

Infrared laser-induced isotope-selective dissociation of mixed $(\text{CF}_3\text{Br})_m\text{Ar}_n$ van der Waals clusters

A.N. Petin, G.N. Makarov

Abstract. The paper presents the results of studies of IR laser-induced bromine-isotope-selective dissociation of small mixed $(\text{CF}_3\text{Br})_m\text{Ar}_n$ van der Waals clusters ($m = 1, 2$ and $1 \leq n \leq 5$ is the number of molecules and atoms in the clusters, respectively). The experiments used a pulsed CO_2 laser to excite clusters and a quadrupole mass spectrometer to detect a molecular cluster beam. The research method is based on the selective vibrational excitation of clusters by IR laser radiation, leading to their predissociation. The possibilities of implementing bromine-isotope-selective dissociation of clusters are considered. The experimental setup and research method are briefly described. The results of determining the cluster dissociation efficiency and selectivity as functions of the energy and frequency of laser radiation are presented. It is shown that resonant vibrational excitation of clusters makes it possible to induce their isotope-selective dissociation. Thus, using a $\text{CF}_3\text{Br}/\text{Ar}$ mixture with a pressure ratio of 1/200, the enrichment factors of the ^{79}Br isotope are found to be $K_{\text{enr}}(^{79}\text{Br}) = 1.15 \pm 0.04$ and 0.95 ± 0.03 under cluster irradiation conditions on the $9\text{R}(30)$ ($\nu = 1084.635 \text{ cm}^{-1}$) and $9\text{R}(24)$ ($\nu = 1081.087 \text{ cm}^{-1}$) lines, respectively. The achieved dissociation selectivities for the clusters are, respectively, 1.16 ± 0.05 and 0.95 ± 0.04 . The results obtained suggest that this method can be used to separate isotopes in molecules containing isotopes of heavy elements, which have a slight isotopic shift in the 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

Currently, active research is being underway, aimed at the development of low-energy methods of molecular laser isotope separation (MLIS) (MLIS methods) [1–11]. The main goal of these studies is to search for efficient and low-cost methods for separation of uranium isotopes and other elements. One of the ways to further develop MLIS methods is the use of low-energy physicochemical processes, the activation energy of which does not exceed 0.3–0.5 eV [1–11]. Such activation energies are characteristic of physicochemical processes of adsorption and desorption of molecules on the surface, including on the surface of large clusters, as well as of

the processes of dissociation and fragmentation of weakly bound van der Waals molecules (clusters) [1]. Now, the technique of separation of isotopes by laser excitation (SILEX) is being developed in the USA to produce enriched uranium [12–16]. The principles of this technique are not disclosed, but we can assume with high probability that it is based on low-energy processes [17]. According to the developers, SILEX is also applicable to separate isotopes other elements (for example, silicon, boron, sulphur, carbon, and oxygen) [1, 12, 14].

To date, much work has been done to study low-energy MLIS methods (see, for example, review [1] and references therein). Alternative methods are also being investigated [1, 18, 19]. The most promising approaches to the implementation of low-energy MLIS methods are IR laser-induced isotope-selective suppression of the molecule clustering under gas-dynamic expansion at the nozzle exit and IR laser-induced isotope-selective dissociation of weakly bound van der Waals clusters [1]. These methods are considered in some detail in [20–24] using the example of SF_6 molecules. They showed the possibility of separating sulphur isotopes using the methods of selective suppression of the clustering of SF_6 molecules and the dissociation of clusters of these molecules in gas-dynamic jets by radiation from a cw CO_2 laser.

Van der Waals molecules are characterised by the fact that one of the intramolecular bonds in them is much weaker than the others. The difference in the binding energies is so great that the energy of the vibrational quanta corresponding to the chemical bonds of the monomer molecules contained in van der Waals molecules is greater than the dissociation energy of the weak van der Waals bond. As a result, such a molecule becomes metastable under vibrational excitation of any monomer and experiences vibrational predissociation.

This property of van der Waals molecules is of great interest for the development of low-energy MLIS methods [1]. For example, the binding (dissociation) energy of E_b van der Waals molecules consisting of polyatomic molecules is in the range from 0.1 to 0.5 eV, and the dissociation energy of van der Waals molecules consisting of a polyatomic molecule and a noble gas atom does not exceed 0.1 eV [25–28]. The absorption by a molecule of one or several quanta of IR radiation with a wavelength of about 10 μm , for example, CO_2 laser radiation, leads to weak-bond dissociation.

In some cases, the absorption spectra of dimers and small clusters (homogeneous or mixed) can be significantly narrower than the absorption spectra of unclustered molecules and form rather narrow bands localised near the vibrational frequencies of the monomer molecules that make up the clusters [25–28]. This allows one to selectively excite and dissociate

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Received 19 November 2018
Kvantovaya Elektronika 49 (6) 593–599 (2019)
Translated by I.A. Ulitkin

ate clusters (most often dimers) containing selected isotomers, and thereby to separate isotopes [1].

Even at an early stage of the development of laser isotope separation methods, the method of isotope-selective cluster dissociation was patented by Nobel Prize winner Yuan Tseh Lee as a new method for separating isotopes of various elements [29]. The isotope-selective IR dissociation of Ar–BCl₃ van der Waals molecules in a beam using a cw CO₂ laser was studied in [30] and the possibilities of practical application of the method for the isotope separation were discussed.

The dissociation of UF₆ clusters by IR radiation was examined in [31]. The experiments were performed to ‘clean’ a molecular beam from clusters by the MLIS method based on the IR multiphoton dissociation of molecules in a gas-dynamically cooled molecular flow. The use of the method of IR vibrational predissociation of van der Waals clusters to separate uranium isotopes was considered in [32].

The above processes were studied in detail in recent papers [33–39] using the example of CF₃I, SF₆, and CF₃Br molecules. Apatin et al. [33] (see also review [34]) investigated the control of clustering of CF₃I molecules as a result of resonant vibrational excitation of molecules and clusters by IR radiation of a cw CO₂ laser during gas dynamic expansion of a mixture of CF₃I molecular gas with argon and xenon carrier gases. In the case of gas-dynamic expansion in a mixture with argon, isotope-selective suppression of the clustering of CF₃Br [35, 36] and SF₆ molecules [37] was demonstrated. Makarov et al. [38] examined the bromine-isotope-selective suppression of the clustering of CF₃Br molecules with atoms of an argon carrier gas. Lokhman et al. [39] studied isotope-selective IR dissociation of homogeneous and mixed (SF₆)_mAr_n van der Waals clusters. The results obtained in [33–39] suggest that the processes in question can be used as the basis for the development of low-energy MLIS methods.

This paper studies the process of bromine-isotope selective IR dissociation of small (CF₃Br)_mAr_n molecular van der Waals clusters in a beam formed during gas-dynamic expansion of a CF₃Br/Ar mixture by radiation from a pulsed CO₂ laser. The choice of the CF₃Br molecule is substantiated in detail in [35, 36] and is mainly due to the fact that it has a very small isotopic shift (~ 0.248 cm⁻¹ [40]) for CF₃⁷⁹Br and CF₃⁸¹Br molecules in the spectrum of the laser-excited vibration ν_1 (~ 1085 cm⁻¹ [40]). Therefore, the results obtained are of particular interest in terms of clarifying the possibility of using this method for separation of isotopes in molecules that have a slight isotopic shift in the spectra of excited vibrations, which is characteristic of molecules containing isotopes of heavy elements. For example, for the ²³⁵UF₆ and ²³⁸UF₆ isotomers, the isotopic shift in the spectrum of the vibration ν_3 (~ 627 cm⁻¹ [41]) is also small and is about 0.6 cm⁻¹ [41].

In this work, we measured the dependences of the enrichment factors, the efficiency and selectivity of cluster dissociation on the gas parameters above the nozzle and the laser radiation parameters, and found the conditions under which the maximum values of the cluster dissociation selectivity are reached.

2. Experimental

2.1. Experimental setup

The schematic of the setup is shown in Fig. 1. It contains a high-vacuum chamber with a pulsed molecular cluster beam source, a KMS-01/250 quadrupole mass spectrometer for

detecting beam particles, and a frequency-tunable pulsed CO₂ laser with a pulse energy of up to 3 J to excite clusters. The setup also comprises a personal computer for controlling a mass spectrometer, a system for synchronising a laser pulse with a pulse of a molecular cluster beam, and a data acquisition and processing system. The upper limit of the detected mass numbers of the mass spectrometer is $m/z = 300$ amu. A VEU-6 secondary electron multiplier tube is used to detect ions in the mass spectrometer. The chambers of the molecular beam source and quadrupole mass spectrometer are pumped out by turbomolecular pumps to a pressure of no more than 10⁻⁵ Torr and $\sim 10^{-7}$ Torr, respectively.

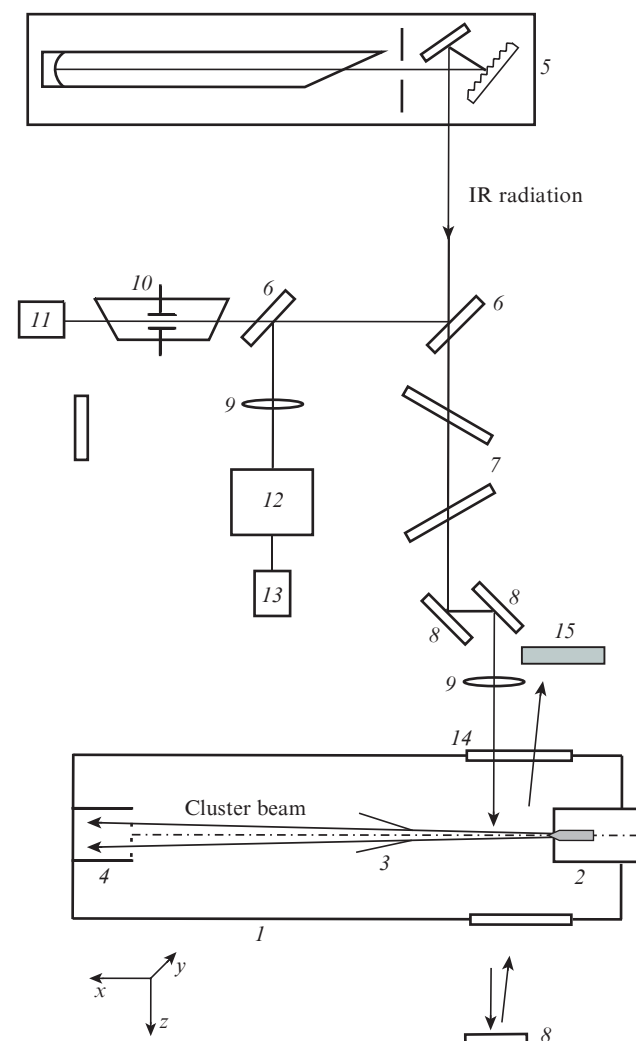


Figure 1. Scheme of the experimental setup: (1) vacuum chamber; (2) pulse nozzle; (3) cone-shaped diaphragm; (4) quadrupole mass spectrometer; (5) pulsed CO₂ laser; (6) beam splitters; (7) attenuators; (8) plane mirrors; (9) lenses; (10) opto-acoustic detector; (11, 13) photodetectors; (12) monochromator; (14) NaCl windows; (15) laser absorber.

(CF₃Br)_mAr_n clusters were generated in the chamber during gas-dynamic cooling of the gas mixture of the studied CF₃Br molecules with the argon carrier gas as a result of its supersonic expansion through a General Valve pulsed nozzle with an exit hole diameter of 0.8 mm. The pulse repetition rate of the nozzle opening was equal to 1 Hz. The duration of the nozzle opening pulse at half maximum was 400–450 μs,

depending on the gas pressure and composition above the nozzle. The gas pressure above the nozzle varied in the range of 1.5–3 atm. A cluster beam was cut from the central part of the supersonic flow using a cone-shaped diaphragm (hole diameter 3 mm), located at a distance of 50 mm from the nozzle. Then, the thus formed beam was directed to the ionisation chamber of the mass spectrometer. The distance from the nozzle exit to this chamber was 250 mm. IR laser radiation was introduced into the chamber with a molecular cluster beam through a NaCl window using copper mirrors and a focusing cylindrical lens with a focal length of 940 mm.

The laser radiation intersected the molecular cluster beam at an angle of about 90°. To increase the irradiated area of the beam, the radiation transmitted through the chamber was reflected back at a small angle by a flat copper mirror. The IR laser spot size in the centre of the beam, determined by two passes of radiation, was 7.8 × 32 mm. The distance from the nozzle to the middle of the irradiation zone was 1.7 cm. During the time of flight of the particles to this zone, the cluster formation process was fully completed [33–39]. To attenuate the laser pulse energy, plane-parallel CaF₂ plates were used. The frequency of the CO₂ laser was tuned by the absorption lines of ammonia using an optoacoustic detector. Due to the relatively large aperture of the laser beam, about 1/3 (along the *x* axis) of a pulsed cluster beam was irradiated (Fig. 2).

2.2. Isotope separation method

The basis of the laser isotope separation method in question is the process of isotope-selective vibrational excitation of (CF₃Br)_{*m*}Ar_{*n*} clusters by IR laser radiation, which leads to their heating and dissociation.

Homogeneous and mixed (CF₃Br)_{*m*}Ar_{*n*} clusters have very small isotopic shifts in the IR absorption and dissociation spectra (~0.245 cm⁻¹) [26, 40]. In addition, these spectra are strongly broadened due to the predissociation process. The IR dissociation spectra of homogeneous clusters (CF₃Br)_{*m*} with a full width at half maximum of about 15 cm⁻¹ [26, 42, 43] resemble almost structureless bands. As a result, the dissociation spectra of clusters containing different isotopomers of CF₃Br molecules strongly overlap. Therefore, it is practically impossible to induce isotope-selective IR dissociation of homogeneous (CF₃Br)_{*m*} clusters by laser radiation.

Another situation is realised in the case of small mixed (CF₃Br)_{*m*}Ar_{*n*} clusters. Their IR dissociation spectra are uniformly broadened bands having a relatively small width (about 3.5 cm⁻¹ at half maximum [26]). The spectra are located in the region of the CO₂ laser generation in the band at λ ≈ 9.6 μm (see Fig. 4 below). As a result, using a number of laser radiation lines, for which there is a maximum difference in the intensities of the IR dissociation spectra of clusters containing different isotopomers of CF₃Br molecules, it is possible, in principle, to induce their isotope-selective dissociation, which is the main goal of our work.

In order to select the laser emission lines, with the use of which we can expect selective dissociation of clusters, we analysed the IR dissociation spectrum of (CF₃Br)_{*m*}Ar_{*n*} clusters, presented in [26]. In work [26], mixed clusters were obtained using a highly diluted mixture of CF₃Br molecules with argon and helium carrier gases (with a pressure ratio CF₃Br: Ar: He = 1:1000:4050). The total gas pressure above the nozzle was equal to 7.8 atm. Under these conditions, mainly mixed clusters containing one or two CF₃Br molecules and several argon

atoms were generated [44]. The spectrum of IR dissociation of clusters was measured in [26] by the yield of the ArBr⁺ ion product.

Based the spectrum presented in [26], we estimated the expected selectivity of the IR dissociation of clusters upon irradiation on a number of lines of a CO₂ laser. To this end, the ratios of the yields of ArBr⁺ ions were measured during IR dissociation of clusters by radiation on selected lines for two IR dissociation spectra (given in [26]) and the same spectrum shifted to the low-frequency region by the value of the CF₃Br isotopic shift (~0.25 cm⁻¹). The intensities of these spectra were normalised taking into account the natural content of CF₃Br isotopomers (50.56% for CF₃⁷⁹Br and 49.44% for CF₃⁸¹Br). The obtained estimated selectivity values for a number of laser generation lines are given in Table 1 along with our experimental data (see Section 3). The maximum differences in the yields of ArBr⁺ ions are observed for 9R(24) (*ν* = 1081.087 cm⁻¹) and 9R(30) (*ν* = 1084.625 cm⁻¹) lines. In this case, the intensity differences of the ion signals for these two lines have opposite signs in accordance with the IR dissociation spectra of clusters containing different CF₃Br isotopomers. Under irradiated on these lines of the CO₂ laser, one should expect isotopic selectivity in the dissociation of clusters. The maximum value of selectivity is determined (and limited from above) by the ratio of the intensities of the Ar⁷⁹Br⁺ and Ar⁸¹Br⁺ ion signals in the spectral dependences of the dissociation yield of the clusters. It follows from Table 1 that the maximum expected selectivities of the process of dissociation of clusters for the above laser lines are 0.89 ± 0.06 and 1.19 ± 0.07, respectively.

Table 1. Results of studies of the isotope-selective dissociation of mixed (CF₃Br)_{*m*}Ar_{*n*} van der Waals clusters by radiation on some CO₂-laser lines during gas-dynamic expansion of the CF₃Br/Ar mixture with a pressure ratio of 1/200 and a total gas pressure above the nozzle of 3 atm. The measured selectivities were obtained at an excitation radiation energy density of 0.04 J cm⁻².

Laser line	Line frequency/cm ⁻¹	Expected selectivity	Measured selectivity
9R(24)	1081.087	0.89 ± 0.06	0.95 ± 0.04
9R(26)	1082.296	1.05 ± 0.05	1.04 ± 0.05
9R(28)	1083.478	1.18 ± 0.06	1.14 ± 0.06
9R(30)	1084.635	1.19 ± 0.07	1.16 ± 0.04

The method for determining the selectivity of cluster dissociation and the enrichment (depletion) factor of a beam by bromine isotopes upon resonant IR laser irradiation was as follows. The Ar⁷⁹Br⁺ and Ar⁸¹Br⁺ ion signals from mixed (CF₃Br)_{*m*}Ar_{*n*} clusters were measured in the absence of beam irradiation and upon its irradiation. The measured ionic mass peaks of the Ar⁷⁹Br⁺ and Ar⁸¹Br⁺ fragments were approximated by Gaussian functions. The isotopic selectivity of dissociation of clusters containing the ⁷⁹Br isotope relative to clusters containing the ⁸¹Br isotope was determined by the formula

$$\alpha(^{79}\text{Br}/^{81}\text{Br}) = \beta_{79}/\beta_{81}, \quad (1)$$

where β₇₉ and β₈₁ are, respectively, the dissociation yields of CF₃⁷⁹Br–Ar and CF₃⁸¹Br–Ar clusters in the irradiated volume of the jet, which were calculated from the relations

$$S_{\text{IL}} = S_{\text{I0}}(1 - \beta_{79}\Gamma), \quad (2)$$

$$S_{2L} = S_{20}(1 - \beta_{81}\Gamma), \quad (3)$$

where S_{1L} and S_{2L} are, respectively, the areas under the Gaussian curves for the $\text{Ar}^{79}\text{Br}^+$ and $\text{Ar}^{81}\text{Br}^+$ ion signals under laser irradiation of the beam; S_{10} and S_{20} are the same areas in the absence of irradiation; and Γ is the ratio of the irradiated volume to the entire volume of the cluster beam. Note that in the experiments we used the mass spectrometer to analyse the composition of only the irradiated part of the cluster beam. Therefore, in our case, the condition $\Gamma = 1$ was met.

From relations (1)–(3), we can obtain the final expression for calculating the isotopic selectivity of cluster dissociation:

$$\alpha(^{79}\text{Br}/^{81}\text{Br}) = \frac{1 - S_{1L}/S_{10}}{1 - S_{2L}/S_{20}}. \quad (4)$$

The enrichment (depletion) factor of the cluster beam with the ^{79}Br isotope was calculated by the formula

$$K_{\text{enr}}(^{79}\text{Br}) = \frac{S_{1L}/S_{2L}}{S_{10}/S_{20}}. \quad (5)$$

The synchronisation of the laser pulse with the molecular beam pulse was controlled by the temporal position of the maximum of the ‘burning out’ amplitude of the dip in the $^{79}\text{BrAr}^+$ ion signal (Fig. 2).

3. Results and discussion

Before the measurements, we created the conditions for obtaining mixed clusters. It should be noted that, in contrast to the conditions for the formation of homogeneous clusters $(\text{CF}_3\text{Br})_m$ [33, 34], mixed $(\text{CF}_3\text{Br})_m\text{Ar}_n$ clusters require a much stronger cooling of the particles of the expanding jet [44, 45]. This is due to the fact that the binding energy of CF_3Br molecules among themselves in a homogeneous $(\text{CF}_3\text{Br})_m$ cluster (0.25–0.3 eV [46]) is significantly higher than the binding energy of CF_3Br molecules with argon atoms in a mixed cluster $(\text{CF}_3\text{Br})_m\text{Ar}_n$, which does not exceed 0.1 eV [1, 47]. As a result, the jet temperature necessary for the formation of mixed $(\text{CF}_3\text{Br})_m\text{Ar}_n$ clusters should be significantly lower than the temperature required for the formation of homogeneous $(\text{CF}_3\text{Br})_m$ clusters [47]. Taking this fact into account, in this work we used a highly diluted mixture of a molecular CF_3Br gas with argon. Studies were performed with a $\text{CF}_3\text{Br}/\text{Ar}$ mixture at a pressure ratio of 1/200 and a total gas pressure above the nozzle of 1.5 or 3 atm.

Under these conditions, mixed clusters containing a small number ($m = 1, 2$) of CF_3Br molecules and several ($n = 1–5$) argon atoms were effectively formed [44]. At the same time, the probability of forming large-sized homogeneous $(\text{CF}_3\text{Br})_m$ clusters was small [44]. The use of a small total gas pressure above the nozzle and a rather dilute mixture allowed us to obtain small mixed clusters and also made it possible to reach higher separation parameters (enrichment factors and selectivities) for the cluster dissociation process [39].

Figure 2 shows the time dependences (time-of-flight spectra) of the cluster $\text{Ar}^{79}\text{Br}^+$ ion signal in the absence of irradiation of the cluster beam and in the case of its irradiation on the 9R(28) line ($\nu = 1083.48 \text{ cm}^{-1}$) at an excitation energy density of 0.06 J cm^{-2} . The total gas pressure above the nozzle is 1.5 atm. One can see that during the irradiation of the beam, a dip is ‘burned out’ in the dependence. The depth of the dip

is determined by the dissociation yield of the clusters, which depends on the energy density of the exciting radiation, on the basis of relation (2). The position and width of the dip can help determine the size of the irradiated part of the cluster beam.

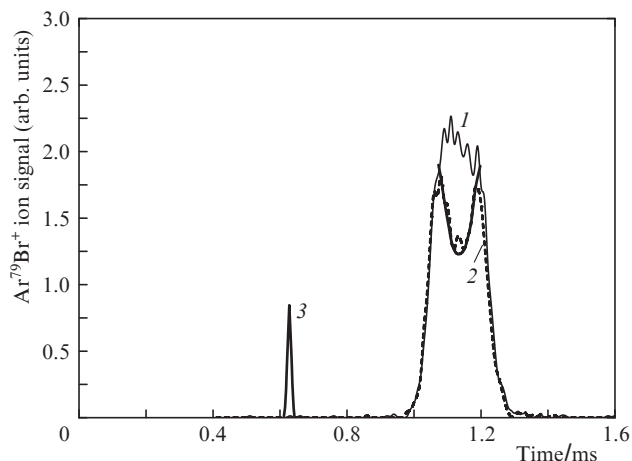


Figure 2. Time dependences of $\text{Ar}^{79}\text{Br}^+$ ion signals (1) in the absence of irradiation of the jet and (2) in the case of its irradiation on the 9R(28) line ($\nu = 1083.48 \text{ cm}^{-1}$) at an energy density of 0.06 J cm^{-2} . The pressure of the $\text{CF}_3\text{Br}/\text{Ar}$ mixture above the nozzle is 1.5 atm. Peak (3) is the electric pickup from a laser pulse; the thick solid line is the result of interpolation.

Figure 3 shows the measured dependences of the difference between the ion signals $S_{10} - S_{1L}$ on the energy density Φ of the exciting radiation for a number of laser lines whose frequencies fall into the IR dissociation band of mixed clusters. These dependences were obtained for all laser lines in the 9R(18)–9R(30) range. It can be seen that for several radiation lines, close to the maximum of the spectrum of the IR dissociation of clusters (Fig. 4), the measured dependences at an energy density of $\Phi \geq 0.2 \text{ J cm}^{-2}$ tend to saturation.

Based on the dependences shown in Fig. 3, we obtained spectral dependences of the signal difference $S_{10} - S_{1L}$ at different energy densities of exciting radiation. Figure 4 shows such a

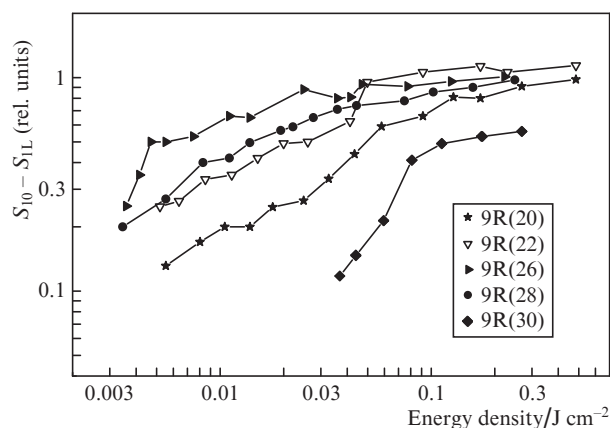


Figure 3. Dependences of the difference between the $\text{Ar}^{79}\text{Br}^+$ ion signals on the energy density of laser radiation for several laser lines. The pressure of the $\text{CF}_3\text{Br}/\text{Ar}$ mixture above the nozzle is 1.5 atm.

dependence at an energy density of $\Phi = 0.008 \text{ J cm}^{-2}$ and, for comparison, the spectral dependence of the $\text{Ar}^{79}\text{Br}^+$ ion signal borrowed from [26]. One can see that both dependences coincide quite well. However, it should be noted that in [26] the spectrum was measured in a linear (in terms of the power or energy density of exciting radiation) regime of IR dissociation of clusters, while in our case the saturation effects were manifested (see Fig. 3). It is probably for this reason that we obtained a slightly wider and slightly red-shifted spectral dependence of the difference $S_{10} - S_{1L}$ between the signals. These nonlinear effects, of course, could also lead to a decrease in the cluster dissociation selectivity.

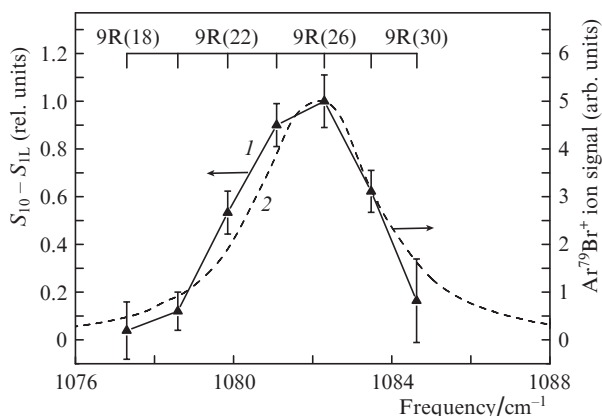


Figure 4. Frequency dependences of (1) the difference between the $\text{Ar}^{79}\text{Br}^+$ ion signals at an energy density of 0.008 J cm^{-2} and a 1.5 atm pressure of the $\text{CF}_3\text{Br}/\text{Ar}$ mixture above the nozzle, as well as of (2) the $\text{Ar}^{79}\text{Br}^+$ ion signal (borrowed from [26]).

Figure 5 shows the mass spectra of $\text{Ar}^{79}\text{Br}^+$, Ar_3^+ and $\text{Ar}^{81}\text{Br}^+$ cluster fragments ($m/z = 119, 120$ and 121 amu, respectively) in the absence of jet irradiation and in the case of its CO_2 laser irradiation on the 9R(28) line ($\nu = 1083.48 \text{ cm}^{-1}$) at an energy density of 0.054 J cm^{-2} . The total gas pressure above the nozzle was 3 atm. The shown spectra are the results of averaging over ten mass spectral scans in the mass number range $m/z = 119 - 121$ amu with a resolution of 0.05 amu. The laser radiation on the 9R(28) is more strongly absorbed by $\text{CF}_3^{79}\text{Br}-\text{Ar}$ clusters than by $\text{CF}_3^{81}\text{Br}-\text{Ar}$ clusters. One can see from Fig. 5 that when the beam is irradiated, the cluster $\text{Ar}^{79}\text{Br}^+$ ion signal ($m/z = 119$ amu) decreases more strongly than the $\text{Ar}^{81}\text{Br}^+$ ion signal ($m/z = 121$ amu). This confirms the process of isotope-selective dissociation of $\text{CF}_3^{79}\text{Br}-\text{Ar}$ clusters with respect to $\text{CF}_3^{81}\text{Br}-\text{Ar}$ clusters. In the case shown in Fig. 5b, the enrichment factor $K_{\text{enr}}(^{79}\text{Br}) = 0.88$ is obtained in the cluster beam. In this case, the selectivity of the cluster dissociation process is $\alpha(^{79}\text{Br}/^{81}\text{Br}) = 1.15$.

Figure 6 presents the dependences of the selectivity $\alpha(^{79}\text{Br}/^{81}\text{Br})$ of the dissociation process of $(\text{CF}_3\text{Br})_m\text{Ar}_n$ clusters on the frequency at excitation energy densities of 0.04 and 0.08 J cm^{-2} . One can see that higher selectivity values are observed at lower energy densities, which is probably due to the transition to the linear regime of cluster excitation. When a cluster beam is excited by radiation on the 9R(26) line, near which the maximum of the IR spectrum of cluster dissociation is localised and for which the difference in spectral intensities is minimal for clusters containing different CF_3Br isotopes (see also Table 1), the selectivity is close to unity. The selectivity is maximal on the wings of the spectrum of the IR

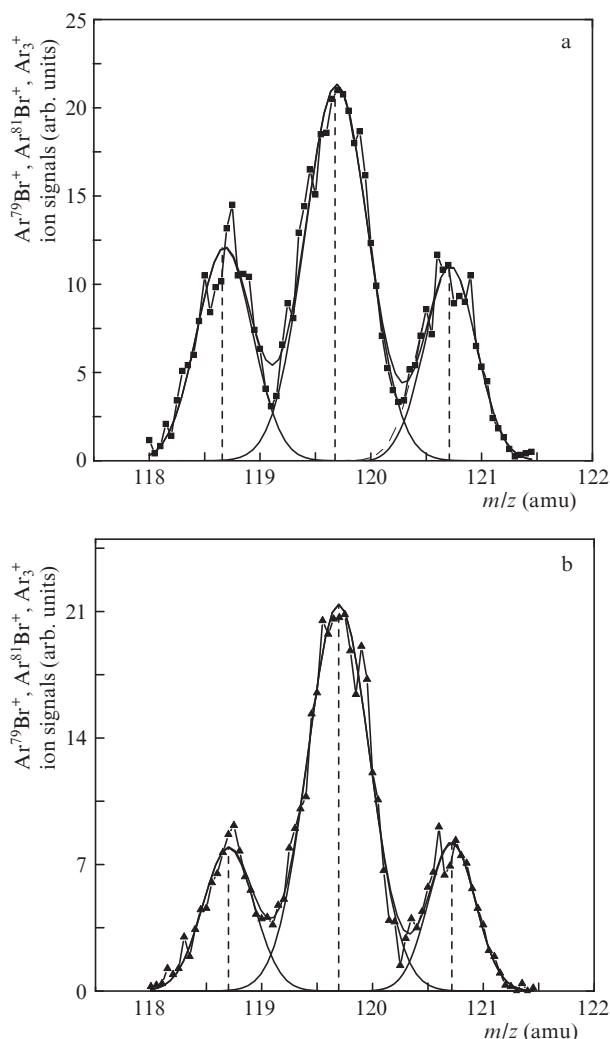


Figure 5. Mass spectra of $\text{Ar}^{79}\text{Br}^+$, Ar_3^+ and $\text{Ar}^{81}\text{Br}^+$ cluster fragments ($m/z = 119, 120$ and 121 amu) (a) in the absence of jet excitation and (b) in the case of excitation by CO_2 laser radiation on the 9R(28) line ($\nu = 1083.479 \text{ cm}^{-1}$) at an energy density of 0.054 J cm^{-2} . A mixture of $\text{CF}_3\text{Br}/\text{Ar}$ was used at a pressure ratio of 1/200 and a total gas pressure above the nozzle of 3 atm. The experimental spectra are approximated by Gaussian curves.

dissociation of clusters, where the gradient of the spectral dependence of the yield of ArBr^+ ions is large. At the frequency of the 9R(24) line, the dissociation selectivity ($^{79}\text{Br}/^{81}\text{Br}$) is less than unity, and at the frequency of the 9R(30) line, it is greater than unity, which corresponds to the frequency position of the maxima of the IR dissociation spectra of the clusters. Thus, in these experiments, we demonstrated the possibility of enrichment (or depletion) of a cluster beam with any of the bromine isotopes.

Note that the main purpose of this work was to investigate the possibility of dissociation by bromine isotope-selective dissociation of mixed $(\text{CF}_3\text{Br})_m\text{Ar}_n$ clusters using a CO_2 laser. The obtained results, in our opinion, clearly demonstrate this possibility. However, there are a large number of unknown parameters of the method in question. They include, in particular, the following: the concentration and temperature of clusters in the region of interaction with laser radiation, the cluster size distribution, and the width of the IR absorption and the dissociation spectra of clusters of a certain size. To reach high values of enrichment factors and selectivi-

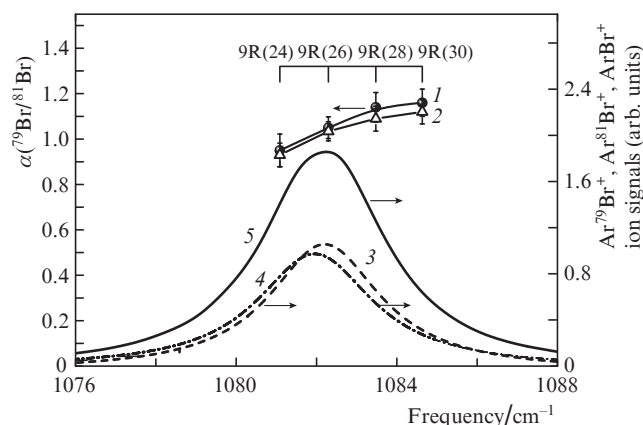


Figure 6. Dependences of the selectivity of dissociation of $(\text{CF}_3\text{Br})_m\text{Ar}_n$ clusters at an energy density of (1) 0.04 and (2) 0.08 J cm^{-2} ($\text{CF}_3\text{Br}/\text{Ar}$ mixture pressure above the nozzle is 3 atm), as well as of (3) $\text{Ar}^{79}\text{Br}^+$ and (4) $\text{Ar}^{81}\text{Br}^+$ ion signals and of (5) the total ArBr^+ ion signal (borrowed from [26]) on the frequency of exciting laser radiation.

ties of the process of IR dissociation of clusters, one needs to optimise and consider all these factors.

4. Conclusions

We have studied bromine-isotope-selective IR dissociation of mixed $(\text{CF}_3\text{Br})_m\text{Ar}_n$ van der Waals clusters in a beam by a pulsed CO_2 laser. We have obtained the dependences of the efficiency and selectivity of cluster dissociation on the frequency and energy density of laser radiation. For a number of radiation lines, the parameters of selective IR dissociation of clusters – enrichment factor and selectivity coefficient – have been measured.

It is shown that the resonant vibrational excitation of $(\text{CF}_3\text{Br})_m\text{Ar}_n$ clusters by CO_2 laser radiation makes it possible to induce their bromine isotope-selective dissociation. Thus, using the $\text{CF}_3\text{Br}/\text{Ar}$ mixture with a pressure ratio of 1/200, the enrichment factors of ^{79}Br , $K_{\text{enr}}(^{79}\text{Br}) = 1.15 \pm 0.04$ and 0.95 ± 0.03 , are obtained under irradiation of these clusters, respectively, on the 9R(30) ($\nu = 1084.635 \text{ cm}^{-1}$) and 9R(24) ($\nu = 1081.087 \text{ cm}^{-1}$) lines. The achieved selectivities for the cluster dissociation are 1.16 ± 0.05 and 0.95 ± 0.04 , respectively.

The results obtained suggest that this method can be used to separate isotopes in molecules containing isotopes of heavy elements, which have a slight isotopic shift in the IR absorption spectra.

The isotope-selective dissociation of clusters, in principle, can be used to construct a scheme for the process of isotope separation. One of the possible scenarios for its implementation is as follows. At the first stage, selective IR dissociation of clusters containing the selected isotopomers of molecules is carried out, which leads to their propagation in a beam inside a solid angle that is larger than the solid angle within which the heavier clusters with nontarget molecules propagate. At the second stage, the target molecules are spatially separated from the cluster beam occurs. When implementing this separation process, in order to achieve a maximum separation factor, it is necessary to ensure not only high optical selectivity of the IR dissociation of clusters, but also sufficiently high selectivity in the spatial separation of target molecules from the cluster beam.

Acknowledgements. The authors are deeply grateful to D.G. Poidashev and E.A. Ryabov for their assistance and helpful discussions.

This work was partially supported by the Russian Foundation for Basic Research (Grant No. 18-0200242).

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