# Suppression of clustering of $CF_3Br$ molecules with argon atoms by $CO_2$ laser radiation in gas-dynamic expansion of a $CF_3Br-Ar$ mixture: bromine isotope selectivity

G.N. Makarov, N.-D.D. Ogurok, A.N. Petin

***Abstract.*** **We present the study of suppressing the clustering of $CF_3Br$ molecules with argon atoms under gas-dynamic expansion of the $CF_3Br-Ar$ mixture at a nozzle exit by a cw $CO_2$ laser. The main attention is paid to the analysis of possibility of implementing the selective control of bromine isotope clustering. The method relies on the vibrational excitation of molecules with the laser radiation, which leads to the suppression of their clustering with argon atoms. The experimental setup and the method of study are briefly described. The results of evaluation of the efficiency and selectivity of suppression of molecular–atomic clustering for different compositions of the gas above the nozzle and separations between the irradiation zone and the nozzle exit section are presented. It is shown that under the resonance vibrational excitation of gas-dynamically cooled $CF_3Br$ molecules at the nozzle exit one can implement bromine isotope selective suppression of clustering of molecules with argon atoms. It is found that by controlling the clustering of $CF_3Br$ molecules with argon atoms one can implement considerably higher enrichment and selectivity factors than in the case of controlling the clustering of $CF_3Br$ molecules with each other. Thus, using the $CF_3Br-Ar$ mixture (the ratio of pressures $1:100$ and $1:200$) the enrichment factors for the bromine isotopes $K_{enr}(^{81}Br) = 1.50 \pm 0.13$ and $1.30 \pm 0.09$, respectively, were obtained under the conditions of irradiating the jet at the $9R(30)$ line of the laser ($v = 1084.635$ cm$^{-1}$). The selectivity $\alpha$ of the suppression of clustering of $CF_3Br$ molecules with argon atoms, achieved in this case, amounted to $4.02 \pm 0.19$ and $2.31 \pm 0.11$, respectively. The results show that the method allows one to selectively control the clustering of molecules, comprising isotopes of heavy elements that possess a small isotopic shift in the IR absorption spectra.**

***Keywords:*** *atoms, molecules, clusters, beams of molecules and clusters, laser spectroscopy, laser-induced selective processes in molecules and clusters, laser separation of isotopes.*

## 1. Introduction

Recently, the development of low-energy molecular laser isotope separation (MLIS) has been actively studied [1–9]. The

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main goal of these studies is the search for efficient and low-cost methods for separating isotopes of uranium, as well as other elements. The reason is that the development of the method of selective IR multiphoton dissociation (MPD), well known [10–12] and successfully used in practice to separate carbon isotopes [13–15], in application to uranium is constrained by the high energy consumption of the process, the absence of high-efficiency and high power laser systems and a number of other factors [1]. Thus, for example, to dissociate a $UF_6$ molecule the absorption of nearly 40–45 quanta of IR radiation with the wavelength 16 μm is necessary, i.e., the energy absorption amounts to 3.1–3.5 eV per molecule.

One of the ways of further development of MLIS methods is to use low-energy physical and chemical processes, for which the activation energy does not exceed 0.3–0.5 eV [1–5]. Such activation energies are typical for physical and chemical processes of molecular adsorption and desorption of a surface, including the surface of large clusters, as well as for the processes of dissociation and fragmentation of weakly bound van der Waals molecules [1]. At present in the USA the technology of separation of isotopes by laser excitation (SILEX) is being developed for uranium isotopes [16–19]. The principles of this technology are not disclosed, but with great probability, it is based on low-energy processes [20]. According to the authors' statements, the SILEX technology is also applicable to separate the isotopes of silicon, boron, sulphur, carbon, oxygen, and other elements [1, 16, 18].

To date considerable work has been carried out on the study of low-energy methods of laser isotope separation (LEMLIS) (see, e.g., review [1] and references therein), as well as the alternative methods [1, 21, 22]. One of the approaches to LEMLIS implementation is the method of selective control of molecular clustering in gas-dynamic jets using IR lasers [1]. In Refs [23–27] the authors demonstrate the possibility to separate sulphur isotopes using the methods of selective suppression of clustering of $SF_6$ molecules and dissociating the clusters of these molecules in gas-dynamic jets using a cw $CO_2$ laser radiation. Van den Bergh [27] also mentions that similar experiments were performed with the $CF_3Br$ molecule, but the results of these experiments are not presented.

Apatin et al. [28] studied the control of clustering of $CF_3I$ molecules due to resonance vibrational excitation of molecules and clusters with the IR radiation of a cw $CO_2$ laser in gas-dynamic expansion of the molecular gas $CF_3I$ in a mixture with argon and xenon carrier gases. The obtained results show that the control of cluster formation in molecular beams can be used to separate isotopes.

Apatin et al. [8] investigated the conditions for $(CF_3Br)_n$ cluster formation ($n$ is the number of molecules in the cluster) under gas-dynamic expansion of the $CF_3Br-Ar$ mixture in a

pulsed jet and demonstrated the possibility of selective control of molecular clustering using IR radiation. In this paper, the beam of molecules and clusters was detected using a time-of-flight mass spectrometer with UV laser ionisation of particles. This did not allow recording the ion peaks of large cluster fragments $[CF_3Br_2^+, (CF_3Br)_2^+]$ of the initial clusters $(CF_3Br)_n$. The enrichment factor and the selectivity were measured using the mass spectra of fragment ions $Br_2^+$, which essentially limited the accuracy of evaluating these parameters. In our paper [9], the detection of particles was implemented using a quadrupole mass spectrometer. This allowed the detection sensitivity to be increased and the measurements to be performed using a few peaks of cluster ion fragments. Hence, the bromine isotope selective control of $CF_3Br$ molecule clustering was studied in more detail and with higher precision. In Ref. [9] we also studied the degree of suppression of such clustering as a function of the laser radiation power. It was shown that within the power range up to 5 W this function is close to linear. This fact shows that in this power range mainly the linear absorption of the IR radiation by $CF_3Br$ molecules takes place.

The $CF_3Br$ molecule was chosen for the investigation for a few reasons. First, it is characterised by very small ($\sim 0.248$ cm$^{-1}$) [29]) isotopic shift between the isotopomers $CF_3^{79}Br$ and $CF_3^{81}Br$ in the spectrum of the vibration $v_1$ ($\sim 1085$ cm$^{-1}$ [29]) excited by laser radiation. In this connection, the results obtained in the study of the $CF_3Br$ molecule are of particular interest for clarifying the possibility to apply the considered method to the isotope separation in the case of a small isotopic shift in the excited vibration, which is typical for the molecules comprising isotopes of heavy elements. Thus, e.g., for the $^{235}UF_6$ and $^{238}UF_6$ isotopomers the isotopic shift in the spectrum of the vibration $v_3$ ($\sim 627$ cm$^{-1}$ [30]) is also small and amounts to $\sim 0.6$ cm$^{-1}$ [30].

Second, by many physical and chemical properties and symmetry type, the $CF_3Br$ molecule is like the $CF_3I$ molecule. The $CF_3I$ molecule and its clusters $(CF_3I)_n$ are studied very well in the context of multiphoton excitation of molecules [31, 32] and cluster fragmentation with IR and UV laser radiation [33–39]. The $(CF_3I)_n$ clusters are relatively easy to detect due to the presence of molecular and atomic ions $I_2^+$ and $I^+$ in their mass spectrum, produced in the process of multiphoton excitation of clusters by UV laser radiation [33–35]. The $CF_3Br$ molecules are easily excited by the radiation of a $CO_2$ laser [40, 41] and easily join into clusters [8]. The $(CF_3Br)_n$ clusters can be detected also by the presence of molecular ions $Br_2^+$ and products of molecular ions decay, i.e., the atomic ions $Br^+$ [8]. As shown in Ref. [9], the $(CF_3Br)_n$ clusters can be detected also by other ions of cluster fragments.

An important circumstance for the choice of the $CF_3Br$ molecules as an object of study is that thanks to the ratio of the content of $CF_3Br$ isotopomers in the nature, the experimental measurements are essentially simplified. The percentage of $CF_3^{79}Br$ and $CF_3^{81}Br$ in the natural mixture is comparable and amounts to 50.56% and 49.44%, respectively. This significantly simplifies mass spectrometric detection of the isotope ratio for the bromine atoms that arise as products of dissociation of molecules and clusters $(CF_3Br)$ and $(CF_3Br)_nAr_m$, since in the mass spectrum both isotopomers have ion signals of $Br^+$ and $Br_2^+$ with nearly similar magnitude.

The aims of the present paper are to study the possibility of bromine isotope selective control of the clustering of $CF_3Br$ molecules with argon atoms; to find the conditions under which the resonance vibrational excitation of molecules

essentially affects the nucleation process for the mixed clusters $(CF_3Br)_nAr_m$ and/or their growth under the gas-dynamic expansion of $CF_3Br$–Ar mixture; to determine the conditions for achieving the maximal effects of isotope-selective suppression of the clustering of $CF_3Br$ molecules with argon atoms and dissociation of small mixed clusters.

## 2. Experiment

### 2.1. Experimental setup

The experimental setup (Fig. 1) comprises the high-vacuum chamber with a pulsed source of molecular and cluster beam, a KMS-01/250 quadrupole mass spectrometer (produced and upgraded by 'Shibbolet' Co., Ryazan, Russia). The upper limit of the recordable mass number range of the mass spectrometer was $m/z = 300$ amu ($z$ is the degree of ionisation). The ions were detected by a VEU-6 secondary electron multiplier. The chambers of the molecular beam source and the quadrupole mass spectrometer were evacuated using turbomolecular pumps to a pressure not exceeding $10^{-5}$ Torr and $\sim 10^{-7}$ Torr, respectively. The control of the mass spectrometer was implemented by means of a personal computer. To excite molecules and clusters in the jet, we used a cw frequency-tunable $CO_2$ laser. The setup also comprises a pulse synchronisation system and a data acquisition and processing system.
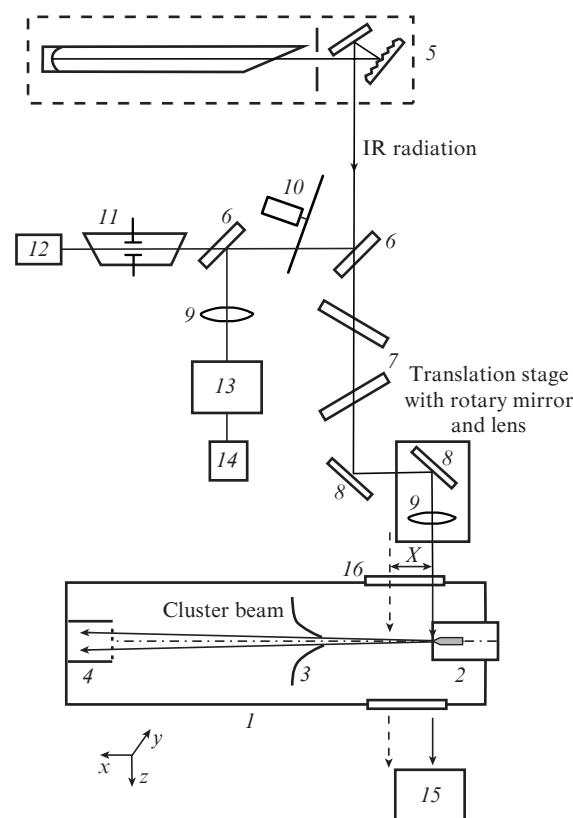


**Figure 1.** Schematic of the experimental setup:
(*1*) vacuum chamber; (*2*) pulsed nozzle; (*3*) skimmer; (*4*) quadrupole mass spectrometer; (*5*) cw CO$_2$ laser; (*6*) beam splitter; (*7*) attenuators; (*8*) plane mirror; (*9*) lens; (*10*) mechanical modulator; (*11*) optoacoustic detector; (*12*, *14*) radiation detectors; (*13*) monochromator; (*15*) power meter (movable); (*16*) NaCl window.

The beam of CF$_3$Br molecules and clusters was generated in the chamber of the source by gas-dynamic cooling of the mixture of the gas of molecules under study with the carrier argon gas as a result of hypersonic expansion through a modified (see [28]) pulsed nozzle of the General Valve type with the exit hole diameter of 0.22 mm. The repetition rate of the pulses produced by the nozzle amounted to 1 Hz. The FWHM duration of the open-nozzle pulse was equal to $450-600$ µs depending on the pressure and gas composition. The gas pressure above the nozzle varied within the range $1.5-3$ atm. Using a skimmer (Beam Dynamics, Model 1, a nozzle exit diameter of 0.49 mm) installed at the distance of 35 mm from the nozzle, the molecular/cluster beam was cut from the central part of the supersonic jet emitted from the nozzle and arrived at the ionisation chamber of the quadrupole mass spectrometer. The distance between the nozzle and the mass spectrometer chamber was 250 mm.

The cw CO$_2$ laser used to control the molecular clustering provides a radiation power of 7 W and has a semi-confocal cavity. By means of copper mirrors and a focusing spherical lens of NaCl with a focal length $f = 200$ mm, the IR laser radiation was launched into the chamber of the molecular-cluster beam via a NaCl window (Fig. 1). The diameter of the IR radiation beam spot at the lens focus amounted to $\sim 0.5$ mm. The laser beam crossed the molecular/cluster beam at an angle of 90° and could be shifted along its axis with a translation stage. Attenuators were used to change the power of laser radiation. The maximal power of radiation input into the chamber amounted to about 5 W; the IR radiation transmitted through the chamber was recorded by a power meter. The CO$_2$ laser operated at 9R-branch (near 9.2 µm). As shown in Ref. [8], the maximal value of selectivity in the process of molecular clustering suppression can be observed when the particles are irradiated by the 9R(30) line of the laser (at a frequency of 1084.365 cm$^{-1}$). Therefore, in the present paper this line was used to irradiate the particles in the jet. The tuning of the CO$_2$ radiation frequency to the 9R(30) line was controlled by an MS 2004 monochromator-spectrograph (SOL Instruments, Belarus, Minsk) and an optoacoustic receiver filled with ammonia (the lines of ammonia IR absorption served as reference marks for tuning).

## 2.2. Method of study

The idea of laser control of the process of cluster formation consists in preliminary (before the beginning of clustering process) vibrational excitation of molecules, including those of the given sort, under gas-dynamic expansion at the nozzle exit. As a result, in the process of subsequent condensation the accumulated vibrational energy suppresses (prevents) the clustering of excited molecules. Besides that, under the appropriate choice of the place of irradiating particles at the jet axis in the space in front of the skimmer (see Fig. 1) one can implement dissociation of small clusters (dimers) and thus control the process of molecular clustering [8, 9, 28]. In this case, it is required to provide (e.g., by choosing the appropriate conditions of the gas expansion) preferable formation of dimers and the absence of larger-size clusters.

In the process of gas clustering under its gas-dynamic expansion at the nozzle exit, one can select a few stages (Fig. 2), occurring in different domains of the jet [8, 9, 28], listed below.

Domain I is characterised by fast cooling of translational and internal degrees of freedom of molecules with the energy
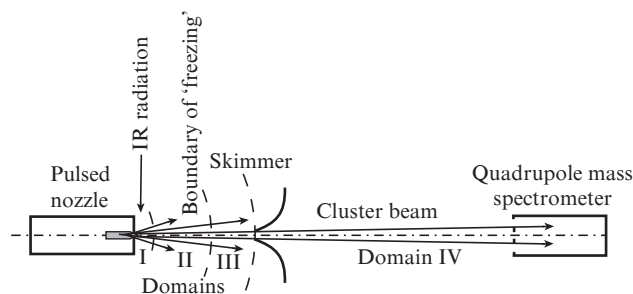


**Figure 2.** Formation of a cluster beam under the conditions of a pulsed jet.

transfer into the kinetic energy of the directed jet motion and the medium transition to the oversaturated state, which leads to the formation of seed clusters.

Collision domain II is characterised by gas-dynamic cooling of molecules and the growth of clusters in the jet with some heating of the system at the expense of the condensation energy.

In domain III after the 'freezing' zone, the particles exhibit collision-free motion and the cluster system stabilises.

Domain IV is located between the skimmer and the mass spectrometer, where the beam particles freely propagate.

To study the effect of the resonance IR excitation of the jet molecules on the cluster beam formation at different stages of clustering, it is necessary to irradiate the particles in the corresponding domains of the jet and to detect the changes in the beam parameters in the detection zone. The signal of the cluster component of the beam may decrease for several reasons [8, 9, 29].

If the jet is irradiated in domain I, then due to IR excitation of molecules the local increase in temperature is possible, which will inhibit the formation of seed clusters. Ideally, this can prevent further clustering of the molecules. Under strong dilution of the molecules with the inert gas, when the probability of the collision between the molecules is small, the clustering of the excited molecules can be selectively suppressed.

If the particles are exposed to IR laser radiation in domain II, the vibrational heating will take place for both the molecules and the clusters that have already appeared in the jet. In this case, partial fragmentation of the clusters is possible. The heating of particles occurs against the background of their gas-dynamic cooling (particularly, in the presence of a carrier gas) and further modifications of the jet cluster composition (the growth of clusters, the evolution of their size distribution). If the particles are irradiated in the collision-free domain III, the effect of IR radiation is mainly reduced to the heating of clusters and their fragmentation, which is reflected in the appropriate reduction of the signal from cluster component of the beam.

Thus, the excitation of the jet particles by the resonance IR laser radiation in domains I–III can lead to both the suppression of molecular clustering and to the dissociation of the already formed clusters, depending on the particular localisation of jet irradiation [8, 9, 28].

## 3. Results and discussion

In contrast to the conditions for the formation of homogeneous clusters (CF$_3$Br)$_n$, the formation of mixed clusters (CF$_3$Br)$_n$Ar$_m$ requires significantly stronger cooling of particles in the diverging jet. This is due to the fact that the binding

energy of $CF_3Br$ molecules in a homogeneous cluster $(CF_3Br)_n$ (0.25–0.3 eV [35]) considerably exceeds the energy of binding the molecule $CF_3Br$ with the argon atoms in the mixed cluster $(CF_3Br)_nAr_m$ (not exceeding 0.1 eV [1, 39]). Due to this fact, the jet temperature, necessary for the formation of mixed clusters $(CF_3Br)_nAr_m$ should be essentially lower than for the formation of homogeneous clusters $(CF_3Br)_n$ [42]. With this fact taken into account, in the present paper we used a strongly diluted mixture of the molecular $CF_3Br$ gas with argon. The studies were carried out with the $CF_3Br–Ar$ mixtures having a pressure ratio 1: $N$, where $N = 100$ or $N = 200$, and a total pressure of the gas above the nozzle 1.5 atm.

For such parameters of the gas above the nozzle, mixed clusters containing a small ($n = 1–2$) number of $CF_3Br$ molecules are rather efficiently produced, whereas the probability of the formation of homogeneous clusters $(CF_3Br)_n$ of larger size was small. Moreover, the small total pressure of the gas above the nozzle and sufficiently strong dilution of the mixture facilitate the achievement of larger values of the separation parameters (selectivities and enrichment factors) for the process of molecular clustering suppression. At a large total pressure of the gas above the nozzle and not strong dilution, the processes of gas heating and vibration–vibrational energy exchange between the isotopomers of $CF_3Br$ lead to a decrease in the enrichment factors and selectivities [8, 9].

In the experiments we measured and analysed the ion signals of the mixed cluster fragments $BrAr^+$ ($m/z = 119$ and 121 amu) both in the absence of jet irradiation and under the irradiation by a $CO_2$ laser. From these measurements, we determined the enrichment factors for the chosen isotopes of bromine in the cluster beam, as well as the depletion (exhaustion) of the beam with clusters due to the jet irradiation. Between the peaks of cluster fragments $^{79}BrAr^+$ ($m/z = 119$ amu) and $^{81}BrAr^+$ ($m/z = 121$ amu) in the mass spectrum, the ion peak $Ar_3^+$ ($m/z = 120$ amu) of the argon clusters was detected with confidence (see Figs 4 and 5).

Figure 3 shows the effect of IR radiation on the molecular cluster beam when using the $CF_3Br–Ar$ mixtures with the pressure ratios 1:100 and 1:200. The figure presents the dependences of the magnitude of the cluster $^{79}BrAr^+$ ion signal (normalised to the value of this signal in the unirradiated jet) on the distance $X$ from the zone of the jet irradiation to the nozzle exit. In both cases, the total pressure above the nozzle is equal to 1.5 atm. The particles of the jet exiting from the nozzle were irradiated by the focused radiation of the $CO_2$ laser at a frequency of 1084.635 cm$^{-1}$ [the line 9R(30)] at different distances $X$ from the nozzle exit. The above frequency of laser oscillation is close to the frequency of vibrations $v_1$ in the molecules $CF_3^{79}Br$ (1084.77 cm$^{-1}$) and $CF_3^{81}Br$ (1084.52 cm$^{-1}$) [29]. It lies between Q-branches in the IR absorption spectra of the above molecules, and at low temperatures, when the Q-branches are well resolved, finds itself at the long-wavelength edge of the Q-branch of the $CF_3^{79}Br$ molecule (the detuning 0.134 cm$^{-1}$) [29]. For each particular position of the irradiation zone (the value of $X$) the mass spectra of the ion signals $^{79}BrAr^+$, $Ar_3^+$ and $^{81}BrAr^+$ ($m/z = 119$, 120, and 121 amu) were recorded.

When the jet is irradiated immediately at the exit from the nozzle at point $X = 0$ (the laser beam touching the nozzle), the molecules are not cooled yet, and their concentration, and, therefore, the collision frequency, is great. The radiation of the $CO_2$ laser mainly excites the $CF_3^{79}Br$ molecules, but due to the reasons mentioned above, the excitation energy is transferred to the $CF_3^{81}Br$ molecules as well. As a result, all
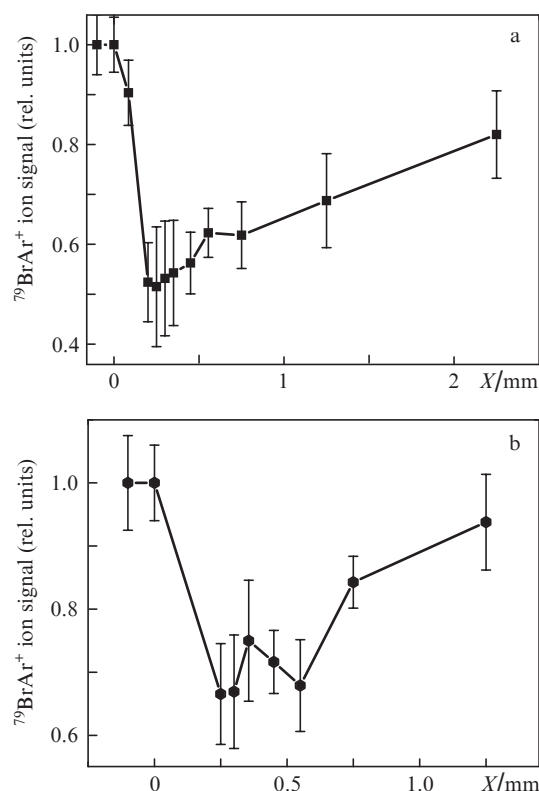


**Figure 3.** Dependence of the magnitude of $^{79}BrAr^+$ cluster ion signal (normalised to the value of this signal in the unexposed jet) on the distance $X$ from the zone of the jet laser irradiation to the exit of the nozzle for the mixtures $CF_3Br–Ar$ with the pressure ratios (a) 1:100 and (b) 1:200. The total pressure of the gas above the nozzle here and in Figs 4–6 equals 1.5 atm.

molecules $CF_3Br$ and the atoms of the carrier gas are strongly heated. In this case, the process of cluster formation is significantly suppressed. The ion peaks of the cluster fragments $^{79}BrAr^+$ as well as $^{81}BrAr^+$ in the mass spectrum of the beam strongly decrease (Fig. 3). The sharp intensity decrease of $^{79}BrAr^+$ and $^{81}BrAr^+$ cluster ion peaks at a slight displacement of the jet irradiation zone from the nozzle exit, in our opinion, is related to small (much smaller than the laser beam spot size) spatial dimension of the cluster formation zone (see below).

When the domain of the jet irradiation of the nozzle is moved away to a distance of $0.25 \leqslant X \leqslant 1.25$ mm, where the cooling of molecules and cluster formation occurs, the selective suppression of clustering of molecules with argon atoms is possible, since the concentration of molecules in this region is small. The selectivity of the IR radiation at the 9R(30) line with respect to the $CF_3Br$ isotopomers entering the formed mixed clusters $(CF_3Br)_nAr_m$ is practically absent. This is due to the overlap of IR absorption spectra of the $CF_3^{79}Br$ and $CF_3^{81}Br$ isotopomers, contained in the cluster 'pack', and the large width of the IR absorption spectra of the clusters [43]. Thus, in this domain the clustering of the molecules with argon atoms is suppressed, including the selective one, together with the dissociation of small (seed) $(CF_3Br)_nAr_m$ clusters [1, 8, 9]. If the jet is irradiated with the laser at the distance $X \geqslant 1.5$ mm, then the formed clusters are nonselectively dissociated [8, 9]. Due to the small power of the laser radiation (no more than 5 W), the probability of dissociation (fragmentation) of clusters is not great. Hence, under the jet

irradiation the amplitudes of the $^{79}BrAr^+$ and $^{81}BrAr^+$ ion peaks decrease (as compared to the amplitudes in the absence of irradiation) not very strongly, nearly by 20% and 10% in the cases shown in Figs 3a and 3b, respectively. Note that with the increasing dilution of $CF_3Br$ with argon, the region with the maximal suppression of molecular clustering becomes narrowed and shifts to the nozzle exit. This is related to the acceleration of the process of cooling of $CF_3Br$ molecules under gas-dynamic expansion due to stronger dilution with the carrier gas. The region where selective control of molecular clustering is possible is also narrowed and shifted towards the nozzle exit.

Therefore, the selective influence of IR radiation on the clustering of one of the chosen isotopomers of $CF_3Br$ can be observed only within a narrow range of distances from the irradiation zone to the nozzle, where the cooling of molecules occurs and the clusters only begin to appear. In Fig. 3, this range is estimated as 0.25–1.25 mm. In this region, one can find the selective influence of IR radiation on the formation of clusters, and, as a result, a stronger decrease in the amplitude of the $^{79}BrAr^+$ ion peak as compared to the ion peak $^{81}BrAr^+$.

Figure 4 presents the mass spectra of cluster fragments $^{79}BrAr^+$, $Ar_3^+$, and $^{81}BrAr^+$ ($m/z$ = 119, 120, and 121 amu) in the absence of jet irradiation (Fig. 4a) and with irradiation by

a $CO_2$ laser at the 9R(30) line (the frequency 1084.635 cm$^{-1}$), the power of radiation being ~4.6W (Fig. 4b). The $CF_3Br-Ar$ mixture with the pressure ratio 1:100 was used. The total pressure above the nozzle amounted to 1.5 atm. The jet was irradiated at the distance $X$ = 0.45 mm from the nozzle exit. Figure 5 presents similar spectra in the case of using the $CF_3Br-Ar$ mixture with the pressure ratio 1:200 and the total pressure 1.5 atm above the nozzle. The jet was irradiated at the distance $X$ = 0.3 mm from the nozzle exit, the power of laser radiation being ~3.8 W. The presented spectra are a result of averaging over ten mass spectra scans in the above-mentioned range of mass numbers with the resolution 0.05 amu. The laser radiation at the 9R(30) line is stronger absorbed by the $CF_3{}^{79}Br$ molecules. From Figs 4 and 5 one can see that under irradiation of the jet the cluster ion signal $^{79}BrAr^+$ ($m/z$ = 119 amu) decreases much stronger than the $^{81}BrAr^+$ ion signal ($m/z$ = 121 amu). This fact confirms the process of selective suppression of clustering of the $CF_3{}^{79}Br$ molecules with the argon atoms.

Figure 6 presents the results of evaluating the enrichment factors $K_{enr}(^{79}Br)$ in the cluster beam in the case of using the $CF_3Br-Ar$ mixtures with the pressure ratios 1:100 and 1:200 and the total pressure of gas above the nozzle 1.5 atm in both cases. The results are obtained by detecting the mixed cluster ion signals $^{79}BrAr^+$ and $^{81}BrAr^+$ ($m/z$ = 119 and 121 amu,
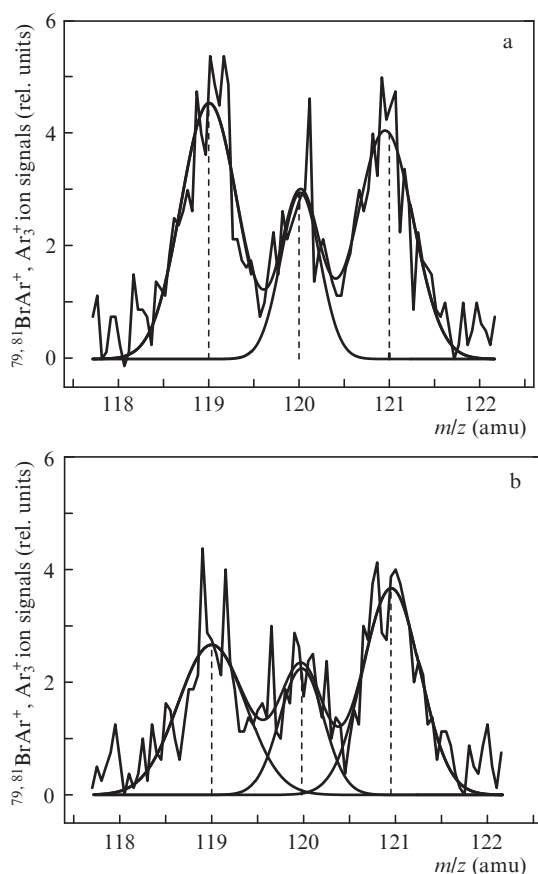


**Figure 4.** Mass spectra of cluster fragments $^{79}BrAr^+$, $Ar_3^+$, and $^{81}BrAr^+$ ($m/z$ = 119, 120, and 121 amu) (a) in the absence of the jet irradiation and (b) with the irradiation by the $CO_2$ laser at the 9R(30) line (the frequency 1084.635 cm$^{-1}$) with a laser power of ~4.6 W. The $CF_3Br-Ar$ mixture with the pressure ratio 1:100 was used. The irradiation of the jet was executed at the distance $X$ = 0.45 mm from the nozzle. The experimental spectra are approximated by Gaussian curves.
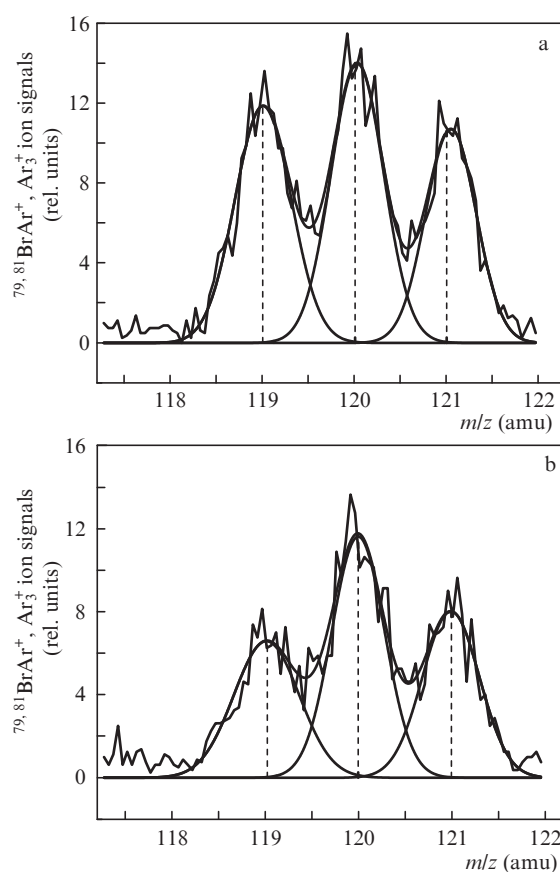
**Figure 5.** Mass spectra of the cluster fragments $^{79}BrAr^+$, $Ar_3^+$, and $^{81}BrAr^+$ ($m/z$ = 119, 120, and 121 amu) (a) in the absence of the jet irradiation and (b) with the irradiation by the $CO_2$ laser at the 9R(30) line (the frequency 1084.635 cm$^{-1}$) with a laser power of ~3.8 W. The $CF_3Br-Ar$ mixture with the pressure ratio 1:200 was used. The jet was irradiated at the distance $X$ = 0.3 mm from the nozzle. The experimental spectra are approximated by Gaussian curves.
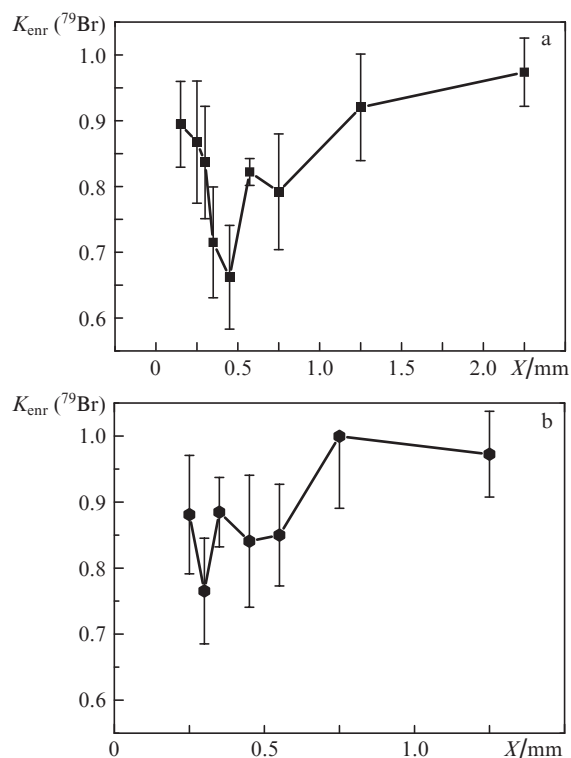
**Figure 6.** Dependences of the enrichment factor $K_{enr}(^{79}Br)$ on the distance to the jet irradiation zone in the case of irradiating the mixtures $CF_3Br-Ar$ with the pressure ratio (a) 1:100 and (b) 1:200 and the radiation power of the $CO_2$ laser (a) 4.6 W and (b) 3.8 W.

respectively) and averaging the data of ten intensity measurements in the mass spectra. The jet irradiation was performed with the line 9R(30) of the laser (frequency 1084.635 cm$^{-1}$). The enrichment factor $K_{enr}(^{79}Br)$ of the cluster beam with the isotope $^{79}Br$ was determined as the ratio of concentrations of bromine isotopes, contained in the mixed clusters $(CF_3Br)_nAr_m$ and measured after the irradiation of the molecular jet with the $CO_2$ laser, to the ratio of initial concentrations of the bromine isotopes in the mixture $CF_3Br-Ar$, measured in the mass spectrum before the irradiation. The concentrations of bromine atoms before and after the irradiation of the jet were assumed proportional to the corresponding ion signals in the mass spectrum. Thus,

$$K_{enr}(^{79}Br) = \frac{(I_{119}/I_{121})_{las\,on}}{(I_{119}/I_{121})_{las\,off}}, \qquad (1)$$

where $I_{119}$ and $I_{121}$ are the intensities of the $^{79}BrAr^+$ and $^{81}BrAr^+$ signals, respectively. To determine the ion signals entering Eqn (1), the experimental ion peaks were approximated by Gaussian curves (see Figs 4, 5) and the area under them was evaluated by integration. We define the selectivity $\alpha$ of the process of $CF_3Br$ molecules clustering suppression as the ratio of the probability of clustering suppression for $CF_3{}^{79}Br$ molecules to that for $CF_3{}^{81}Br$, i.e., $\alpha = \beta_{79}/\beta_{81}$. The quantities $\beta_{79}$ and $\beta_{81}$, in analogy with the yield of dissociation of molecules caused by the laser IR multiphoton excitation [10–12], describe the relative decrease of the $CF_3{}^{79}Br$ and $CF_3{}^{81}Br$ molecules content in the composition of the mixed clusters $(CF_3Br)_n/Ar_m$ of the detected cluster beam.

Since the jet irradiation results in the selective suppression of clustering predominantly for $CF_3{}^{79}Br$, the enrichment factor, determined according to Eqn (1) is smaller than unity. In our case, the beam is depleted with the $^{79}Br$ atoms and enriched with the $^{81}Br$ atoms. The enrichment coefficient of the cluster beam for the atoms $^{81}Br$ is equal to the inverse of $K_{enr}(^{79}Br)$.

Table 1 presents the determined enrichment factors, selectivities, and degrees of the beam depletion with $^{79}Br$ isotopes (the values of the residual ion signals $^{79}BrAr^+$), obtained from the measurement of the abovementioned cluster ion peaks under the particular experimental conditions. For comparison, we also present some data of Ref. [9] related to the control of clustering of $CF_3Br$ molecules. From the presented data, it follows that by controlling the clustering of $CF_3Br$ molecules with argon atoms one can achieve much higher enrichment factors and selectivities than by controlling the clustering of $CF_3Br$ molecules among themselves. One of the possible causes of this fact is that, as already noted above, the clustering of molecules among themselves occurs in the jet at significantly higher temperature, and therefore, greater concentration of particles, than the clustering of molecules with argon atoms. Therefore, the optical selectivity of the $CF_3Br$ molecule excitation (and, therefore, the selectivity of suppression of molecular clustering) in the second case is higher than in the first one.

Note that increasing the dilution of the molecular gas with the carrier gas one could expect the enrichment factor to increase due to stronger cooling of the gas and the corresponding narrowing of molecular absorption spectra, as well the decreased in the rate of vibrational energy exchange between the isotopomers $CF_3{}^{79}Br$ and $CF_3{}^{81}Br$. However, no such dependence was observed in our study. In our opinion, this is because the increased degree of the gas dilution strongly

**Table 1.** Results of the study of selective suppression of clustering of the $CF_3Br$ molecules among themselves (from Ref. [9]) and with argon atoms (the present study, shown in boldface) under gas-dynamic expansion of the $CF_3Br-Ar$ mixtures under different conditions of the experiment. The jet irradiation was executed with the radiation of the $CO_2$ laser at the 9R(30) line (the frequency 1084.635 cm$^{-1}$), the total pressure of the gas above the nozzle 1.5 atm.

| $p_{CF_3Br}:p_{Ar}$ | Laser power/W | Measured ion peak | $m/z$ (amu) | Value of residual signal | $K_{enr}(^{79}Br)$ | $\alpha(^{81}Br_2/^{79}Br)$ | Nozzle pulse duration/μs | $X$/mm |
|---|---|---|---|---|---|---|---|---|
| 1:10 | 5.0 | $Br_2^+$ | 158, 160, 162 | 0.37±0.11 | 0.84±0.07 | 1.18±0.04 | 450 | 0.45 |
| 1:10 | 4.9 | $CF_3Br_2^+$ | 227, 229, 231 | 0.38±0.03 | 0.98±0.03 | 1.03±0.02 | 450 | 0.55 |
| 1:30 | 5.0 | $CF_3Br_2^+$ | 227, 229, 231 | 0.47±0.02 | 0.95±0.02 | 1.12±0.01 | 450 | 0.45 |
| 1:30 | 5.1 | $CF_3Br_2^+$ | 296, 298 | 0.31±0.04 | 0.90±0.06 | | 450 | 0.45 |
| **1:100** | **4.6** | **$BrAr^+$** | **119, 121** | **0.62±0.07** | **0.67±0.05** | **4.02±0.19** | **600** | **0.45** |
| 1:100 | 3.9 | $CF_3Br_2^+$ | 296, 298 | 0.54±0.08 | 0.90±0.05 | | 450 | 0.45 |
| **1:200** | **3.8** | **$BrAr^+$** | **119, 121** | **0.67±0.09** | **0.77±0.09** | **2.31±0.11** | **600** | **0.3** |
| 1:200 | 3.8 | $CF_3Br_2^+$ | 296, 298 | 0.59±0.03 | 0.88±0.04 | | 600 | 0.3 |

diminishes the size of the region in which it is possible to control the molecular clustering (contracting this region to a point). As a result, the region of 'localisation' of the effect becomes significantly smaller than the diameter ($\sim$0.5 mm) of the laser beam spot (see Fig. 3b), which undoubtedly leads to the reduction of the selectivity of clustering suppression.

Using the obtained results, we can make some estimates that allow better understanding of the relation between the parameters of the process studied by us. Based on the IR absorption spectrum of the laser-excited isotopomers of $CF_3Br$ molecules measured in Ref. [29] at a low ($\sim$50 K) temperature and a small (50–60 MHz) width of the laser radiation spectrum, we estimated the optical selectivity of exciting $CF_3{}^{79}Br$ relative to $CF_3{}^{81}Br$ at the laser radiation frequency as 25–30. The actual selectivities, obtained by us, are significantly smaller than this value. This is due to the following reasons. First, due to the high concentration of molecules in the excitation zone, efficient vibration–vibrational energy exchange between the $CF_3{}^{79}Br$ and $CF_3{}^{81}Br$ molecules may occur. Apparently, this is the main reason of the selectivity loss in the process of molecular clustering. Second, in the zone of molecular excitation near the exit from the nozzle, the jet is not yet cold enough, the temperature of the particles being probably significantly higher than 50 K and, therefore, the optical selectivity of the particle excitation is smaller than the value presented above. Besides that, because of a rather large size of the laser beam spot ($\sim$0.5 mm) the region of irradiation of the particles considerably exceeds the region of localisation of the maximal selectivity of molecular excitation both in concentration and in temperature. In the rapidly diverging jet, these parameters strongly vary even within the limits of the irradiation region itself.

In conclusion, note that the main goal of the present study was to investigate the possibility of bromine isotope selective control of clustering of $CF_3Br$ molecules with argon atoms. The obtained results, in our opinion, clearly demonstrate this possibility. At the same time, many unknown or not yet studied characteristics and parameters of the considered method exist. In particular, they include the concentration and temperature of the gas in the jet, the structure of IR absorption spectra of $CF_3Br$ isotopomers near the frequency, at which the laser excites them, and the rate of vibration energy exchange between $CF_3Br$ isotopomers.

To obtain higher selectivity values for the process of controlling the $CF_3Br$ molecule clustering with argon atoms, it is necessary to optimise the process and to take all the factors mentioned above into account, which is a subject of further studies.

The isotope-selective suppression of $CF_3Br$ molecules clustering among themselves and with argon atoms, in principle, can be used to separate isotopes. One of the possible ways to implement this process is to suppress selectively the clustering of the chosen isotope modification of molecules at the first stage. These molecules will propagate in the beam within the solid angle, significantly exceeding the angle of propagation for colder and heavier clusters, containing nontarget molecules, so that at the second stage further spatial separation of target molecules from the cluster beam is possible. In this separation scheme, the achievement of a maximal separation factor requires providing not only high optical selectivity of IR excitation of necessary isotopic modifications of the molecules, but also sufficiently high selectivity of the spatial separation of the nontarget molecules from the cluster beam.

## 4. Conclusions

The process of suppression of $CF_3Br$ molecules clustering with argon atoms under the gas-dynamic expansion of the $CF_3Br-Ar$ mixture at the exit of the nozzle using the cw $CO_2$ laser radiation is studied. The dependences of the molecular–atomic clustering suppression efficiency on the gas composition above the nozzle, as well as on the distance between the jet irradiation zone and the nozzle exit are obtained. It is shown that one can selectively control the process of clustering of $CF_3Br$ molecules with argon atoms by irradiating the jet at the 9R(30) line of the $CO_2$ laser radiation (1084.635 cm⁻¹).

It is shown that due to the resonance vibrational excitation of gas-dynamically cooled $CF_3Br$ molecules at the exit from the nozzle using the radiation of the $CO_2$ laser one can implement bromine isotope-selective suppression of clustering of $CF_3Br$ molecules with argon atoms. Using the $CF_3Br-Ar$ mixtures with pressure ratios 1:100 and 1:200 and a total pressure of gas above the nozzle 1.5 atm, we obtained the enrichment factors $K_{enr}({}^{79}Br) \approx 0.67\pm0.05$ and $K_{enr}({}^{79}Br) \approx 0.77\pm0.09$, respectively. The selectivity of the processes $\alpha$ amounted to $4.02\pm0.19$ in the first case and to $2.31\pm0.11$ in the second one.

It is found that the clustering of $CF_3Br$ molecules with argon atoms allows much greater enrichment factor and selectivity than the clustering of molecules $CF_3CBr$ among themselves (see Table 1).

The obtained results on the control of $CF_3Br$ molecules clustering with argon atoms allow a conclusion that using the studied method one can selectively control the clustering of molecules comprising isotopes of heavy metals ($OsO_4$, $WF_6$, $UF_6$) that have small isotopic shifts ($\sim$0.25 cm⁻¹) in the IR absorption spectra.

We emphasise that we have found relatively large values of the enrichment factor and selectivity. For example, in the analogous experiments on the selective dissociation of the ${}^{32}SF_6$ and ${}^{34}SF_6$ molecules with the isotopic shift in the excited vibration $\nu_3$ amounting to $\sim$17 cm⁻¹ the value of $K_{enr} \approx 2$ was achieved [23]. At the same time, we would like to note that the enrichment factors and selectivities of the process of suppressing the clustering of $CF_3Br$ molecules with argon atoms obtained by us are affected by many factors, a number of which, apparently, could reduce the values measured by us.

Probably, the conditions of irradiation, i.e., the gas pressure above the nozzle, the laser power, the degree of spatial overlapping of the IR laser beam with the region of maximal localisation of the effect, were not optimal for achieving the maximal selectivity. The diameter of the laser beam spot ($\sim$0.5 mm) was comparable with or even greater than the size of this region. Moreover, the results of the measurements were significantly affected by the instabilities of the frequency and mode structure of the $CO_2$ laser radiation. Probably, these factors, alongside with nonlinear processes of ionisation and fragmentation of clusters in the mass spectrometer, led to a relatively great error in the measurement of intensities of mass peaks. Careful optimisation of experimental parameters (the conditions of gas exit, the location and size of irradiation site) and the parameters of laser radiation are expected to allow a considerable increase in the enrichment factors and selectivity of the process.

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