

Selective IR multiphoton dissociation of molecules in a pulsed gas-dynamically cooled molecular flow interacting with a solid surface as an alternative to low-energy methods of molecular laser isotope separation

G.N. Makarov, A.N. Petin

Abstract. We report the results of studies on the isotope-selective infrared multiphoton dissociation (IR MFD) of SF₆ and CF₃I molecules in a pulsed, gas-dynamically cooled molecular flow interacting with a solid surface. The productivity of this method in the conditions of a specific experiment (by the example of SF₆ molecules) is evaluated. A number of low-energy methods of molecular laser isotope separation based on the use of infrared lasers for selective excitation of molecules are analysed and their productivity is estimated. The methods are compared with those of selective dissociation of molecules in the flow interacting with a surface. The advantages of this method compared to the low-energy methods of molecular laser isotope separation and the IR MPD method in the unperturbed jets and flows are shown. It is concluded that this method could be a promising alternative to the low-energy methods of molecular laser isotope separation.

Keywords: atoms, molecules, clusters, molecular and cluster beams, laser spectroscopy, laser-induced selective processes, laser isotope separation.

1. Introduction

In recent years, the research have been actively carried out, aimed at the development of low-energy (activation energy less than 1 eV) methods of molecular laser isotope separation (LEM MLIS) induced by IR laser radiation, including heavy elements (see, e.g., the reviews [1, 2] and references therein). This is primarily due to the fact that the SILEX (Separation of Isotopes by Laser Excitation) laser technology, which is probably based on the IR-laser-induced low-energy processes [2, 3], is actively implemented in the United States into the uranium enrichment production. This is also explained by the fact that the development of the well-known method of isotope-selective infrared multiphoton dissociation (IR MPD) of molecules as applied to heavy elements, including uranium, is constrained by the high energy consumption of the process, lack of high-efficiency and high-power laser systems, and

other factors. This method has been brought to practical implementation. A production on carbon isotope separation using IR MPD of CF₂HCl molecules (Freon-22) [4–8] was put into operation and then worked in Kaliningrad, Russia. The dissociation of UF₆ molecule requires the absorption of 40–50 quanta of IR radiation with a wavelength of 16 μm, i.e. the energy of 3.5–4.5 eV. The absence of highly efficient and high-power tunable laser systems capable of generating radiation with a wavelength near 16 μm complicates the works on isotope-selective IR MPD of UF₆ molecules. At the same time, the studies in this direction are being continued (see, e.g., [9]).

We should note that since the 1970s, the attempts have been launched in the United States to design effective laser systems for uranium isotope separation, which could have been run in a batch production. However, the engineering difficulties have not been overcome, and the works in this direction have been largely terminated. Similar attempts of developing more cost-effective methods of uranium enrichment compared to the traditional gaseous diffusion method, which is now becoming unattractive because of high energy consumption, had been undertaken in some other countries (England, Germany, France, South Africa, Japan, Australia). Most of these projects were also closed in the late 1990s. Currently, a construction of four new uranium enrichment plants has started in the United States, three of which will use the advanced technologies based on centrifugation, whilst the laser enrichment based on the SILEX technology is planned to be used at the fourth plant. The SILEX laser technology is strictly classified [2, 3].

In the case of low-energy methods, the process activation energy should not exceed 1 eV. This energy is typical for physicochemical processes of adsorption and desorption of molecules on a surface, including that coated by molecules or clusters and on a surface of large clusters, and also for the processes of dissociation and fragmentation of the weakly bound van der Waals molecules.

To date, many approaches to the development of the LEM MLIS using IR lasers [2] have been suggested. These include the use of selective heterogeneous processes on a surface, which are induced by continuous radiation of CO₂ or CO lasers [10–12], and also the use of the processes of selective IR vibrational pre-dissociation of the van der Waals molecules [13–17] and selective control over clustering of molecules by means of IR laser radiation in gas-dynamically cooled jets and flows [15–18]. An application of selective dissociative capture of low-energy electrons by molecules and also selection of the molecules embedded into nanodroplets (clusters) of superfluid helium have been considered in [19]

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and [20–22], respectively. In the context of application for isotope separation, the processes of interaction of vibrationally highly excited and unexcited molecules with those condensed on a cold surface (clusters) have been studied in [23, 24]. With the same purpose, the processes of selective capture of molecules by clusters [25] and disintegration of weakly bound van der Waals clusters in collisions with vibrationally excited molecules [26, 27] have been considered.

The method of isotope separation based on capture of low-energy electrons by molecules [19] and the recently proposed methods of molecular selection involving clusters and nanoparticles [25–27] are still poorly studied, not efficient enough and difficult to implement in practice [2]. The method of selecting molecules embedded into helium nanodroplets [20–22] is also not efficient enough and complicated for practical implementation. However, some approaches may form a basis for the LEM MLIS development. These approaches include the use of heterogeneous processes on the surface with application of continuous and pulsed IR lasers [12, 23, 24] for molecule excitation, and also the processes of molecular clustering suppression and dissociation of clusters in the gas-dynamically cooled jets and flows and their combinations [15–18]. Probably, these are the latter processes that make a basis of the SILEX technology [1–3].

In this paper, the above-mentioned methods are analysed and compared with the method of selective IR MPD of molecules in a pulsed, gas-dynamically cooled molecular flow interacting with a solid surface, including nonequilibrium conditions of a pressure shock [28–33]. The results of analysis of the previously obtained data on isotope-selective dissociation of the SF₆ molecules in a pressure shock are presented.

Estimates of the method productivity are derived. It is shown that the method productivity significantly exceeds that of the low-energy methods of molecular laser isotope separation, and also the productivity of the IR MPD method in the unperturbed jets and flows. Based on the effectiveness estimates of the isotope separation methods in specific experiments, and also using the results of comparative analysis of these methods, it is concluded that the method of selective IR MPD of molecules in the nonequilibrium shock conditions can be considered as a promising alternative to the low-energy methods of molecular laser isotope separation.

2. IR MPD of molecules in a pulsed gas-dynamically cooled molecular flow interacting with a solid surface

Isotope-selective IR MPD of molecules in a pulsed gas-dynamically cooled molecular flow interacting with a solid surface has been thoroughly investigated in [28–33] as applied to SF₆ and CF₃I molecules. It is shown that the excitation of molecules in the nonequilibrium conditions emerging in front of the shock surface is accompanied with a high product yield and high selectivity at a relatively low excitation energy density (less than 1.5–2 J cm⁻²). Such energy densities are significantly (3–5 times) less than those required for dissociation of molecules in the unperturbed jets and flows. Therefore, despite the fact that the approach developed in papers [28–33] is based on the process of molecular dissociation, the moderate value of the energy density required for dissociation allows consideration of this approach on a par with the low-energy methods of molecular laser isotope separation. Let us consider the foundation of this approach and some results.

2.1. Nonequilibrium conditions in a pressure shock

Rapid gas cooling during its expansion in gas-dynamic jets and flows results in the violation of thermodynamic equilibrium between different degrees of freedom because of the differences in the characteristic times of translational, rotational and vibrational relaxation: $\tau_{tr} \leq \tau_{rot} \leq \tau_{vib}$. A deviation from the local equilibrium depends on the number z_{col} of collisions required for relaxation of a given degree of freedom. For polyatomic molecules, the relation $z_{tr} \leq z_{rot} \leq z_{vib}$ is usually fulfilled; therefore, the corresponding effective temperatures satisfy the condition [34]

$$T_{1tr} \leq T_{1rot} \leq T_{1vib}. \quad (1)$$

The nonequilibrium conditions being inverse to relations (1) can be realised in the pressure shock [35, 36] due to the differences in translational, rotational, and vibrational rates of molecular relaxation [37]. Whith the pressure shock formed by the interaction of a pulsed gas-dynamically cooled molecular flow with a solid surface, these conditions have the form

$$T_{2tr} \geq T_{2rot} \geq T_{2vib}. \quad (2)$$

Here, due to a large time of vibrational–translational relaxation (for example, the rate constant $p\tau_{V-T}$ for SF₆ is about 150 μs Torr [38], the rate constant $p\tau_{V-T}$ for CF₃I is about 350 ± 100 μs Torr [39]), the vibrational temperature of molecules in the pressure shock, in case a pulsed flow of rarefied gas is used, is virtually identical to the vibrational temperature of molecules in the incident flow ($T_{2vib} \approx T_{1vib}$), while the translational and rotational temperatures of the molecules in the pressure shock are much higher than those in the incident flow: $T_{2tr} > T_{1tr}$ and $T_{2rot} > T_{1rot}$. Thus, new nonequilibrium conditions emerge in the pressure shock, which are characterised by the fact that the vibrational temperature of molecules is substantially less compared to the translational and rotational temperatures. Under these conditions the selective dissociation of SF₆ and CF₃I molecules has been investigated in [28–33].

2.2. Experimental

The scheme of the instalation is shown in Fig. 1. To obtain a molecular flow, a pulsed nozzle of the ‘current loop’ type [40] is used, with an aperture diameter of 0.75 mm and a pulse opening time of about 100 μm (FWHM). The gas pressure above the nozzle is varied in the range of 0.1–3.5 atm. The output nozzle has a conical shape, with an apex angle of 60°. The cone height is 15 mm.

The number of molecules flowing from the nozzle in a single pulse depends on the gas pressure above the nozzle, and in the experiments described is ranged from 5 × 10¹⁵ to 5 × 10¹⁷ molecules per pulse [30, 32]. The nozzle can operate both in the single-pulse regime and with a pulse repetition rate up to 1 Hz. The vacuum chamber, in which the molecular flow is formed, is pumped to the pressure of (1–2) × 10⁻⁶ Torr. The molecular flow is formed by means of two thin metal strips attached to the output cone of the nozzle so that they form a dihedron with a rib parallel to the *y* axis. The strips have a variable radius of curvature in the *xz* plane.

A solid surface (plates of KBr, CaF₂ and LiF crystals transparent to the luminescence of HF* molecules) is placed at a distance *x* = 50–150 mm from the nozzle perpendicular

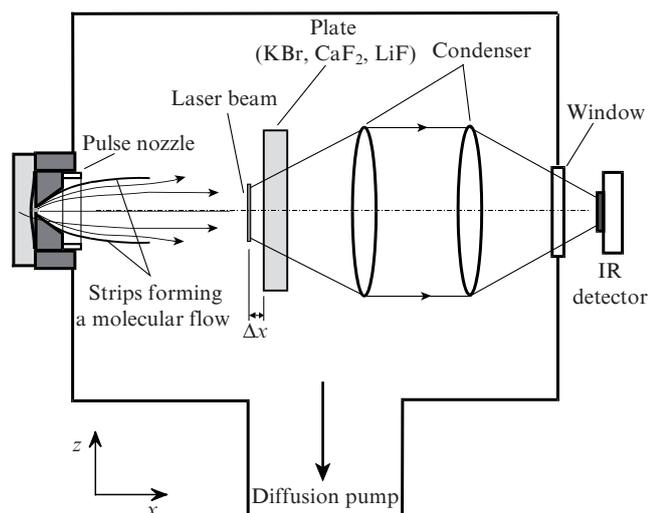


Figure 1. Schematic of the experimental installation. The laser beam is directed along the y axis [28].

to the flow direction. As a result of interaction of the supersonic molecular flow with a surface, a pressure shock [35, 36] with substantially nonuniform, nonstationary and nonequilibrium characteristics is formed in front of the surface. The length of the shock front, which by the order of magnitude is equal to the mean free path of molecules [35], constitutes 0.2–5 mm under the conditions of the experiments in question [30–32].

Molecules are excited by means of tunable pulsed radiation from a CO_2 laser with pulse energy of about 3 J. We have studied the dissociation of molecules both in the case when molecules are excited in the unperturbed flow (in the absence of a surface on the flow path) and in the case of the flow incident on a surface, including the stage preceding the interaction with the surface and shock formation, and directly in the pressure shock itself. In the flow incident on a surface, molecules are excited at a distance $\Delta x \approx 50$ –70 mm from the surface, and in the pressure shock – at a distance $\Delta x = 1.5$ –8 mm from the surface. The laser beam is focused by a cylindrical lens with a focal length of 12 cm, with the lens axis parallel to the surface. The laser beam cross section in the lens focus represents a rectangle of 0.18×12.5 mm (Fig. 1).

2.3. The research method

The dissociation of SF_6 molecules is investigated by means of detecting the HF^* luminescence ($\lambda \approx 2.5$ μm). The vibrationally excited HF^* molecules are formed in the reaction of fluorine atoms (the primary products of SF_6 dissociation) with hydrogen or methane [41]. The HF^* luminescence intensity is well correlated with the yield of SF_6 dissociation [42]. The luminescence is detected using the IR receiver on the basis of PbS, with a detector area of 1×1 cm (the bandwidth is about 16 kHz). In the case of molecule excitation in the flow incident on a surface, the HF^* luminescence is observed both from the zone of molecule excitation, and from the pressure shock that is formed in front of the surface, where vibrationally excited molecules are dissociated by collisions with each other. At small distances from the molecular excitation zone of the surface ($\Delta x \leq 20$ mm), the luminescence pulses from these two areas are not resolved in time by the IR

receiver. In this case, the integrated HF^* luminescence signal is measured.

In these experiments, the SF_4 product yield and the factor of its enrichment by the ^{34}S isotope have also been measured. The procedure of collection and IR analysis of the products and original gas remaining after irradiation in the process of molecule dissociation in the gas-dynamic flow is described in detail in [43]. The enrichment factor in SF_4 appears as

$$K_{34}^{\text{prod}} = \frac{[^{34}\text{SF}_4]}{[^{32}\text{SF}_4]} \frac{1}{\zeta}, \quad (3)$$

where $[^{34}\text{SF}_4]/[^{32}\text{SF}_4]$ is the concentration ratio of molecules in the SF_4 product; and $\zeta = ^{34}\text{S}/^{32}\text{S} \approx 0.044$ is the ratio of percentage compositions for sulfur isotopes in the original SF_6 gas. The concentration ratio of $^{34}\text{SF}_4$ and $^{32}\text{SF}_4$ in the product has been measured by infrared absorption spectra (the oscillation ν_6 of the SF_4 molecule; $\nu_6 \approx 728$ cm^{-1} for $^{32}\text{SF}_4$ [44]), in which the shift of absorption bands for the $^{34}\text{SF}_4$ and $^{32}\text{SF}_4$ isotopes constitutes ~ 12.3 cm^{-1} [45].

In the experiments with CF_3I molecule, the yield of the C_2F_6 product and the coefficient of its enrichment by ^{13}C isotope have been measured. These measurements have been conducted on the basis of analysis of IR spectra and mass spectra of the products, and also of original gas remaining after irradiation. The isotopic composition of C_2F_6 has been determined by the ion fragment C_2F_5^+ . The enrichment coefficient in C_2F_6 is

$$K_{13}^{\text{prod}} = \frac{2I_{121} + I_{120}}{(I_{120} + 2I_{119})\zeta}, \quad (4)$$

where I_{119} , I_{120} and I_{121} are the mass-peak intensities of the ion C_2F_5^+ ; and $\zeta = ^{13}\text{C}/^{12}\text{C} \approx 0.011$ is the ratio of percentage compositions of carbon isotopes in the original CF_3I gas.

2.4. Analysis of some results

Figure 2a shows the dependence of the HF^* luminescence intensity on the gas pressure above the nozzle when SF_6 molecules are excited in the unperturbed flow [curve (1)] and in the flow incident on a surface [curve (2)]. Figure 2b presents the dependence of the ratio R of experimental intensity values represented by curves (2) and (1) on pressure. It can be seen that for all investigated gas pressures above the nozzle, provided the molecules are excited in the flow incident on a surface, the HF^* luminescence intensity is significantly (5–9 times) greater than that in the case of molecular excitation in the unperturbed flow. A particularly large difference occurs at the gas pressures above the nozzle in the range from about 0.25 to 1.25 atm. This is probably due to the fact that, in this pressure range, optimal conditions for the collision-stimulated dissociation of vibrationally excited molecules getting into the pressure shock are realised. At lower gas pressures above the nozzle the intense shock in front of the surface is not yet formed, and therefore the role of molecular dissociation collisions is small [30]. Apparently, at higher gas pressures above the nozzle, the process of vibrational–translational relaxation starts to compete with the process of molecular dissociation due to collisions in the pressure shock.

It is also found [29, 30, 32] that in the case of excitation of SF_6 molecules in the pressure shock and also in the flow incident to a surface, the HF^* luminescence intensity in a wide

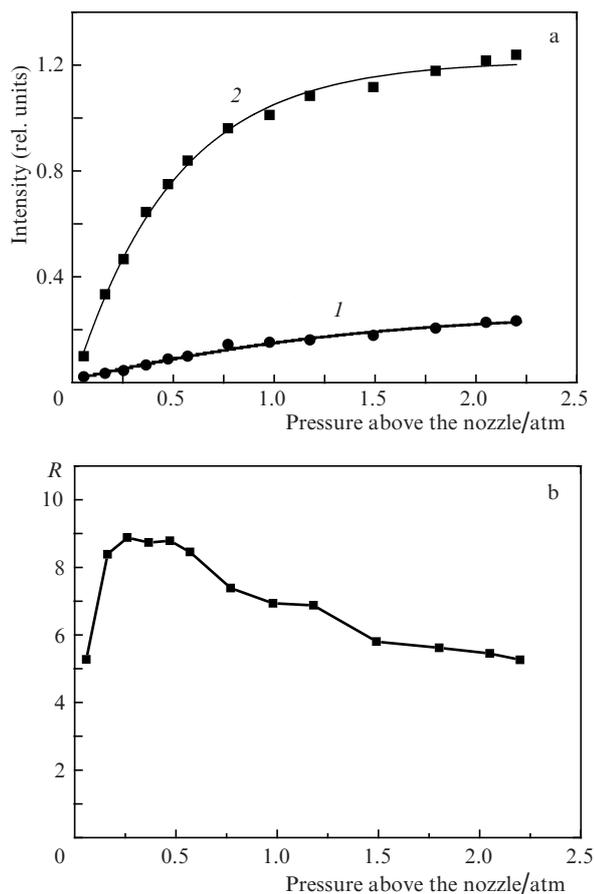


Figure 2. (a) Intensity of HF* luminescence as a function of the total gas pressure above the nozzle [in the case of SF₆ excitation in a mixture with CH₄ ($p(\text{SF}_6)/p(\text{CH}_4) = 1$) in the unperturbed flow (1) and in the flow incident on a surface (2). The total gas pressure above the nozzle is 2.4 atm, the distance from the nozzle to the surface [for curve (2)] is $x = 51$ mm, $\Delta x = 2.5$ mm. The molecules are excited at a frequency of 945.98 cm^{-1} [10P(18) line of the CO₂ laser] at the radiation energy density of $\Phi = 7.3 \text{ J cm}^{-2}$ averaged over the irradiation volume [30, 32]. (b) Ratio R of the intensities of HF* luminescence in the flow incident on a surface and in the unperturbed flow as a function of the total gas pressure above the nozzle. Obtained on the basis of the data given in [30].

range of energy densities is significantly greater than in the case of excitation in the unperturbed flow (Fig. 3a). The HF* luminescence intensity in the flow incident on a surface is about 3–7 times (in the pressure shock – more than 30 times) higher than that in the unperturbed flow. This difference becomes even more significant when the excitation energy density does not exceed 3 J cm^{-2} (Fig. 3b), which indicates a very significant contribution to the total yield of molecular dissociation caused by collisions in the pressure shock at low energy densities. These results testify that in exciting molecules in the pressure shock, likewise as in the flow incident on a surface, the product yield is much greater compared to the case of molecular excitation in the unperturbed flow.

Direct measurements of the yield of final products (SF₄ and C₂F₆) and the process selectivity (product enrichment ratio) in the case of excitation of SF₆ and CF₃I molecules in the flow interacting with a surface and in the unperturbed flow have been performed in [29, 30, 32] and [31], respectively. Some results are given in Table 1 below. It is shown that in the case of excitation of SF₆ molecules in the flow incident on a surface, the SF₄ yield is 2.5 times (in the shock – about 12

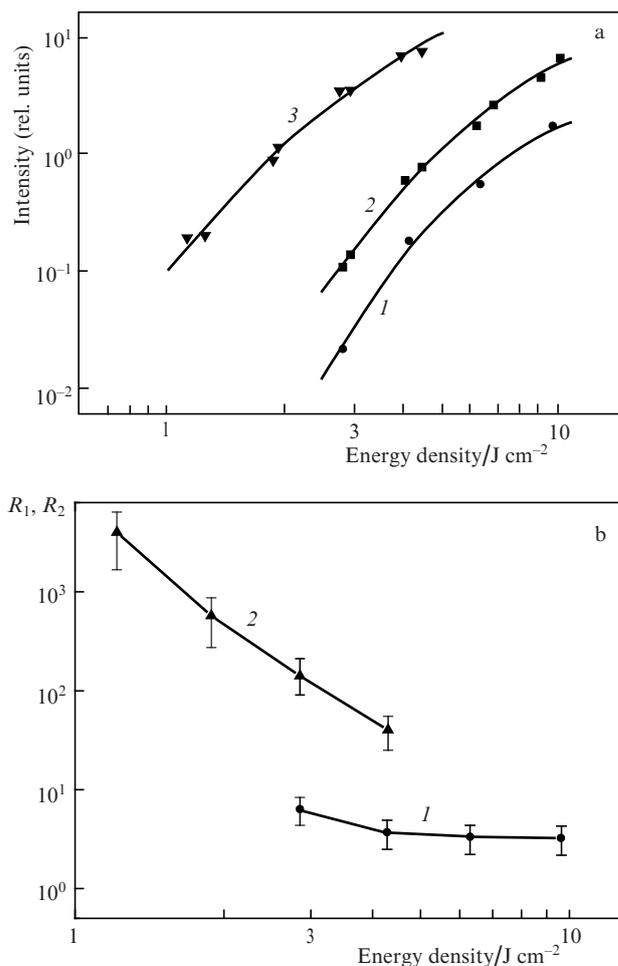


Figure 3. (a) Intensity of HF* luminescence as function of the energy density in the case of SF₆ excitation in a mixture with CH₄ ($p(\text{SF}_6)/p(\text{CH}_4) = 1$) in the unperturbed flow (1), in the flow incident on a surface (2), and in the pressure shock (3). The total gas pressure above the nozzle is 2.4 atm, the distance from the nozzle to the surface [curves (2) and (3)] is $x = 51$ mm, $\Delta x = 2.5$ mm. The molecules are excited at a frequency of 945.98 cm^{-1} [10P(18) line of the CO₂ laser] [30, 32]. (b) Ratios R_1 and R_2 of the intensities of HF* luminescence in the flow incident on a surface (1) and in the pressure shock (2), relatively, to the intensity of HF* luminescence in the unperturbed flow as functions of the density of exciting laser radiation. Obtained on the basis of the data given in [30].

times) greater than in the unperturbed flow. In the case of excitation of CF₃I in the flow incident on a surface, the C₂F₆ yield is 2.5 times (in the shock – about 14 times) greater compared to the unperturbed flow. It was found that in excitation of SF₆ in the unperturbed flow at an energy density of 10 J cm^{-2} , the enrichment ratio is $K_{34}^{\text{prod}} = 17 \pm 5$, while in the flow incident on a surface $K_{34}^{\text{prod}} = 15 \pm 3$, and in the pressure shock $K_{34}^{\text{prod}} = 14 \pm 3$. Exciting CF₃I in the unperturbed flow at an energy density of 1.5 J cm^{-2} , the enrichment ratio is $K_{13}^{\text{prod}} = 21 \pm 3$, in the flow incident on a surface $K_{13}^{\text{prod}} = 19 \pm 3$, and in the pressure shock $K_{13}^{\text{prod}} = 15 \pm 3$. Thus, the dissociation selectivity of molecules in the flow incident on a surface and in the shock is only slightly (less than by 25%–30%) less than that in the unperturbed flow, whereas the product yield is significantly (more than by order of magnitude) greater.

The product yield increase in excitation of molecules in the flow incident on a surface is due to the fact that a large portion of molecules vibrationally excited below the dissociation threshold is dissociated as a result of mutual collisions

Table 1. The yield of the SF₄ and C₂F₆ products and the coefficients of their enrichment by the ³⁴S and ¹³C isotopes in the case of excitation of SF₆ and CF₃I molecules in the unperturbed flow, in the flow incident on a surface, and in the pressure shock [30, 31].

Gas composition and pressure above the nozzle/atm	CO ₂ laser line	Energy density/J cm ⁻²	Yield of SF ₄ , C ₂ F ₆ (rel. units)			Enrichment coefficients (K_{34}^{prod} , K_{13}^{prod})		
			Unperturbed flow	Flow incident on a surface	Pressure shock	Unperturbed flow	Flow incident on a surface	Pressure shock
SF ₆	1.25	10P(16)	12	1 ± 0.2	2.5 ± 0.5	12 ± 3		
	1.25	10P(36)	10				17 ± 5	15 ± 3
CF ₃ I	1.5	9R(12)	1.3	1 ± 0.2	2.5 ± 0.5	14 ± 3		
	1.5	9P(20)	1.5				21 ± 3	19 ± 3

when getting into the shock. The integral dissociation selectivity in this case is quite high because the molecules are excited in the incident gas-dynamically cooled flow. If the molecules are excited directly in the pressure shock, the product yield increase is conditioned by the increase in temperature, gas density and molecular dissociation yield. In turn, an increase in the yield of molecular dissociation is, firstly, stimulated by more efficient excitation of molecules in the pressure shock, and, secondly, by a larger contribution of collisional dissociation of molecules which are excited by the IR pulse below the dissociation limit and do not dissociate in the unperturbed flow because of a small collision frequency [30, 32]. A relatively high selectivity in the pressure shock is a consequence of the fact that vibrational temperature of molecules remains quite low. It has been shown [33] that vibrational temperature of molecules rather than rotational temperature represents a dominating factor in the selectivity formation process.

3. Evaluation of the method efficiency and its comparison with the efficiency of other methods

A comparison of the efficiency of all above-considered methods of molecular laser isotope separation on the basis of any objective criteria seems rather complicated at this stage of the studies. This is explained by the lack of required experimental data on basic separation parameters, including in particular, the selectivity and yield of the products, irradiation geometry and laser radiation parameters.

In paper [14], the estimates have been proposed as applied to the case of deriving the enriched ¹⁰BCl₃ product by the method of selective vibrational pre-dissociation in a continuous flow. These estimates show that although about 70% of Ar-¹⁰BCl₃ molecules can be removed from a molecular beam by means of a continuously running CO₂ laser, this only represents a small fraction of the total number of ¹⁰BCl₃ molecules in the beam. The concentration of van der Waals dimers in the beam constitutes only a few percent of the total concentration of BCl₃ gas above the nozzle. This implies that separation of 1 mole of ¹⁰BCl₃ in the natural isotopomeric mixture, provided that the experimental installation (nozzle diameter – of 50 μm, total gas pressure above the nozzle – about 7 atm) is employed, would require several years of continuous irradiation, gas recirculation and collection of products. At the same time, according to the authors, the productivity of such an installation is easy to increase (for example, by 100 times) by using large vacuum pumps and large-diameter nozzle apertures. This would reduce the required time up to a few days [14]. In paper [21], the productivity of the method of selecting the molecules embedded into the helium nanodroplets has been evaluated. The estimates have been made for the case of

sulfur isotope separation by the example of SF₆ molecules. The estimates given in [21] proceed from the intensities of the really obtained helium cluster beams and the productivity of the diffusion pumps used for that purpose. It is shown that the yield of the enriched ³⁴SF₆ product is about 10¹³ molecules s⁻¹, or 3.6 × 10¹⁶ molecules h⁻¹, which is equivalent to approximately 0.01 mg h⁻¹. This is a very poor productivity, even taking into account that the estimates have been only conducted for a single small installation on the basis of a single diffusion pump.

The product yield estimates related to the use of the well-known method of IR MPD of molecules in the gas-dynamically cooled jets and flows have been derived in [21]. We should note that the product yield typical for this method is also not very large. For instance, in the laser separation of uranium isotopes by means of the IR MPD method as applied to UF₆ molecules, for more effective gas cooling in the gas-dynamic flows, a rather lean mixture of UF₆ molecules is used in the carrier gas (the concentration ratio of UF₆ molecules and the carrier gas is less than 0.01 [46, 47]). At the same time, for effective excitation and dissociation of molecules, quite large laser power densities are required (at least greater than 1 J cm⁻² to ensure dissociation of pre-excited molecules), which reduces the irradiation pulse ratio down to the values not exceeding 0.001 [21].

Apparently, a high ($s \approx 3-5$) selectivity may be only obtained at a low dissociation yield ($\beta \leq 0.01$). Taking into account the fact that in contrast to the methods discussed above, the chamber pressure being two orders higher (circa 10⁻² Torr) is permissible in the case of isotope separation by IR MPD of molecules in the gas-dynamic flows, and herewith the flows being two orders larger ($\sim 10^{22}$ particles s⁻¹) can be implemented; the estimates [21] indicate that the yield of products may constitute approximately 10¹⁵ molecules s⁻¹, or 3.6 × 10¹⁸ molecules h⁻¹. This is about two orders of magnitude greater than in the framework of the method operating with helium nanodroplets.

The productivity estimation of the isotope separation method based on the selective IR-laser-induced suppression of clustering of the molecules in the gas-dynamic jets and flows [15–18] is problematic due to the lack of necessary data. Given that in this method, in order to achieve an acceptable selectivity, a highly diluted mixture of molecules in the carrier gas must be used (the concentration of molecules in the mixture is no more than 0.5%–1% [15, 18]), and the zone dimensions of the flow laser irradiation should be small (limited by several nozzle calibres) [2], we may suppose that the method efficiency is apparently not very high.

Using the results of [30, 32], let us estimate the productivity of the method of molecular dissociation in the pressure shock, described in this paper. Consider the example of SF₆

Table 2. Productivity estimates for a series of methods of molecular laser isotope separation in specific experiments.

Method	Molecules for which estimates have been conducted	Operation regime, laser pulse repetition rate	Estimated productivity/mg h ⁻¹	References
Selective vibrational pre-dissociation of van der Waals molecules	¹⁰ BCl ₃	CW CO ₂ laser	1–1.5	[14]
Selection of molecules embedded into helium nanodroplets	³⁴ SF ₆	Pulsed CO ₂ laser, 500 Hz	≤0.01	[21]
Selective IR MPD of molecule in the gas-dynamically cooled molecular flow	²³⁵ UF ₆	Pulsed CO ₂ laser, 500 Hz	1–2	[21]
Selective IR MPD of molecules under nonequilibrium conditions of the pressure shock	³⁴ SF ₆	Pulsed CO ₂ laser, 100 Hz	50–75	Present paper
Selective IR MPD of molecules in the flow incident on a surface	³⁴ SF ₆	Pulsed CO ₂ laser, 100 Hz	20–30	Present paper

dissociation and obtaining the enriched ³⁴SF₄ product in the conditions of a particular experiment with measured parameters of the molecular flow [30]. Thus, when the SF₆ pressure above the nozzle is 2 atm, the number of molecules outgoing from the nozzle per one pulse is $N_{f1} \approx 6 \times 10^{16}$ [30, 48]. The flow volume is $V_{f1} \approx 30 \text{ cm}^3$, average concentration of molecules in the flow is $N_1 \approx 2 \times 10^{15} \text{ cm}^{-3}$. Average concentration of SF₆ molecules in the pressure shock is $N_2 \approx 2.8 \times 10^{16} \text{ cm}^{-3}$ [30, 48]. The length of the shock front in the case of SF₆ molecules is ~3 mm. At a moderate laser energy density, it is possible to irradiate the gas volume defined by the geometric cross section of the focused laser beam (for example, ~1.5 mm × 20 mm) and by the length of the irradiated zone along the surface (~10 cm), i.e. the gas volume is $V_{\text{exc}} \approx 3 \text{ cm}^3$.

The concentration of ³⁴SF₆ molecules (4.2% in the natural isotopomeric mixture) in the irradiated volume is $\sim 1.2 \times 10^{15} \text{ cm}^{-3}$, while the total number of molecules is equal to 3.6×10^{15} . At the density of laser radiation energy $\Phi \approx 1.5 \text{ J cm}^{-2}$, the dissociation yield of molecules in the pressure shock is ~0.3. This follows from the fact that the HF* luminescence signal in the pressure shock at $\Phi \approx 1.5 \text{ J cm}^{-2}$ corresponds to that of the unperturbed molecular flow at $\Phi \approx 6.5\text{--}7 \text{ J cm}^{-2}$ (see Fig. 2a), when the dissociation yield of SF₆ molecules exceeds 0.3 [49]. Consequently, the number of ³⁴SF₆ molecules that dissociate per a single pulse constitutes $\sim 1.1 \times 10^{15}$. With no regard to the losses in chemical reactions, at a pulse repetition rate, for example, of 100 Hz, it is possible to obtain $\sim 4 \times 10^{20}$ of ³⁴SF₄ molecules during one hour of irradiation, or $\sim 10^{22}$ molecules per day, which constitutes circa 1.6×10^{-2} mole or ~1.8 g of ³⁴SF₄. This is significantly (by approximately two orders) greater than the estimated values given for the case of enrichment of the ¹⁰BCl product by the method of selective vibrational pre-dissociation of the clusters of Ar – ¹⁰BCl₃, by about four orders greater than that in the case of enrichment of ³⁴SF₆ molecules using the helium nanodroplets, and by about one and half – two orders greater than in the case of IR MPD of UF₆ molecules. The results of all above-cited evaluations are summarised in Table 2. The estimates relevant to the case of molecular excitation in the flow incident on a surface are also presented in this Table. The method efficiency in this case is quite high. We should draw attention to the fact that the estimates of the method parameters have been derived at a laser pulse repetition rate of 100 Hz.

Note that a CO₂ laser with a pulse energy of 0.5–1.0 J is suitable for implementation of the process of IR MPD of

molecules in the pressure shock. Herewith, due to relatively high selectivity of dissociation process (in the case of SF₆ molecules – about 14, see Table 1), no more than 1.5%–2.5% of the laser energy is absorbed under the above-described conditions. The vacuum chamber pressure at the level of $(0.5\text{--}1) \times 10^{-3}$ Torr is satisfactory for this method, and therefore the isotope separation process can be scaled by using, for instance, a series of round or slotted pulse nozzles.

4. Conclusions

We have described a method and presented results of the studies on isotope-selective IR MPD of molecules in a pulsed gas-dynamically cooled molecular flow interacting with a solid surface, including, in the nonequilibrium conditions of a pressure shock. An analysis of the results obtained has been conducted. The evaluation results are compared with those derived for a series of the low-energy methods of molecular laser isotope separation. It is shown that the productivity of the method considered in this work significantly exceeds the productivity of the low-energy methods, and also the productivity of the method of IR MPD of molecules in the unperturbed jets and flows.

Another important advantage of this method, as compared with the high-energy methods of molecular laser isotope separation, is the easiness of its implementation in practice. High efficiency and simplicity of this method have been demonstrated in the experiments [28–33], in which the conditions for obtaining a large product yield at a relatively high process selectivity have been rather easily implemented.

The measurements of the product yield and selectivity have been performed in the experiments using the really produced enriched gas collected into a cuvette, not by mass spectrometric detection of these parameters in the on-line regime as it was the case in many other methods considered. It is also important that the CO₂ lasers with moderate pulse energy are suitable for implementation of this method in practice. Therefore the isotopic-selective IR multiphoton dissociation of molecules in a pulsed gas-dynamically cooled molecular flow interacting with a solid surface, including, in the nonequilibrium conditions of a pressure shock, can be regarded as a promising alternative to the low-energy methods of molecular laser isotope separation.

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