

Efficient two-stage laser enrichment up to 99% of carbon-13 isotope by IR multiphoton dissociation of Freon molecules

V.B. Laptev, S.V. Pigul'skii

Abstract. A new method for two-stage laser enrichment of carbon-13 (^{13}C) by isotope-selective IR multiphoton dissociation of Freon molecules is considered, which makes it possible to achieve a concentration of ^{13}C up to 99% or higher with high productivity. At the first stage, as a result of the selective dissociation of CF_2HCl (Freon-22) molecules, it is expected to obtain a C_2F_4 dissociation product enriched in ^{13}C up to 30%–50%. At the second stage, CF_2Br_2 (Freon-12B2) is proposed to be used as a working substance, which is synthesised from enriched C_2F_4 , and the enrichment process is carried out by selective deep ‘burning-out’ of the ^{12}C -containing component. Experiments on multiphoton dissociation of Freon-12B2 with an initial $^{13}\text{CF}_2\text{Br}_2$ concentration of 30% in a mixture with oxygen by pulsed CO_2 laser radiation are performed. It is shown that reaching a $^{13}\text{CF}_2\text{Br}_2$ concentration of no lower than 99% is possible at high values of the elementary separation act parameters: 15%–18% dissociation yield and 40–75 selectivity for $^{12}\text{CF}_2\text{Br}_2$ molecules.

Keywords: carbon-13, laser enrichment, ^{13}C -enriched Freon-12B2, selective ‘burning-out’ of a ^{12}C -containing component.

1. Introduction

Since the 1950s, the world production of the stable carbon-13* isotope has been constantly growing and by 2018 amounted to about 600 kg per year [1, 2]. This is mainly due to the fact that in medical practice pharmacological drugs labelled with the carbon-13 (^{13}C) isotope are being actively introduced and widely applied, which makes them indispensable for diagnosing various diseases by methods of breath tests and magnetic resonance [3]. Carbon-13 is also used as a starting material for positron emission tomography [2]. The ever-growing demand for the ^{13}C isotope requires the development of its production, including on new principles. The method for isotope separation based on isotope-selective multiphoton dissociation (MPD) of molecules by IR laser radiation has been brought for carbon isotopes to industrial implementation and has proved its competitiveness compared to traditional methods [1, 4, 5]. In particular, the Ugl'erod complex (ZAO Gaz-Oil, Kaliningrad) in the early 2000s produced up to 30 kg of

carbon-13 per year, which at that time accounted for about a third of the world production [2].

At the same time, practice has shown that laser enrichment of ^{13}C in one stage is economically advantageous only up to a concentration of 30%–50% [5]. Therefore, there is a need to use the second stage of enrichment, at which the ^{13}C concentration of 99% that is necessary for medical purposes is reached. At the second stage, both traditional enrichment methods (low-temperature distillation, gas centrifuges, etc.) and the laser method can be used. The use of the laser method for the enrichment of ^{13}C from 30%–50% to 99%, in our opinion, is more appropriate for the following reasons. Firstly, traditional enrichment methods are characterised by high capital and energy costs, as well as a long period for the separation cascade to reach a stationary operation regime. Secondly, the estimated cost of the product in the laser method, according to preliminary estimates, should be noticeably lower than in the first stage of enrichment from the natural carbon-13 content of 1.1% to ~30%, which is associated with significantly lower (about 30 times) amounts of the working substance. In addition, the final enriched product (CO_2 or CO) produced by laser technology will have a natural concentration of oxygen isotopes. The catalogue price of such a product is much higher. For classical methods, this ratio is violated. Thus, the task of developing an efficient laser technology for enriching carbon-13 to 99% at the second stage is very urgent.

2. Review of previous works

Since the 1980s, many researchers around the world have been studying the possibility of obtaining highly enriched carbon-13. Various options for solving this problem were considered. Attempts were made to achieve high concentrations of ^{13}C already at the first stage. The principal possibility of obtaining ^{13}C with a concentration of up to 96%–98% in one stage was demonstrated in laboratory experiments on the isotopically selective MPD of Freon-22 (CF_2HCl) [6, 7]. However, in these studies, the experimental conditions were chosen in such a way as to ensure the maximum selectivity of the separation process. The dissociation efficiency and, consequently, the process productivity were extremely low. It became clear that high concentrations of ^{13}C could only be achieved with high productivity by using at least two laser enrichment stages.

In works [8–21] dedicated to the development of various options for implementing the second stage of laser enrichment, three main directions are considered. The first direction is separate enrichment processes at the first and second stages with an intermediate cycle of isolation of the product enriched

*The natural abundance of heavy carbon-13 isotope is 1.1%.

V.B. Laptev, S.V. Pigul'skii Institute of Spectroscopy, Russian Academy of Sciences, ul. Fizicheskaya 5, 108840 Moscow, Troitsk, Russia; e-mail: laptev@isan.troitsk.ru

Received 29 November 2021
Kvantovaya Elektronika 52 (4) 371–375 (2022)
Translated by M.A. Monastyrsky

in ^{13}C and its chemical conversion into a compound suitable for use at the second stage [8–10]. The second way is to combine the enrichment process with simultaneous chemical synthesis inside the laser separation reactor of the working substance for the second stage [8, 11–13]. To do this, an additional chemical compound (acceptor) is added to the working substance of the first stage, in reactions with which the radicals formed during IR MPD produce the product enriched in ^{13}C , which is necessary for the second stage. The third method makes it possible to completely combine the first and second enrichment stages and the chemical conversion cycle in a single reactor. This is achieved by adding the acceptor to the first-stage working substance, upon interaction with which a substance is formed, which, along with the first one, isotope-selectively dissociates under the action of laser radiation of the same frequency [14–21].

The first way of organising a two-stage separation process was studied in [9, 10]. Freon-22 (CF_2HCl) with an increased concentration of $^{13}\text{CF}_2\text{HCl}$ molecules (32.6% [10]) was synthesised from the first-stage product tetrafluoroethylene (C_2F_4) enriched in ^{13}C . In this case, in work [10], in contrast to work [9], a reactor with enriched Freon-22 was located inside the CO_2 laser resonator in the same way as in an industrial plant [4, 5]. It was found that an increase in the initial concentration of $^{13}\text{CF}_2\text{HCl}$ to 32.6% and a corresponding increase in the resonator losses do not lead to the generation failure, and the entire system operates stably. As a result of the experiments, the final ^{13}C concentration of $99.55\% \pm 0.5\%$ was reached in the C_2F_4 dissociation product; however, the degree of depletion and dissociation yield of the desirable $^{13}\text{CF}_2\text{HCl}$ component were low ($\sim 5\%$ and about 0.04%, respectively). Such low parameters of the enrichment process indicate the inefficiency of this scheme.

The second method of the process organisation, combining at the first stage the enrichment and chemical synthesis of the working substance for the second stage, was implemented by adding bromine radicals as an acceptor to the working compounds [8, 11–13]. From the standpoint of the process technology, the presence of bromine in the laser separation reactor is undesirable due to its high chemical activity and adsorption capacity.

The third way to organise a two-stage process with an intracavity reactor was studied in our work [21]. The addition of hydrogen iodide to Freon-22 as an acceptor led to the formation of an intermediate product, CF_2HI , which dissociated selectively with respect to ^{13}C during irradiation at the same laser radiation frequency. This made it possible to achieve a ^{13}C concentration of $98\% \pm 1.5\%$ in the final CF_2H_2 product. However, it turned out that this scheme, in addition to the difficulties associated with the use of chemically aggressive hydrogen iodide and partial loss of ^{13}C in the intermediate CF_2HI product, has one more significant drawback. With an intracavity placement of the reactor, the fluence of laser radiation, and, consequently, the efficiency of multiphoton dissociation of CF_2HCl significantly decreased with accumulation of enriched products in the reactor.

Thus, almost all the studied schemes for the implementation of the second stage of laser enrichment are based on the selective dissociation of the ^{13}C -containing component of compounds pre-enriched with ^{13}C . It turned out that in this way it is difficult to realise a high productivity of the enrichment process, since the required final concentration of ^{13}C (99%) was either not achieved or had a low process productivity and a low degree of depletion of the ^{13}C -containing

component [10]. Obtaining the required degree of the desirable isotope depletion and further use of the ^{13}C -enriched residual gas are the main problems of the second laser stage scheme, in which the selective dissociation of the ^{13}C -containing component is carried out.

The method of carbon-13 enrichment based on the selective 'burning-out' of an undesirable ^{12}C -containing component, which was first proposed in work [22] and developed in works [23–25], was also studied. A theoretical analysis of the enrichment method based on the 'burning out' of an undesirable isotope is given in [26] when choosing the optimal scheme for organising the separation process. In this selective multiphoton dissociation method, the component with ^{12}C is converted into products, and the residual gas is enriched in the desirable ^{13}C -containing component. In experiments on MPD of CF_3I [22, 23, 25], CF_3Br [24], and CF_2HCl [25] molecules with a natural ^{13}C content of 1.1%, the fundamental possibility of implementing such a scheme was demonstrated. In work [22], after irradiation, a concentration of $^{13}\text{CF}_3\text{I}$ molecules equal to 86% was reached in the residual gas. In work [23], the concentration of $^{13}\text{CF}_3\text{I}$ molecules was 70%, while the macroscopic amount of the isotopic mixture of CF_3I molecules amounted to 2 g. Similar experiments were conducted with CF_3Br [24] and CF_2HCl [25] molecules, also with the initial ^{13}C content of 1.1%. In work [24], the achieved concentration of $^{13}\text{CF}_3\text{Br}$ was 90%.

At the same time, the method of selective 'burning-out' of an undesirable ^{12}C -containing component for compounds with a natural ^{13}C content has an extremely low efficiency. Firstly, the maximum concentration of ^{13}C reached in the experiments did not exceed 90%. Secondly, to achieve a ^{13}C concentration of 99%, 99.99% of the substance must be processed, which dramatically increases energy consumption. Thirdly, due to the huge amount of dissociation products, they must be continuously removed from the reactor, since they can affect the dissociation selectivity. This is extremely inconvenient from the viewpoint of process technology.

3. Proposed method for implementing a two-stage ^{13}C enrichment process

Based on the foregoing, we can conclude that the problem of efficient production of carbon-13 with 99% enrichment by using only a laser method has essentially remained unsolved. We propose a new approach, which consists in using the method of deep selective 'burning-out' of the ^{12}C -containing component at the second stage of enrichment, while Freon-12B2 (CF_2Br_2), pre-enriched by ^{13}C up to 30%–50%, is supposed to be used as the working substance of the laser process [27].

The use of CF_2Br_2 is explained by the relatively simple chemical synthesis of this compound from tetrafluoroethylene, which is a product of the first-stage enrichment [5, 28]. This is the first advantage of this approach. In addition, the results of preliminary experiments on the IR MPD of Freon-12B2 with a natural ^{13}C content of 1.1%, which we have performed previously [29], show that the spectral properties of CF_2Br_2 allow us to achieve high values of the elementary separation act parameters (yield and dissociation selectivity with respect to the ^{12}C -containing component) at a low fluence of laser radiation.

Another advantage is that a much smaller amount of substance (50%–70% of the main ^{12}C -containing component) will be processed when using pre-enriched Freon-12B2 in

order to achieve the required ^{13}C -concentration of 99% at the second stage. This should significantly reduce the amount of dissociation products and energy consumption.

However, the principal advantage of the method of deep selective ‘burning-out’ of the ^{12}C -containing component for ^{13}C enrichment is the possibility of achieving any final ^{13}C concentration in the residual gas, including 99% or higher.

Thus, the purpose of these experiments was to study the process of ^{13}C enrichment with deep ‘burning-out’ of the ^{12}C -containing component in Freon-12B2 with enrichment in ^{13}C 30% under the action of pulsed CO_2 laser radiation. During the experiment, the main parameters of the separation elementary act (yield and selectivity of dissociation) were measured and optimised depending on the irradiation conditions. It was shown that at high values of the separation act parameters, the concentration of $^{13}\text{CF}_2\text{Br}_2$ molecules of at least 99% in the residual gas is reliably achieved.

4. Experiment

The amount of Freon-12B2 enriched with ^{13}C to 30%, required for experiments, was synthesised by laser conversion of enriched CF_2HCl (^{13}C concentration of 30%) in a bromine medium. The content of the main substance in the synthesised CF_2Br_2 product was about 96%. IR spectra of enriched Freon-12B2 were obtained and isotopic shifts relative to ^{13}C were measured in the absorption bands of vibrational modes $\nu_1 = 1090\text{ cm}^{-1}$, $\nu_6 = 1153\text{ cm}^{-1}$, and $\nu_8 = 831\text{ cm}^{-1}$ [30].

The ^{12}C -selective multiphoton dissociation of CF_2Br_2 was performed by tuning the CO_2 laser radiation frequency to the long-wavelength wing of the absorption band $\nu_1 = 1090\text{ cm}^{-1}$ corresponding to the symmetric vibration of the $^{12}\text{CF}_2$ group. In the experiments, the kinetics of changes in the concentration of each isotopic component was measured as a function of the number of laser pulses under different irradiation conditions (radiation frequency, CF_2Br_2 pressure, and O_2 acceptor gas pressure). The concentration of each component was used to determine the yield and dissociation selectivity, as well as their change in the enrichment process. Selective dissociation of CF_2Br_2 in an oxygen environment resulted in the conversion of the ^{12}C -containing component predominantly into the COF_2 dissociation product, while the remaining CF_2Br_2 was enriched in ^{13}C to a concentration of 99% or higher.

A Specord-M82 computerised dual-beam IR spectrophotometer was used to determine the concentration of each component at a high concentration of $^{12}\text{CF}_2\text{Br}_2$ (from 70% to about 5%). The concentrations were measured from the intensity of the absorption bands of ^{12}C - and ^{13}C -containing components of the $\nu_8 = 831\text{ cm}^{-1}$ ($^{12}\text{CF}_2\text{Br}_2$) mode, since the bands of isotopic components are well resolved only for this mode. When the content of $^{12}\text{CF}_2\text{Br}_2$ was reduced below 5%, a highly sensitive Clarus 500 chromatograph/mass spectrometer was used. The ^{12}C and ^{13}C concentrations were measured by mass peaks with a mass-to-charge ratio of $m/e = 129, 130$ from $^{12}\text{CF}_2^{79}\text{Br}^+$ and $^{13}\text{CF}_2^{79}\text{Br}^+$ fragment ions.

The experimental procedure was as follows. For irradiation, we used a stainless steel cell with KBr windows 11.2 cm long, pre-pumped by a forevacuum pump through a nitrogen trap to a residual pressure of 7.5×10^{-3} Torr (1 Pa). The cell was filled with a mixture of enriched CF_2Br_2 with a 30% concentration of ^{13}C and oxygen. Next, the gas mixture was sequentially irradiated with portions of N pulses. After each

series of laser pulses, the MPD yields and selectivity were determined. The selectivity of dissociation with respect to the ^{12}C component was determined as the yield ratio $\alpha(12/13) = \beta_{12}/\beta_{13}$. Dissociation yields β_i ($i = 12, 13$) were calculated from the partial pressure of each component before ($p_{i,0}$) and after (p_i) irradiation with N laser pulses. Here $p_{i,0}$ was taken as the current partial pressure of the components before the onset of a new series of laser pulses. To calculate β_i , the following formula was used [31]:

$$\beta_i = \Gamma^{-1}[1 - (p_i/p_{i,0})^{1/N}], \quad (1)$$

where Γ is the ratio of the irradiated volume to the cell volume.

5. Results and discussion

The results of ^{12}C -selective multiphoton dissociation of CF_2Br_2 under sequential irradiation of a sample of the $\text{CF}_2\text{Br}_2 + \text{O}_2$ gas mixture are shown in Fig. 1, which demonstrates the IR spectra of the absorption bands of ^{12}C - and ^{13}C -containing ν_8 -mode components. It can be seen that the $^{12}\text{CF}_2\text{Br}_2$ band decreases with irradiation until it almost completely disappears, while the $^{13}\text{CF}_2\text{Br}_2$ band changes insignificantly. When calculating the concentration of $^{13}\text{CF}_2\text{Br}_2$, we took into account the contribution of the R-branch of the $\nu_6 = 774\text{ cm}^{-1}$ band [32] from the $^{12}\text{COF}_2$ dissociation product accumulated in the mixture during irradiation.

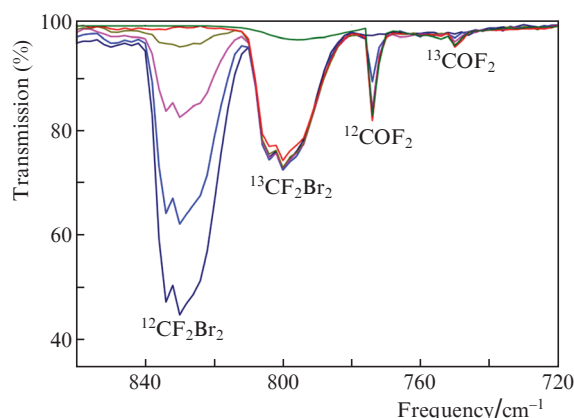


Figure 1. (Colour online) IR spectra of absorption bands of ν_8 modes of $^{12}\text{CF}_2\text{Br}_2$ and $^{13}\text{CF}_2\text{Br}_2$ under sequential laser irradiation of the $\text{CF}_2\text{Br}_2 + \text{O}_2$ mixture at a frequency of 1084.6 cm^{-1} [CO_2 laser generation line 9R(30)] and a fluence of 2.6 J cm^{-2} . Initial pressures are: CF_2Br_2 , 1 Torr; and O_2 , 30 Torr. The green line corresponds to the R-branch of the ν_6 band for $^{12}\text{COF}_2$ at the end of irradiation.

The kinetics of reducing the concentration of the ‘burnt-out’ $^{12}\text{CF}_2\text{Br}_2$ component with increasing number of laser pulses is shown in Fig. 2 for two laser radiation frequencies. Note that in both cases, with an approximately equal number of pulses (300–350), a $^{12}\text{CF}_2\text{Br}_2$ concentration of less than 1% and, accordingly, a $^{13}\text{CF}_2\text{Br}_2$ concentration of more than 99% are reliably achieved. This is not surprising, since the MPD yields of the $^{12}\text{CF}_2\text{Br}_2$ molecules at both frequencies, as shown below, are approximately equal.

The dependences of the dissociation yields β_{12} and β_{13} of the $^{12}\text{CF}_2\text{Br}_2$ and $^{13}\text{CF}_2\text{Br}_2$ molecules and the selectivity $\alpha(12/13) = \beta_{12}/\beta_{13}$ on the number of laser pulses under succes-

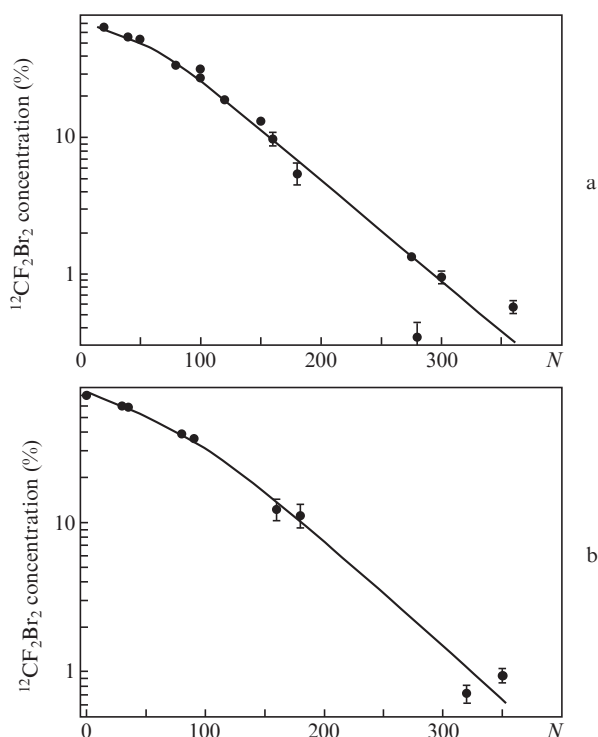


Figure 2. (Colour online) Dependences of the concentration of $^{12}\text{CF}_2\text{Br}_2$ on the number of laser pulses during sequential irradiation of the $\text{CF}_2\text{Br}_2 + \text{O}_2$ mixture with laser radiation at a frequency of (a) 1078.6 and (b) 1084.6 cm^{-1} [CO_2 laser generation lines 9R(20) and 9R(30), respectively] and a fluence of 2.6 J cm^{-2} . Initial pressures are: CF_2Br_2 , 1 Torr; and O_2 , 30 Torr.

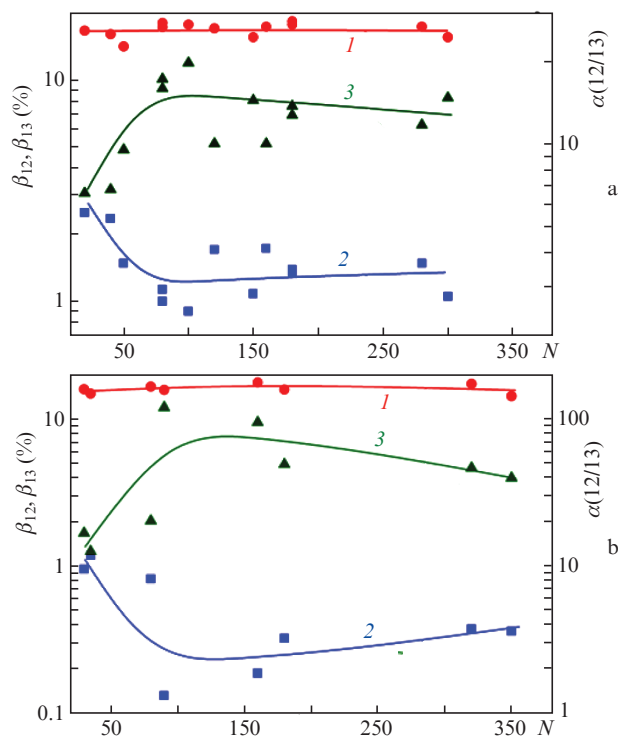


Figure 3. (Colour online) Dependences of dissociation yields (1) β_{12} and (2) β_{13} and selectivity $\alpha(12/13)$ (3) on the number of laser pulses during sequential irradiation of the $\text{CF}_2\text{Br}_2 + \text{O}_2$ mixture with laser radiation at a frequency of (a) 1078.6 and (b) 1084.6 cm^{-1} [CO_2 laser generation lines 9R(20) and 9R(30), respectively] and a fluence of 2.6 J cm^{-2} . Initial pressures are: CF_2Br_2 , 1 Torr; and O_2 , 30 Torr.

sive irradiation of the $\text{CF}_2\text{Br}_2 + \text{O}_2$ mixture are shown in Fig. 3. Three main points that are characteristic of these dependences deserve discussion. First, let us pay attention to the high (15%–18%) dissociation yields β_{12} with respect to the ‘burnt-out’ $^{12}\text{CF}_2\text{Br}_2$ component, which are achieved at a very moderate laser radiation fluence of 2.6 J cm^{-2} . In the long run, this makes it possible to implement high productivity of the enrichment process. In addition, the value of β_{12} virtually does not depend on the current concentration of $^{12}\text{CF}_2\text{Br}_2$. Second, an increase in the laser radiation frequency leads to a significant increase in the selectivity of dissociation: from 13–15 at 1078.6 cm^{-1} to 40–75 at 1084.6 cm^{-1} . As a result, the losses of the desirable $^{13}\text{CF}_2\text{Br}_2$ component significantly decrease (from 40%–50% to ~15%), while the enrichment process productivity proportionally increases. Third, at both laser radiation frequencies, there is a part of selectivity growth at the onset of irradiation. It is within this initial part that the $^{12}\text{CF}_2\text{Br}_2$ and $^{13}\text{CF}_2\text{Br}_2$ concentrations are equalised. This can be seen by comparing the kinetic dependences of the $^{12}\text{CF}_2\text{Br}_2$ concentration and selectivity shown in Figs 2 and 3. Thus, a significant reserve for reducing the losses of a component with the desirable isotope $^{13}\text{CF}_2\text{Br}_2$ consists in using enriched CF_2Br_2 with a ^{13}C concentration of 50% and higher.

The increase in the MPD selectivity $\alpha(12/13) = \beta_{12}/\beta_{13}$ at the initial stage of CF_2Br_2 irradiation is, in our opinion, due to the influence of inter-isotope vibrational–vibrational (VV) exchange [31], which leads to the transfer of vibrational energy from selectively excited $^{12}\text{CF}_2\text{Br}_2$ molecules to $^{13}\text{CF}_2\text{Br}_2$ molecules during the laser pulse action. When the concentration of $^{12}\text{CF}_2\text{Br}_2$ molecules is still high (70%), the portion of vibrational energy transferred to $^{13}\text{CF}_2\text{Br}_2$ molecules is also

large, which contributes to an increase in the dissociation yield of $^{13}\text{CF}_2\text{Br}_2$. With an increase in the number of laser pulses, the concentrations of $^{12}\text{CF}_2\text{Br}_2$ and $^{13}\text{CF}_2\text{Br}_2$ align, and the proportion of vibrational energy transferred to $^{13}\text{CF}_2\text{Br}_2$ molecules decreases, which manifests itself in a decrease in the dissociation yield of $^{13}\text{CF}_2\text{Br}_2$ and a corresponding increase in selectivity (see Fig. 3).

The assumption about the decisive role of the VV exchange in the growth of dissociation selectivity at the initial stage of the ‘burning-out’ of $^{12}\text{CF}_2\text{Br}_2$ molecules is confirmed by the kinetic dependences of the dissociation yields β_{12} and β_{13} and selectivity $\alpha(12/13)$ with an increase in the pressure of CF_2Br_2 to 4 Torr (Fig. 4). It can be seen that with an increase in pressure from 1 to 4 Torr, the dissociation selectivity $\alpha(12/13)$ sharply decreases at the beginning of irradiation from 13–15 to 3 (compare Figs 3b and 4).

One more useful feature of the proposed method for obtaining highly enriched (99% and higher) carbon-13 should be noted. Due to the finite MPD selectivity of $^{12}\text{CF}_2\text{Br}_2$ molecules, the COF_2 dissociation product is slightly enriched with ^{13}C . For example, at a CO_2 laser radiation frequency of 1084.6 cm^{-1} , at the end of irradiation, the concentration of $^{13}\text{COF}_2$ reaches ~5%. The COF_2 product readily hydrolyses to form CO_2 enriched in ^{13}C , which can then be used as a working substance for traditional separation methods.

6. Conclusions

A new method for arranging a two-stage process of carbon isotope separation is considered, which allows us to obtain carbon-13 with a concentration of at least 99% with high pro-

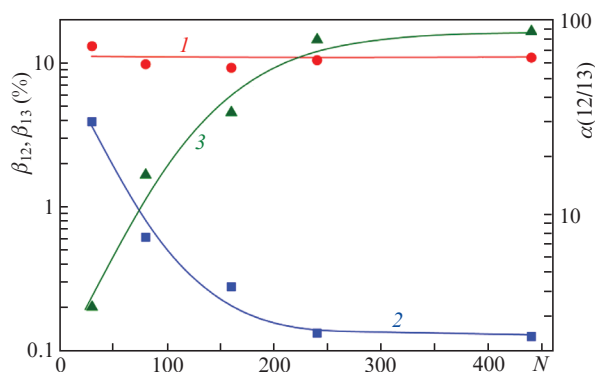


Figure 4. (Colour online) Dependences of (1) β_{12} and (2) β_{13} dissociation yields and the selectivity $\alpha(12/13)$ (3) on the number of laser pulses in sequential irradiation of a $\text{CF}_2\text{Br}_2 + \text{O}_2$ mixture by laser radiation at a frequency of 1084.6 cm^{-1} [CO_2 laser generation line 9R(30)] and a fluence of 2.6 J cm^{-2} . Initial pressures are: CF_2Br_2 , 4 Torr; and O_2 , 30 Torr.

ductivity. For this purpose, we propose to use Freon-12B2 (CF_2Br_2) with 30% and higher enrichment in ^{13}C as a working substance for the second enrichment stage, which is quite simply synthesised from enriched ^{13}C of the first stage, and also use, for enrichment in ^{13}C , the method of selective deep ‘burning-out’ of the ^{12}C -containing component.

Experiments have been carried out on multiphoton dissociation of Freon-12B2 with a 30% initial concentration of $^{13}\text{CF}_2\text{Br}_2$ molecules in a mixture with oxygen by pulsed radiation from CO_2 laser. The possibility has been shown of reaching a 99% and higher concentration of $^{13}\text{CF}_2\text{Br}_2$. The main separation elementary act parameters – the MPD yield and selectivity with respect to ^{12}C -containing component – have been measured in the process of its ‘burning-out’. High yield values for $^{12}\text{CF}_2\text{Br}_2$ component ($\beta_{12} = 15\%–18\%$) and selectivity [$\alpha(12/13) = 40–75$] have been obtained at a moderate laser radiation fluence of 2.6 J cm^{-2} . The obtained results allow us to hope for the further development of an effective, purely laser process for producing carbon-13 with the required ^{13}C concentration of at least 99%.

References

- Baranov V.Yu. (Ed.) *Izotopy: svoystva, poluchenie, primeneniye* (Isotopes: Properties, Production, Application) (Moscow: Fizmatlit, 2005) Vol. 1.
- Khoroshilov A.V. *J. Phys.: Conf. Ser.*, **1099**, 012002 (2018).
- El'man A.R., Korneeva G.A., Noskov Yu.G. *Ros. Khim. Zh.*, **LVII**, 3 (2013).
- Baranov V.Yu., Dyad'kin A.P., Malyuta D.D., Kuzmenko V.A., Pigil'skii S.V., Mezhevov V.S., Letokhov V.S., Laptev V.B., Ryabov E.A., Yarovoy I.V., Zarin V.D., Podoryashy A.S. *Proc. SPIE*, **4165**, 314 (2000).
- Pigul'skii S.V. Doct. Diss. (Moscow: Scientific and Technological Centre for Unique Instrumentation of the Russian Academy of Sciences, 2009).
- Gauthier M., Cureton C.G., Hackett P.A., Willis C. *Appl. Phys. B*, **28**, 43 (1982).
- Evseev A.V., Laptev V.B., Pureskii A.A., Ryabov E.A., Furzikov N.P. *Sov. J. Quantum Electron.*, **18** (3), 385 (1988) [*Kvantovaya Elektron.*, **15**, 606 (1988)].
- Abdushelishvili G.I., Avatkov O.N., Bagratashvili V.N., Baranov V.Yu., Bakhtadze A.B., Velikhov E.P., Vetsko V.M., Gverdtseteli I.G., Dolzhikov V.S., Esadze G.G., Kazakov S.A., Kolomiiski Yu.R., Letokhov V.S., Pigul'skii S.V., Pismennyi V.D., Ryabov E.A., Tkeshelashvili G.I. *Sov. J. Quantum Electron.*, **12** (4), 459 (1982) [*Kvantovaya Elektron.*, **9**, 743 (1982)].
- Gauthier M., Outhouse A., Ishikawa Y., Kutschke K.O., Hackett P.A. *Appl. Phys. B*, **35** (3), 173 (1984).
- Apatin V.M., Laptev V.B., Ryabov E.A., Petin A.N. *Khim. Vys. Energ.*, **37** (2), 133 (2003).
- Arai S., Watanabe T., Ishikawa Y., Oyama T., Hayashi O., Ishii T. *Chem. Phys. Lett.*, **112** (3), 224 (1984).
- Arai S., Sugita K., Ma P., Ishikawa Y., Kaetsu H., Isomura S. *Chem. Phys. Lett.*, **151**, 516 (1988).
- Arai S., Sugita K., Ma P., Ishikawa Y., Kaetsu H., Isomura S. *Appl. Phys. B*, **48**, 427 (1989).
- Velichko A.M., Nadeikin A.A., Nikitin A.I., Pimenova N.V., Talroze V.L. *Khim. Vys. Energ.*, **21** (3), 251 (1987).
- Ma P., Sugita K., Arai S. *Chem. Phys. Lett.*, **137** (6), 590 (1987).
- Ma P., Sugita K., Arai S. *Appl. Phys. B*, **49**, 503 (1989).
- Ma P., Sugita K., Arai S. *Appl. Phys. B*, **51**, 103 (1990).
- Ma P., Sugita K., Arai S. *Appl. Phys. B*, **50**, 385 (1990).
- Baranov V.Yu., Dyad'kin A.P., Kuz'menko V.A. *Khim. Vys. Energ.*, **25**, 181 (1991).
- Laptev V.B., Ryabov E.A. *Khim. Vys. Energ.*, **33**, 406 (1999).
- Dyad'kin A.P., Kuz'menko V.A., Laptev V.B., Pigul'skii S.V., Ryabov E.A. *Khim. Vys. Energ.*, **34**, 371 (2000).
- Bittenson S., Houston P.L. *J. Chem. Phys.*, **67**, 4819 (1977).
- Fuss W., Schmid W.E. *Ber. Bunsenges Phys. Chem.*, **83**, 1148 (1979).
- Avatkov O.N., Vetsko V.M., Esadze G.G., Kaminskii A.V., Tkeshelashvili G.I. *Sov. J. Quantum Electron.*, **8**, 1119 (1981) [*Kvantovaya Elektron.*, **11**, 668 (1981)].
- Kojima H., Fukumi T., Nakajima S., Maruyama Y., Kosasa K. *Chem. Phys. Lett.*, **95**, 614 (1983).
- Velikhov E.P., Letokhov V.S., Makarov A.A., Ryabov E.A. *Sov. J. Quantum Electron.*, **6**, 317 (1979) [*Kvantovaya Elektron.*, **9** (2), 179 (1979)].
- Laptev V.B., Pigul'skii S.V. RF Patent No. 2712592 (2020).
- Baranov V.Yu., Dyad'kin A.P., Kuz'menko V.A., Pigul'skii S.V. *Proc. 5th All-Russian (Int.) Sci. Conf. 'Physico-Chemical Processes In the Selection of Atoms and Molecules'* (Zvenigorod, 2000) p. 77.
- Laptev V.B. *Proc. 10th Int. Sci. Conf. 'Physico-Chemical Processes In the Selection of Atoms and Molecules'* (Zvenigorod, 2005) p. 94.
- Laptev V.B., Pigul'skii S.V. *Khim. Vys. Energ.*, **52**, 215 (2018).
- Velikhov E.P., Baranov V.Yu., Letokhov V.S., Ryabov E.A., Starostin A.N. *Impul'snye CO₂-lazery i ikh primeneniye dlya razdeleniya izotopov* (Pulsed CO_2 Lasers and Their Application for Isotope Separation) (Moscow: Nauka, 1983).
- Shimanouchi T. *J. Phys. Chem. Ref. Data*, **6**, 993 (1972).