

CARBON ISOTOPE SELECTIVE SEPARATION FROM MPD OF CF_3Br WITH A TEA CO_2 LASER

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Pure CF_3Br and mixtures of this substance with monoatomic (He, Ar and Xe), homonuclear diatomic (H_2 , D_2 , N_2), polyatomic gases (CF_4) and NO have been irradiated with a TEA CO_2 laser. Carbon-13 enrichment factor and carbon-13 selectivity have been estimated from the mass spectrometric analysis of the undissociated CF_3Br as a function of excitation wavelength, fluence, temperature and pressure. The irradiating wavelength is a crucial parameter to achieve enrichment. The nature of the added gas also affects considerably selectivity. Best enrichment is achieved in mixtures with NO due to its radical-like character.

Keywords: CO_2 laser; carbon isotope separation; CF_3Br ; multiphoton dissociation

1. INTRODUCTION

The process of isotopic selective multiphoton dissociation (MPD) of polyatomic molecules in the gas phase has been amply studied by several authors [1–9]. Pure CF_3Br and mixtures with different gases have been also studied by MPD [10–15]. These studies reveal that the wavelength is the most relevant parameter to attain selectivity. They also show that when pressure is increased, the enrichment disappears and the presence of added gases does not affect substantially the selectivity.

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We have also studied the MPD of pure CF_3Br and mixtures with monoatomic, diatomic and polyatomic gases [16–18]. Our results corroborate the effect of wavelength and pressure observed in previous studies, although most of these experiments have been carried out with static cells and sharp focusing, while ours and some others [19, 20] have been performed with a long and narrow cell as a waveguide reactor, and constant fluence. Due to these different experimental conditions, the results cannot be compared in detail.

Abdushelishvili *et al.* [21] have studied the effect of adding NO on the MPD of CF_3I . They found that the presence of NO considerably increases the observed CF_3I molecule dissociation yield but has only a slight effect on the selectivity of the process. We have confirmed that NO acts as an acceptor of CF_3 radicals by studying $\text{CF}_3\text{Br} + \text{NO}$ mixtures, but in our case the added NO does produce a remarkable effect on the carbon-13 enrichment.

2. EXPERIMENTAL

Figure 1 shows the experimental apparatus. The TEA CO_2 laser is a modified Lambda Physics EMG 200 that can be tuned. It is filled with $\text{N}_2:\text{CO}_2:\text{He}$ at 60:80:320 Torr. The operating mode is TEM_{00} . An aperture of variable diameter is introduced in the cavity and allows to select the energy per shot. The maximum energy per pulse is 200 mJ for the 9P18 line. The laser pulse consists of a 80 ns spike followed by a low intensity microsecond tail. The repetition rate of the laser was 32 shots per minute. The laser beam is brought to the stainless steel cell (1 meter long and 1.8 mm diameter) with KBr windows by a collection of mirrors and is focused at the entrance by a KCl lens of 120 cm focal length.

A metallic support bears the cell and allows it to cool to different bath temperatures. A slush bath of heptane/decane/liquid nitrogen allows us to reach 188 K.

Two Gentec detectors mod. 200 are placed before and after the gas cell to measure the input and output energies. The ratio of these measurements reaches a value of 60% in the worst cases. The spot size diameter at the entrance of the cell is approximately 0.45 mm, and has been determined by using the areas of the burn patterns on heat sensitive paper. The cavity is evacuated at 10^{-6} Torr. The windows

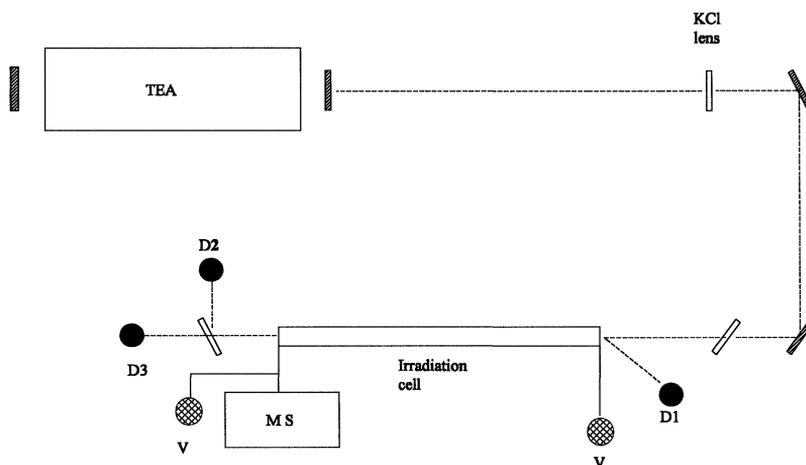


FIGURE 1 Experimental apparatus. (TEA: pulsed CO₂ laser; D₁, D₂, and D₃: IR detectors; V: vacuum and gas supply; MS: mass spectrometer).

and valves for the gas supply are mounted as close as possible to the ends of the irradiation cell to decrease the non irradiated volume. The relation of both volumes is approximately 1 to 1.

A MKS Baratron which has an output of 1 mV per mTorr is used at the entrance of the cell to control the pressure until 1 Torr. For higher pressures another Baratron is used.

The dissociation products are analyzed with a SXP Elite mass spectrometer from Fisons capable of detecting 1 ppm of masses up to 300 amu. The electrons are accelerated with an energy of 70 eV and the generated ions are positive. The mass spectrometer region is kept at a pressure of 10⁻⁹ Torr.

CF₃Br (Praxair) and NO (Air Liquide) have been used without further purification.

3. RESULTS AND DISCUSSION

To measure the enrichment of the process we use the enrichment factor of the residual CF₃Br, β , defined as:

$$\beta = \frac{(I_{149}/I_{148})_{\text{after irradiation}}}{(I_{149}/I_{148})_{\text{before irradiation}}}$$

where I_{149} and I_{148} are, respectively, the mass peak intensities of $^{13}\text{CF}_3^{79}\text{Br}$ and $^{12}\text{CF}_3^{79}\text{Br}$.

Under all the experimental conditions studied, the observed β values are smaller than 1, what shows that carbon-13 bearing molecules are preferentially dissociated.

When possible, we have also estimated the selectivity factor, α_{13} , that is a direct measurement of the reaction yield ratio for the two isotopic species of the reactant, and is defined as [15]:

$$\alpha_{13} = \frac{V_{13}}{V_{12}} = 1 + \frac{\ln \beta_{\text{reactant}}}{\ln f}$$

where V_i is the reaction yield of $^i\text{CF}_3\text{Br}$, and

$$f = \frac{[^{12}\text{CF}_3\text{Br}]_{\text{after irradiation}}}{[^{12}\text{CF}_3\text{Br}]_{\text{before irradiation}}}.$$

The results have been obtained as the averaging of at least 3 measurements under the same experimental conditions, and the error bars reflect their statistical deviation.

A. Wavelength Effect

Figure 2 shows the enrichment factor, β , for different irradiation wavenumbers ranging from 1035.5 cm^{-1} to 1053.9 cm^{-1} , 9P32 and 9P12 CO_2 laser lines respectively, for pure CF_3Br . A minimum β value, maximum enrichment, is reached around 1046.9 cm^{-1} , 9P20 CO_2 laser line. The enrichment quickly disappears when the laser is changed to shorter or longer wavelengths. We attribute the carbon-13 selectivity observed to the near resonance of the ν_1 mode of the $^{13}\text{CF}_3\text{Br}$ molecule, at 1058 cm^{-1} [22]. There is a difference between the absorption and dissociation maxima of 11 cm^{-1} towards the red, as usual [1].

As it can be inferred from the absorption spectrum of CF_3Br that appears in Figure 3, the absorption coefficient of the ν_1 mode of $^{13}\text{CF}_3\text{Br}$ is considerably larger than that of the $3\nu_3$ mode of $^{12}\text{CF}_3\text{Br}$, what explains the observed selective dissociation of the first isotopic species.

Beta values for some 1:3 ($\text{CF}_3\text{Br} + \text{X}$) representative mixtures are also shown in Figure 2. As it can be seen, the dependence of the

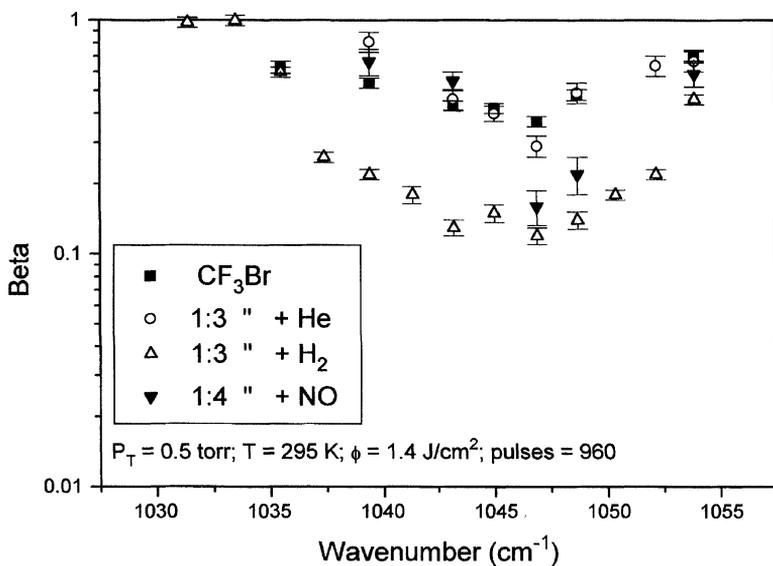


FIGURE 2 Enrichment factor, β , for pure CF_3Br and some representative mixtures under the experimental conditions that are indicated.

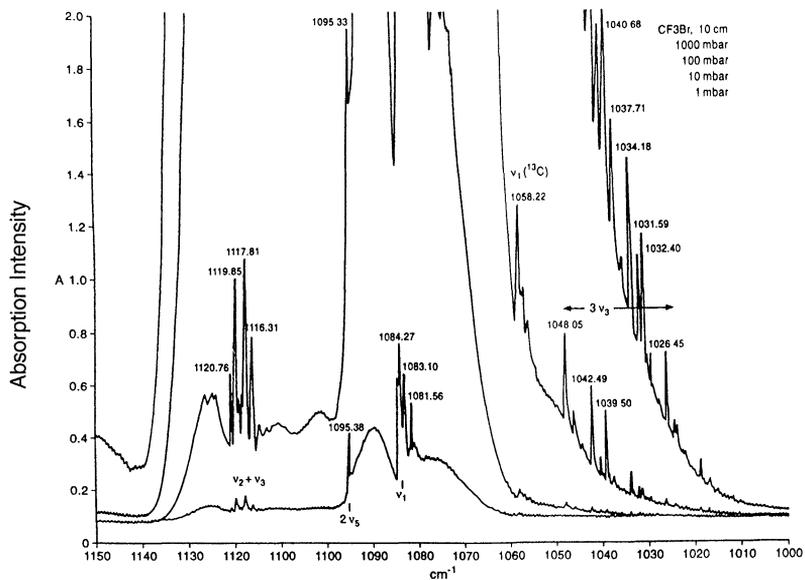


FIGURE 3 Infrared absorption spectrum of CF_3Br .

enrichment factor, β , with wavenumber is similar to the one observed for pure CF_3Br , as expected.

B. Effect of the Gas Added to CF_3Br in the Mixtures

Table I shows the enrichment factor for the pure substance and 1:3 mixtures with monoatomic gases: He, Ar and Xe. To compare these results in detail, it is necessary to choose those total pressure values that correspond to the same partial pressure of CF_3Br . No variation is observed in the enrichment because of the presence of these monoatomic gases. Therefore, we conclude that they act as spectators, due to the lack of vibro-rotational structure.

Figure 4 shows the enrichment factor for the pure substance and 1:3 mixtures with homonuclear diatomic gases: H_2 , D_2 and N_2 . A remarkable improvement of the enrichment is observed in these mixtures, being most noticeable in those prepared with H_2 . It seems that diatomic gases relax more efficiently $^{12}\text{CF}_3\text{Br}$ molecules through collisions, allowing the $^{13}\text{CF}_3\text{Br}$ species to be preferentially dissociated.

In Table I it is shown the enrichment factor for pure CF_3Br and 1:3 mixtures with CF_4 . No effect is observed on the enrichment when this gas is added, what can be explained by considering that, due to its near resonance with all the isotopic species of CF_3Br , it relaxes with similar efficiency both isotopic species: $^{12}\text{CF}_3\text{Br}$ and $^{13}\text{CF}_3\text{Br}$.

C. Effect of NO Addition

Figure 5 shows that adding NO to CF_3Br instead of H_2 improves the enrichment except at the lowest pressure, 0.5 Torr. This improvement is remarkable for total pressures between 1 and 4 Torr.

TABLE I Enrichment factor, β , for 1:3 mixtures with monoatomic gases and CF_4 . Irradiating line: 9P20, room temperature, $1.4\text{J}/\text{cm}^2$ of fluence and 960 pulses

P_T/Torr	8	6	4	3	2	1	0.5
Mixture							
CF_3Br				0.86	0.69	0.46	0.44
$\text{CF}_3\text{Br} + \text{He}$	0.78		0.43		0.30		0.29
$\text{CF}_3\text{Br} + \text{Ar}$	0.68		0.48		0.35		0.35
$\text{CF}_3\text{Br} + \text{Xe}$	0.68		0.52		0.48		0.29
$\text{CF}_3\text{Br} + \text{CF}_4$	0.76		0.59	0.47	0.42	0.30	0.26

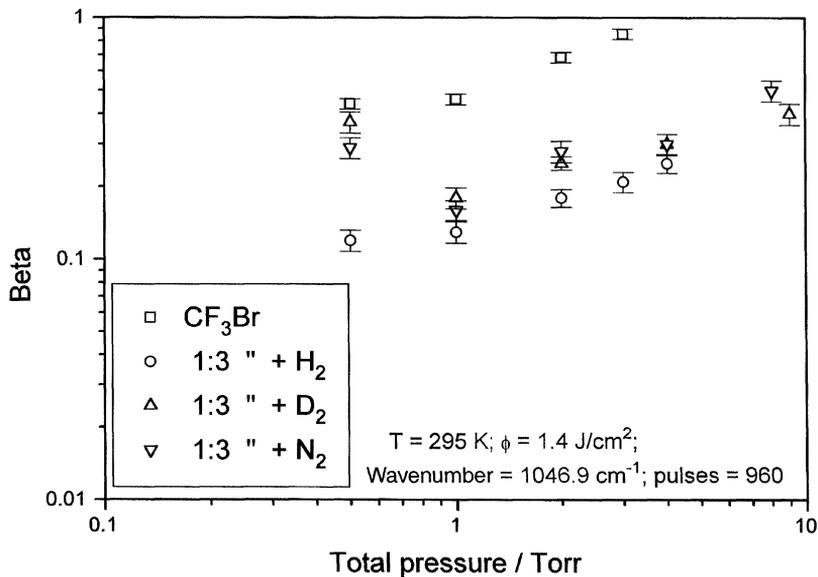


FIGURE 4 Enrichment factor, β , as a function of total pressure for pure CF_3Br and mixtures with homonuclear diatomic gases. Experimental conditions are indicated.

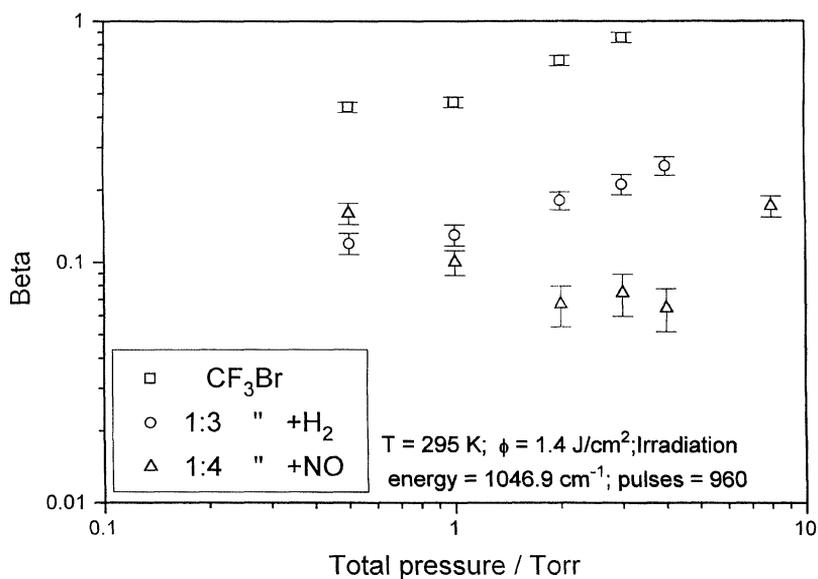
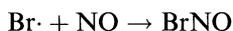
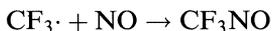
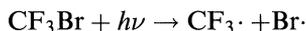


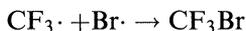
FIGURE 5 Enrichment factor *versus* total pressure for the pure substance, a 1:3 $\text{CF}_3\text{Br} + \text{H}_2$ mixture and a 1:4 $\text{CF}_3\text{Br} + \text{NO}$ mixture. The experimental conditions are the same as in Figure 4.

The different behaviour of NO compared with the other gases studied could be based on its radical-like structure that makes it an excellent trapper of the radical photodissociation fragments.

It is believed that in the presence of NO the following reactions take place [21]:



These reactions avoid the following recombination of the fragments:



which contributes to the loss of enrichment in the other mixtures studied.

Figure 6 shows the enrichment factor for 1:x ($x = 2.2, 4, 6$ and 7.3) mixtures of $\text{CF}_3\text{Br} + \text{NO}$ as a function of total pressure. Maximum

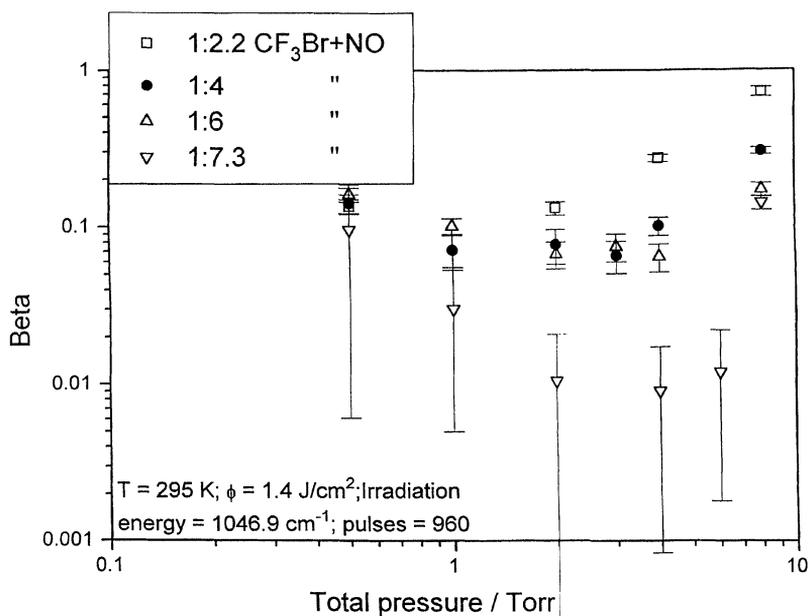


FIGURE 6 Enrichment factor *versus* total sample pressure for NO mixtures with different proportions. 9P20 irradiating line, room temperature, 1.4 J/cm^2 of fluence and 960 pulses.

enrichment is achieved for the most diluted sample and for total pressures between 1 and 4 Torr. We believe that the enrichment will improve still further with more diluted samples, but we cannot corroborate it because we are in the detection limit of our mass spectrometer with 1:7.3 mixtures, as it is inferred from the large error bars. In any case, at higher dilutions the number of CF_3Br molecules is so small that the efficiency of the process would be rather poor.

We have also estimated the selectivity factor [16], α_{13} , which also reaches a maximum in the pressure range from 1 Torr to 4 Torr, as it is shown in Figure 7. For higher pressures α decreases abruptly and, as usual, the process is not further selective.

D. Effect of Other Variables

We have estimated the enrichment factor for pure CF_3Br at different fluences, whose values are affected of a 20% error: 0.94, 1.4 and 1.7 J/cm^2 [17]. It can be seen in Figure 8 that enrichment factor values

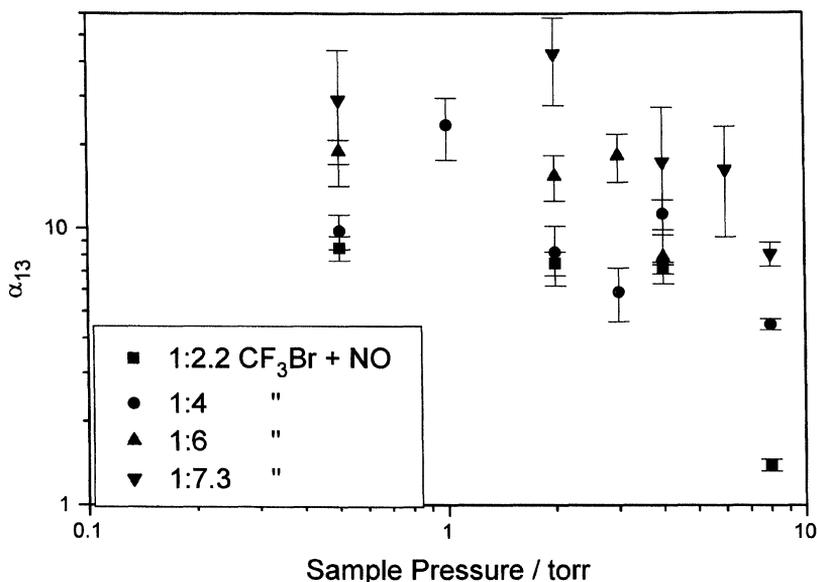


FIGURE 7 Selectivity factor, α_{13} , for NO mixtures with different proportions. 9P20 irradiating line, room temperature, 1.4 J/cm^2 of fluence and 960 pulses.

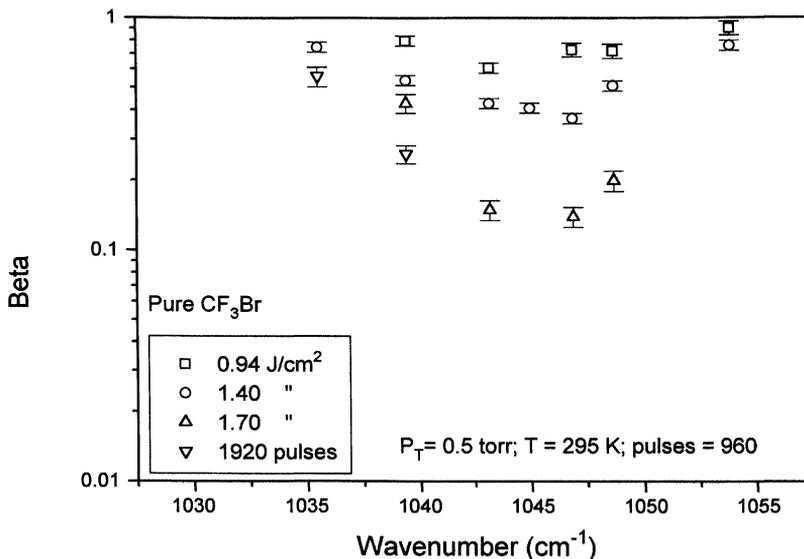


FIGURE 8 Enrichment factor for pure CF₃Br at different fluences. 9P20 irradiating line, room temperature and 960 pulses.

decrease when fluence is increased, what means that the enrichment of the process augments with fluence. This trend is observed for most wavelengths, being specially noticeable at those that give higher selectivity values. It seems that, with fluences between 0.94 and 1.7 J/cm², maximum possible enrichment is not achieved. The behaviour of the enrichment factor with fluence is similar for all the mixtures studied [18].

The dissociation probability, DP, for the isotopic species ¹²CF₃Br and ¹³CF₃Br at the fluences indicated above has been estimated for nitrogen mixtures. DP increases with fluence for the majority of the wavelengths studied, but the increase observed for ¹³CF₃Br is larger than the one observed for ¹²CF₃Br, what confirms the improvement achieved in the enrichment at higher fluences.

The enrichment factor, β , at different temperatures has been estimated for pure CF₃Br [17], and mixtures [17, 18]. In both cases it is observed that the enrichment improves when decreasing the temperature from 295–188 K for the most selective wavelengths,

1046.9 and 1048.7 cm^{-1} , and remains practically unchanged for the other ones studied.

In the case of NO mixtures, we have been able to estimate the selectivity factor, α_{13} , which augments appreciably when temperature decreases [16].

A decrease in the enrichment is observed when total pressure increases from 0.5 Torr to 10 Torr [16–18]. This fact can be explained by the enlargement of the number of collisions during the laser pulse when total pressure augments. This increase of collisions favours the ergodic distribution of the absorbed energy and, consequently, entails a loss of selectivity.

E. Efficiency of the Carbon Isotopic Separation Process

In order to estimate the efficiency of the separation process in NO mixtures, we define the following function:

$$C_R = \alpha_{13} \times [P_{\text{CF}_3\text{Br}}]_{\text{before irradiation}}$$

where the first factor takes account of the efficiency of the selective dissociation, and the second, of the number of particles susceptible of dissociation.

We consider that the maximum values of C_R give the optimum pressure conditions for carbon isotopic separation. Table II shows the estimated values of this function in the mixtures studied. Under the present experimental conditions, best results are obtained for the most diluted samples, 1:7.3, and 6 Torr of total pressure.

TABLE II C_R values, in Torr, for the NO mixtures studied. Irradiating line: 9P20, room temperature, 1.4 J/cm² of fluence and 960 pulses

P_T/Torr	8	6	4	3	2	1	0.5
Mixture							
1:2.2	3.50	–	9.00	–	4.69	–	1.33
1:4	7.20	–	9.04	3.54	3.30	4.74	0.98
1:6	–	–	4.51	7.85	4.43	–	1.33
1:7.3	12.96	19.56	13.92	–	10.33	–	1.75

4. CONCLUSIONS

1. The irradiating wavelength is a crucial parameter to obtain selectivity.
2. The addition of a radical trapper like NO improves significantly the enrichment.
3. The MPD process is more selective than it could be inferred from our previous results. The recombination of the radicals formed in the dissociation masks the selectivity of the initial MPD process. The presence of NO avoids this recombination preserving the selectivity of the multiple photon dissociation.
4. Maximum enrichment is achieved in the most diluted $\text{CF}_3\text{Br} + \text{NO}$ mixtures (1:7.3).
5. Although lowering the temperature does not influence noticeably the enrichment factor, β , its effect on the α values is significant.
6. An efficient experimental method for obtaining carbon isotopes has been established.

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References

- [1] Lyman, J. L., Rockwood, S. D. and Freund, S. M. (1977). *J. Chem. Phys.*, **67**, 4545.
- [2] Bitterson, S. and Houston, P. L. (1977). *J. Chem. Phys.*, **67**, 4819.
- [3] Gauthier, M., Hackett, P. A., Drouin, M., Pilon, R. and Willis, C. (1978). *Can. J. Chem.*, **66**, 2227.
- [4] Drouin, M., Gauthier, M., Pilon, R., Hackett, P. A. and Willis, C. (1978). *Chem. Phys. Letters*, **60**, 16.
- [5] Ambartzumian, R. V., Letokhov, V. S., Makarov, G. An. and Puretzky, A. A. (1978). *X International Quantum Electronic Conference*, Atlanta, Georgia, 29th May – 1st June, Paper N-8.
- [6] Sudbo, A. S., Schulz, P. A., Grant, E. R., Shen, Y. R. and Lee, Y. T. (1979). *J. Chem. Phys.*, **70**, 912.
- [7] Sugita, K., Ma, P., Ishikawa, Y. and Arai, S. (1991). *Appl. Phys. B*, **52**, 266.
- [8] Parthasarathy, V., Sarkar, S. K., Pushpa, K. K., Rao, K. A., Rama Rao, K. V. S. and Mittal, J. P. (1993). *Appl. Phys. B*, **56**, 101.

- [9] Hattori, M., Ishikawa, Y., Mizuta, K., Arai, S., Sugimoto, S., Shimizu, Y., Kawanishi, S. and Suzuki, N. (1992). *Appl. Phys. B*, **55**, 413.
- [10] Avatkov, O. N., Laptev, V. B., Ryabov, E. A. and Furzikov, N. P. (1985). *Sov. J. Quantum Electron.*, **15**(3), 375.
- [11] Parthasarathy, V., Sarkar, S. K., Iyer, N. V., Rama Rao, K. V. S. and Mittal, J. P. (1993). *Appl. Phys. B*, **56**, 321.
- [12] Abzianidze, T. G., Egiazarov, A. S., Petrov, A. K. and Samsonov, Y. N. (1981). *Sov. J. Quantum Electron.*, **11**, 343.
- [13] Abdushelishvili, G. I., Avatkov, O. N., Bagratashvili, V. N., Baranov, V. Y., Bakhtadze, A. B., Velikhov, E. P., Vetsko, V. M., Gverdtsiteli, I. G., Dolzhikov, V. S., Esadze, G. G., Kazakov, S. A., Kolomiiskii, Y. R., Letokhov, V. S., Pigul'skii, S. V., Pis'mennyi, V. D., Ryabov, E. A. and Tkeshelashvili, G. I. (1982). *Sov. J. Quantum Electron.*, **12**, 459.
- [14] Borsella, E., Clementi, C., Fantoni, R., Giardini-Guidoni, A. and Palucci, A. (1983). *Nuovo Cimento*, **73A**, 364.
- [15] Cantrel, C. D., Freund, S. M. and Lyman, J. L. (1979). *Laser Handbook*, Stitch, M. L. (Ed.). North Holland Publishing Co, p. 514.
- [16] del Barrio, J. I., Fernández C  zar, R., G-Tablas, F. M. (1998). *J. Phys. Chem. A*, **102**, 3215.
- [17] del Barrio, J. I., Fern  ndez C  zar, R., Mart  n, E., G-Tablas, F. M. and Fuss, W. (1996). *Appl. Phys. B*, **63**, 51.
- [18] del Barrio, J. I., Fern  ndez C  zar, R. and G-Tablas, F. M. (1997). *Chem. Phys. Lett.*, **270**, 71.
- [19] Sarkar, S. K., Nayak, A. K., Rama Rao, K. V. S. and Mittal, J. P. (1990). *J. Photochem. Photobiol. A: Chemistry*, **54**, 159.
- [20] del Bello, U., Fuss, W., Kompa, K. L. and G-Tablas, F. M. (1989). *J. Chem. Phys.*, **90**(6), 3055.
- [21] Abdushelishvili, G. I., Avatkov, O. N., Bakhtadze, A. B., Vetsko, V. M., Tkeshelashvili, G. I., Tomilina, V. I., Fedoseev, V. N. and Kolomisskii, Y. R. (1981). *Sov. J. Quantum Electron.*, **11**, 326.
- [22] Fuss, W., Private communication.