

Brome isotope selective control of CF₃Br molecule clustering by IR laser radiation in gas-dynamic expansion of CF₃Br – Ar mixture

V.M. Apatin, V.N. Lokhman, G.N. Makarov, N.-D.D. Ogurok, E.A. Ryabov

Abstract. We report the results of research on the experimental control of CF₃Br molecule clustering under gas-dynamic expansion of the CF₃Br–Ar mixture at a nozzle exit by using IR laser radiation. A cw CO₂ laser is used for exciting molecules and clusters in the beam and a time-of-flight mass-spectrometer with laser UV ionisation of particles for their detection. The parameters of the gas above the nozzle are determined (compositions and pressure) at which intensive molecule clustering occurs. It is found that in the case of the CF₃Br gas without carrier when the pressure P_0 above the nozzle does not exceed 4 atm, molecular clusters actually are not generated in the beam. If the gas mixture of CF₃Br with argon is used at a pressure ratio 1 : N , where $N \geq 3$, and the total pressure above the nozzle is $P_0 \geq 2$ atm, then there occurs molecule clustering. We study the dependences of the efficiency of suppressing the molecule clustering on parameters of the exciting pulse, gas parameters above the nozzle, and on a distance of the molecule irradiation zone from the nozzle exit section. It is shown that in the case of resonant vibrational excitation of gas-dynamically cooled CF₃Br molecules at the nozzle exit one can realise isotope-selective suppression of molecule clustering with respect to bromine isotopes. With the CF₃Br–Ar mixtures having the pressure ratio 1 : 3 and 1 : 15, the enrichment factors obtained with respect to bromine isotopes are $k_{\text{enr}} \approx 1.05 \pm 0.005$ and $k_{\text{enr}} \approx 1.06 \pm 0.007$, respectively, under jet irradiation by laser emission in the 9R(30) line (1084.635 cm⁻¹). The results obtained let us assume that this method can be used to control clustering of molecules comprising heavy element isotopes, which have a small isotopic shift in IR absorption spectra.

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

1. Introduction

Isotopes of chemical elements are widely known to be used in scientific investigations and various applications: medicine, nuclear power engineering, semiconductor production, and other fields [1]. The advent of lasers stimulated interest in their use for isotope separation. Already in the early 1970s, the employment of first ruby and neo-

dimium glass lasers made it possible to make first experiments on laser isotope separation [2–4]. Creation of IR lasers, in particular, pulsed CO₂ lasers opened the possibility of using laser radiation for affecting a vibrational subsystem of molecules, which gave a chance to carry out first experiments on laser isotope separation by the method of selective two-stage IR–UV photodissociation of molecules [5].

Development and production of high-power, high-repetition-rate CO₂ lasers (see monograph [6] and references therein), discovery of multiphoton dissociation (MPD) of molecules by IR laser radiation [7, 8], and demonstration of the isotopic selectivity of the IR MPD process [9, 10] raised interest to studying laser isotope separation [11–16]. From a great number of laser methods for isotope separation suggested presently, the best results have been obtained with the MPD of molecules by IR radiation of high-power pulsed CO₂ lasers. On a basis of this method, production of carbon isotopes has been started successfully in Russia (Kaliningrad) [17–19].

Note that the interest in laser isotope separation was mainly related to studying possible efficient and competitive laser methods for separating uranium isotopes in atomic power engineering. Since the 1970s, the USA and other countries (England, Germany, France, South Africa, Japan, Australia) undertook serious efforts on developing technologies for laser separation of uranium isotopes with employment of either atomic vapour (AVLIS – atomic vapour laser isotope separation), or UF₆ molecules (MLIS – molecular laser isotope separation). A review of results obtained can be found in [20, 21], respectively, and also in [22]. However, for a number of reasons, in the late 1990s most projects on laser isotope separation in the frameworks of these approaches have been closed.

One of the factors determining the efficiency of laser IR multiphoton dissociation of molecules [15–19] for separating isotopes of heavy element including uranium is relatively high energy consumption of the process. For example, dissociation of UF₆ molecule requires absorption of approximately 40 quanta of IR radiation at a wavelength of 16 μm, that is, the absorption energy of ~3.1 eV per molecule. Hence, one of the ways for further improvement of the MLIS approach is the employment of low-energy physical–chemical processes possessing an activation energy of at most 0.3–0.5 eV [23–28]. It is mainly related to the fact that the technology of uranium isotope separation is being presently developed in the USA, which is based on the SILEX method (separation of isotopes by laser excitation) [29–32]. Although the principles of this method are untold, it is probably based on one of such low-energy approaches.

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Thus, investigations aimed at the development of low-energy methods for laser isotope separation (LEMLIS) appropriate for heavy elements are actual and needed. In the case of LEMLIS, the activation energy should not exceed 0.5–1 eV. Such energies are inherent in physical–chemical processes of molecule adsorption and desorption on a surface (including that of large clusters), and in dissociation and fragmentation of loosely coupled van der Waals molecules [23]. The SILEX technology is probably based on low-energy methods hypothetically related to isotope-selective processes, which suppress molecule clustering and/or small-cluster dissociation under gas-dynamic expansion of gas (UF_6 with carrier) at the nozzle exit [33]. The activation energy of these processes is not above 0.3–0.5 eV. According to developers, the SILEX technology is also applicable to separating isotopes of other elements (silicon, boron, sulphur, carbon, oxygen, etc.) [23, 29, 31].

Works [34–39] demonstrate the possibility of selecting sulphur isotopes by using the method of selective suppression of SF_6 molecule clustering and dissociation of SF_6 molecule clusters in gas-dynamic jets by radiation of a cw CO_2 laser (see also review [23] and references therein). As applied to the development of low-energy methods of laser isotope separation, the authors of Refs [40–43] investigate the processes of molecule and cluster interaction in crossing beams and consider the possibility of realising IR-laser-induced selective processes of capturing vibrationally excited and unexcited SF_6 molecules by large xenon clusters [40, 41] and disintegration of small weakly coupled van der Waals clusters (argon, krypton, nitrogen) in collisions with vibrationally excited SF_6 molecules [42, 43] for isotope selection. The control of clusterisation process is investigated in [44] for CF_3I molecules by resonance vibrational excitation of molecules and clusters using IR radiation of a cw CO_2 laser in gas-dynamic expansion of CF_3I gas mixtures with argon and xenon gas-carriers at the nozzle exit. The results obtained show that the method employed to control the process of cluster generation in molecular beams can be used for isotope selection.

In the present work we present investigation results on controlling the processes which suppress clustering of CF_3Br molecules and dissociation of small clusters. This molecule was chosen for the study because it has a very small isotopic shift (approximately 0.248 cm^{-1}) for $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$ isotopomers in the spectrum of vibration ν_1 ($\sim 1085\text{ cm}^{-1}$) [45] excited by laser radiation. Thus, the results obtained with the CF_3Br molecule are interesting from the viewpoint of possible employment of this method for separating isotopes in molecules having a small isotopic shift in an excited vibration, which is typical of molecules comprising heavy elements. For example, for $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ isotopomers, the isotopic shift for vibration ν_3 ($\sim 627\text{ cm}^{-1}$) is also small and equals approximately 0.6 cm^{-1} [21].

The choice of the CF_3Br molecule is also related to the fact that in many physical and chemical properties and the type of symmetry, it is similar to the CF_3I molecule. The latter molecule and its clusters ($(\text{CF}_3\text{I})_n$ (n is the number of molecules in a cluster)) are well studied in the cases of IR multiphoton excitation [46, 47] and cluster fragmentation by IR and UV laser radiation [48–53]. The $(\text{CF}_3\text{I})_n$ clusters can be relatively easily detected because molecular and atomic ions I_2^+ and I^+ comprised in their mass-spectra are formed in the process of cluster multiphoton excitation by UV laser radiation [48–50]. Molecules CF_3Br are also well excited by CO_2 -laser radiation

[54, 55] and, as will be shown below, easily form $(\text{CF}_3\text{Br})_n$ clusters, which can be detected by molecular ions Br_2^+ and products of molecular ion decay, namely, atomic ions Br^+ that are formed under cluster multiphoton excitation by UV radiation (see Section 3.1).

One more reason for choosing the CF_3Br molecule as the object of investigation is the fact that the natural content of CF_3Br isotopomers substantially simplifies experimental measurements. The natural contents of $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$ are comparable and equal to 50.56% and 49.44%, respectively. This substantially simplifies mass-spectrometric detection of the isotopic ratio for bromine atoms, which are dissociation products of the CF_3Br molecule and clusters, because Br^+ ion signals in mass-spectra are approximately equal for both isotopomers.

The present work is aimed at determining conditions, in which the resonance vibration excitation of CF_3Br molecules by IR laser radiation substantially affects the process of $(\text{CF}_3\text{Br})_n$ cluster generation and/or their growth in gas-dynamic expansion of the CF_3Br mixture with argon and finding the optimal conditions in which molecule clustering is isotopically suppressed.

2. Experimental setup and investigation method

The experimental setup and investigation method are thoroughly described in recent work [44]. Briefly recall the main features important for experiments with the CF_3Br molecule. The experimental setup (Fig. 1) comprises a high-vacuum chamber with a pulsed source of a molecular-cluster beam, a photoionisation time-of-flight mass-spectrometer, and a cw frequency-tunable CO_2 laser. A turbo-molecular pump evacuates chambers of the molecular beam source and mass-spectrometer to a pressure of 10^{-5} and 10^{-7} Torr, respectively. Pulsed UV and IR lasers, a pulse synchronising system, and a data acquisition and processing system are also included in the setup.

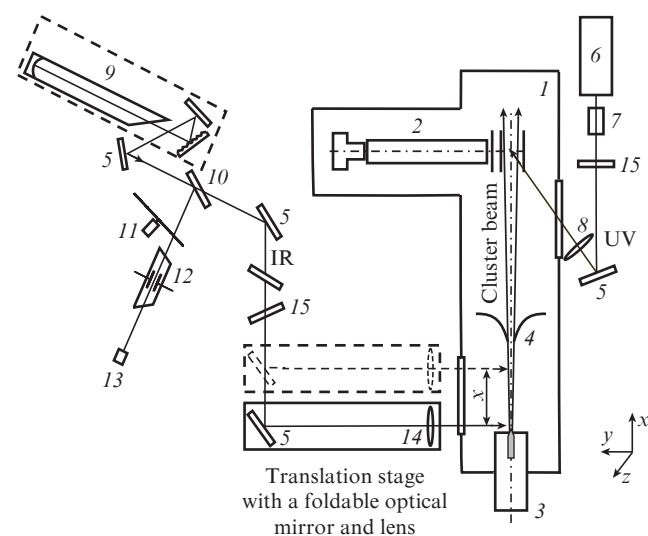


Figure 1. Schematic of the experimental setup: (1) vacuum chamber; (2) mass-spectrometer; (3) pulsed nozzle; (4) skimmer; (5) plane mirror; (6) dye laser pumped by XeCl-laser radiation; (7) BBO crystal; (8) lens; (9) cw CO_2 laser; (10) beam splitter; (11) mechanical modulator; (12) optical-acoustic detector with ammonia; (13) radiation sensor; (14) lens; (15) light attenuators.

The cw CO₂ laser used for controlling molecule clustering had a semiconfocal cavity. The laser power was 10–12 W. Copper mirrors and a focusing spherical lens made of NaCl with a focal length $f = 200$ mm directed the IR radiation of the laser to the chamber of the molecular-cluster beam through a BaF₂ window (see Fig. 1). The diameter of IR radiation spot in a lens focal plane was approximately 0.5 mm. The laser beam crossed the molecular-cluster beam at an angle of 90°. Light attenuators varied the laser output power. The maximal laser radiation power introduced into the chamber was 6 W. The CO₂ laser emitted on 9R-branch lines near $\lambda = 9.2$ μm .

A molecular-cluster CF₃Br beam was generated in the source chamber, where the gas mixture of investigated molecules with the argon gas-carrier was subjected to gas-dynamic cooling in the result of supersonic expansion through a modified (see [44]) pulsed nozzle of the General Valve type with the exit hole diameter of 0.22 mm. The nozzle pulse repetition frequency was 0.5 Hz. The FWHM duration of open nozzle pulse was about 400 μs . A gas pressure above the nozzle P_0 varied in the range 1.5–5 atm. A molecular (cluster) beam was separated from a central part of the supersonic jet produced by the nozzle by using a skimmer (of the Beam Dynamics type, Model 1, with a hole diameter of 0.66 mm), which was placed at a distance of 38.5 mm from the nozzle. The beam formed in this way passed to the chamber of the time-of-flight mass-spectrometer. At a distance of 96.5 mm from the skimmer input hole, the beam crossed mutually perpendicular axes of the mass-spectrometer and the beam of the UV laser ionising the molecules.

Molecules and clusters in the beam were ionised by the second harmonic of a pulsed dye laser pumped by an excimer XeCl laser. The resulting UV radiation was focused to the chamber by a spherical lens with a focal length $f = 120$ mm. The diameter of the UV radiation waist at the lens focus was approximately 0.12 mm, and the spectral width of the radiation line was about 1.0–1.5 cm^{-1} . The range of the UV radiation wavelength was $\lambda_{\text{UV}} \approx 225\text{--}237$ nm. This combined employment of the UV multiphoton ionisation and mass-spectrometer detection of molecules and clusters in the beam makes it possible to diagnose cluster beams and study laser IR and UV cluster fragmentation [44, 48–53].

The approach to laser control of molecule clustering realised in the present work comprises preliminary (prior to the onset of the clustering process) vibrational excitation of molecules, including those of particular type, under gas-dynamic expansion at the nozzle output. In the result, in the following condensation the stored vibrational energy prevents (suppresses) clustering of excited molecules. In addition, the appropriate choice of the irradiation position of particles at the beam axis in space in front of the skimmer (see Fig. 1) allows one to perform dissociation of small clusters (dimers), which can be used to control the process of molecule clustering. In the latter case, it is necessary to provide (for example, by choosing the appropriate gas expansion conditions) preferable generation of dimers without clusters of large size.

In the process of gas clustering under gas-dynamic expansion at the nozzle output, several phases are distinguished (Fig. 2), which mainly occur in different beam domains [44].

Domain I near the nozzle exit is characterised by the fastest cooling of translational and internal degrees of freedom of molecule with the energy transfer to the kinetic energy of the beam directed motion transfer of matter to supersaturated state, which leads to generation of seed clusters.

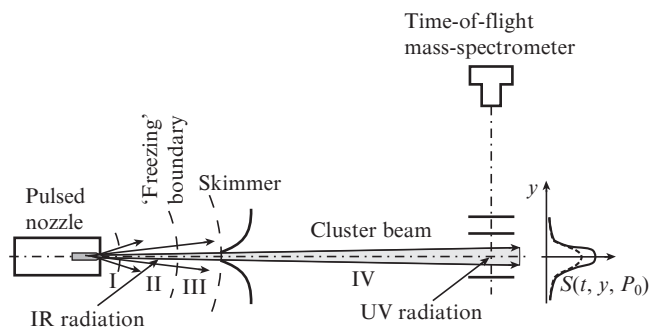


Figure 2. Cluster beam formation in the conditions of a pulsed jet.

Collision domain II of the expanding jet is characterised by continuing gas-dynamic cooling, on the one hand, and cluster growing in a jet with certain heating of the system due to the condensation energy, on the other hand.

In domain III after the 'freezing' zone, there occurs a transfer to collision-free motion of particles and stabilisation of the cluster system.

In domain IV between the skimmer and detection region in the time-of-flight mass-spectrometer, the cluster jet formed by the skimmer from a central beam part freely propagates. The beam properties in the detection zone are determined by its geometrical divergence, composition, and velocity distribution of particles to the instant of passing across the skimmer.

For studying the influence of resonance IR excitation of jet molecules on formation of a cluster beam at various stages of clustering it is necessary to irradiate the particles in the corresponding jet domains on a trajectory of the flux that forms the cluster beam and to detect changes of beam parameters in the detection zone. A reduction of the cluster component signal may occur in several ways [44].

If a temperature in domain I locally increases due to IR excitation of molecules, which prevents origin of seeds, then ideally this will cancel further molecule clustering. In the case where molecules are highly diluted by an inert gas and the probability of their collisions is small, clustering of excited ('target') molecules can be selectively suppressed.

If IR radiation affects the particles in domain II then the molecules and clusters generated in the jet to this instant will be vibrationally heated. In this case, partial fragmentation of clusters is possible. Note that particle heating occurs against the background of competing gas-dynamic cooling of the particles (especially in the case of a gas-carrier) and certain further change of jet cluster composition (cluster growing, evolution of size distribution).

Particle irradiation in domain III, where collisions are absent, the action of IR radiation mainly reduces to cluster heating and fragmentation, which is revealed in the corresponding signal fall of the beam cluster component.

3. Results and discussion

3.1. Investigation of CF₃Br clustering, detection of molecules and clusters

The process of CF₃Br molecule clustering was investigated in particular conditions of the present experiment in order to find the optimal conditions for controlling clustering by the laser. With this aim, mass-spectra of the molecular (cluster)

beams were detected and analysed, which were obtained for CF_3Br both without a gas-carrier and with an argon gas-carrier. The experiments were performed at various total gas pressures over the nozzle and various ratios of the gas pressure in the $\text{CF}_3\text{Br}-\text{Ar}$ 1 : N mixture, where $N = 3, 10, 15, 79$.

Typical mass-spectra of molecular (cluster) beams are shown in Fig. 3. It was found that in the case of CF_3Br without a carrier and at $P_0 \leq 4$ atm, clusters in the beam are not actually produced. Indeed, the results presented in the figure show that in this case the mass-spectrum has no Br_2^+ ion peaks inherent in clusters $(\text{CF}_3\text{Br})_n$, whereas if CF_3Br is used with a gas-carrier, the peaks of the Br_2^+ molecular ion are observed. Hence, as in the case of $(\text{CF}_3\text{I})_n$ cluster UV multiphoton ionisation, the presence of the Br_2^+ ion while using the $\text{CF}_3\text{Br}-\text{Ar}$ mixture confirms the fact that $(\text{CF}_3\text{Br})_n$ clusters are generated in the beam. The $\text{CF}_3\text{Br}-\text{Ar}$ mixtures with a distinct pressure ratio as well as energy variation of the UV radiation pulse at $\lambda_{\text{UV}} = 232.5$ nm did not result in a substantial increase in the Br_2^+ ion signal although the peak values for other ions (CF^+ ,

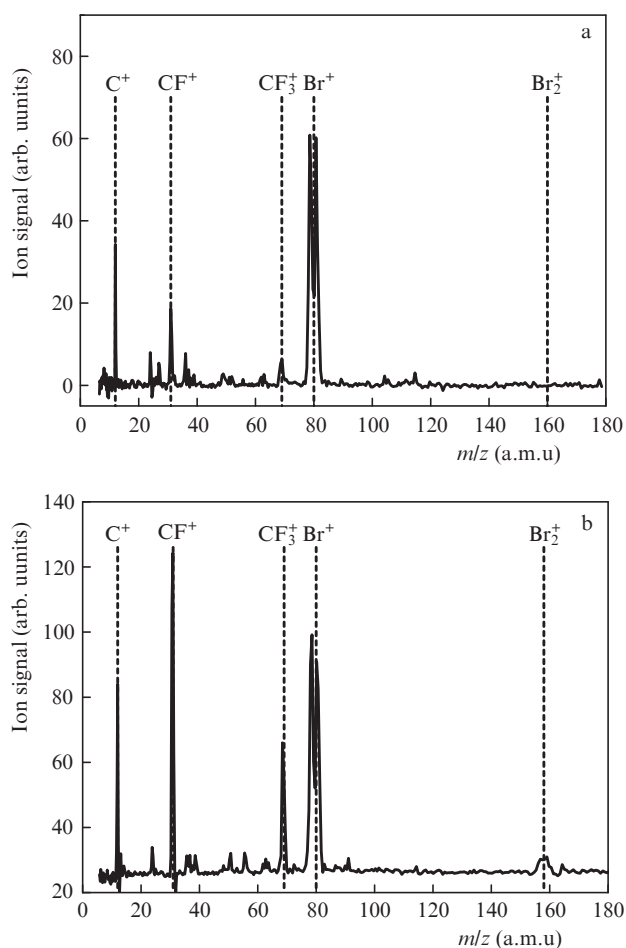


Figure 3. Ion mass-spectra of (a) the CF_3Br molecular (cluster) beam at $P_0 = 4$ atm, $E_{\text{UV}} = 400 \mu\text{J}$, $\lambda_{\text{UV}} = 232.5$ nm and (b) the $\text{CF}_3\text{Br}:\text{Ar} = 1:15$ mixture at $P_0 = 2$ atm, $E_{\text{UV}} = 430 \mu\text{J}$, $\lambda_{\text{UV}} = 232.5$ nm.

CF_3^+ , and Br^+) changed in this case.

Note that if the CF_3Br gas over the nozzle is used without a carrier then the probability of cluster generation in the beam is small; the ion signals of CF_3^+ , CF^+ and C^+ fragments in the mass-spectrum are substantially smaller than that of Br^+ (Fig. 3a). However, when the mixture of CF_3Br with argon is

used (and the probability of molecule clustering is high due to stronger cooling), the amplitudes of ion peaks for CF_3^+ , CF^+ and C^+ fragments and for the atomic bromine Br^+ are comparable (Fig. 3b). This is an additional evidence of molecule clustering when the gas mixture of CF_3Br and argon expands.

In studying the influence of IR radiation on molecule clustering the main attention was paid to a change in the composition ratio for bromine isotopes ^{79}Br and ^{81}Br in the beam, and Fig. 4 shows dependences of the ion signals for $^{79}\text{Br}^+$ on the UV radiation wavelength in the cases considered above. One can see that the dependences are different. In the molecular beam CF_3Br [Fig. 4, curve (1)], intensive ion peaks of $^{79}\text{Br}^+$ are observed at the resonance wavelengths $\lambda_{\text{UV, res}} \approx 232.5$ and 233.5 nm [56, 57], whereas at other wavelength the amplitude of the $^{79}\text{Br}^+$ peak is 5–10 times less. At nonresonant wavelengths, the amplitudes of other ion fragments CF_3^+ , CF^+ , and

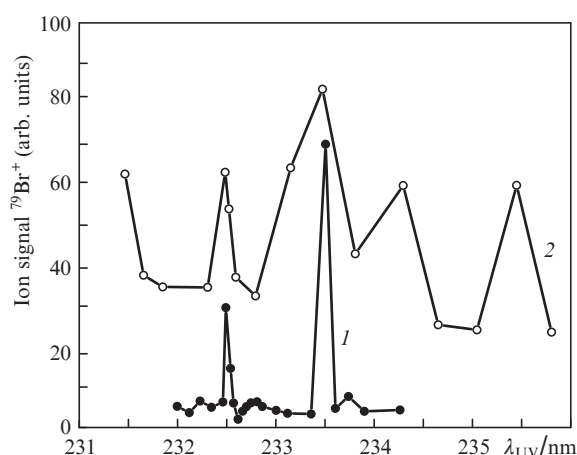


Figure 4. Dependence of the $^{79}\text{Br}^+$ ion signal on the wavelength of UV radiation for a CF_3Br molecular beam at $P_0 = 4$ atm and $E_{\text{UV}} = 430 \mu\text{J}$ (1) and similar dependence for the $(\text{CF}_3\text{Br})_n$ cluster beam in the case of mixture $\text{CF}_3\text{Br}:\text{Ar} = 1:15$ at $P_0 = 2$ atm and $E_{\text{UV}} = 405 \mu\text{J}$ (2).

C^+ are also substantially less.

In the case of a cluster beam $(\text{CF}_3\text{Br})_n$ [Fig. 4, curve (2)], the ion peak $^{79}\text{Br}^+$ is observed at all wavelengths of the studied range 231.5–236 nm, and the peak amplitude is greater as compared to the case of the molecular beam. The dependence of the $^{79}\text{Br}^+$ peak amplitude on the UV radiation wavelength is weaker than in the case of the molecular beam, although there is a noticeable structure (with a contrast of about 2). This is one more important argument for the fact that we deal with a cluster beam $(\text{CF}_3\text{Br})_n$. Thus, results given in Fig. 4 confirm generation of a cluster beam when the gas mixture of CF_3Br and gas-carrier are used over the nozzle. Hence, we may assert that if the mass-spectrum of the beam has ion peaks Br_2^+ and the amplitudes of $^{79}\text{Br}^+$ and $^{81}\text{Br}^+$ ion peaks weakly depend on the UV radiation wavelength, then the beam comprises mainly $(\text{CF}_3\text{Br})_n$ clusters. The weak spectral dependence of ion peak amplitudes, seemingly, relates to line broadening due to interaction between molecules in clusters.

In the cases of both a CF_3Br molecular beam and a $(\text{CF}_3\text{Br})_n$ cluster beam, the ion peaks Br^+ have the maximal amplitudes at the wavelength $\lambda_{\text{UV}} = 233.495$ nm. Probably, at this UV radiation wavelength, a resonance two-quantum transition in CF_3Br molecules is observed from the ground state to a decay state with the following absorption of one more such quantum by molecules and further transition to

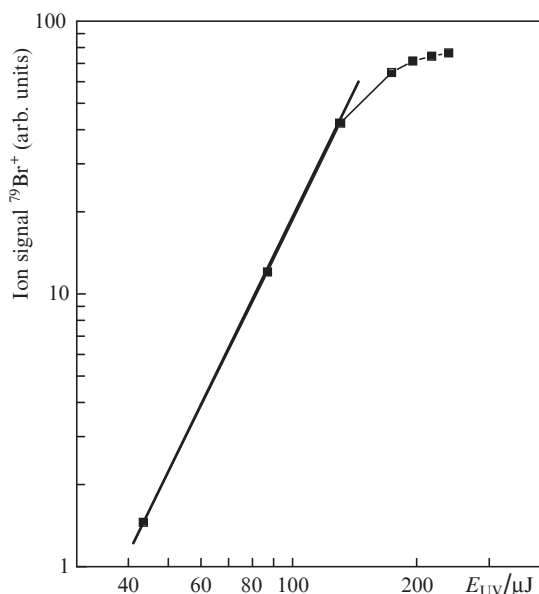


Figure 5. Dependence of the $^{79}\text{Br}^+$ ion signal on the UV pulse energy in the case of $(\text{CF}_3\text{Br})_n$ clusters in the beam. Clusters were generated by using the $\text{CF}_3\text{Br}:\text{Ar} = 1:8$ mixture at $P_0 = 4$ atm; $\lambda_{\text{UV}} = 233.494$ nm.

autoionising state, where molecules finally decay [56, 57]. A three-quantum absorption of UV radiation at this wavelength well agrees with the almost cubic dependence of the $^{79}\text{Br}^+$ ion signal on the UV radiation pulse energy obtained in our experiments (Fig. 5).

3.2. Study of CF₃Br molecule clustering control

Prior to discussing the results obtained, note that the selective control of molecule clustering by radiation of a cw CO₂ laser [34–39] was studied in the SF₆–Ar mixtures in the proportions of 1:100 or 1:200. It was explained by the fact that in strongly diluted mixtures the probability of vibrational energy transfer from a laser-excited SF₆ isotopomer to an unexcited isotopomer reduces. In this way, one can enhance the selectivity of radiation action on molecules and increase the enrichment factor. Nevertheless, in this case the efficiency of the process (the goal product yield) substantially falls [23, 58]. In addition, in the conditions where the molecular gas is so much diluted by a gas-carrier, the linear dimension of the domain of molecule clustering (along the x axis of molecular jet propagation) strongly reduces (almost converting to point) near the nozzle exit. In this domain, the laser beam with finite transversal dimensions of the emission ‘spot’, principally, can selectively control molecule clustering [23, 44, 58]. For example, the length of this domain in [34–39] was only about 0.2 mm.

Mixtures in our experiments on controlling CF₃Br molecule clustering were not strongly diluted, namely, these were CF₃Br–Ar mixtures with the pressure ratios of 1:3 and 1:15. In photoionisation at the UV radiation wavelengths that are resonant for CF₃Br molecules, not only clusters, but also unclustered molecules contribute into the Br⁺ ion signals. In view of this fact, the experiments were carried out in the conditions of particle photoionisation at a nonresonant wavelength of UV radiation ($\lambda_{\text{UV}} = 233$ nm). In this case, the contribution of jet unclustered molecules into Br⁺ ion signals is minimal [see Fig. 4, curves (1) and (2)]. With the radiation at

$\lambda_{\text{UV}} = 233$ nm we investigated CF₃Br–Ar = 1:3 mixtures. For a comparison, we have also investigated the CF₃Br–Ar = 1:15 mixture in the conditions of photoionising beam particles at the resonance UV radiation wavelength ($\lambda_{\text{UV}} = 233.49$ nm).

The influence of IR radiation action on a molecular cluster beam is shown in Fig. 6. Jet particles leaving the nozzle were irradiated at a wavelength of 1084.635 cm⁻¹ [9R(30) line] by focused radiation of a cw CO₂ laser at various distances x from the nozzle exit. This value of the laser emission frequency is close to the vibrational frequencies ν_1 of CF₃⁷⁹Br (1084.77 cm⁻¹) and CF₃⁸¹Br (1084.52 cm⁻¹) molecules [45]. It is between Q-branches of IR absorption spectra of the mentioned molecules and is shifted to the red from the frequency of the Q-branch for the CF₃⁷⁹Br molecule by approximately 0.134 cm⁻¹ [45]. Particles were ionised by UV radiation at the nonresonant wavelength $\lambda_{\text{UV}} = 233$ nm. For each particular coordinate x of the point, at which jet particles were irradiated, the time-of-flight spectra of $^{79}\text{Br}^+$ and $^{81}\text{Br}^+$ ion signals were recorded. In addition, the energy E_{UV} and power of CO₂ laser radiation introduced into the vacuum chamber were

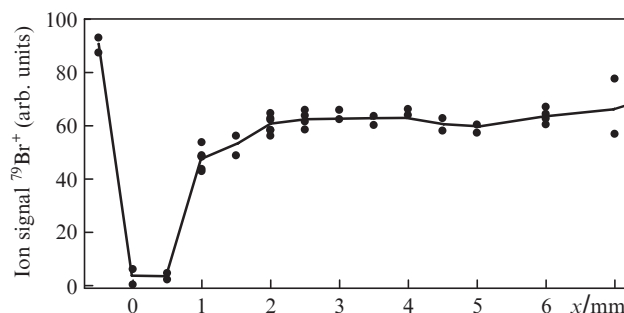


Figure 6. Dependence of the $^{79}\text{Br}^+$ ion signal on the distance of the irradiation zone from the nozzle exit under gas-dynamic expansion of the CF₃Br:Ar = 1:3 mixture. Particles in the jet were irradiated at a frequency of 1084.635 cm⁻¹ [R9(30) line] at the laser power $W_{\text{IR}} = 4.5$ W; $P_0 = 3$ atm, $E_{\text{UV}} = 264$ μJ, $\lambda_{\text{UV}} = 233.018$ nm.

measured.

If the jet is irradiated just at the nozzle exit at point $x = 0$ (the laser beam touches the nozzle) where molecules have not been cooled yet, their concentration is high and, hence, there are many collisions, then the CO₂-laser radiation excites mainly CF₃⁷⁹Br molecules; however, the excitation energy is also transferred to CF₃⁸¹Br molecules due to reasons mentioned above. As a result, all CF₃Br molecules and atoms of the gas-carrier are strongly heated. The beam ‘breaks’ and clusters are not generated. Ion peaks of $^{79}\text{Br}^+$ and $^{81}\text{Br}^+$ are absent in the beam mass-spectrum.

At longer distances of the irradiated domain from the nozzle $0.5 \leq x \leq 3$ mm, where molecules cool down and clusters are generated, clustering may be selectively suppressed, because the molecule concentration in this case is small. Actually, there is no selectivity of IR radiation in the 9R(30) line with respect to CF₃Br isotopomers, which are included in generated clusters, because IR absorption spectra of the CF₃Br isotopomers comprised in the generated clusters are superimposed, and the width of cluster IR absorption spectra is large [59]. Thus, molecule clustering in this zone (including selective clustering) is suppressed, and small (seed) clusters are dissipated [23, 44]. If the jet is irradiated by the laser at

distances $x \geq 3$ mm, then there occurs nonselective dissociation of clusters [44]. The probability of cluster dissociation (fragmentation) is low due to a small laser power. As a result, the amplitudes of the ion peaks $^{79}\text{Br}^+$ ($^{81}\text{Br}^+$) reduce (as compared to the amplitudes in a nonirradiated jet) not very much, i.e. approximately by 35%–40% (see Fig. 6).

Hence, selective action of IR radiation on clustering of one of the chosen CF_3Br isotopomers can only be observed in a narrow range of irradiation zone distances from the nozzle where molecules are cooled and clusters just begin to arise. In Fig. 6 this range of distances is estimated as $x = 1.5$ – 2.5 mm.

Just in this domain we expected to observe selective influence of IR radiation in the lasing line R9(30) on clustering and, as a result, reduction of the $^{79}\text{Br}^+$ ion peak amplitude relative to the $^{81}\text{Br}^+$ ion peak.

We determined the enrichment factor k_{enr} as the ratio of the initial concentrations of bromine isotopes in the CF_3Br –Ar mixture measured in a mass-spectrum of the beam prior to irradiation (I) to the ratio of the bromine isotope concentrations measured after irradiating (II) the molecular jet by the CO_2 -laser radiation. The bromine atomic concentrations prior to and after irradiation were assumed proportional to the corresponding ion signals in the mass-spectrum. Hence,

$$k_{\text{enr}} = \frac{{}^{79}\text{Br}^+ \cdot {}^{81}\text{Br}^+(\text{I})}{{}^{79}\text{Br}^+ \cdot {}^{81}\text{Br}^+(\text{II})}. \quad (1)$$

While taking these measurements we encountered two difficulties. The first one is as follows. Our system for processing measurement results was capable of calculating the area under each ion peak in a mass-spectrum; however, in the only case where the peaks are clearly separated in the spectrum and the integration limits under a particular peak are definite. In our case, bases of $^{79}\text{Br}^+$ and $^{81}\text{Br}^+$ ion peaks were superimposed and it was impossible to definitely separate the boundaries for integration. Thus, in calculating the enrichment factors it was assumed that the concentrations of Br isotopes are proportional to the corresponding amplitudes of bromine ion peaks obtained in ion mass-spectra.

The second problem was that in multiple repeated measurements of the amplitudes of bromine ion signals without jet irradiation, the ion peak amplitudes of Br isotopes noticeably varied. Sometimes, the ion signal for $^{81}\text{Br}^+$ was greater than for $^{79}\text{Br}^+$, although the content of the $\text{CF}_3^{79}\text{Br}$ isotopomer in the initial mixture is higher than that of $\text{CF}_3^{81}\text{Br}$ (the natural content ratio is approximately 1.023). Probably, the problem mentioned is related to the close to unity content ratio for ^{79}Br and ^{81}Br isotopes, insufficient stability of UV laser radiation (frequency and energy), and difference in absorption spectra of CF_3Br isotopomers [56, 57].

In view of these facts, we had to collect measurement statistics for estimating the enrichment factor k_{enr} . For determining the initial content ratio for ^{79}Br and ^{81}Br we have taken 2400 measurements in various days. The influence of CO_2 -laser radiation at the 9R(30) line (1084.635 cm^{-1}) on generation of clusters comprising molecules with the ^{79}Br isotope was studied by taking 800 measurements of ion signals at each irradiation point. The result of determining the enrichment factor k_{enr} in the case of the CF_3Br :Ar = 1:3 mixture is presented in Fig. 7. At point $x = 2$ mm, this factor reaches $k_{\text{enr}} \approx 1.05 \pm 0.005$. For the CF_3Br :Ar = 1:15 mixture the estimated enrichment factor value of 1.06 ± 0.007 is reached at point $x = 0.25$ mm, and already at $x = 0.5$ mm the selective influence of

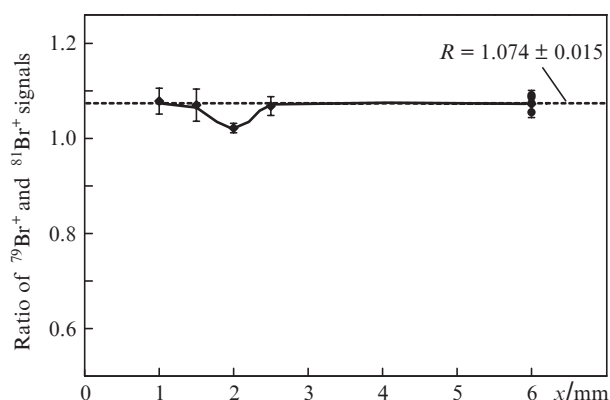


Figure 7. Dependence of the ratio of $^{79}\text{Br}^+$ and $^{81}\text{Br}^+$ ion signals on the distance of the IR-laser irradiation zone from the nozzle exit under gas-dynamic expansion of the CF_3Br :Ar = 1:3 mixture. Particles in the jet were irradiated at a frequency of 1084.635 cm^{-1} [R9(30) line] at a laser power $W_{\text{IR}} = 4.5 \text{ W}$; $P_0 = 3.1 \pm 0.1 \text{ atm}$, $E_{\text{UV}} = 264 \mu\text{J}$, $\lambda_{\text{UV}} = 233.018 \text{ nm}$. The ratio of bromine isotope contents in the initial (not irradiated) mixture CF_3Br (R) measured by the mass-spectra is 1.074 ± 0.015 .

IR radiation on molecule clustering is almost absent. For the CF_3Br :Ar = 1:3 mixture the domain for controlling molecule clustering by IR radiation is substantially wider ($\Delta x \approx 1 \text{ mm}$).

We have also obtained dependences of the $^{79}\text{Br}^+$ ion signal amplitude on a 9R-branch line frequency of CO_2 -laser radiation for jet irradiation at various distances from the nozzle (Fig. 8). These dependences give information about the frequencies of maximal IR absorption for cooled CF_3Br molecules in a jet. One can see that the strongest absorption of IR radiation is observed in the 9R(30) line, which is well matched

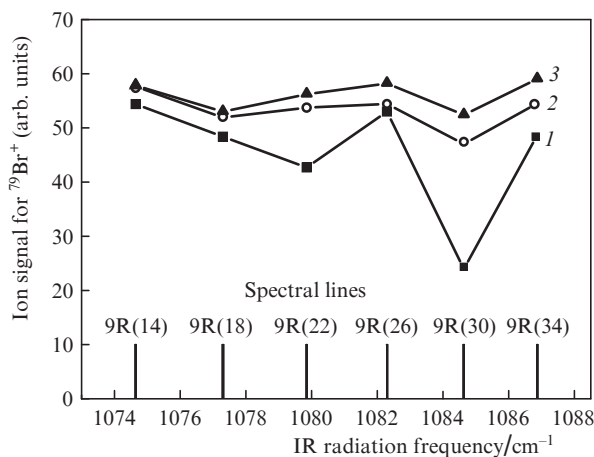


Figure 8. Dependences of the $^{79}\text{Br}^+$ ion signal on the frequency of the 9R-branch line of CO_2 -laser radiation when the molecular jet was irradiated at the distances from nozzle of (3) 0.5, (2) 1, and (3) 3 mm. The CF_3Br :Ar = 1:3 mixture was used at $P_0 = 3.1 \pm 0.1 \text{ atm}$; $E_{\text{UV}} = 264 \mu\text{J}$, $\lambda_{\text{UV}} = 233.018 \text{ nm}$.

with the Q-branch of CF_3Br molecules [45].

In our opinion, the results presented above conclusively confirm that isotopic-selective laser control is possible for the process of molecule clustering and, consequently, isotope selection by this method even at rather small isotopic shifts $\sim 0.25 \text{ cm}^{-1}$ in a vibrationally excited molecule. This conclusion is confirmed by observations of isotopic selectivity only

in the case of exact matching of CO₂-laser radiation with a 'resonance' isotopomer, 'correct sign' of the enrichment factor, and strong localisation of this effect at the expected point on the beam axis. Isotopic selectivity is also observed at high dilution of CF₃Br by argon (1 : 15); the localisation domain of the effect, as expected, moves towards the nozzle. This fact additionally confirms that isotopic-selective control for CF₃Br molecule clustering is possible.

The values of realised enrichment factors are not relatively high: $k_{\text{enr}} \approx 1.05$ and 1.06 . Note that in similar experiments on selective ³²SF₆ and ³⁴SF₆ molecule condensation where the isotopic frequency shift in the excited vibration ν_3 is about 17 cm⁻¹, the enrichment factor reached $k_{\text{enr}} \approx 2$ [34]. The comparatively small value of k_{enr} in our experiments, seemingly, is determined by several factors. In particular, the radiation conditions are not optimal: the degree of gas dilution and its pressure over the nozzle, degree of IR radiation overlapping with the domain of the maximal localisation of the effect, and rate of exchange by vibrational energy between isotopomers. Instabilities of the CO₂-laser radiation frequency and width of ionising UV radiation might substantially affect the results. We assume that thorough optimisation of the experimental parameters such as conditions of gas flow, irradiation position and domain, and laser radiation parameters will noticeably increase the enrichment factor.

4. Conclusions

CF₃Br molecule clustering is studied in gas-dynamic expansion of a CF₃Br–Ar mixture at the nozzle exit. The method is described for detecting molecules and clusters in a beam by a time-of-flight mass-spectrometer with particle ionisation by a UV laser pulse. Gas parameters over the nozzle (compositions and pressure) are determined, at which intensive molecule clustering occurs. It is shown that in the case of the CF₃Br gas without a carrier at $P_0 \leq 4$ atm, molecular clusters actually are not generated in the beam. If a gas mixture of CF₃Br–Ar with the pressure ratio 1 : N ($N \geq 3$) is used at $P_0 \geq 2$ atm, then there occurs intensive CF₃Br molecule clustering.

The procedure for controlling CF₃Br molecule clustering under gas-dynamic expansion of a CF₃Br–Ar mixture at the nozzle exit by using IR laser radiation is studied. Dependences are obtained of the efficiency of suppressing molecule clustering on the parameters of exciting laser radiation, gas parameters over the nozzle, and the distance of molecule irradiation zone from the nozzle exit. The conditions are found, in which molecule clustering can be selectively controlled. It is found that the process of CF₃Br molecule clustering can be selectively controlled by irradiating the jet by CO₂-laser radiation in the 9R(30) line (1084.635 cm⁻¹).

It is shown that due to resonance vibrational excitation of gas-dynamically cooled CF₃Br molecules at the nozzle exit by IR laser radiation one can realise isotopic-selective (with respect to bromine isotopes) suppression of molecule clustering. In the conditions of jet irradiation at a wavelength of the 9R(30) line (1084.635 cm⁻¹) in the CF₃Br : Ar = 1 : 3 mixture at $P_0 = 3.1$ atm, the obtained enrichment factor with respect to the ⁸¹Br isotope is $k_{\text{enr}} = 1.05 \pm 0.005$, and in the CF₃Br : Ar = 1 : 15 mixture (at the same total pressure) it is $k_{\text{enr}} = 1.06 \pm 0.007$.

In view of the fact that CF₃⁷⁹Br and CF₃⁸¹Br isotopomers are characterised by a small frequency isotopic shift in the IR absorption spectrum of vibration ν_1 , the results obtained give

a hope to use this method to selectively control molecule clustering for molecules comprising isotopes of heavy elements (OsO₄, WF₆, UF₆).

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