

## **$^{13}\text{C}$ separation by IRMPD of $\text{CF}_2\text{HCl}$ molecules with a powerful $\text{CO}_2$ -TEA laser**

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**Abstract.** The single pulse separation parameters in IRMPD of  $\text{CF}_2\text{HCl}$  molecules have been obtained in relation with the laser fluence, the number of laser pulses, and the gas pressure. The measurements have been carried out using a fixed laser line (9P22) and an ordinary shape of the laser pulses.

**Keywords.** Laser isotope separation; multiphoton dissociation.

### **1. Introduction**

Laser isotope separation (LIS) by infrared multiphoton dissociation (IRMPD) has been investigated to compete with classical existing processes for several isotope species such as  $^{34}\text{S}$ ,  $^{18}\text{O}$ ,  $^{15}\text{N}$  and  $^{13}\text{C}$ . For  $^{13}\text{C}$  separation,  $\text{CF}_2\text{HCl}$  is most interesting as the working substrate because of its low price.

Several groups are trying to find a workable photochemical separation for  $^{13}\text{C}$  by IRMPD of  $\text{CF}_2\text{HCl}$  (Outhouse *et al* 1985; Evseev *et al* 1985; Arai *et al* 1989). There is general agreement that practical scale enrichment of  $^{13}\text{C}$  requires a two-stage process, whereby the first stage enriches the concentration of the  $^{13}\text{C}$  from its natural abundance to 30–60%, and the second makes it higher (90%) (Outhouse *et al* 1985). Since the energy consumption is large in the first stage of the separation process that must be well optimized.

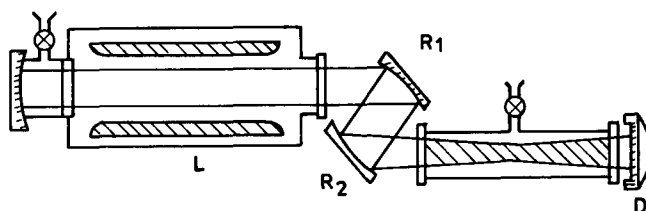
We wish to report on the IRMPD of the  $\text{CF}_2\text{HCl}$  for the  $^{13}\text{C}$  separation in the ordinary shape  $\text{CO}_2$ -TEA laser pulses. We studied the dependence of the isotopic decomposition fractions ( $f_{12}$  and  $f_{13}$ ), energy expenditure per separated atom ( $\epsilon$ ) and the amount of  $^{13}\text{C}$  separated per pulse ( $m_{13}$ ) on the number of laser pulses and of the gas pressure at different fluences in the laser beam. This data obtained per pulse complete the feature of macroscopic parameters reported by Deac *et al* (1990).

### **2. Experimental set-up**

A  $\text{CO}_2$  laser built by us was used in the experiments described below. The main performances of this laser and the characteristics of the generated pulses were detailed in Deac *et al* (1988) and Deac *et al* (1990). Long term operation at the moderate repetition rates (5 Hz) was achieved by combination of several design features including

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**Figure 1.** Optical arrangement used in experiment: L – CO<sub>2</sub>-TEA laser including tuning system, R<sub>1</sub> and R<sub>2</sub> – totally reflecting mirrors with the focal lengths of 6 m and 1.2 m respectively. C – irradiation cell; D – pyroelectric detector.

forced transverse gas flow, intrahead gas cooling and CO<sub>2</sub> regeneration in the external circuit containing Pd/alumina catalyst.

All the experiments were carried out at a fixed laser frequency (1045 cm<sup>-1</sup>) and an ordinary shape of the laser pulse (100 ns FWHM high power peak followed by a 1-μs tail, which contains twice as much energy as the peak). Laser tuning at the 9P22 laser line was performed by inserting in the laser cavity a 10 cm length cell filled with 10–20 Torr of SF<sub>6</sub> (Datkevitch *et al* 1976).

As shown in figure 1, two concave mirrors focus the initial 2 × 2.5 cm<sup>2</sup> laser beam into the reaction cell, giving a cross-section of about 1 cm<sup>2</sup> in the beam waist. A simple pyrex tube, of 43 mm inner diameter and 2.21 total volume, terminated with NaCl windows was used throughout the experiment.

The <sup>13</sup>C isotopic concentration both in residual gas (C<sub>R</sub>) and in the dissociation product (C<sub>P</sub>) was measured with a mass-spectrometer (MS) VARIAN MAT-311. In order to improve the measurement precision, we determined the isotopic ratio <sup>13</sup>C/<sup>12</sup>C in C<sub>2</sub>F<sub>4</sub> from the intensity of the signals both at *m/e* = 81, 82 and 83 (corresponding to <sup>12</sup>C<sub>2</sub>F<sub>3</sub><sup>+</sup>, <sup>12</sup>C<sup>13</sup>CF<sub>3</sub><sup>+</sup> and <sup>13</sup>C<sub>2</sub>F<sub>3</sub><sup>+</sup> respectively) and at *m/e* = 100, 101 and 102 (corresponding to similar ions of the parent molecule). Isotope ratios <sup>13</sup>C/<sup>12</sup>C in CF<sub>2</sub>HCl were determined from the intensities of the signals at *m/e* = 51 and 52 (<sup>12</sup>CF<sub>2</sub>H<sup>+</sup> and <sup>13</sup>CF<sub>2</sub>H<sup>+</sup>).

Besides the MS method we also used a gas-chromatograph (GC) DC-DIF-8 built in our institute, equipped with a 1.5 length column packed with Porapak-Q at 90°C in order to determine the amount of dissociation products.

Calibration of the GC and MS response was achieved with aliquots of C<sub>2</sub>F<sub>4</sub> corresponding to the amount produced in substrates used in the irradiations. In order to do this, we prepared C<sub>2</sub>F<sub>4</sub> by irradiating gas samples until a complete dissociation of CF<sub>2</sub>HCl was obtained.

### 3. Results and discussion

In the first stage of the experiments we irradiated 10 Torr of CF<sub>2</sub>HCl samples by an increasing number of laser pulses, each having 6.4 J at the front of the cell. From the value of C<sub>P</sub> and C<sub>R</sub> measured by MS after each run we calculated the dissociation fractions *f*<sub>12</sub> and *f*<sub>13</sub>, corresponding for two isotopic species respectively. The results are plotted in figure 2.

One can observe from figure 2 that *f*<sub>12</sub> and *f*<sub>13</sub> are independent of the number of laser pulses, at least in the investigated domain.

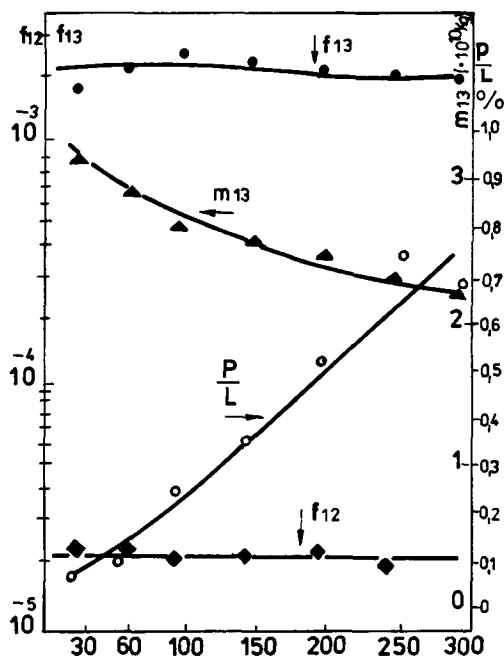


Figure 2. The dependence on the number of laser pulses of: relative yield  $P/L$  (○); isotopic dissociation fractions  $f_{12}$  (◆) and  $f_{13}$  (●); and the amount of separated  $^{13}\text{C}$  per pulse  $m_{13}$  (▲).

The relative dissociation yield in the ordinary separation method is given by Kojima *et al* (1983).

$$\frac{P}{L} = \frac{1}{1+r_0} [(1 - (1 - f_{12})^n) + r_0(1 - (1 - f_{13})^n)] \quad (1)$$

where  $r_0$  is the ratio of the natural abundances.

For small dissociation fractions and for moderate value of  $n$ , the terms  $(1 - f)^n$  from (1) can be developed in series to give:

$$\frac{P}{L} = \frac{n}{1+r_0} (f_{12} + r_0 f_{13}). \quad (2)$$

Therefore, one can expect a linear dependence of  $P/L$  on  $n$ , as is evident from experimental values plotted in figure 2. This means that the obtainable quantity of dissociated product ( $P$ ) is directly proportional to the number of laser pulses, but continuous decrease of the process selectivity causes decrease of the amount of the separated  $^{13}\text{C}$  per pulse ( $m_{13}$ ).

One can see from figure 2 that after irradiation with 300 pulses  $m_{13}$  is 1.5 times smaller than after 30 pulses.

We must mention here that after irradiation with 300 laser pulses,  $^{13}\text{C}$  concentration in residual gas ( $C_R$ ) decreases from 1.1% (the natural abundance) to 0.6%. This means an extraction of 42% for  $^{13}\text{C}$  from  $\text{CF}_2\text{HCl}$ , a value obtainable by classical separation methods.

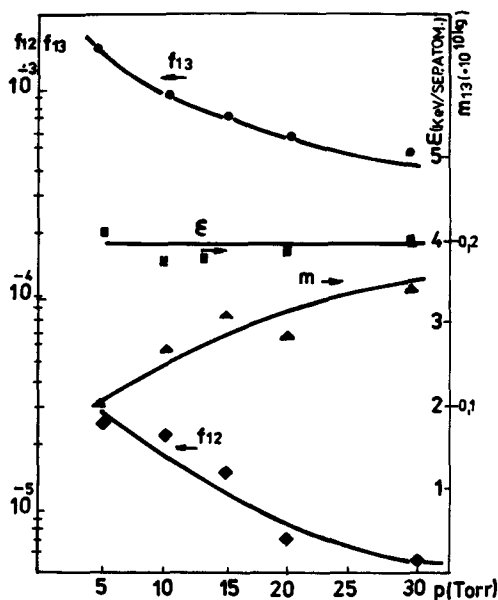


Figure 3. The dependence of  $f_{12}$  (◆),  $f_{13}$  (●),  $m_{13}$  (▲) and energy expenditure  $\epsilon$  (■) on the gas pressure. Each run was carried out by using 3000 pulses of 4 J/pulse measured before passing through the cell.

In the same irradiation geometry but using a lower incident energy of 4.5 J/pulse, the values of  $f_{12}$  and  $f_{13}$  were found to be three times smaller, proving that dissociation fractions are strongly dependent on the laser fluences (Outhouse *et al* 1985).

In the second stage of the experiment we investigated the dependence of the same parameters on the gas pressure for two different energies of the laser pulses: 4 J and 6.1 J (when entering the cell), using 3000 and 200 laser pulses respectively. The results are plotted in figures 3 and 4 respectively.

As one can see from results depicted in figure 3,  $f_{12}$  and  $f_{13}$  exhibit a monotonic decrease from  $f_{13} = 4 \cdot 10^{-3}$  and  $f_{12} = 3 \cdot 10^{-6}$  for  $p = 5$  Torr, to  $f_{13} = 4 \cdot 10^{-5}$  and  $f_{12} = 6 \cdot 10^{-7}$  for  $p = 30$  Torr. Increase of the ratio  $f_{13}/f_{12}$  with pressure explains the increase of the selectivity.

The effect of pressure on  $m_{13}$  is also shown in figure 3. In a previous paper (Deac *et al* 1990) we demonstrated that  $p \cdot P/L$  remains constant over the entire range of pressure, thus the separated  $m_{13}$  will increase with the pressure only because the process selectivity increases as well.

Energy expenditure ( $\epsilon$ ) per separated atom remains constant in the investigated pressure range, within the limits of experimental error (figure 3).

The behaviour of these parameters is consistent with the measurements reported by Outhouse *et al* (1985) in neat  $\text{CF}_2\text{HCl}$  and by Arai *et al* (1989) for a mixture of  $\text{CF}_2\text{HCl}$  and  $\text{Br}_2$ .

For 6.4 J/pulse (figure 4)  $f_{13}$  maintains the same characteristics, while  $f_{12}$  exhibits a minimum around of 15 Torr, due to the mechanism of thermal decomposition (Deac *et al* 1990). The value of  $m_{13}$  increases and then levels off because the process selectivity is strongly attenuated. By the same reason  $\epsilon$  abruptly increases with the pressure.

The present results demonstrate that for excitation with normal  $\text{CO}_2$  laser pulses,

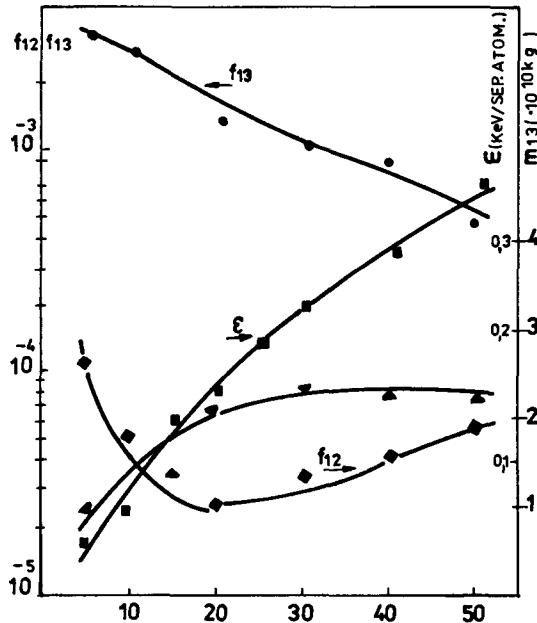


Figure 4. The dependence of  $f_{12}$  (◆),  $f_{13}$  (●),  $m_{13}$  (▲) and energy expenditure  $\epsilon$  (■) on the gas pressure. Each run was carried out by using 200 pulses each of 6.1 J/pulse.

the  $^{13}C$  mass separated per pulse cannot increase much more by increasing the gas pressure because of the occurrence of the thermal decomposition. It would be therefore necessary to find other ways to improve the process figures of merit.

## References

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