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ATOMS, MOLECULES, OPTICS

EFFICIENT ISOTOPE-SELECTIVE IR LASER MULTIPHOTON DISSOCIATION OF $^{11}BCL_3$ MOLECULES IN A MIXTURE WITH SF_6 SERVING AS A SENSITIZER AND AN ACCEPTOR OF RADICALS

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Abstract. The results of studies of isotope-selective laser infrared (IR) multiphoton dissociation (MPD) of $^{11}BCl_3$ molecules in a natural mixture with $^{10}BCl_3$ by the radiation from a pulsed CO_2 laser in the case of their irradiation with a sensitizer – SF_6 molecules, which are simultaneously acceptors of radicals – Cl atoms formed during dissociation of BCl_3 molecules are presented. A strong increase in the efficiency of dissociation of $^{11}BCl_3$ molecules was discovered when they were irradiated with SF_6 molecules compared to the case of irradiation without SF_6. The main parameters of isotope-selective IR multiphoton dissociation of BCl_3 molecules were measured – the dissociation yields of $^{11}BCl3$ (β_{11}) and $^{10}BCl_3$ (β_{10}), as well as the selectivity of dissociation of $^{11}BCl_3$ molecules relative to $^{10}BCl_3$ molecules ($\alpha(^{11}B/^{10}B)$). The dependences of these parameters on the pressures of the irradiated gases BCl_3 and SF_6, as well as on the energy density and frequency of the exciting laser radiation were obtained. The main products formed upon irradiation of the mixture of BCl_3 and SF_6 molecules used – SF_5Cl, BCl_2F, $BClF_2$ and BF_3 – have been identified. A significant (several times) increase in the yield and selectivity of dissociation of $^{11}BCl_3$ molecules was observed, as well as a significant decrease in the threshold dissociation energy density when they were irradiated with SF_6 compared to the case of irradiation without SF_6. This opens up the possibility of implementing single-frequency isotope-selective laser MPD of $^{11}BCl_3$ molecules in unfocused laser beams at moderate (no more than 4–5 J/cm^2) excitation energy density. The results obtained are important and relevant in terms of the application of the described method for the development of laser technology for the separation of boron isotopes.

Keywords: atoms, molecules, clusters, boron trichloride, molecular and cluster beams, laser spectroscopy, laser-induced selective processes in molecules and clusters, laser separation of isotopes, laser physics

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1. INTRODUCTION

Recently, there has been a great interest in laser separation of boron isotopes [1–5], which is associated with their use in important industries, as well as in medicine [6–10]. In nature, boron is contained in the form of two isotopic modifications: ^{10}B (about 19.8%) and ^{11}B (about 80.2%) [6–10]. Boron isotopes have similar physicochemical properties and are perfect but they differ in their nuclear and physical properties. The isotope ^{10}B has a very large thermal neutron capture cross section, about 3837 bn [9, 11] (1 bn = 10^{-24} cm^2). For most nuclides, this cross section is close to units or fractions of a barn. Therefore, materials enriched with isotope containers for the transportation and storage of neutron-emitting materials, highly sensitive neutron detectors, as well as in ^{10}B (boric acid, boron carbide and other compounds) are widely used in nuclear power engineering in control and protection systems of nuclear reactors, in the manufacture of systems of biological protection of personnel from thermal neutrons. Compounds containing an isotope ^{10}B, are used in neutron capture therapy in oncology.

Isotope ^{11}B is used in the electronic industry as an alloying component in the production of semiconductor products [8–10].

Industrial enrichment of boron isotopes is carried out using traditional separation technologies of low-temperature BF_3 rectification or chemical isotope exchange using anisole technology [7–9]. However, classical methods of separation of boron isotopes are characterized by high capital and energy costs associated with a large number of separation elements, as well as a long period of the release of the separation cascade to the stationary mode of operation. There are no industrial technologies for the production of isotope ^{10}B in Russia today. At the same time, there is a renaissance of nuclear energy, and plans for its accelerated development are widely discussed. In this regard, the development of fundamentally new laser methods and effective boron isotope separation technology is an important and urgent task.

The most effective and well-developed method of molecular laser isotope separation today is considered to be the method of isotope selective infrared multiphoton dissociation of molecules (IR MFD) by pulse-periodic radiation CO laser [12–16]. This method has been brought to practical realization in Russia. At the end of the last century and at the beginning of this century, the Uglerod laser complex consisting of four laser modules for laser enrichment of the carbon-13 (^{13}C) isotope based on the IC MFD of CF_2HCl (freon-22) molecules was created and successfully operated in Kaliningrad [17–19]. In the early 2000s, it produced up to 30 kg of carbon-13 per year. It has been shown that the laser method is quite competitive in comparison with traditional methods [19]. Therefore, when implementing the technological process of separation of boron isotopes, it is advisable to use this method.

For molecular laser separation of isotopes using available efficient pulsed CO_2 lasers, it is necessary that the IR absorption fields of the selected molecules fall within the range of CO_2 laser generation and have a comparatively large ($\geqslant$ 5–10 cm^{-1}) isotopic shift. Due to technological considerations, it is important that the dissociation products be gaseous. In addition, it is desirable that the efficient isotope-selective dissociation of the selected molecules was carried out at a low energy density of laser radiation. The number of boron- containing molecules that meet these requirements is limited. Therefore, experiments on the atomic separation of boron isotopes have so far been carried out with only a few compounds with boron trichloride (BCl_3) [20–33], chloroethylene dichloroborane ($HC_1C = CHBC_{12}$) [34–37] and the $BCl_3 \bullet CH_3SH$ complex [38].

The most suitable starting compound for laser separation of boron isotopes is the gaseous chemical compound BCl_3, which is produced by industry. Stripes of IR absorption of ν_3 vibrations of $^{11}BCl_3$ molecules ($\approx$ 954.2 cm^{-1}) and $^{10}BCl_3$ ($\approx$ 993.7 cm^{-1}) [39] resonate with the P- and R-branches, respectively 10.6-microns of the CO_2 laser generation band (see Figure 2a below). Isotopic shift between the indicated IR absorption bands of $^{11}BCl_3$ molecules and $^{10}BCl_3$ is $\Delta\nu_{is} \approx 39.5$ cm^{-1} [39]. It was using BCl_3 that the isotope-selective laser IR MFD of molecules was first demonstrated [20]. In a large number of subsequent works [21–33] the selective dissociation of BCl_3 molecules was studied in detail in the radiation field of a powerful pulsed CO_2 laser using different radical acceptors (H_2, NO, H_2S, D_2S, HBr, etc.) to suppress the association process of the radicals formed during dissociation of BCl_3 molecules BCl_2 and Cl atoms [22].

It has been shown that oxygen is a good radical acceptor in terms of obtaining relatively high selectivity values and the release of BCl_3 molecules [20, 23–25]. The final products of IR MFD of BCl_3 molecules and subsequent chemical reactions in the case of oxygen use are B_2O_3 and Cl_2 [23]. Solid connection B_2O_3 in the form of a film is deposited on the walls and windows of the cuvette in which the gas is irradiated. It has been established [23, 29], that radical acceptors practically do not lead to any significant increase in the selectivity and yield of BCl_3 dissociation, as well as a decrease in the threshold of molecular dissociation.

The studies also showed that for effective IR MFD of BCl_3 molecules, rather high energy densities of ambient laser radiation ($\geqslant$ 20 J/cm^2) are required [29, 30], which is mainly due to the high binding energy of the molecule ($\approx$ 110 kcal/mol [40]). Therefore, IR dissociation of molecules is possible only by focused laser beams. At the same time, the use of focused laser beams leads, as a rule, to a decrease in the isotopic selectivity of the molecule dissociation process [12–14].

When BCl_3 molecules of natural isotopic composition were excited by single-frequency laser radiation, the dissociation selectivity of $^{10}BCl_3$ and $^{11}BCl_3$ molecules was $\alpha(^{10}B/^{11}B) \leqslant 8$ and $\alpha(^{11}B/^{10}B) \leqslant 2.5$, respectively [28–30]. The yields of dissociation of molecules (in terms of the volume of gas irradiated by the laser in the cuvette) were small [30],

$$\beta_{10} \approx \beta_{11} \leq (2 - 8) \cdot 10^{-2}.$$

Significantly higher selectivity and dissociation rates of BCl_3 molecules ($\alpha(^{10}B/^{11}B) > 8$; $\beta_{10} \geq 10\%$; $\beta_{11} \geq 20\%$) were observed in the case of their excitation and dissociation by two-frequency laser IR radiation [41,42]. With two-frequency excitation, the threshold of molecular dissociation also significantly decreased (to values of $\Phi_1, \Phi_2 \geq 2$–3 J/cm^2). However, the implementation of the technological process of the laser separation of boron isotopes using two- frequency dissociation of molecules is very difficult in practice.

Recently, we have discovered that with isotope-selective laser IR MFD of the BCl_3 molecule, in the case of using SF_6 molecules as a radical acceptor, which at one time are effective sensitizers for BCl_3 molecules, a significant increase in the selectivity and dissociation yield of $^{11}BCl_3$ molecules, as well as a significant decrease in the threshold energy density of dissociation by single-frequency IR radiation [5] take place. As a result, it becomes possible to carry out single-frequency isotope-selective dissociation of molecules $^{11}BCl_3$ in unfocused laser beams at a moderate (3–5 J/cm^2) excitation energy density, which is very important when implementing the technological process of laser separation of boron isotopes in practice. This paper presents the results of a broader and more detailed study of this process.

2. EXPERIMENT AND RESEARCH METHOD

2.1 Experimental installation

The scheme of the experimental installation is shown in Fig. 1. The installation included a frequency-tunable pulsed CO_2 laser, forming-optical, stainless steel gas cuvette for irradiation of the studied molecules with a length of 112 mm, with a volume of 24.2 cm^3, with windows made of KBr, calorimetric (TPI-2–5) and pyroelectric (SensorPhysics Model 510) radiation receivers for measuring incoming and transmitted energy through the cuvette. The pulse of the CO_2 laser radiation consisted of an anterior peak of about 80 ns in half-height and the tail section had a duration of about 750 ns, which contained about a third of the energy of the laser pulse. The collimation of the laser beam into the irradiated cuvette was carried out by a long-focus (f = 100 cm) lens. The energy of the laser radiation in the pulse ranged from 0.7 to 3.0 J, depending on the frequency of generation and the partial composition of the laser mixture. The laser radiation frequency was adjusted in the range of 929.0–985.5 cm^{-1}. To link the frequency of the CO_2 laser emission lines, an optical-acoustic receiver with a reference gas was used NH_3. Transverse distribution of energy density and the cross-sectional area of the laser beam was determined using a microprobe by scanning its laser beam sections in mutually perpendicular directions at the inlet and outlet of the cuvette.

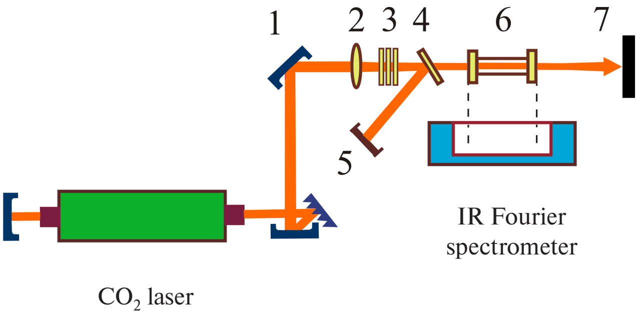

Fig. 1. Scheme of the experimental installation: 1 mirror; 2 long-focus lens; 3 laser radiation attenuators; 4 dividing plate; 5 radiation receiver; 6 cuvette with irradiated gas; 7 radiation absorber

2.2 Research method

The main part of the experiments on isotope-selective dissociation of BCl_3 molecules was carried out when adjusting the frequency of CO_2 laser radiation to the 10P32 line (frequency 932.96 cm^{-1}), which coincides with the long-wavelength wing of the absorption band of the ν_3 oscillation of $^{11}BCl_3$ molecules ($\approx$ 954.2 cm^{-1} [39]). The absorption band of the oscillation ν_3 of SF_6 molecules ($\approx$ 948 cm^{-1} [43]) is approximately 6.2 cm^{-1} is shifted to the low-frequency side from the center of the absorption band of $^{11}BCl_3$ molecules (see Fig. 2).

With laser multiphoton IR excitation of molecules $^{11}BCl_3$ and SF_6 their IR absorption bands shift due to the anharmonicity of vibrations to the red side (towards the laser radiation frequency) and come into optimal resonance with the laser field [44, 45, 46, 47, 48]. Effective multiphoton IR excitation of both types of molecules occurs, including molecules SF_6, absorbed energy from which is transferred to molecules $^{11}BCl_3$. Since the absorption bands of the molecules SF_6 and $^{11}BCl_3$ practically coincide, the process of *V–V* vibrational-vibrational exchange of energy between them has a resonant character and occurs very efficiently [46, 49, 50]. This leads to an increase in the yield of the dissociation of $^{11}BCl_3$ molecules. The mechanisms and probability of vibrational energy transfer during simultaneous multiphoton IR laser excitation of molecules in a two-component molecular medium were considered in more detail (using the example of a mixture of CF_2HCl/CF_3Br molecules) in recent works [46, 48]. It should be noted that since the dissociation energy of SF_6 molecules ($\approx$ 92 kcal/mol [51]) is less than the dissociation energy of BCl_3 molecules, at high excitation energy densities, dissociation of SF_6 molecules also occurs.

Laser IR MFD of $^{11}BCl_3$ molecules proceeds according to the scheme

$$^{11}BCl_3 + nh\nu \rightarrow {}^{11}BCl_2 + Cl, \qquad (1)$$

where $nh\nu$ is the number of absorbed laser IR photons.

Upon irradiation of the molecules, the dissociation products were enriched with isotope ^{11}B, and the residual gas BCl_3 was enriched with isotope ^{10}B. The dissociation yields, which represent the fractions of molecules decayed in the irradiated volume in one laser pulse, were determined by changes in the intensity of the bands in the IR absorption spectra for each of the isotopic components of BCl_3. Absorption spectra were measured using the FT-801 infrared Fourier spectrometer. The dissociation outputs of β_{11} and β_{10} were calculated from the partial pressure of each component of $^{i}BCl_3$ ($i = 10{,}11$) before ($p_{i,0}$) and after (p_i) irradiation with laser pulses using the ratio

$$\beta_i = \Gamma^{-1}[1 - (p_i / p_{i,0})^{1/N}], \qquad (2)$$

where $\Gamma \approx 0.083$ is the ratio of the irradiated volume ($V_{irr} \approx 2.0$ cm^3) to the volume of the cuvette ($V_{cell} = 24.2$ cm^3), N is the number of irradiation pulses. Since the IR absorption bands of $^{11}BCl_3$ and SF_6 molecules overlap (Fig. 2 c), the measurement of gas flow $^{11}BCl_3$ by the IR absorption spectrum required special attention. Measurements of the intensity of the absorption band of $^{11}BCl_3$ molecules before and after irradiation were carried out at a frequency of ≈ 954.2 cm^{-1} (approximately in the maximum of the absorption band $^{11}BCl_3$), at which practically no contribution from the absorption of SF_6 molecules at the pressures used in the experiment was made (Fig. 2b). The selectivity of $\alpha(^{11}B/^{10}B)$ was defined as the ratio of the yields of dissociation of molecules $^{11}BCl_3$ and $^{10}BCl_3$:

$$\alpha(^{11}B/^{10}B) = \beta_{11}/\beta_{10}. \qquad (3)$$

3. RESEARCH RESULTS AND THEIR DISCUSSION

3.1 Dependences of yields and selectivity of BCl_3 dissociation on SF_6 pressure

The main parameters of the isotope-selective laser IR MFD of the BCl_3 molecule: the dissociation yields of $^{11}BCl_3$ (β_{11}) and $^{10}BCl_3$ (β_{10}), molecules, as well as the selectivity of the dissociation of $^{11}BCl_3$ molecules with respect to molecules $^{10}BCl_3$ $\alpha(^{11}B/^{10}B)$ were measured in the experiments. The dependences of these parameters on the pressures of the irradiated gases BCl_3 and SF_6, as well as on the energy density and frequency of the incident laser radiation, are obtained.

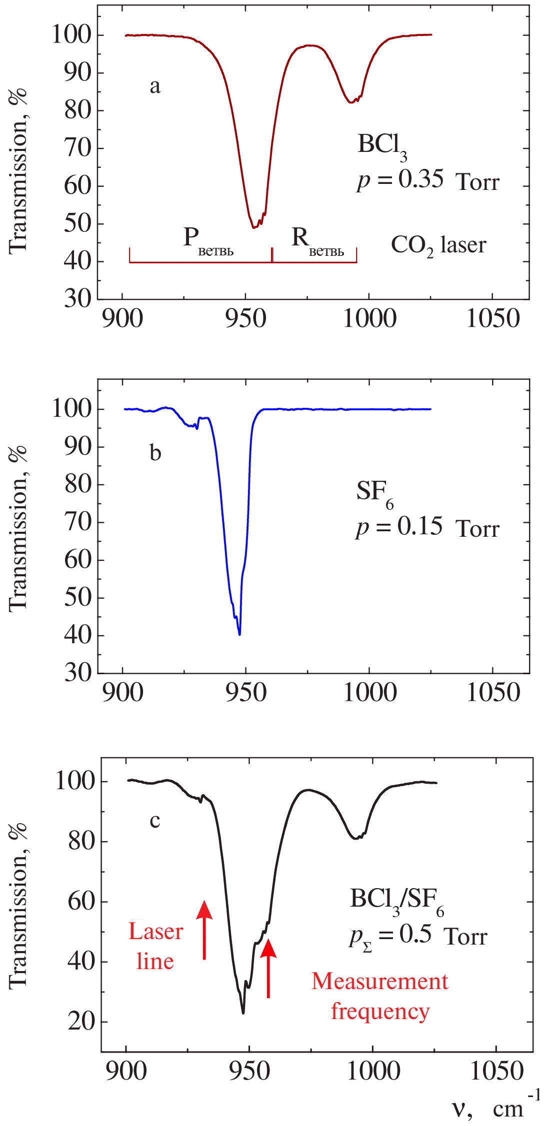

Fig. 2. A ν_3 molecule vibration IR absorption bands, $^{11}BCl_3$ and $^{10}BCl_3$. The pressure of BCl_3 in the cuvette is 0.35 Torr, the length of the cuvette is 11.2 cm. b IR absorption band of vibrations of ν_3 SF_6 molecules. The pressure of SF_6 in the cuvette is 0.15 Torr. c e IR absorption bands of vibrations of 3 molecules $^{10}BCl_3$, $^{10}BCl_3$ and SF_6. The pressure of BCl_3 in the cuvette is 0.35 Torr, SF_6 is 0.15 Torr

Figure 3 shows the results reflecting the measurement methodology. The bands of IR absorption of ν_3 oscillations of $^{11}BCl_3$ molecules, $^{10}BCl_3$ and SF_6 molecules before irradiation (1) and after irradiation (2) are shown. Also the bands of IR absorption of vibrations ν_1 (≈ 851.4 cm^{-1}) and ν_8 (≈ 909.1 cm^{-1}) of the resulting SF_5Cl product [52,53] are shown. The initial pressure of BCl_3 in the cuvette is 0.35 Torr, SF_6 is 0.15 Torr. The energy density of the exciting laser radiation is 1.91 J/cm^2. The number of irradiation pulses is N = 1800. In addition to SF_6Cl we also found (IR absorption

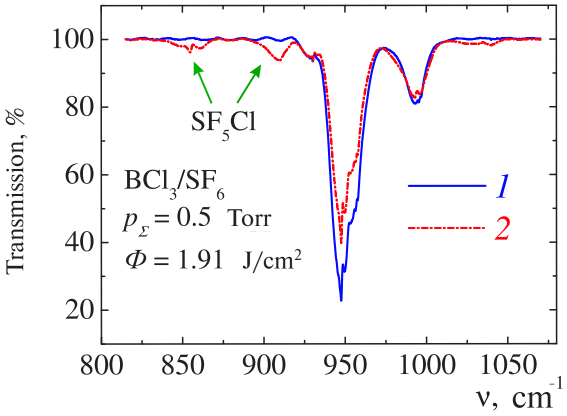

Fig. 3. (In outline color) IR absorption bands of vibrations of ν^3 molecules $^{11}BCl_3$, $^{10}BC_{13}$ and SF_6 molecules before irradiation (*1*) and after irradiation (*2*) with a laser. The IR absorption bands of the resulting SF_5Cl product with band centers at frequencies 851.4 cm^{-1} (oscillation ν_1) and 909.1 cm^{-1} (oscillation ν_8) [52, 53]. Initial pressure of BC13 in the ditch is 0.35 Torr, SF_6 0.15 Torr. energy density of exciting laser radiation is 1.91 J/cm^2. The number of irradiation pulses $N = 1800$

spectra of other products are not shown in Fig. 3) BCl_2F, $BClF_2$ and BF_3 molecules in the resulting products.

Fig. 4 shows the dependences of the dissociation yields of $^{11}BCl_3$ (β_{11}) and $^{10}BCl_3$ (β_{10}) molecules, as well as the selectivity of dissociation of $^{11}BCl_3$ molecules in relation to $^{10}BCl_3$ ($\alpha(^{11}B/^{10}B)$) molecules) on pressure SF_6 in the range 0.05–2.0 Torr at a fixed pressure of BCl_3, equal to 0.35 Torr and an exciting radiation energy density of $\Phi \approx 2.1$ J/cm^2. It can be seen that in the investigated pressure range SF_6 the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules depend, respectively, on the values of $\beta_{11} \approx 4.5 \cdot 10^{-4}$ and $\beta_{10} \approx 3.4 \cdot 10^{-4}$ when irradiating BCl_3 molecules without SF_6 to the values of $\beta_{11} \approx 8.5 \cdot 10^{-2}$ and $\beta_{10} \approx 7.2 \cdot 10^{-2}$ in the case of irradiation of BCl_3 with SF_2 at pressure 2.0 Torr.

Thus, it follows from the results shown in Fig. 4a that when irradiating BCl_3 molecules in a mixture with SF_2 an increase in the yields of BCl_3 molecules is observed by more than two orders of magnitude. Note the sharp increase (by more than an order of magnitude) of dissociation yield of $^{11}BCl_3$ molecules when adding to 0.35 Torr of BCl_3 only 0.1 Torr of SF_6. This also means that due to the use of SF_6, the threshold energy density of dissociation of $^{11}BCl_3$ molecules is significantly reduced. The increase in the dissipation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules with an increase in SF_6 pressure in the 0.5–2.0 Torr region is monotonous and reflects the process of increasing the amount of energy transferred to BCl_3 molecules from laser excited SF_6 molecules.

The selectivity of dissociation of $^{11}BCl_3$ molecules with respect to $^{10}BCl_3$ molecules dramatically increases-from the value $\alpha(^{11}B/^{10}B) \approx 1.3$ in the case of irradiation of molecules without SF_6 to the value $\alpha(^{11}B/^{10}B) \approx 7$–8 in the case of irradiation of molecules with SF_6 at a pressure of 0.15–0.2 Torr. With a further increase in the pressure of SF_6 to 0.4 Torr, the selectivity rapidly decreases to the value $\alpha(^{11}B/^{10}B) \approx 3.0$ and then slowly decreases to the value $\alpha(^{11}B/^{10}B) \approx 1.0$ at pressure $SF_6 \geq 1.5$ Torr. Rapid reduction of selectivity $\alpha(^{11}B/^{10}B)$ in the range of 0.15–0.4 Torr is probably associated with a sharp decrease in the amount of energy transferred to $^{11}BCl_3$ molecules from SF_6 molecules. The reason for this may be the release of energy from the laser-induced mode of ν_3 SF_6 (resonant with the oscillation of $^{11}BCl_3$ molecules) into other modes of the molecule as a result of the process of intramolecular intermolecular-the oscillatory-vibrational V–V relaxation of energy, as well as the flight of excited SF_6 molecules from the irradiation zone

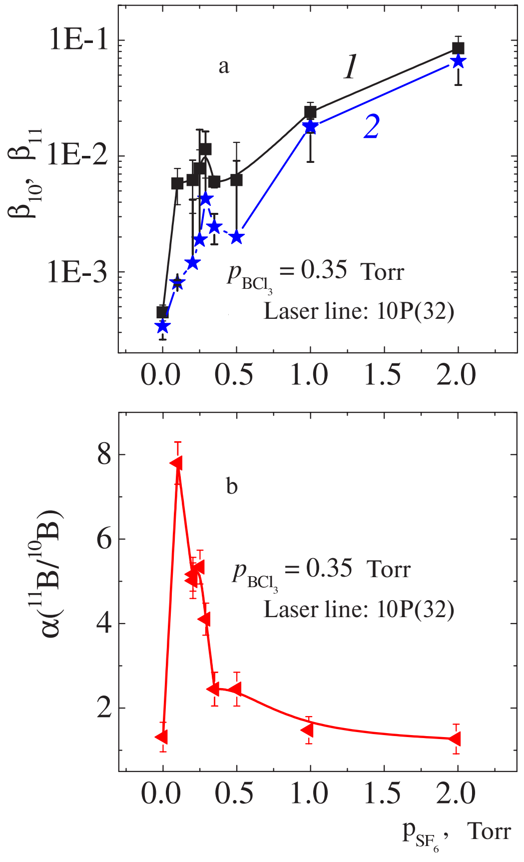

Fig. 4. Dependences of dissociation yields β_{11} (curve 1) and β_{10} (curve 2) (*a*), as well as the selectivity of dissociation ($^{11}B/^{10}B$) (*b*) on the pressure of SF_6 at a fixed pressure of BCl_3, equal to 0.35 Torr and the energy density of the ambient radiation of 2.1 J/cm^2

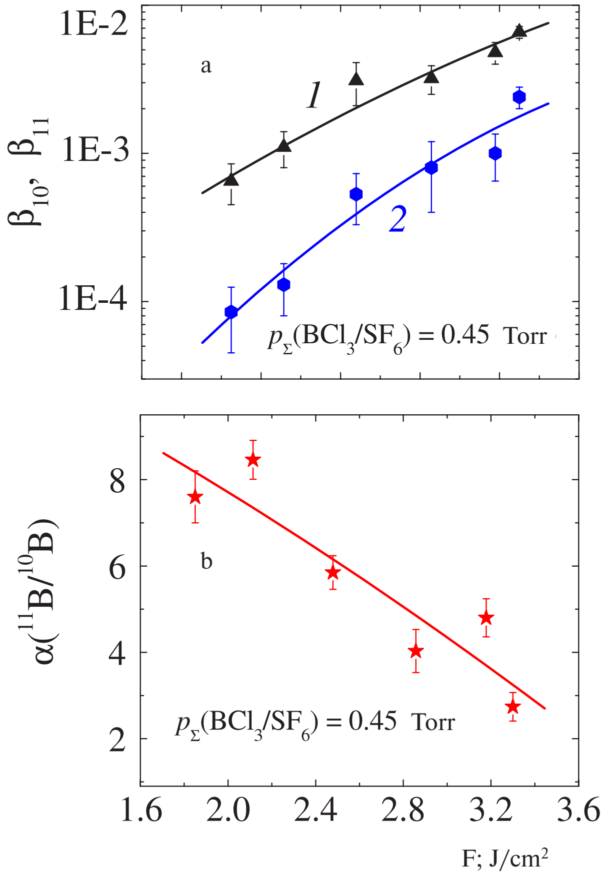

Fig. 5. Dependences of dissociation outputs β_{11} (curve 1) and β_{10} (curve 2) (a), as well as the selectivity of the dissociation $\alpha(^{11}B/^{10}B)$ (b) from the energy density of the exciting laser radiation. Gas pressure in the cuvette: 0.35 Torr BCl_3+0.1 Torr SF_6

and the relaxation of their vibrational energy upon collision with the walls of the cuvette.

Our estimates show that the average free path $\langle l \rangle$ of SF_6 molecules (at a pressure of 0.15 Torr) mixed with molecules BCl_3 (0.35 Torr) in a two-component mixture is $\langle l \rangle \le 0.25$ mm. The diameter of the laser beam in the irradiation zone of the molecules was about 0.5 cm, and the diameter of the cuvette was 1.4 cm. Therefore, at the specified free path length of SF_6 molecules the departure of particles from the beam did not significantly affect the decrease in the energy transferred to the $^{11}BCl_3$ molecules. In our opinion, the process of intramolecular intermodular vibrational-vibrational V–V energy relaxation is more likely to decrease the proportion of energy transferred to $^{11}BCl_3$ molecules from SF_6 molecules. In SF_6 molecules, it proceeds with a velocity constant $p\tau_{V-V} \le 1$ μs ·Torr in the case of not strongly excited molecules [54]. In the case of strongly excited molecules, this process as well as the process of vibrationally translational V–T relaxation energy flows much faster [54, 55].

A decrease in the selectivity of dissociation of $^{11}BCl_3$ molecules with an increase in SF_6 pressure at high pressures is associated with an acceleration of the processes of vibrational energy exchange between irradiated molecules. Thus, in the case of irradiation of BCl_3 at a pressure of 0.35 Torr in a mixture with SF_6, the maximum values of the dissociation selectivity $\alpha(^{11}B/^{10}B)$ are achieved at a pressure of SF_6 in the range of 0.15–0.25 Torr. At the same time, the selectivity of $\alpha(^{11}B/^{10}B)$ in the case of irradiation with SF_6 is more than 3–5 times greater than in the case of irradiation of molecules BCl_3 without SF_6.

3.2 Dependences of the yields and selectivity of BCl_3 dissociation on the energy density of exciting laser radiation

It should be noted that the dependence of yields and selectivity of dissociation of BCl_3 molecules on the energy density of exciting laser radiation using an unfocused irradiation geometry in single-frequency radiation that is of great interest in terms of practical applications has not been previously studied. This is due to the fact that the high energy densities necessary for effective dissociation of molecules are difficult to realize without radiation focusing, since they lead to the destruction of the cuvette windows, in which molecules are irradiated. We obtained such dependences using the unfocused geometry of the BCl_3 radiation precisely due to a significant increase in the dissociation efficiency of BCl_3 molecules due to the use of a sensitizer and a radical acceptor of SF_6 molecules. Fig. 5 shows the dependences of the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules, as well as selectivity of the dissociation of $\alpha(^{11}B/^{10}B)$ from the energy density of the exciting laser radiation in the range from 1.8 to 3.4 J/cm^2. A mixture of 0.35 Torr BCl_3 + 0.15 Torr SF_6 molecules was irradiated. It can be seen that the dissociation yields of BCl_3 molecules grow rapidly with increasing excitation energy density. Such a rapid increase in dissociation yields is explained by [12–14], that due to the high binding energy of molecules at the indicated laser radiation energy densities, the dissociation process has an over-threshold character and is relatively far from saturation.

Selectivity of dissociation of $\alpha(^{11}B/^{10}B)$ molecules of $^{11}BCl_3$, on the contrary, decreases sharply with increasing excitation energy density. At the same time, for all studied energy densities, the selectivity of dissociation using SF_6 is significantly (2–5 times) higher than without SF_6.

The observed behavior of the dependence of the outputs of dissociation and selectivity on the energy density of stray laser radiation is characteristic of the isotope-selective IR MFD process of a large number of molecules [12–14, 16].

3.3 Dependences of the yields and selectivity of BCl_3 dissociation on the frequency of exciting laser radiation

Fig.6a, b show the dependences of the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$, molecules, as well as the selectivity of $\alpha(^{11}B/^{10}B)$ dissociation on the frequency of exciting laser radiation in the region P-branches of the 10.6-μm CO_2 laser generation band (in the range from 932.96 to 949.5 cm^{-1}). The results of individual measurements in the area of the R-branch of CO_2 laser radiation are also presented (on the frequency is 971.9 cm^{-1}). A mixture of molecules was irradiated (0.35 Torr BCl_3+0.15 Torr SF_6 at an energy density of 2.5 J/cm^2 of exciting radiation. It can be seen that the maximum yields of dissociation of molecules $^{11}BCl_3$ and $^{10}BCl_3$ are observed in the frequency range of 935–948 cm^{-1}, and the maximum selectivity in the region of 932.96 cm^{-1} (on the 10*P*(32) laser generation line).

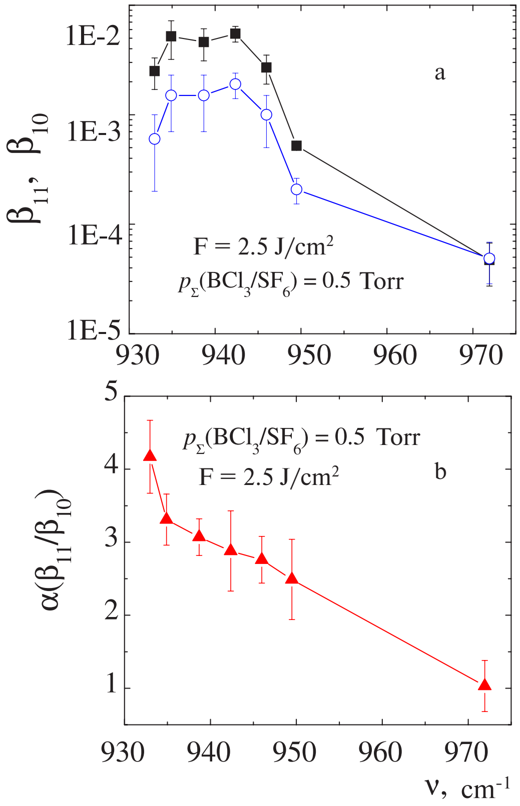

Fig. 6. Dependences of $^{11}BCl_3$ and $^{10}BCl_3$ molecular dissociation yields (a), as well as the selectivity of dissociation $\alpha(^{11}B/^{10}B)$ (b) on the frequency of exciting laser radiation. A mixture of molecules was irradiated, 0.35 Torr BCl_3+0.15 Torr SF_6 at an energy density of 2.5 J/cm^2 of ambient radiation

The obtained dependences of the dissociation yields of BCl_3 molecules on the frequency of exciting laser radiation correlate fairly well with the analogous data obtained earlier in the work [28, 30] using the molecule irradiation geometry by focused laser radiation. The significant difference between the data obtained by us and the results of the works [28,30] is that both the results of dissociation of $^{11}BCl_3$ and $^{10}BCl_3$, molecules and the selectivity of dissociation of $^{11}BCl_3$, molecules obtained by us are significantly higher than similar values obtained in [28, 30].

In these works [28, 30], the dependences of the dissociation results of $^{11}BCl_3$ and $^{10}BCl_3$ molecules on the frequency of exciting laser radiation were measured using oxygen radicals as an acceptor. Maximum output value of the dissociation of $^{11}BCl_3$ molecules during the rearrangement of the laser radiation frequency in the region of the P-branch of the 10.6-μm CO_2 laser generation band (in the range from 956.2 to 925 cm^{-1}) was only 4–5 times greater compared with the minimum value observed in the frequency range 956.2 cm^{-1}. In our experiments, the dissociation yield of $^{11}BCl_3$ molecules increased nearly 40–50 times compared to the minimum value in the specified range. Selectivity of $^{11}BCl_3$ molecules dissociation at all frequencies in the area of the 10.6-μm P-branch of the CO_2 laser generation band with an energy density of 2.5 J/cm^2 of excitatory radiation used is approximately 1.5–2.2 times higher than that observed in [28, 30].

It should be noted that in the case of irradiation of BCl_3 molecules in a mixture with SF_6 the processes of vibrational V–V energy exchange between $^{11}BCl_3$ and SF_6 molecules, which occur under conditions of relatively high density of the irradiated gas (total pressure 0.5–1.5 Torr), make a very large contribution to increasing the yield and selectivity of $^{11}BCl_3$ dissociation.

Processes of collisions of excited molecules BCl_3 and SF_6 lead, together with the processes of resonant radiation excitation for $^{11}BCl_3$ and SF_6 molecules, to a strong increase in the dissociation yields of $^{11}BCl_3$ when they are irradiated in a mixture with SF_6 compared with the case of irradiation without SF_6. The role of vibrational-vibrational energy exchange between molecules, including those of different types, is especially high in the presence of almost resonant vibrational levels of molecules [50], and this was realized in our experiments. The probability of a transition from state 1 to state 2 induced by a time-dependent perturbation $V(t)$ in

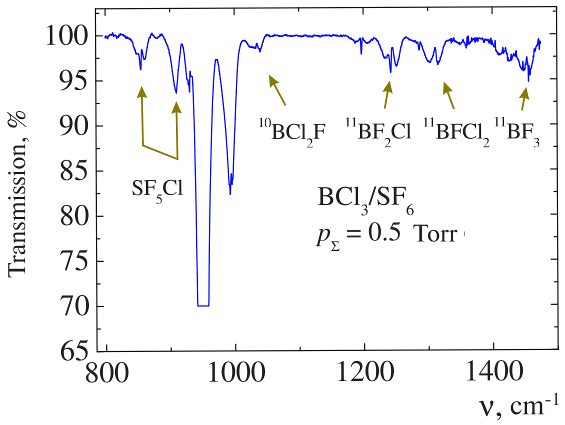

Fig. 7. IR absorption bands of products formed as a result of laser IR MFD of BCl_3 molecules in combination with SF_6 and subsequent chemical reactions. A mixture of 0.35 Torr BCl_3 + 0.15 Torr SF_6 molecules was irradiated

the first order of the Born–Oppenheimer approximation is given by [56] the expression

$$P_{12}(t) = \hbar^{-2}\left|\int_{-\infty}^{+\infty}\langle 1|V(t)|2\rangle \exp(i\Delta\omega t)dt\right|^2. \qquad (4)$$

In contrast to the processes of oscillatory-translational V –T relaxation, when the frequency difference Δω between states 1 and 2 is large (relaxation of the vibrational energy of a molecule in translational degrees of freedom occur through low-frequency modes of the molecule), in the processes of vibrational–vibrational V–V energy exchange, the frequency difference Δω of transitions between states may be insignificant or even zero for resonant transitions. Such long- acting dipole-dipole interactions can induce almost resonant processes of vibrational-vibrational V–V energy exchange [50]. This leads to an efficient transfer of energy between colliding molecules (see, for example, work [49] and the references therein).

Fast processes of almost resonant vibrational-vibrational V–V energy exchange between molecules as a result of long-range dipole-dipole interaction [49] already during the exciting laser pulse as if create a very dense “network” of inhabited vibrational-rotational levels, consisting of energy levels of both types of molecules. As a result, additional resonant channels arise to excite molecules through a sequence of vibrational-rotational transitions of both types of molecules, which leads to more efficient excitation of them up to the dissociation boundary.

The frequency dependences of the dissociation results of $^{11}BCl_3$ and $^{10}BCl_3$ molecules obtained by us, as well as the selectivity of dissociation of $^{11}BCl_3$ molecules, show that it is precisely due to the resonant energy transfer from SF6 molecules (the IR absorption band of which coincides well with the IR absorption band of $^{11}BCl_3$ molecules) to $^{11}BCl_3$ molecules that a strong increase in the efficiency of isotopic selective dissociation of $^{11}BCl_3$ molecules takes place. This is manifested in a significant increase in the yield and selectivity of dissociation of molecules and a decrease in the threshold energy density of their dissociation.

3.4 Identification of resulting products

Gaseous products that were formed as a result of laser IR MFD of BCl_3 molecules in a mixture with SF_6 and subsequent chemical reactions were identified by their IR absorption spectra in the spectral range from about 750 to 3600 cm^{-1}. In most of the experiments carried out, the partial pressures of the irradiated gases of BCl_3 and SF_6 in the cuvette were in the range of 0.1–1.0 Torr, and the pressure ratio of BCl_3/ SF_6 was approximately from 5/1 to 1/10. It is established that the composition and quantity of the products formed depends on the ratio of the partial pressures of the source gases BCl_3 and SF_6, as well as the degree of their production during irradiation.

So, with small outputs of $^{11}BCl_3$ ($\leq$ 15–20%) the main end products were SF_6Cl and $^{11}BCl_2F$ (Fig. 7). If spending over 20–30% of $^{11}BCl_3$, and also at partial pressures of SF_6 significantly exceeding the partial pressure of BCl_3, the composition of the products formed was much wider: SF_6Cl, $^{11}BCl_2F$ and $^{10}BCl_2F$, $^{11}BClF_2$ and $^{10}BClF_2$. With even higher BCl_3 consumption (at least 35–40%), the main end products were SF_6Cl, $^{11}BF_3$ and $^{10}BF_3$, while the content of BCl_2F and $BClF_2$ molecules in the products was insignificant.

The predominant formation of the BF_3 product is probably explained by the fact that under conditions of high temperature of the mixture at the moments of laser pulse irradiation and the presence of fluorine atoms in the reaction volume (as part of the SF_6 acceptor), an effective process of their substitution of chlorine atoms in BCl_2F and $BClF_2$ molecules occurs takes place.

4. CONCLUSION

Isotope-selective laser IR MFD of $^{11}BCl_3$ molecules has been studied in a natural mixture with $^{10}BCl_3$ in the case of their irradiation with a sensitizer resonantly absorbing laser radiation and an SF_6 radical acceptor. A strong increase in the dissociation efficiency of $^{11}BCl_3$ molecules was found in the case of irradiation with SF_6 compared with the case of irradiation without SF_6. The dependences of the basic parameters of the isotope-selective laser IR MFD of BCl_3 molecules, selectivity and dissociation yields, on the pressure of SF_6, as well as on the energy density and frequency of exciting laser radiation.

Based on the obtained dependences of the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules, as well as the dissociation selectivity of $\alpha(^{11}B/^{10}B)$ from SF_6 pressure, on the energy density and frequency of exciting radiation, it was found that a strong increase in the efficiency of isotope-selective dissociation of $^{11}BCl_3$ molecules occurs due to the resonant transfer of energy from SF_6 molecules to $^{11}BCl_3$ molecules.

The main products that are formed as a result of laser IR dissociation of BCl_3 molecules in a mixture with SF_6 and subsequent chemical reactions have been identified. It is established that the main products are SF_5Cl, BCl_2F, $BClF_2$ and BF_3.

It has been shown that when irradiated with BCl_3 in a mixture with SF_6, the yield of dissociation of $^{11}BCl_3$ molecules increases significantly (by 1–2 orders of magnitude) and the selectivity of dissociation (2–5 times), as well as the threshold energy density of dissociation decreases significantly (by about an order of magnitude) compared with the case of irradiation BCl_3 without SF_6. This opens up the possibility of implementing a single-frequency isotope-selective laser IR dissociation of $^{11}BCl_3$ molecules in unfocused laser beams at moderate (no more than 4–5 J/cm^2) of the excitation energy density.

The results obtained are important and relevant in terms of the application of the described method for the development of laser technology for the separation of boron isotopes, since it becomes possible to obtain a highly ^{10}B isotope-enriched molecular gas BCl_3 due to the dissociation of $^{11}BCl_3$ molecules in the natural in a natural mixture with $^{10}BCl_3$.

In conclusion, we note that the studied process is also applicable to other molecules, including $^{10}BCl_3$ molecules. So, in the case of isotope-selective laser IR MFD of $^{10}BCl_3$ molecules, CH_3F, C_2H_4, SiH_4 or SiH_3F molecules can probably be used as a sensitizer and radical acceptor, which probably have strong absorption bands near the $^{10}BCl_3$ molecule absorption bands [53].

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