

# SINGLE PULSE CARBON-13 ENRICHMENT OF CF<sub>3</sub>I UNDER IR MPD IN A SHORT GAS DYNAMIC FLOW

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An experimental approach is described for obtaining highly enriched residual gas under IR multiphoton dissociation (MPD) of molecules in one cycle of irradiation. The approach is based on utilization of a pulsed molecular flow of small length ( $\Delta x_{fl} \leq 1$  cm). The use of a short flow length leads to high values of the dissociation yield of molecules ( $\beta \approx 1$ ) in the whole volume of the flow. Owing to this, high enrichment of the residual gas is achieved in one cycle of irradiation. The isotopically-selective dissociation of CF<sub>3</sub>I in the pulsed gasdynamic flow of a small length was studied. About 400-fold enrichment of the <sup>13</sup>C isotope in the residual gas was obtained following irradiation of a molecular flow of CF<sub>3</sub>I of natural isotope composition by a single laser pulse. The selectivity of dissociation was measured to be  $\alpha \geq 10$ .

*Keywords:* Laser isotope separation; selective IR multiphoton dissociation of molecules; pulsed molecular beams and flows

## 1. INTRODUCTION

The important problem in laser isotope separation by the IR MPD of molecules [1, 2] is increase of selectivity, especially in the case of molecules with a small isotope shift (like OsO<sub>4</sub>, UF<sub>6</sub>...).

The most effective means to increase the selectivity of the dissociation is the cooling of the mixture of isotopomers in gasdynamic jets or flows [3–5]. However, in flow conditions problems appear connected with the collection of the products. Because of high

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chemical activity of the radicals formed in the course of dissociation of molecules and their small concentration in the flow conditions, it is rather difficult to realize the formation and effective collection of the products. Reactions on the walls can dominate and change fundamentally the kinetics and the channels of product formation.

Besides, in the case of dissociation of molecules with a small isotope shift the achievable selectivities are as a rule rather small ( $\leq 3-5$ ). As a result it is impossible to obtain highly enriched product in one cycle of irradiation of initial gas. Therefore, in many cases it is preferable to dissociate molecules containing unwanted isotopes in the mixture and thereby enrich the desirable isotope in the residual gas.

However, in the case of gas dynamic jets and flows, high enrichment factors in the residual gas are impossible to obtain, if circulation of the gas to allow multi-fold irradiation is not realized. So, in the case of continuous molecular flow, which moves along the  $x$ -axis with the mean velocity  $\nu_X$ , one can irradiate by the laser only the part  $\eta$  of molecules as determined by the expression:

$$\eta = \frac{\Delta x_L f}{\nu_X}, \quad (1)$$

where  $\Delta x_L$  is the laser beam size in the direction of  $x$ -axis, and  $f$  is the repetition rate of the laser pulses. Here we have assumed that the laser beam is directed perpendicular to the  $x$ -axis, and the flow in the directions of  $y$ - and  $z$ -axis is confined and totally irradiated by the laser.

With the pulsed-periodic  $\text{CO}_2$ -lasers [6] one can realize the parameters  $\Delta x_L \simeq 1$  cm and  $f \simeq 500$  Hz. With a characteristic mean velocity of molecular flow  $\nu_X \simeq 5 \cdot 10^4$  cm/s the fraction of irradiated molecules will be  $\eta \simeq 10^{-2}$ . (Here we have taken into account the fact, that the  $\text{CO}_2$ -laser pulse duration is  $\tau_p \leq 1 \mu\text{s} \ll \Delta x_L / \nu_X$ , and therefore during the irradiating pulse the position of the flow in the space will be practically not changed). If the dissociation yield is equal to  $\beta \approx 0.2$ , then the fraction of dissociated molecules in the flow will be  $\eta\beta = \eta\beta \simeq 2 \cdot 10^{-3}$ . Consequently, the enrichment factor in the residual gas in one cycle of irradiation will be very small.

The situation is better when pulsed molecular flows are used. With a characteristic opening time of the pulsed nozzle  $\tau_{\text{noz}} \simeq 200 \mu\text{s}$  the

molecular flow will have the length  $\Delta x_{\text{fl}} \simeq \nu_{\text{X}} \tau_{\text{noz}} \simeq 10$  cm. In this case a single laser pulse can irradiate  $\eta = \Delta x_L / \Delta x_{\text{fl}} \simeq 0.1$  part of the molecules in the flow. With  $\beta \simeq 0.2$  we will obtain  $\eta_{\beta} \simeq 2 \cdot 10^{-2}$ . However, this is still rather small fraction, and consequently, the enrichment factor in the residual gas will be small as well.

In principle another situation is reached, when dissociation is carried out in a short pulsed gas dynamic flow ( $\Delta x_{\text{fl}} \leq 1$  cm), which one can obtain by means of a pulsed nozzle with a short opening time ( $\tau_{\text{noz}} \leq 20$   $\mu$ s). In this case one can subject all the flow to irradiation by a highly intense IR laser. The enrichment factor in the residual gas will be mainly determined by the dissociation yield of the resonantly excited molecules. With the dissociation yield  $\beta \simeq 1$  one can obtain high enrichment factors in the residual gas as a result of irradiation of a mixture of isotopomers by a single laser pulse even at moderate selectivities, *i.e.*,  $\alpha \geq 3$ .

Since the absorption spectra of molecules are narrowed due to cooling in the gasdynamic flow [5], one can obtain comparatively high selectivity ( $\alpha \geq 5-10$ ) even at high energy fluences. Owing to this the dissociation of the desired isotopic component is limited.

Such an approach has been developed in this work and its possibilities studied using the CF<sub>3</sub>I molecule. About 400-fold enrichment of the residual gas by <sup>13</sup>C isotope was obtained under irradiation of CF<sub>3</sub>I of natural isotope composition ( $\simeq 1.1\%$  of <sup>13</sup>C,  $\simeq {}^{12}\text{C}/{}^{13}\text{C} \simeq 90$ ) in a molecular flow by a single laser pulse. The dissociation yield of <sup>12</sup>CF<sub>3</sub>I molecules and the selectivity of the dissociation in this experiment were measured to be  $\beta_{12} \simeq 1$  and  $\alpha \geq 10$ , accordingly.

## 2. THE CHOICE OF THE OBJECT FOR STUDY

The CF<sub>3</sub>I molecule was chosen for study on the following reasons. It has a rather low dissociation energy ( $\simeq 2.3$  eV [7]) and effectively dissociates at moderate energy fluences  $\Phi \leq 4$  J/cm<sup>2</sup> [8–11]. Therefore, with this molecule it is easy to realize the conditions at which the dissociation yield  $\beta \simeq 1$  can be achieved. In the dissociation of CF<sub>3</sub>I stable products (C<sub>2</sub>F<sub>6</sub> and I<sub>2</sub>) are formed. The IR multiphoton excitation (MPE) and dissociation (MPD) of this molecule are rather

well studied [8–12]. The IR multiphoton absorption of  $\text{CF}_3\text{I}$  was also investigated [13] under molecular beam conditions.  $\text{CF}_3\text{I}$  has been considered [14] as a starting substance for the large scale laser separation of carbon isotopes. Furthermore, the IR absorption spectra of  $^{12}\text{CF}_3\text{I}$  and  $^{13}\text{CF}_3\text{I}$  isotopomers are well studied and the isotope shifts in these spectra are measured [15], making it easier to choose selective frequencies.

### 3. THE RELATION BETWEEN THE PARAMETERS OF THE SEPARATION PROCESS IN CONDITIONS OF THE PRESENT EXPERIMENT

In conditions when all the molecular flow is irradiated by the laser the concentrations of molecules in a two-component mixture after the action of a laser pulse will be:

$$N_1 = N_{10}(1 - \beta_1), \quad (2)$$

$$N_2 = N_{20}(1 - \beta_2), \quad (3)$$

where  $N_{10}$  and  $N_{20}$  are the concentrations of isotopomers in an initial mixture,  $\beta_1$  and  $\beta_2$  are the dissociation yields of these molecules, accordingly.

Let the laser radiation be in resonance with the molecules marked by index 1. Then  $\beta_1 > \beta_2$ . The selectivity of the dissociation will be:

$$\alpha = \beta_1/\beta_2. \quad (4)$$

The enrichment factor in the residual gas will be determined by the expression:

$$K_2^{\text{res}} = \frac{N_2/N_1}{N_{20}/N_{10}} = \frac{N_2 N_{10}}{N_{20} N_1}, \quad (5)$$

or, taking in to account (2), (3) and (4) it will be:

$$K_2^{\text{res}} = \frac{1 - \beta_2}{1 - \beta_1} = \frac{1 - \beta_1/\alpha}{1 - \beta_1} \quad (6)$$

The enrichment factor in the products will be equal to:

$$K_1^{\text{prod}} = \frac{N_{1\text{prod}}}{N_{2\text{prod}}} \bigg/ \frac{N_{10}}{N_{20}} = \frac{\beta_1 N_{10}}{\beta_2 N_{20}} \bigg/ \frac{N_{10}}{N_{20}} = \beta_1 / \beta_2 = \alpha \quad (7)$$

Therefore, to obtain the highly enriched product it is necessary to realize a rather high selectivity in the dissociation process, which is not easily achieved in many cases even with cooled gas.

However, one can obtain (even at moderate selectivities  $\alpha \geq 3$ ) highly enriched residual gas. As follows from relation (6), the enrichment factor  $K_2^{\text{res}}$  depends only slightly on the selectivity  $\alpha$  (if  $\alpha \geq 3$ ), but very strongly on the dissociation yield in the region  $\beta_1 \simeq 1$ . It is clearly seen from Figure 1, where the dependences  $K_2^{\text{res}}(\beta_1)$  are shown for different  $\alpha$ . For example, at  $\beta_1 \simeq 0.95$  the change of  $\alpha$  from 2 to  $10^3$  gives rise to the increase of  $K_2^{\text{res}}$  only from about 10 to about 20. However, practically independent of  $\alpha$  (if  $\alpha \geq 3$ ),  $K_2^{\text{res}}$  reaches high values at  $\beta_1 \rightarrow 1$ . So, at  $\alpha = 5$ , the increase of  $\beta_1$  from 0.9 to 0.99 results in increase of  $K_2^{\text{res}}$  from about 10 to about 100. At  $\beta_1 \rightarrow 1$   $K_2^{\text{res}} \rightarrow \infty$ .

Consequently, if experimental conditions are realized in which all the molecular flow is subjected to irradiation by the laser and the dissociation yield of resonantly excited molecules reaches the value  $\beta \simeq 1$ , then a high degree of enrichment can be obtained in the residual gas as a result of irradiation by a single laser pulse. These are conditions were realized in the present experiments.

#### 4. EXPERIMENTAL

A scheme of the experimental setup is shown in Figure 2a. To obtain a short molecular flow a "current loop" type pulsed nozzle [16] was used. The opening time of the nozzle was about 18  $\mu\text{s}$  (at half maximum). The diameter of the nozzle aperture was 0.75 mm. The CF<sub>3</sub>I pressure in the nozzle  $p_0$  could be varied from 1 to 5 atm. The number of molecules,  $N$ , flowing from the nozzle per pulse depended on  $p_0$  and at  $p_0 \simeq 2$  atm  $N$  was equal to about  $10^{16}$  molecules/pulse. The nozzle could operate both in single pulse regime and at repetition rate up to 1 Hz.

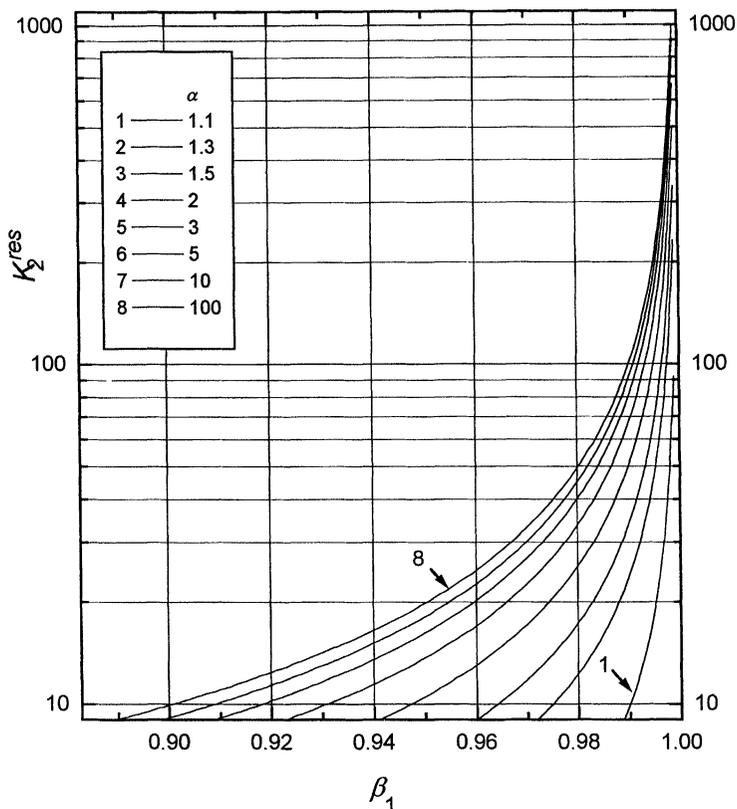


FIGURE 1 The dependence of the enrichment factor in the residual gas  $K_2^{\text{res}}$  on the dissociation yield  $\beta_1$  (in the region  $0.9 \leq \beta_1 < 1$ ) at different values of selectivity  $\alpha$  in the case of irradiation of two-component mixture of isotopomers in conditions  $\beta_1 > \beta_2$ .

The vacuum chamber ( $V_{\text{ch}} \approx 20\ell$ ) in which the molecular flow was formed was pumped down to a pressure  $p \leq 10^{-5}$  Torr by a turbomolecular pump (TMP-500, 500 l/s). The pressure in the chamber was measured by an ionization detector (PMI-10). The number of molecules  $N$  was determined from the increase in pressure,  $\Delta p$ , in the vacuum chamber after  $n$  pulses of the nozzle, carried out with the pump closed off:

$$N = (p_{\text{fin}} - p_{\text{in}}) V_{\text{ch}}/nkT = \Delta p V_{\text{ch}}/nkT, \quad (T \approx 300 \text{ K}) \quad (8)$$

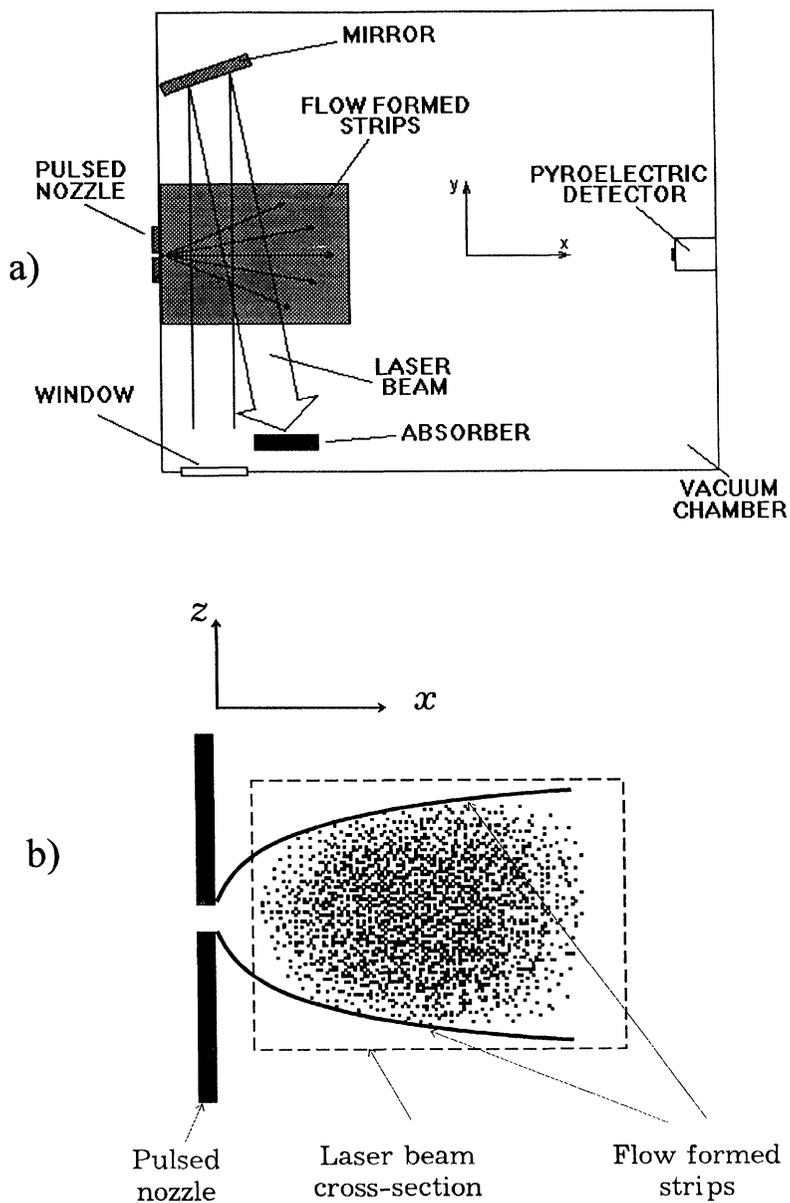


FIGURE 2 The scheme of the experimental setup and the geometry of irradiation of the molecular flow by the laser.

The opening time of the nozzle,  $\tau_{\text{noz}}$ , and the mean flow velocity,  $\nu_x$ , were determined with a pyroelectric detector using a time of flight technique [17, 18]. The mean  $\text{CF}_3\text{I}$  flow velocity in the excitation zone was  $\nu_x = (400 \pm 20)\text{m/s}$  [19].

The molecular flow was formed (Fig. 2b) with the help of two thin ( $100\ \mu\text{m}$ ) metallic strips. In the plane  $xz$  they had a variable radius of curvature. The maximum angle of opening of the strips (near the nozzle exit) was about  $60^\circ$ . The dimensions of the strips were  $2.5 \times 2.5\text{cm}^2$ . The minimum distance between the strips (near the nozzle excite) was about 1.5 mm and the maximum one was about 8 mm. Since the pulse of molecules flowing from the nozzle had the length  $\Delta x_{\text{fl}} \simeq \nu_x \tau_{\text{noz}} \simeq 7.2\text{mm}$ , it was totally enclosed in the space between the strips. Exactly at the moment when the molecules flew through this space they were subjected to irradiation.

Excitation was carried out using a line to line tunable TEA  $\text{CO}_2$ -laser. The energy in the laser pulse was up to 3 J. The laser radiation was slightly focused ( $f_L = 1\text{m}$ ) and directed into the vacuum chamber in the region between the strips which confined the molecular flow. The laser beam was perpendicular to the flow axis. The shortest distance from the nozzle exit to the excitation zone was about 3 mm. In the excitation region the laser beam cross-section was about  $6 \times 6\text{mm}^2$ . In the  $y$ - and  $z$ -direction the laser beam irradiated all the space between the strips, while in the  $x$ -direction its size  $\Delta x_L \simeq 6\text{mm}$  was less than the flow length  $\Delta x_{\text{fl}} \simeq 7.2\text{mm}$ . In order to irradiate all the flow, the laser beam was reflected by small angle back, so that the length of the irradiating volume in the  $x$ -direction was about 12 mm. Therefore, all the molecular flow could be irradiated by highly intensive IR laser radiation. The energy fluence in the excitation zone was up to  $8\text{J/cm}^2$ . At such energy fluence the dissociation yield of  $\text{CF}_3\text{I}$  is practically equal to unit [11, 14].

The synchronization of the  $\text{CO}_2$ -laser, the pulsed nozzle and the detection system was carried out with the help of the generator of delayed pulses GI-1.

## 5. THE PROCEDURE OF COLLECTION OF THE RESIDUAL GAS AND PRODUCTS AND THEIR ANALYSIS

In addition to the main pump outlet the vacuum chamber had another (bypass) pump outlet, in which a liquid nitrogen trap, a gas cell with

small trap and a manometer were assembled. The vacuum chamber could be pumped also through this channel. We used in this channel a forvacuum pump.

The procedure of irradiation and collection of the gas was as follows. At first the vacuum chamber and the nitrogen trap were pumped down to about  $10^{-5}$  Torr by turbomolecular pump. After that the pump channel was closed, the cryogenic trap was cooled and the irradiation of CF<sub>3</sub>I molecules in the flow was started. The residual CF<sub>3</sub>I gas and the products (mainly C<sub>2</sub>F<sub>6</sub>) were collected in the trap.

The irradiation cycle consisted of from 50 to 500 pulses. During the irradiation time the pressure in the vacuum chamber did not increase above  $10^{-2}$  Torr. For example, the increase of pressure in the vacuum chamber for 500 pulses was equal to  $\Delta p_{\text{ch}} = \Delta N_{\Sigma} kT / V_{\text{ch}} \simeq 7 \cdot 10^{-3}$  Torr. (Here  $\Delta N_{\Sigma} = 5 \cdot 10^{18}$  is the number of molecules delivered from the nozzle into the chamber for 500 pulses and  $V_{\text{ch}} \simeq 2 \cdot 10^4 \text{ cm}^3$  is the volume of the vacuum chamber). The effective pressure of the CF<sub>3</sub>I molecules in the irradiation zone was  $p_{\text{eff}} = NkT / V_{\text{fl}} \simeq 0.2$  Torr ( $V_{\text{fl}} \simeq 1 \text{ cm}^3$  is the volume of the flow).

After the irradiation cycle was finished, the vacuum chamber was filled with oxygen to pressure of about 1 Torr. After a while the gas from the chamber was slowly pumped through the bypass channel. In this way only the oxygen was pumped while the CF<sub>3</sub>I and C<sub>2</sub>F<sub>6</sub> collected in the trap. Following this, gas from the trap was transferred into the gas cell for the analysis.

The analysis of the gas was carried out using a "Specord-75 IR" IR spectrophotometer. The absorption of the gas in the region from 600 to 1400  $\text{cm}^{-1}$ , where the most intensive absorption bands of CF<sub>3</sub>I and C<sub>2</sub>F<sub>6</sub> lie, was recorded. The enrichment of the residual gas in the <sup>13</sup>C or <sup>12</sup>C isotope was determined on the IR absorption of CF<sub>3</sub>I in the region of the  $\nu_4$  vibrational band (1187  $\text{cm}^{-1}$  for the <sup>12</sup>CF<sub>3</sub>I [15]), where the absorption spectra of <sup>12</sup>CF<sub>3</sub>I and <sup>13</sup>CF<sub>3</sub>I isotopomers are rather well resolved ( $\Delta\nu_{\text{is}} \simeq 33 \text{ cm}^{-1}$  [15]). More accurately the enrichment factor in the residual CF<sub>3</sub>I as well as in the product C<sub>2</sub>F<sub>6</sub> was determined from mass-spectra taken with MX-7303 mass-spectrometer. The isotope composition of CF<sub>3</sub>I was determined on the CF<sub>3</sub>I<sup>+</sup> ion peaks ( $m/e = 196$  and  $197$ ) and the isotope composition of the C<sub>2</sub>F<sub>6</sub> was done on C<sub>2</sub>F<sub>5</sub><sup>+</sup> ion peaks ( $m/e = 119$ ,  $120$  and  $121$ ).

## 6. RESULTS AND DISCUSSION

The excitation of  $\text{CF}_3\text{I}$  was carried out in the  $\nu_1$  vibrational band ( $1075\text{ cm}^{-1}$  for the  $^{12}\text{CF}_3\text{I}$  and  $1047.1\text{ cm}^{-1}$  for the  $^{13}\text{CF}_3\text{I}$ ,  $\Delta\nu_{\text{is}} \simeq 27.9\text{ cm}^{-1}$  [15]). The  $^{12}\text{CF}_3\text{I}$  molecules were excited by the  $9\text{R}(10) - 1071.9\text{ cm}^{-1}$  or  $9\text{R}(12) - 1073.3\text{ cm}^{-1}$  laser lines, while the  $^{13}\text{CF}_3\text{I}$  molecules were excited by the  $9\text{P}(24)$  line -  $1043.2\text{ cm}^{-1}$ . As it was shown in [13], the  $9\text{R}(10)$  and  $9\text{R}(12)$  lines are optimal for the dissociation of  $^{12}\text{CF}_3\text{I}$  molecules in the pulsed jet.

The results obtained are shown in Figures 3(a–d). Figure 3a presents the absorption spectrum of nonirradiated  $\text{CF}_3\text{I}$  molecules. The ratio of isotopomers in the mixture was measured to be natural. Figure 3b shows the spectrum of the  $\text{CF}_3\text{I}$  molecules irradiated in the flow by the  $9\text{R}(10)$  laser line at a fluence  $\Phi \simeq 8\text{ J/cm}^2$ . In this experiment the laser beam crossed the molecular flow only in one direction. The reflecting mirror was not mounted. Therefore not all the molecules in flow were irradiated by the laser ( $\Delta x_L < \Delta x_{\text{fl}}$ ,  $\Delta x_L \simeq 6\text{ mm}$ ,  $\Delta x_{\text{fl}} \simeq 7.2\text{ mm}$ ). Almost 7-fold enrichment of the residual  $\text{CF}_3\text{I}$  in the  $^{13}\text{C}$  isotope was obtained ( $K_{13}^{\text{res}} \simeq 6.8$ ). Figure 3c shows the absorption spectrum of the  $\text{CF}_3\text{I}$  irradiated in the flow by the  $9\text{R}(12)$  laser line under conditions where all molecules were excited by the laser (reflecting mirror was mounted). The excitation energy fluence was  $\Phi \simeq 3.5\text{ J/cm}^2$ . At such energy fluence the dissociation yield of  $\text{CF}_3\text{I}$  is less than unity. More than 5-fold enrichment of the residual gas in the  $^{13}\text{C}$  isotope was observed ( $K_{13}^{\text{res}} \simeq 5.2$ ). Finally, Figure 3d presents the absorption spectrum of  $\text{CF}_3\text{I}$  irradiated by the  $9\text{R}(10)$  laser line in conditions, when all the molecules in the flow were excited by intensive laser radiation ( $\Delta x_L \simeq 12\text{ mm}$ ,  $\Phi \simeq 7.5\text{ J/cm}^2$ ). One can see, practically all  $^{12}\text{CF}_3\text{I}$  molecules, which were contained in the natural mixture ( $\simeq 99\%$ ) have dissociated. The residual  $\text{CF}_3\text{I}$  mainly consists of  $^{13}\text{CF}_3\text{I}$  molecules ( $\geq 82\%$ ). In this experiment about 400-fold enrichment of the residual  $\text{CF}_3\text{I}$  by  $^{13}\text{C}$  isotope was obtained. The selectivity of the dissociation was measured to be  $\alpha_{12} \geq 10$ . We could not measure values of  $\alpha_{12} > 10$  because the dynamic range of the measurable intensities of mass peaks in our mass-spectrometer was less than  $10^3$ . The dissociation yield of  $^{12}\text{CF}_3\text{I}$  in this experiment was measured to be  $\beta_{12} \simeq 99.8\%$ .

As described above, under the conditions of the present experiments the measured enrichment factor is not the result of a number of

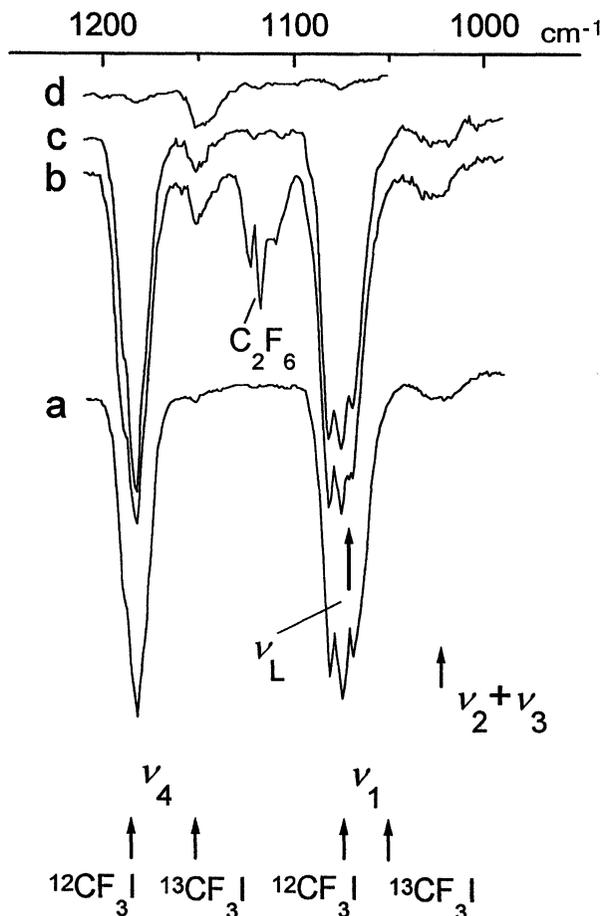


FIGURE 3 The IR absorption spectra of  $\text{CF}_3\text{I}$  molecules of the natural isotope composition without irradiation (a) and after irradiation in the molecular flow under resonant excitation of the  $^{12}\text{CF}_3\text{I}$  molecules (b–d). For the details the reader is referred to the text.

irradiating laser pulses, but it is characteristic of the separation achievable in a single pulse. Consequently, about 400-fold enrichment of the residual  $\text{CF}_3\text{I}$  in the case of Figure 3d was obtained as a result of irradiation of  $\text{CF}_3\text{I}$  flow by a single laser pulse.

When the  $\text{CF}_3\text{I}$  flow was irradiated by the laser lines, which are in resonance with the  $^{13}\text{CF}_3\text{I}$  molecules, the enrichment of the residual

gas in the  $^{12}\text{C}$  isotope took place. For example, the irradiation of  $\text{CF}_3\text{I}$  by the 9P(24) line in conditions similar to those for Figure 3b ( $\Delta x_L \simeq 6$  mm,  $\Phi \simeq 8$  J/cm $^2$ ) resulted in more than 4-fold enrichment of the residual gas in the  $^{12}\text{C}$  isotope ( $K_{12}^{\text{res}} \simeq 4.1$ ). The selectivity of dissociation was measured to be  $\alpha \simeq 11$ . Not very high selectivity in the case of excitation of  $^{13}\text{CF}_3\text{I}$  molecules is mainly connected with the fact that a rather intense combination band  $\nu_2 + \nu_3$  of  $^{12}\text{CF}_3\text{I}$  molecules lies near the  $\nu_1$  vibrational band of  $^{13}\text{CF}_3\text{I}$  [15]. Note, that enrichment factors in the residual gas in the case of excitation of  $^{13}\text{CF}_3\text{I}$  were less compared with those for the case of excitation of  $^{12}\text{CF}_3\text{I}$ . In our opinion, this is connected with that the scrambling reaction of  $^{13}\text{CF}_3$  radicals with the  $^{12}\text{CF}_3\text{I}$  molecules decreased the total dissociation yield of  $^{13}\text{CF}_3\text{I}$ . The quantity of product  $\text{C}_2\text{F}_6$  formed was established to be strongly dependent on the concentration of  $\text{CF}_3\text{I}$  in the flow. This is probably explained by the mechanism of  $\text{C}_2\text{F}_6$  formation *via* pair collisions of  $\text{CF}_3$  radicals.

Using the obtained values  $K_{13}^{\text{res}} \simeq 6.8$  and  $\alpha_{12} \geq 10$  (Fig. 4b) one can estimate the fraction of irradiated molecules in the flow. In the case, where not all the flow is irradiated by the laser  $\beta_1$  should be replaced in relation (6) by  $\beta_{1\text{eff}}$  ( $\beta_{1\text{eff}} = \beta_1\eta$ ). Substitution in (6) the obtained values  $\alpha_{12} = 10$  and  $K_{13}^{\text{res}} \simeq 6.8$  gives  $\beta_{1\text{eff}} \simeq 0.86$ . Since  $\beta_1 = \beta_{12} \simeq 1$ , then  $\eta \simeq 0.86$ . With the relation (6) one can determine also the dissociation yield of the  $^{12}\text{CF}_3\text{I}$  molecules in the case of excitation of  $\text{CF}_3\text{I}$  flow at  $\Phi \simeq 3.5$  J/cm $^2$  (Fig. 4c). Substitution in (6) of the obtained values  $K_{13}^{\text{res}} \simeq 5.2$  and  $\alpha_{12} = 10$  gives  $\beta_{12} \simeq 0.82$ .

## 7. CONCLUSION

A pulsed gas dynamic molecular flow of small length ( $\Delta x_{\text{fl}} \leq 1$  cm,  $\tau_{\text{fl}} \leq 20$   $\mu\text{s}$ ) was used to obtain a high degree of enrichment in the residual gas in single pulse IR MPD. The isotope-selective IR MPD of  $\text{CF}_3\text{I}$  was studied in this fashion. Conditions were realized at which the whole flow could be irradiated by an intense IR laser radiation and the dissociation yield of resonantly excited molecules reached the values  $\beta \simeq 1$ . About 400-fold enrichment of the residual gas in the  $^{13}\text{C}$  isotope was obtained following irradiation of  $\text{CF}_3\text{I}$  of natural isotope

composition in a single laser pulse. The dissociation yield and the selectivity were measured to be  $\beta_{12} \simeq 1$  and  $\alpha_{12} \geq 10$ , accordingly.

Since, in the approach described, high values of the enrichment factors in the residual gas can be obtained at moderate selectivities  $\alpha \geq 2-3$ , it is probably applicable also to the heavy molecules with a small isotope shift. This approach can be applied to the deep cleaning of gases from admixtures. To increase of the productivity of the process and to make more effective use of the laser radiation pulsed slit nozzles will be preferable.

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