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Laser separation of boron isotopes: research results and options for technological implementation

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Abstract. Due to the widespread use of boron isotopes (^{10}B and ^{11}B) in some major industries and medicine, production of these isotopes is now an urgent issue, driving significant interest in the development of effective methods for their separation (enrichment). Research aimed at developing methods for laser isotope separation (LIS) of boron has recently intensified. Results of studies on boron LIS are reviewed. The main concepts of LIS and the necessary conditions for the implementation of laser techniques are briefly discussed. The infrared (IR) absorption spectra underlying laser isotope separation of boron-containing molecules, which are used in experiments on boron LIS, are presented and analyzed. High-energy and low-energy methods of molecular laser separation of boron isotopes, along with the physicochemical processes on which they are based, are considered. The results of early studies of isotope-selective laser IR dissociation of boron trichloride (BCl_3) molecules using various excitation techniques and 2-chloroethenyldichloroborane ($HClC{=}CHBCl_2$), which are of greatest interest for laser separation of boron isotopes, and the results of new studies are reported and discussed. The results of studies of selective IR

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multiphoton dissociation (MPD) of $^{11}BCl_3$ molecules in a natural mixture with $^{10}BCl_3$ molecules upon their irradiation with a sensitizer (SF_6 molecules, which simultaneously perform as acceptors of radicals — Cl atoms formed during dissociation of BCl_3 molecules) are considered. The use of a sensitizer is shown to significantly enhance the efficiency of dissociation of $^{11}BCl_3$ molecules. The results obtained for boron LIS are systematized. Based on the analysis of research results, the optimal methods for the technological implementation of boron LIS in practice are proposed. A brief historical overview of research in laser separation of boron isotopes is given.

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

Dedicated to the 55th anniversary of the Institute
of Spectroscopy of the Russian Academy of Sciences

1. Introduction

Today, boron isotopes are widely used in practice, due to which the development of effective methods for their production and enrichment are relevant and important. Recently, research has been actively conducted that aimed at developing a technology of laser isotope separation (LIS) of boron [1–11]. Natural boron consists of two stable isotopic modifications: boron-10 (^{10}B) and boron-11 (^{11}B) with concentrations of 19.8 and 80.2%, respectively [12–16]. Boron isotopes have similar physicochemical properties, but their nuclear-physical properties are completely different. ^{10}B features a very large cross section for the capture of thermal neutrons, about 3840 b [15, 17] (1 b $= 10^{-24}$ cm^2), while this parameter for the heavy isotope is only about 0.05 b. For most nuclides, this cross section is close to units or fractions of a barn. Thus, the light boron isotope ^{10}B is an effective absorber, while the heavy isotope ^{11}B is a very effective reflector and moderator of neutrons. Both isotopes are used in the nuclear industry. Materials enriched with the ^{10}B isotope (boric acid, boron carbide, and other compounds) are widely employed in nuclear power engineering in control and protection systems of nuclear reactors, in the manufacture of containers for the transportation and storage of neutron-emitting materials, and as highly efficient neutron detectors [18, 19]. The growing need for the ^{10}B isotope is also associated with a large-scale project to convert nuclear power plants to power units operating fast neutron reactors. In medicine, boron-10 is used in neutron-capture cancer therapy [20–22] and in studies of the properties of food products aimed at preventing cancer and other diseases [23]. Interest in the pure boron-11 isotope is associated with its possible use in the electronics industry as an alloying component in the manufacture of semiconductor products [14–16]. Therefore, the development of an effective technology for separating boron isotopes is an urgent task, the solution of which is also driven by the need to create domestic large-scale production of the ^{10}B isotope in Russia. Laser isotope separation can, in principle, be a promising technique for obtaining enriched boron isotopes.

Two well-developed options are available: the atomic technique, AVLIS (Atomic Vapor Laser Isotope Separation) [24–29] and the molecular technique, MLIS (Molecular Laser Isotope Separation) [30–34]. The same name, MLIS, is used for molecular laser isotope separation in Russian-language publications [34, 35]. Both of these options have recently been developed to the level of industrial implementation in the USA using the example of uranium isotope separation [24–34], and in Russia using the example of molecular carbon isotope separation [18, 36–38]. In the case of uranium isotope separation (enrichment) in the atomic technique, metallic uranium vapors were used as the initial substance [24–29], while, in the molecular technique, UF_6 molecules were used [30–34]. The technological implementation of molecular laser separation of carbon isotopes employed CF_2HCl molecules (freon-22) as the initial substance. Among the well-developed techniques of molecular laser isotope separation, it is also worth noting the SILEX (Separation of Isotopes by Laser EXcitation) method [39–43]. In the case of boron LIS, only the molecular option is being studied, using several gaseous boron-containing compounds as the initial substance.

Laser isotope separation is of both academic and applied interest. The fundamental interest in LIS is primarily due to efforts to understand the physicochemical processes underlying laser methods, the main aspects of which relate to the general problem of the interaction of laser radiation with matter. In practical terms, the importance of exploring laser isotope separation, including boron isotopes, is due to the demand for isotopes in industry, science, and medicine [18–23].

Currently, three methods of boron isotope separation are used in industry to enrich the ^{10}B isotope. These methods are based on a chemical exchange reaction [44], low-temperature fractional distillation [45], and gas centrifugation. The starting material in these methods is the gaseous compound BF_3. Boron trichloride, BCl_3, can also be used in gas centrifugation, since it features a fairly high vapor pressure at room temperature, but is much less effective due to the presence of three chlorine isotopes in its composition. However, the use of BF_3 is not economically justified, since 86% of the cost of high-purity ^{10}B is due to the extraction of powder from BF_3 [9]. Therefore, it is necessary to develop alternative methods based on the use of BCl_3.

Reviewed below are the results of studies of boron LIS using various separation techniques: high-energy methods based on isotope-selective multiphoton dissociation (MPD) of BCl_3 and $HClC{=}CHBCl_2$ molecules, low-energy methods based on isotope-selective suppression of molecule clustering (condensation) in gas-dynamic jets and flows by an infrared (IR) laser, and isotope-selective dissociation of small van der Waals clusters. The main objective of the review is to present and analyze the results of boron LIS studies conducted over about half a century using various methods and several starting materials. Much attention is devoted to considering and analyzing the results of recent studies aimed at finding options and clarifying the feasibility of laser methods for separating boron isotopes in practice. The review highlights the achievements and most important results along with the main problems and challenges that researchers encounter on the way to boron LIS, formulates the main avenues for further research, and presents options for the technological implementation of boron LIS.

The review is structured as follows. Section 2 discusses the general concept of LIS and the conditions required for the implementation of laser methods. Section 3 presents existing MLIS methods and the physicochemical processes underlying them. Section 4 outlines the advantages and main parameters of laser isotope separation methods. Section 5 is devoted to the IR absorption spectra of boron-containing molecules, with which the experimental studies were carried out. Section 6 provides a brief historical overview of boron LIS studies. Sections 7–9 present and analyze the results of boron LIS studies using BCl_3 (Sections 7 and 8) and $HClC{=}CBCl_2$ (Section 9) molecules. Presented are the results of studies of the main characteristics of isotope-selective dissociation of molecules: yields and dissociation selectivity, depending on the parameters of the irradiated gas (pressure and composition of the irradiated mixture) and the parameters of the exciting laser radiation (frequency and excitation energy density). Section 8 discusses the results of optimization of isotope-selective dissociation of BCl_3 molecules by means of the use of an optically active sensitizer and an acceptor of SF_6 radicals. Section 10 considers the most promising options for the technological implementation of boron LIS in practice: IR multiphoton dissociation of $HClC{=}CBCl_2$ molecules, dissociation of BCl_3 molecules in a two-frequency IR laser field, and IR multiphoton dissociation of BCl_3 in a mixture with a sensitizer and an acceptor of SF_6 radicals. Section 11 concludes with the main results of the studies and the conclusions drawn from them.

2. Basic concept of laser isotope separation

2.1 Basic principles of laser isotope separation

The basic principles of laser isotope separation are described in detail in recent review [34] (see also earlier publications [46–48]). Here, we only mention them briefly. The basic concept of LIS is the selective action of laser radiation on selected isotopes (or isotopologues) in the original substance (Fig. 1) to alter their physical or chemical properties without affecting other isotopes (or isotopologues) [46, 47]. When two types of atoms or molecules of different isotopic compositions (A and B) have at least one nonoverlapping spectral line in the radiation absorption spectra, an atom or molecule of the selected isotopic composition (e.g., particle A) can be selectively excited with laser radiation. Excitation of particles A changes their chemical and physical properties, and this circumstance can be used to separate a mixture of particles using various approaches based on differences between the characteristics of excited and unexcited particles.

The photochemical approach enables a chemical reaction of excited particles A^* with a suitable reagent to obtain products (AR) before the excited particles begin transiting to the ground state as a result of relaxation or near-resonant energy transfer to particles B due to collisions, thereby creating excited particles B^* (see Fig. 1). On the other hand, the photophysical approach is based on subsequent laser-induced dissociation or ionization of particles that have been selectively excited beforehand. In both approaches, new products are formed, enriched in the selected isotope, which can be separated from the mixture using standard methods. Thus, a common feature of all laser isotope separation methods is the isotope-selective excitation of an electronic or vibrational level of a molecule (or atom) at a quantum transition that has a distinct isotopic shift.

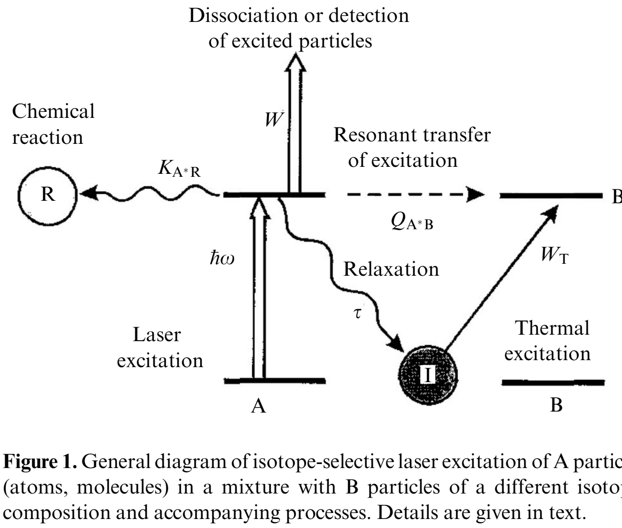

Figure 1. General diagram of isotope-selective laser excitation of A particles (atoms, molecules) in a mixture with B particles of a different isotopic composition and accompanying processes. Details are given in text.

A significant drawback of the photochemical approach is the need to select a reaction with an appropriate activation barrier E_a, and, most importantly, the rate of reaction between the excited particle and the reagent K_{A^*R} must significantly exceed the rate of resonant energy transfer Q_{A^*B} from the excited particle to the unexcited one ($K_{A^*R} \gg Q_{A^*B}$). The latter requirement is very difficult to fulfill, which is why this approach, despite a number of demonstrations, failed to be widely applied. Therefore, in most cases, to 'fix' the first stage of selective excitation, dissociation or ionization of the excited particles is carried out, thereby transferring them to another chemical state (forming radicals or ions). The rate of this additional excitation W can easily be made sufficiently large, much greater than the rate of collisional excitation transfer to another isotope ($W \gg Q_{A^*B}$). In this approach, it is much easier to maintain the selectivity of the primary excitation, and, next, of the subsequent extraction of the target isotope.

2.2 Prerequisites for implementation of laser methods

The following conditions must be fulfilled to apply laser methods of isotope separation [46–48].

(1) Isotopologues of atoms or molecules containing the isotopes to be separated must be in a gaseous state and feature well-resolved isotopic shifts in the electronic or vibrational radiation absorption spectra.

(2) Lasers used for isotope separation must have a sufficiently narrow and tunable spectral emission line to provide preferential excitation of atoms or molecules of the selected isotopic composition.

(3) An effective process for the extraction of the required (target) isotope must be implemented, which acts only on excited atoms or molecules before their relaxation or energy exchange with unexcited particles.

Several approaches are available for isotope-selective excitation of atoms and molecules by laser radiation: one-, two-, and multiphoton processes. The photochemical process is not widely used for the separation of the desired isotope, since it is difficult to find a suitable chemical reaction whose rate would significantly exceed the relaxation rate of pre-excited particles and the rate of near-resonant energy transfer to particles containing other isotopes. However, using intense ultraviolet (UV), visible, or IR laser radiation, it is now possible to develop a number of methods that allow acting on atoms or molecules in an isotope-selective manner. These methods are briefly reviewed in Section 3.

3. Methods of molecular laser isotope separation

MLIS methods (Fig. 2) are divided into two groups (high-energy and low-energy) that differ in the activation energy of the underlying processes. The method of isotope-selective

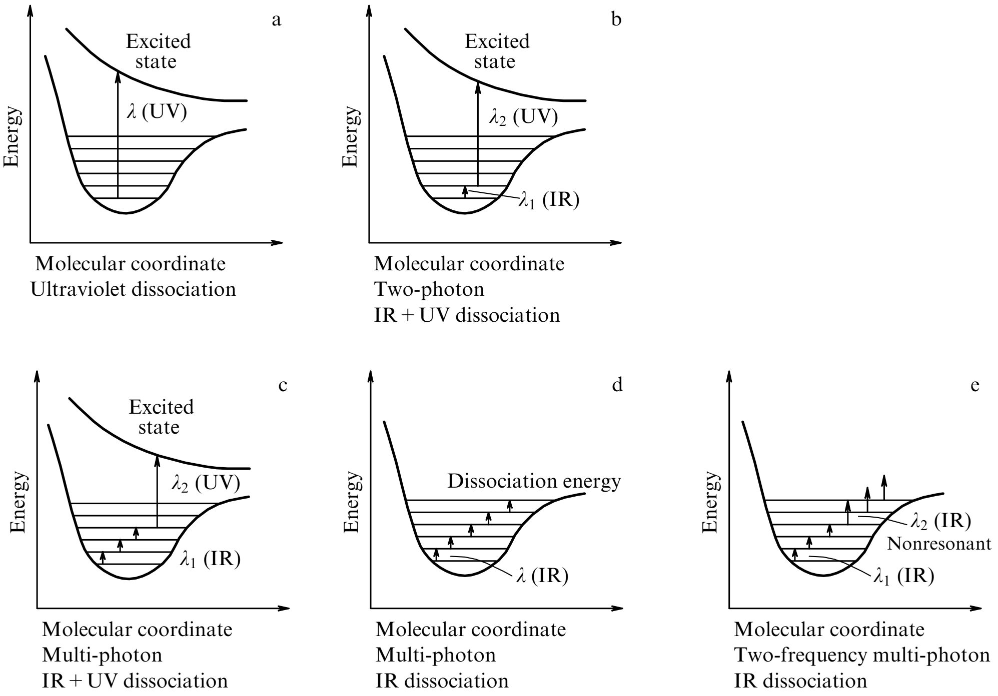

Figure 2. (a–e) Single- and two-frequency processes of molecular laser isotope separation [31, 52].

dissociation of molecules (and selective ionization of atoms) is a high-energy method, since the activation energies of the processes underlying it are fairly high (exceed 3–6 eV). To dissociate a molecule, it is necessary to spend energy comparable to its dissociation energy (approximately 2.5 to 5.0 eV [49, 50]) or even greater. Even more energy is required to ionize atoms (approximately 5 to 10 eV [49, 50]). The dissociation energy of BCl_3 molecules is about 4.8 eV [49, 50] and of UF_6 is about 3.0 eV [51], and the ionization energy, for example, of uranium atoms is ≈ 6.2 eV [49, 50], and boron atoms is ≈ 8.3 eV [49, 50].

3.1 High-energy methods

The set of high-energy MLIS methods includes [31, 47, 52] (see Fig. 2): (a) single-photon dissociation of molecules with UV radiation, (b) two-stage dissociation of molecules with IR + UV radiation, (c) multiphoton IR + UV dissociation, (d) single-frequency multiphoton IR dissociation of molecules, and (e) two- or three-frequency multiphoton IR dissociation of molecules. Methods (a) and (d) are based on single-frequency dissociation of molecules, while methods (b), (c), and (e) employ two-frequency dissociation.

UV dissociation of molecules. In this method (Fig. 2a), isotope-selective UV dissociation of molecules occurs as a result of absorption of laser radiation at the transition from the ground electronic state to an excited state, which is predissociation. The selective process is realized if there is an isotopic shift between the vibrational levels of isotopologues in the ground electronic state, from which the molecules are excited. The separation of isotopes by the method of selective laser photopredissociation of molecules was first examined in [53, 54] (see also review [55]). Moreover, in [53], the separation of isotopes H and D by photopredissociation of formaldehyde molecules (H_2CO) was demonstrated.

Two-stage IR + UV dissociation of molecules. In the two-stage IR + UV dissociation method (Fig. 2b), at the first stage, molecules of the selected isotopic composition (target molecules) are selectively excited to the first vibrational level of the ground electronic state using laser radiation of the IR range λ_1(IR). At the second stage, vibrationally excited molecules undergo dissociation due to UV radiation of the wavelength λ_2(UV) as a result of their excitation from the ground electronic state to the pre-dissociation excited electronic state. The molecules that were not excited by IR radiation do not absorb UV radiation of this wavelength and do not undergo dissociation. This method was first implemented in [56, 57] using the example of two-stage IR + UV dissociation of ammonia molecules and separation of nitrogen isotopes [58, 59].

Multiphoton IR + UV dissociation of molecules. This technique (Fig. 2c) is a development of the two-stage IR + UV dissociation method for polyatomic molecules that can absorb more than one photon from an intense IR laser field. As a result, in contrast to the method presented in Fig. 2b, not only is the first vibrational level populated, but so are higher vibrational levels of the ground electronic state. This leads to a significant increase in the UV absorption cross section for selectively excited molecules, which was first observed using the example of OsO_4 [60] and CF_3I [61] molecules. When molecules are vibrationally excited, the long-wavelength wing of their UV absorption spectrum shifts toward the low-frequency side. The isotopic selectivity of the dissociation process is realized due to the difference between the UV absorption cross sections for vibrationally excited and unexcited molecules.

It should be noted that all methods involving excitation of particles by laser UV radiation are high-energy isotope separation methods.

IR multiphoton dissociation of molecules. The essence of the IR multiphoton dissociation of molecules (Fig. 2d) is that, in an intense IR laser field, despite the anharmonicity of oscillations, the molecule absorbs in a purely radiative way (without collisions) a large number (several ten) of laser photons from the laser pulse field, reaches the dissociation limit, and disintegrates into fragments. Collisionless IR MPD of molecules was first observed in [62, 63] using the example of SiF_4 and BCl_3 molecules, respectively, and isotope-selective IR MPD of molecules was first implemented in [64, 65] using the example of BCl_3 and SF_6 molecules, respectively.

The method of isotope-selective IR MPD of molecules was developed to the level of practical implementation. In 1998–2005, a plant for the separation of carbon isotope ^{13}C based on isotope-selective dissociation of CF_2HCl (freon-22) molecules with a pulse-periodic CO_2 laser was commissioned and is successfully operating in Kaliningrad [36–38].

Two-frequency IR multiphoton dissociation of molecules. In this method (Fig. 2e), two IR fields are used for the dissociation of molecules. In the region of lower vibrational levels, molecules are excited by weak laser radiation of wavelength λ_1(IR), resonant with the vibrations of the molecules. Pre-excited molecules are subsequently dissociated by a stronger field of wavelength λ_2(IR), detuned from resonance with the lower transitions. The pulse of the second laser is usually delayed in time by 0.2–0.5 μs. Thus, this method allows the functions of the IR field to be separated into selective excitation of molecules in the region of lower vibrational levels and excitation in the region of high levels and dissociation of molecules. Since a weak field is used at the resonance stage, the dynamic broadening of the absorption lines of the molecule by the laser pulse field is small. This enables a significant increase in the isotopic selectivity of the dissociation process [66–69]. If the frequency of the dissociating stage is shifted to the red side relative to the linear absorption spectrum of unexcited molecules, the best resonance with vibrationally excited molecules is achieved, since, due to the anharmonicity of vibrations, their absorption spectrum shifts to the red side [70]. As a result, the yield of molecular dissociation is enhanced significantly [68–71]. Thus, the method under consideration enables a significant enhancement of both the isotopic selectivity and the dissociation yield, which is of great importance when applying it for isotope separation in practice. This method, discovered in [66, 67], was subsequently widely used in experiments to examine isotope-selective dissociation of molecules (see, for example, [72–77] and references cited therein).

3.2 Low-energy methods

The activation energies of the processes underlying low-energy methods are approximately an order of magnitude lower than those of high-energy methods [78, 79], being $\leqslant 0.3-0.5$ eV. Such activation energies are characteristic of physicochemical processes of adsorption and desorption of molecules on a surface, including one covered with molecules or clusters, that of large clusters, and of dissociation and fragmentation of weakly bound van der Waals molecules. Of the large number of low-energy MLIS methods proposed to date, two are the most studied and of interest in terms of practical implementation [78, 79]: isotope-selective suppression of molecule clustering and isotope-selective IR vibrational predissociation of weakly bound van der Waals clusters.

3.2.1 Method of isotope-selective suppression of molecule clustering. This method, implemented in molecular jets and flows using IR lasers, is based [78–84] on preliminary (preceding the clustering process) selective vibrational excitation of molecules during gas-dynamic expansion at the nozzle outlet [78, 79]. As a result, the accumulated vibrational energy suppresses the clustering of excited molecules. The process of molecule clustering can also be controlled by dissociation of small clusters (dimers) near the nozzle, in the region of their formation [85–93]. In this case, it is necessary to ensure (for example, by choosing suitable conditions for gas expansion) the preferential formation of dimers and the absence of larger clusters.

The method described was proposed and studied in detail in [80, 82–84] using the example of clustering of SF_6 molecules among themselves and with argon atoms. Today, this technique is considered one of the feasible and most promising LIS methods [78, 79, 94, 95]. The options for using this method for separating uranium isotopes were examined in [94, 95], and, for separating boron isotopes, in [3, 4, 6–9, 96–99]. As a result of applying this method, the cluster beam is depleted of selectively excited molecules and enriched with molecules that are not excited, since free molecules propagate within a significantly wider solid angle than the cluster beam [100].

The method of suppressing (slowing down) the clustering (condensation) of molecules is sometimes designated as SILARC (Separation of Isotopes by Laser Assisted Retardation of Condensation) [94, 95] or CRISLA (Chemical Reaction by Isotope Selective Laser Activation, or (after 1995) Condensation Repression by Isotope Selective Laser Activation).

3.2.2 Method of isotope-selective IR dissociation of van der Waals clusters. This method is based on isotope-selective vibrational IR predissociation of weakly bound van der Waals clusters (molecules), in particular dimers. The binding (dissociation) energies E_b of van der Waals molecules consisting of polyatomic molecules are in the range of 0.1–0.5 eV, while the dissociation energies of van der Waals molecules consisting of a polyatomic molecule and a noble gas atom are $\leqslant 0.1$ eV [101–105]. Absorption by a molecule of one or more IR radiation quanta with a wavelength of about 10 μm, for example, CO_2 laser radiation, leads to its dissociation along a weak bond. The method was patented by Y.T. Lee, the winner of the Nobel Prize in Chemistry in 1986, as a new technique for separating isotopes of various elements [106]. This method was studied in detail in [79, 90–93] in what regards laser separation of uranium isotopes using the example of isotope-selective dissociation of small van der Waals clusters SF_6 and CF_3Br.

During cluster dissociation, due to recoil processes, fragments (monomers) 'escape' from the beam. As a result, in the laboratory coordinate system, the target molecules (dissociation products) propagate within a relatively large solid angle determined by the mass and velocity of the molecules, while nontarget molecules remain in the paraxial segment of the cluster beam. By using specially selected diaphragms (skimmers), different isotopic components can be spatially separated.

3.2.3 Combination of methods of suppression of molecular clustering and cluster dissociation. For isotope separation, a combination of methods of suppression of molecular clustering and cluster dissociation can also be used [34]. Figure 3 shows (using BCl_3 molecules as an example) a diagram of such a two-stage separation process, in which selective suppression of molecular clustering is applied at the first

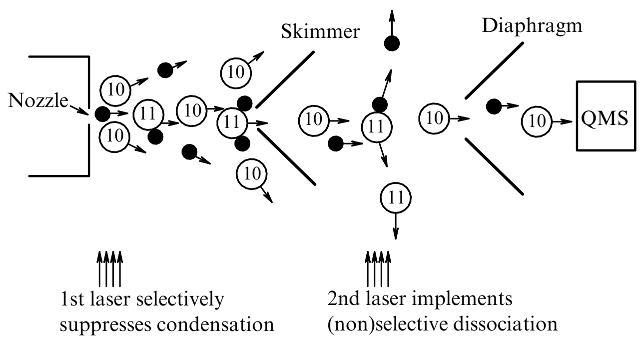

Figure 3. Schematic diagram of two-stage laser separation of boron isotopes. At first stage, clustering is selectively suppressed, and, at second stage, (non)selective dissociation of BCl_3 clusters occurs. Circles with numbers 10 and 11 denote $^{10}BCl_3$ and $^{11}BCl_3$ molecules, while black dots denote argon atoms. QMS is a quadrupole mass spectrometer.

stage, and selective dissociation of clusters, at the second stage. The first laser in a low-pressure chamber selectively excites $^{10}BCl_3$ molecules at the nozzle outlet, thereby suppressing their clustering with argon atoms. Next, a second laser is used in the high-pressure chamber to (non)selectively dissociate clusters containing $^{11}BCl_3$ molecules, which fly out of the beam due to the recoil process. The $^{10}BCl_3$ molecules in this region, even if they absorb IR radiation, hardly leave the beam.

The low-energy methods of isotope-selective suppression of molecule clustering and dissociation of van der Waals clusters discussed in Sections 3.2.1–3.2.3 probably underlie the technology of laser enrichment of uranium isotopes using UF_6 molecules currently under development in the USA and Australia [39–43].

4. Advantages and main parameters of laser methods of isotope separation

4.1 Advantages of laser technologies for isotope separation

Potential advantages of laser methods of isotope separation over conventional methods are [34, 48, 52, 107]:

(1) High selectivity of the elementary act of separation [34, 107]. In many conventional methods, the separation coefficient (selectivity) α in one stage is very small, close to unity. Therefore, to achieve a high degree of enrichment (K), it is necessary to use a large number ($n \gg 1$) of separating stages: $K = \alpha^n \gg 1$. However, isotope-selective ionization of atoms and dissociation of molecules with a laser provide a separation factor of $\alpha \gg 1$ (from about 10 to more than a thousand) [34, 107], making it possible to significantly reduce the number of separating stages or, in some cases, use only one stage.

(2) The desired isotopes can be separated without significant influence on other isotopes of the same elements, even when using an atomic or molecular gas containing several isotopologues as the initial substance. This is realized by choosing tunable laser radiation of a suitable wavelength.

(3) Energy costs per atom of the target isotope are small compared to conventional methods [34, 107].

(4) Universality. With rare exceptions, laser methods can be used with sufficiently high efficiency to separate isotopes of any elements — light, medium, and heavy — unlike conventional methods, whose efficiency depends on the mass of the isotope.

(5) Short startup time of the technology. When using laser methods, stable operation of the separation unit is achieved almost immediately, while, with conventional methods, the startup time of the unit can last several months.

4.2 Laser IR photochemistry of BCl_3 and $HClC{=}CHBCl_2$ molecules and main parameters of laser separation of boron isotopes

During laser IR multiphoton dissociation, BCl_3 molecules decompose according to the following reaction:

$$BCl_3 + nh\nu \to BCl_2 + Cl\,, \tag{1}$$

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

Acceptors are used to bind the resulting radicals (chlorine atoms and BCl_2 molecules) and suppress the radical recombination reaction. To this end, most often oxygen molecules and hydrogen-containing molecules such as H_2 or CH_4 are used. In the presence of radical acceptors (e.g., O_2 or H_2), products (B_2O_3 and Cl_2 or $HBCl_2$ and HCl; see Section 7.3) are formed. The solid product B_2O_3 formed when using oxygen as a radical acceptor is deposited as a film on the walls and windows of the cuvette [108, 109]. Therefore, radical acceptors that form gaseous boron-containing products are preferred. The results of detailed studies of the yield of products in laser IR multiphoton dissociation of BCl_3 molecules using various radical acceptors are presented in Section 7.3.

$HClC{=}CHBCl_2$ molecules decompose as a result of laser IR multiphoton dissociation [110] according to the reaction

$$HClC{=}CHBCl_2 + nh\nu \to BCl_3 + C_2H_2\,. \tag{2}$$

Thus, the products of dissociation of the 2-chloroethenyldichloroborane molecule are the same compounds from which it is synthesized (see Section 9.2).

The main parameters characterizing the MLIS process are (using the standard notations) the dissociation yield of molecules β, selectivity α, and enrichment factors in products and in residual gas (in waste) K. We now define these parameters as applied to BCl_3 molecules.

The dissociation yield, for example, of $^{10}BCl_3$ molecules (β_{10}) upon laser irradiation is determined by the formula

$$N_L(^{10}BCl_3) = N_0(^{10}BCl_3)(1 - \beta_{10}\Gamma)\,, \tag{3}$$

where $N_0(^{10}BCl_3)$ and $N_L(^{10}BCl_3)$ are, respectively, the concentration of $^{10}BCl_3$ molecules in the absence of excitation and upon their excitation by the laser, and Γ is the ratio of the irradiated volume to the total volume of molecular gas in the cuvette.

The selectivity of the dissociation of $^{10}BCl_3$ molecules with respect to $^{11}BCl_3$ molecules is defined as the ratio of the dissociation yields of these molecules:

$$\alpha = \frac{\beta_{10}}{\beta_{11}}\,. \tag{4}$$

The factor of enrichment in the resulting product (for example, in dichloroborane $HBCl_2$) with the ^{10}B isotope with respect to the ^{11}B isotope is defined as the ratio of the concentrations of R_L of the said isotopes in the product ($HBCl_2$) to the ratio of their concentrations R_0 in the initial gas BCl_3:

$$K_{\rm enr}^{\rm pr}\left(\frac{^{10}\rm B}{^{11}\rm B}\right) = \frac{R_{\rm L}}{R_0} = \frac{(^{10}{\rm B}/^{11}{\rm B})_{\rm in\,HBCl_2}}{(^{10}{\rm B}/^{11}{\rm B})_{\rm in\,BCl_3}}\,. \tag{5}$$

The factor of enrichment (depletion) in the residual gas BCl_3 with the $^{11}BCl_3$ isotope with respect to the $^{10}BCl_3$ isotope, taking into account Eqn (3), is defined as

$$K_{\rm enr}^{\rm res}\left(\frac{^{10}\rm B}{^{11}\rm B}\right) = \frac{1-\beta_{10}}{1-\beta_{11}}\,. \tag{6}$$

We also use formulas similar to Eqns (3)–(6) when considering and analyzing the results obtained with other boron-containing molecules.

5. IR absorption spectra of boron-containing molecules under study

The methods of molecular laser separation of boron isotopes are based on the IR absorption spectra of boron-containing molecules used as starting materials. Isotope-selective vibrational excitation and dissociation of molecules are possible if their IR absorption spectra fall within the IR laser generation region and exhibit a distinct isotopic shift. The number of gaseous boron-containing compounds featuring IR absorption spectra with the required conditions is limited. They are boron trichloride, BCl_3, 2-chloroethenyldichloroborane, $HClC{=}CHBCl_2$, and several coordination compounds, including BCl_3 (see Section 7.3 below). In the case of BCl_3 and $HClC{=}CHBCl_2$ molecules, their IR absorption bands and the CO_2 laser emission frequencies significantly overlap [110, 111] (Fig. 4a, b). Boron trichloride, which is produced on an industrial scale, is a commercially available product, while 2-chloroethenyldichloroborane is not commercially manufactured.

5.1 Some properties and IR absorption spectra of boron trichloride

Boron trichloride is a colorless gas (a liquid under normal conditions) with a pungent odor, reacts violently with water, smokes in air, and is toxic. The molecular weight is 117.17 amu, density (at 0 °C) is 1.326 g cm^{-3}, and vapor pressure (at 20 °C) $\approx$ 1.48 atm. The structure of the molecule is trigonal planar. The dipole moment is zero [112].

The infrared absorption spectra of BCl_3 molecules in the region from about 3 to 15 μm have been studied fairly well [113–116]. The $^{11}BCl_3$ and $^{10}BCl_3$ molecules have intense absorption bands centered at about 954.2 cm^{-1} and 993.7 cm^{-1}, respectively, which correspond to asymmetric vibrations of the ν_3 mode of the B–Cl bond. The isotopic shift between these absorption bands is $\Delta\nu_{\rm is} \approx 39.5\ {\rm cm}^{-1}$ [116]. The absorption bands of $^{11}BCl_3$ and $^{10}BCl_3$ molecules coincide well with the P and R branches of the 10.6-μm generation band of the CO_2 laser (Fig. 4a) [111]. It is for this reason that boron trichloride was widely used in early studies of the interaction of laser radiation with a molecular gas to investigate various processes (see Section 6), including isotope-selective multiphoton dissociation by powerful IR laser radiation. The indicated absorption bands of BCl_3 molecules are the most intense in their IR absorption spectrum. The linear absorption coefficient at the band maxima for $^{11}BCl_3$ and $^{10}BCl_3$ molecules is $\alpha_{11} \approx 0.140\ {\rm cm}^{-1}\ {\rm Torr}^{-1}$ and $\alpha_{10} \approx 0.105\ {\rm cm}^{-1}\ {\rm Torr}^{-1}$, respectively [111] (Fig. 4a).

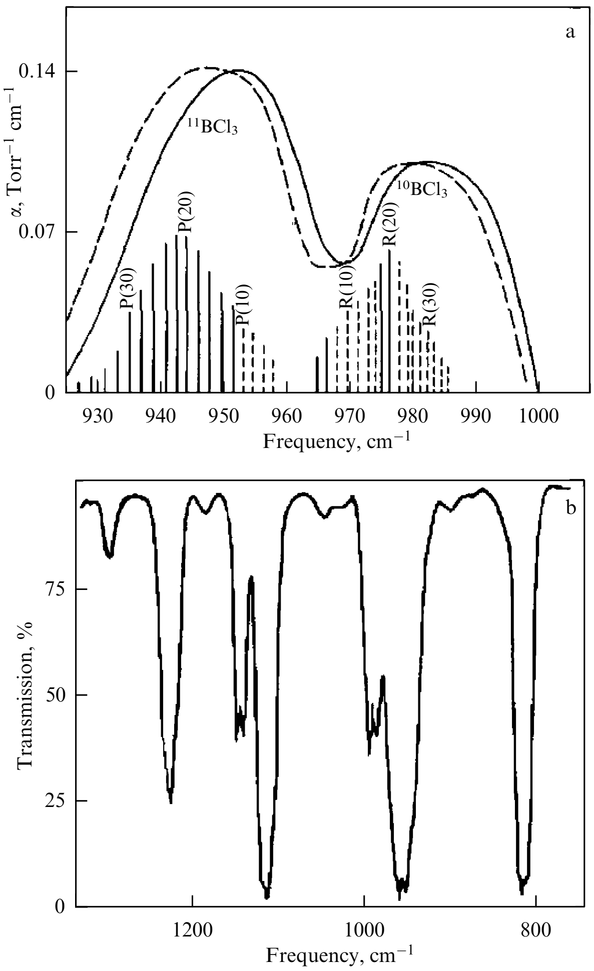

Figure 4. (a) Absorption spectrum of BCl_3 in vicinity of 10.6-μm generation band of a CO_2 laser. Solid curve represents absorption in the ground state. Dashed curve shows absorption of BCl_3 molecules excited to first vibrational level. Solid/dashed lines show CO_2 laser generation lines on which double resonance signals were/were not observed [111]. (b) Fourier spectrum of IR absorption of 2-chloroethenyldichloroborane [110].

5.2 Some properties and IR absorption spectra of 2-chloroethenyldichloroborane

The isotope-selective laser IR dissociation of $HClC{=}CHBCl_2$ molecules was first examined in [110]. The authors of the study synthesized this compound using the Arnold method [117] from two starting materials: boron trichloride and acetylene, taken in a molar ratio of 1:2. The synthesis was carried out in a stream of dry nitrogen at a temperature of 150 °C. The authors studied some of its thermodynamic, physical, and chemical properties and the IR absorption spectrum. In addition, the IR laser-induced isotope-selective dissociation of molecules was examined.

The dipole moment of the molecule was also measured ($\mu = 1.06 \pm 0.05$ D). A comparison of the obtained value with *ab initio* quantum-mechanical calculations showed that the trans-isomer of the molecule was obtained during the synthesis. The cis-isomer dipole moment is significantly higher ($\mu_{\rm cis} = 3.23$ D). The energy of the ground state of the cis-isomer is 1.45 eV greater than that of the trans-isomer. Calculations showed that the trans-isomer is a stable form of the molecule. The pressure of the resulting 2-chloroethenyldi-

Table 1. IR absorption bands of 2-chloroethenyldichloroborane ($C_2H_2BCl_3$) and BCl_3 molecules and their relationship to vibration types [110].

Molecules	Band center, cm^{-1}	Relative strength	Band identification	Change under dissociation of $C_2H_2BCl_3$
$C_2H_2BCl_3$	816	Strong	—	Decreases
$C_2H_2BCl_3$	960	Strong	$\nu_{as}{}^{11}BCl_2$	—
$C_2H_2BCl_3$	992	Medium	$\nu_{as}{}^{10}BCl_2$	Increases
$C_2H_2BCl_3$	1113	Strong	$^{11}B-C$ stretching	Decreases
$C_2H_2BCl_3$	1147	Medium	$^{10}B-C$ stretching	Decreases
$C_2H_2BCl_3$	1226	Strong	—	—
$C_2H_2BCl_3$	1572	Very strong	—	—
BCl_3	957	—	$\nu_3{}^{11}BCl_3$	Increases
BCl_3	994	—	$\nu_3{}^{10}BCl_3$	Increases

chloroborane gas was 56.1 Torr at 28.7 °C, a value which is in good agreement with the data obtained by Arnold [117] (58 Torr at the same temperature). At this pressure and temperature, the vapor density corresponds to a molecular weight of 145.2 amu. This value is slightly greater than the 143.2 amu expected for pure $HClC=CHBCl_2$ gas, which is explained by the authors by the presence of a small amount of impurity. The resulting gas is very reactive with moisture. Hydrolysis with water or aqueous solutions of acids and bases leads to the formation of hydrochloric acid, HCl [118]. The physical and chemical properties of 2-chloroethenyldichloroborane were investigated in [119–122].

The infrared spectrum of 2-chloroethenyldichloroborane was obtained by the authors using a Fourier transform IR spectrometer. The spectrum contains several intense IR absorption bands in the range from about 615 to 1600 cm^{-1} (Table 1). Table 1 also displays a preliminary identification of the bands. Some IR absorption bands, including those in the CO_2 laser frequency range, are shown in Fig. 4b (see also Section 9.2). It should be noted that this compound, like boron trichloride, features very intense absorption bands in the region of 10.6 μm, corresponding to asymmetric vibrations of the ν_3 mode of the B–Cl stretching bond. The vibration frequencies of the $HClC=CH^{11}BCl_2$ and $HClC=CH^{10}BCl_2$ molecules coincide well with the P and R branches of the 10.6-μm CO_2 laser generation band, respectively (Fig. 4b). The maxima of these absorption bands are localized near frequencies of about 960 and 992 cm^{-1}; the isotopic shift between them is $\Delta\nu_{is} \approx$ 32 cm^{-1} [110].

Two intense absorption bands with central frequencies near 1113 and 1147 cm^{-1}, corresponding to the vibration frequencies of the $^{11}B-C$ and $^{10}B-C$ stretching bonds, are also characterized by an isotopic shift of $\Delta\nu_{is} \approx 34\,cm^{-1}$ [110]. The presence of these bands is advantageous when conducting experiments on isotope-selective dissociation of $HClC=CHBCl_2$ molecules, since it is by the decrease in the intensity of these absorption bands that the yields and selectivities of dissociation of two isotopologues can be measured. The absorption bands localized near the frequencies of 960 and 992 cm^{-1} virtually coincide with those of BCl_3 molecules, and their intensities increase as the $HClC=CHBCl_2$ molecules are consumed, since boron trichloride is a product of the dissociation of 2-chloroethenyldichloroborane molecules (see Section 4 and Table 1) [110].

6. Brief historical excursion into research on laser separation of boron isotopes

The beginning of research into the interaction of molecules with intense IR radiation in the late 1960s and early 1970s was closely related to progress on the development of continuous and pulsed IR lasers, especially CO_2 lasers. Good coincidence of the IR absorption bands of BCl_3 molecules with the frequencies of the 10.6-μm generation band of a CO_2 laser and a comparatively high absorption of molecules (Fig. 4a) enabled the use of boron trichloride as a nonlinear absorber for CO_2 lasers at the initial stage. The effect of saturation of BCl_3 absorption was used by N.V. Karlov et al. to study some processes: Q-modulation [123] and control of the radiation frequency [124] of a CO_2 laser, generation of laser radiation [125], self-synchronization of transverse modes of a CO_2 laser [126], and dissociation of BCl_3 molecules [127]. The authors of other studies measured the nonlinear absorption coefficients of BCl_3 on some CO_2 laser radiation lines [128]. Relaxation processes in BCl_3 molecules excited by a CO_2 laser were studied using the double IR resonance method [111]. Narrow nonlinear resonances in BCl_3 were observed using the Lamb dip spectroscopy method [129].

After a relatively powerful CO_2 laser had appeared, experiments were conducted to study its effect on resonantly absorbing molecular gases. The following main areas of their application were outlined: (1) stimulation of chemical reactions, (2) separation of isotopes by double IR + UV excitation of molecules, and (3) exploration of the nature of visible glow arising from the excitation of molecular gases by intense radiation from pulsed CO_2 lasers.

The first studies of the stimulation of chemical reactions by radiation of continuous CO_2 lasers using NH_3 [130] and BCl_3 [131] as an example (see also [132, 133]) showed that the gas strongly 'heats' and dissociates in the laser field, which is accompanied by the glow of the decay products. Excitation and dissociation of molecules in these experiments occurred primarily due to collisional energy exchange. In study [134], the possibility of nonequilibrium radiative-collisional vibrational excitation of molecules by radiation of continuous IR lasers was discussed for the conditions when the time of vibrational energy exchange is significantly shorter than that of vibrational-translational relaxation in the gas. The radiation intensities required for this were 10^2–10^3 W cm^{-2}. However, subsequent experiments showed in [135] that, when continuous laser radiation acts on a molecular gas, a substantially collisional excitation mechanism operates [136–138].

The idea of laser isotope separation by double IR + UV excitation of molecules was first suggested in [139, 140]. Experimentally, IR + UV photodissociation of molecules was observed in [56, 57], and in [58] this method was used for the first time to separate isotopes (nitrogen) as a result of IR + UV excitation of ammonia molecules. Somewhat later, the method of double IR + UV resonance was tested at the Los Alamos Scientific Laboratory to carry out isotope-selective photochemistry with BCl_3 molecules mixed with oxygen [141]. It was shown that, when the mixture is irradiated with combined IR + UV radiation, the reaction between the initial compounds occurs significantly more efficiently than when irradiated with a UV pulse alone, and when irradiated with only an IR laser pulse, the reaction does not occur at all.

The first observation of visible glow during excitation of molecular gases (SiF_4, NH_3, CF_2Cl_2, etc.) by intense pulsed CO_2 laser radiation was reported in [142]. It was shown that, at intensities of 10^8–10^9 W cm^{-2}, below the optical breakdown threshold in the gas, dissociation of molecules occurs. The comparatively short duration of the CO_2 laser pulse ($\approx$ 100 ns) made it possible to conduct experiments under conditions where the influence of collisions on molecular excitation could be disregarded. The kinetics and spectrum of visible luminescence arising from excitation of molecules using a CO_2 laser pulse were studied in [143–145]. However, these experiments were carried out at comparatively high gas pressures (tens of Torr). An important step was made by switching to low gas pressures. In experiments with the SiF_4 molecule [62, 146] (at a gas pressure of $p \leqslant 2$ Torr) and subsequently in experiments with the BCl_3 molecule [63] (at $p \geqslant 0.03$ Torr), collisionless dissociation of molecules was discovered (Fig. 5a–c), and isotopic selectivity of the dissociation process was shown (Fig. 5d, e) [64]. Thus, the possibility of purely radiative collisionless dissociation of an isolated molecule by intense IR laser radiation was demonstrated.

In the early 1970s, all these areas were actively studied at the Institute of Spectroscopy of the USSR Academy of Sciences under the guidance of V.S. Letokhov. The first experiments on detecting selective laser photoionization of rubidium atoms were carried out there [147]. After nitrogen isotope separation experiments and the observation of isotope-selective dissociation of BCl_3 molecules, experiments were carried out on laser separation of sulfur [65] and osmium [60] isotopes using the IR multiphoton dissociation of SF_6 and OsO_4 molecules. The results of these studies clearly showed the great potential of lasers for separating isotopes of various elements and were an important stimulating factor for the initiation and development of uranium LIS projects in many countries (see reviews [34, 78, 79] and references therein). The results obtained at the Institute of Spectroscopy on sulfur LIS using SF_6 molecules were shortly afterwards reproduced at the Los Alamos Scientific Laboratory [148, 149]. From that time on, many experiments on molecular laser isotope separation were focused on a very specific topic — primarily investigating the possibility of using laser methods to separate uranium isotopes using UF_6 molecules (see reviews [34, 35, 78, 79] and references therein).

As for laser separation of boron isotopes, a large number of subsequent studies included a whole range of exploration of isotope-selective laser IR multiphoton dissociation of BCl_3 and $HClC{=}CHBCl_2$ molecules, including those that have been conducted recently. The results obtained are discussed in the following sections.

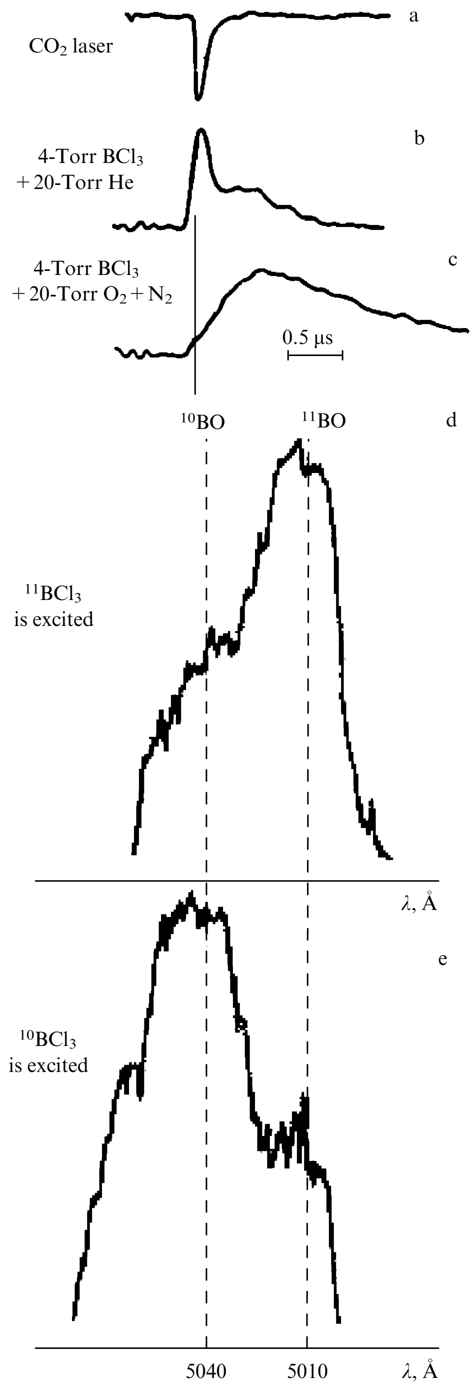

Figure 5. CO_2 laser-induced luminescence in pure BCl_3 gas and in BCl_3 mixed with $O_2{+}N_2$. (a) Excitation pulse from CO_2 laser. (b) Glow pulse in BCl_3. (c) Glow pulse of BO. Emission spectra of ^{10}BO and ^{11}BO at (0.2) $^2\pi_{1/2} \to {}^2\Sigma$ transition upon excitation of $^{11}BCl_3$ (d) and $^{10}BCl_3$ (e) [64].

7. Results of studies on separating boron isotopes using BCl_3 molecules

7.1 First experiments: demonstration and confirmation of selectivity of IR multiphoton dissociation of BCl_3

7.1.1 Demonstration of selectivity of BCl_3 dissociation. In the first experiments [64], in which isotopic selectivity was demonstrated in laser IR multiphoton dissociation of BCl_3, the molecules were excited by a pulsed CO_2 laser with a pulse energy of up to 0.5 J and a pulse duration of 100 ns. A short-focus lens ($f = 5$ cm) was used to focus the laser radiation into a cuvette with gas. The laser-induced luminescence radiation was projected through a cuvette side window onto the entrance slit of an MDR-2 monochromator, which was used to record the emission spectra of radicals and molecules resulting from the dissociation of BCl_3 and subsequent chemical reactions. The spectra obtained were used to identify the products of chemical reactions.

The experiment was carried out with a natural mixture of $^{10}BCl_3$ and $^{11}BCl_3$ isotopologues (with a content ratio of $^{10}BCl_3 : {}^{11}BCl_3 = 1:4.32$). The spectrum of the instantaneous luminescence phase in pure BCl_3 gas lies in the visible region of the spectrum, extends up to 4400 Å, and is continuous with an accuracy of 15 Å. When a mixture of $O_2 + N_2$ gases was added to BCl_3 (in the ratio $O_2 : N_2 = 1:4$), an intense system of bands appeared in the luminescence spectrum, which was identified as the α band of the BO radical [150]. In addition, the shape of the luminescence pulse considerably changed (Fig. 5c). The leading edge of the luminescence pulse in the second case corresponds to the BO formation rate. In the experiments, the CO_2 laser was tuned to the absorption band of the ν_3 vibration of either $^{11}BCl_3$ or $^{10}BCl_3$ molecules.

To determine the selectivity of collisionless dissociation of boron trichloride and the subsequent reaction of the dissociation products with oxygen, a shift in the ^{10}BO and ^{11}BO spectrum was used. The isotopic shift between the R branches of the transition $(0.2)\,{}^2\pi_{1/2} \rightarrow {}^2\Sigma$ of the ^{10}BO and ^{11}BO radicals reaches 30 Å [150]. In the experiment, this particular section of the spectrum was analyzed in two cases: upon excitation of $^{11}BCl_3$ molecules (at a frequency of 938.7 cm^{-1}, line 10P(26) of the laser) and upon excitation of $^{10}BCl_3$ molecules (at a frequency of 978.5 cm^{-1}, line 10R(24) of the laser). In addition, the detection system selected a time interval of 150 ns from the BO glow pulse to measure the spectrum, corresponding to the instantaneous phase of luminescence in pure BCl_3 gas (Fig. 5c). The luminescence spectra of BO radicals in these two cases are displayed in Fig. 5d, e. The spectral resolution was no worse than 8 Å. It is evident that, upon excitation of $^{11}BCl_3$, primarily the ^{11}BO radical is formed, while upon excitation of $^{10}BCl_3$, the ^{10}BO radical is formed. Thus, it was revealed that collisionless dissociation of molecules in a powerful resonant IR field is an isotope-selective process (at least in the case of BCl_3 molecules, characterized by a large (≈ 39.5 cm^{-1} [116]) isotope shift in the IR absorption bands).

7.1.2 Confirmation of selectivity of BCl_3 dissociation. Almost immediately after the isotope selectivity of the BCl_3 dissociation was revealed, active research began aimed at a more detailed study of this phenomenon and confirmation of isotope selectivity. Experiments were conducted to determine the kinetics of luminescence arising from laser IR multiphoton excitation and dissociation of BCl_3 molecules [151–153]. Experiments were also carried out to determine the dependence of the process selectivity on excitation conditions, the type of radical acceptors and buffer gases, and the influence of laser-induced chemical reactions [108, 109]. For example, in [151, 152], the dissociation of BCl_3 molecules and the formation of excited radicals were studied in detail based on the detection of the kinetics of visible luminescence arising from the excitation of BCl_3 molecules in a mixture with buffer or acceptor gases by intense (10^7–10^9 W cm^{-2}) CO_2 laser radiation.

It was found in [151] that at comparatively high intensities of laser radiation ($\approx 10^9$ W cm^{-2}) luminescence is induced without a time delay relative to the laser radiation pulse down to very low pressures ($p < 0.1$ Torr). The luminescence consists of two stages: 'instantaneous,' associated with the dissociation of molecules in a strong field, and 'delayed,' associated with collisions of excited molecules and observed at lower intensities (10^7–10^8 W cm^{-2}) of exciting radiation. It has been shown that the dissociation of BCl_3 molecules in an intense field can be used to initiate an isotope-selective chemical reaction between the BCl_3 dissociation products and oxygen, resulting in the production of an enriched product with an enrichment factor of about 10 for the ^{10}B isotope. It was found that the 'instantaneous' stage of luminescence is purely radiative in nature and is not associated with molecular collisions.

In [152], the kinetics of the formation of electron-excited radicals BO* and BCl* in an intense ($\approx 10^9$ W cm^{-2}) field of a CO_2 laser was investigated. The rate constant of BO* formation in the reaction between the dissociation fragments of BCl_3 molecules with oxygen was estimated to be $K = (8 \pm 4) \times 10^5$ s^{-1} $Torr^{-1}$. The results of [152] show the great potential of photolysis of molecules in an intense IR field as a new method for obtaining high concentrations of radicals at gas pressures down to ≈ 0.03 Torr. In turn, this opens up a way to study high-speed radical reactions, which was demonstrated in [152].

Visible luminescence arising from irradiation of a mixture of $BCl_3 + H_2S$ molecules with intense 10.6-μm radiation from a CO_2 laser was studied in [153]. The emission spectrum was found to contain a molecular bond structure superimposed on the continuum. The intensity of visible luminescence was shown to strongly depend on the power of the exciting laser radiation and contain a component that emerges faster than the time of collisions between particles. The feasibility of using the observed effect for isotope separation is discussed.

In [154], photochemical enrichment of boron isotopes was observed upon irradiation of a mixture of $BCl_3 + H_2S$ (D_2S) molecules with powerful pulsed CO_2 laser radiation (with a pulse energy of 0.1 J and a pulse duration of 300 ns). The mixtures under study contained 2 Torr of BCl_3 and 2–40 Torr of H_2S (D_2S). When a mixture of $BCl_3 + H_2S$ was irradiated at a frequency of 947.7 cm^{-1} (laser generation line 10P(16)), resonant with the absorption band of $^{11}BCl_3$ molecules, an increase in the concentration of $^{10}BCl_3$ molecules in the mixture to 29.2% was observed (the natural concentration of $^{10}BCl_3$ is 19.5%). When irradiating the mixture at a frequency of 982.1 cm^{-1} (laser generation line 10R(30)), resonant with the absorption band of $^{10}BCl_3$ molecules, the concentration of $^{10}BCl_3$ molecules in the mixture decreased to 14.4%. The main products of laser-induced photochemical reactions — $HSBCl_2$ and $DSBCl_2$ — were detected. Thus, study [154] revealed the isotopically selective nature of the studied photochemical reaction.

In [155], studies similar to those described in [154] were carried out. The authors investigated the synthesis of $BHCl_2$ and HCl molecules induced by irradiation with a powerful CO_2 laser with a mixture of $BCl_3 + H_2$ molecules at a pressure ratio of 1:1 and a total pressure of 80 Torr. It was found that the only products of the reaction of excited BCl_3 molecules with H_2 are $BHCl_2$ (dichloroborane) and HCl, and the quantum efficiency of the reaction is approximately 122 laser photons per $BHCl_2$ molecule produced. In the opinion of the

Table 2. Number of BCl_3 isotopologues produced upon irradiation of $^{10}BCl_3$ with various acceptors. Molecules were excited at a frequency of 982.1 cm^{-1} (laser line 10R(30)). BCl_3 pressure is 0.88 Torr; acceptor pressure, 2.3 Torr; irradiation time, 30 min [108].

Acceptor	Amount of $^{11}BCl_3$, Torr	Amount of $^{10}BCl_3$, Torr
O_2	0.27	0.13
C_2D_2	0.25	0.11
HBr	0.16	0.09
NO	0.18	0.06
H_2	0.19	0.05

Table 3. Selectivity α ($^{10}B/^{11}B$) during irradiation of BCl_3 with various acceptors. Molecules were excited at a frequency of 982.1 cm^{-1} (laser line 10R(30)). BCl_3 pressure is 0.88 Torr; acceptor pressure, 2.3 Torr; irradiation time, 30 min [108].

Acceptor	Selectivity $\alpha(^{10}B/^{11}B)$
HBr	2.4
O_2	2.0
C_2D_2	1.8
NO	1.45
H_2	1.2

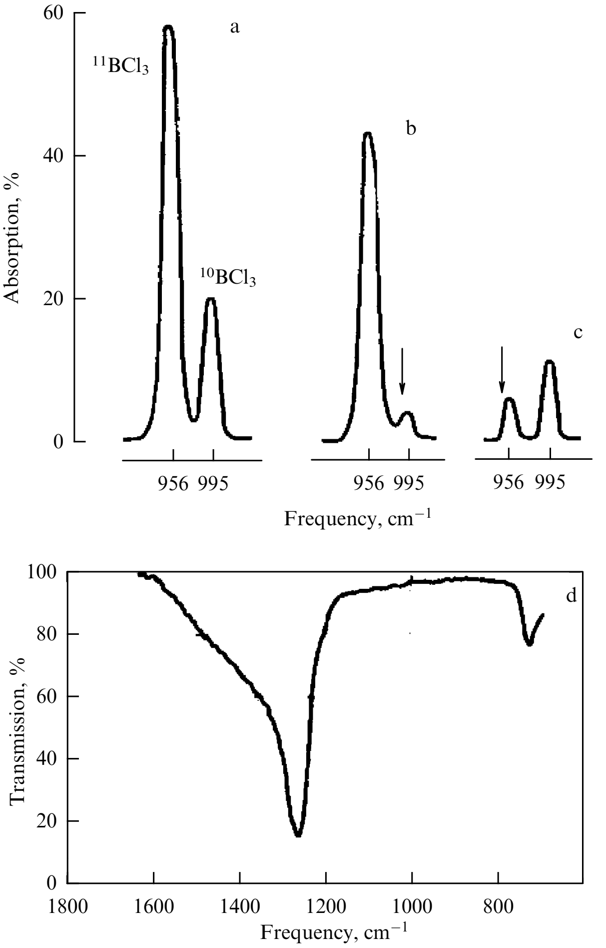

Figure 6. Absorption spectrum of BCl_3 before irradiation (a) and after irradiation upon excitation of $^{10}BCl_3$ (b) and $^{11}BCl_3$ (c). BCl_3 pressure is 0.44 Torr, air pressure, 11 Torr. Excitation frequency is marked with arrows. Irradiation time is 30 min. (d) Spectrum of $^{11}B_2O_3$ film obtained upon excitation of $^{11}BCl_3$ molecules. BCl_3 molecules were irradiated for 3 h [108].

authors, since the endothermic reaction of hydrogen atoms with BCl_3 molecules has a small (≈ 0.08 eV) activation energy, it can occur with vibrationally excited molecules and lead to chain reactions.

Selective laser IR multiphoton dissociation of BCl_3 molecules was studied in detail in [108, 109]. A powerful CO_2 laser with a pulse energy of ≈ 2 J, a pulse duration of 90 ns, and a pulse repetition rate of 1.6 Hz was used to excite the molecules. The laser radiation was focused into a cuvette filled with gas using a lens with a focal length of $f = 120$ mm. The spot size at the lens focus was 2×1.5 mm, which provided a power density of $\sim 10^9$ W cm^{-2} in the focal region. The cuvette length was 120 mm, the diameter was 20 mm, and the windows were made of NaCl. The production of BCl_3 as a result of gas irradiation was determined by the IR absorption spectra of the molecules in the cuvette, recorded before and after their irradiation using an IKS-24 infrared spectrophotometer.

In the experiments, the isotope-selective dissociation of BCl_3 molecules with a natural content of boron isotopes was studied using various radical acceptors: O_2, HBr, C_2D_2, NO, and H_2 (Tables 2 and 3).

The dissociation of molecules was carried out upon excitation of both $^{10}BCl_3$ and $^{11}BCl_3$ molecules. The isotopic selectivity of excitation and dissociation of molecules was clearly demonstrated (Fig. 6a–c).

The dependences of the enrichment factors on the BCl_3 pressure and the radical acceptor pressure were studied. The efficiency of processing was determined to be up to 25% of the laser-excited $^{11}BCl_3$ molecules in the reaction volume per pulse. It was shown that, if oxygen radical acceptors are used, the final product of BCl_3 molecule dissociation and subsequent chemical reactions is a solid compound B_2O_2 (Fig. 6d), which is deposited on the walls and windows of the cuvette in the form of a film.

7.1.3 Subsequent studies.

Subsequent studies [5, 156–161] examined the main parameters of isotope-selective laser IR multiphoton dissociation of BCl_3 molecules and their dependence on the parameters of the exciting laser radiation [156–158] and the irradiated gas [158–161] on the pressure of the BCl_3 gas itself, and the pressure and type of radical acceptors [158–160]. Experiments were carried out on isotope-selective dissociation of van der Waals clusters Ar-BCl_3 [162], on IR MPD of BCl_3 molecules in a mixture with hydrogen using catalysts [163, 164], and on the use of a free-electron laser for MPD of BCl_3 molecules [165]. Experiments were conducted on laser separation of boron isotopes by the IR MPD method for molecules using the $BCl_3 \bullet CH_3SH$ complex [166]. Experiments on two-frequency laser IR MPD of BCl_3 molecules [167, 168] were carried out. Molecules of 2-chloroethyldichloroborane [110] were synthesized and experiments on isotope-selective IR MPD of 2-chloroethyldichloroborane molecules [110, 169–172] were conducted. Schemes were proposed and calculations were made on enrichment of boron isotopes using a low-energy method of suppressing (slowing down) the condensation of BCl_3 molecules in a mixture with carrier gases [3, 4, 6–9, 96–99]. Recent studies investigated in detail isotope-selective laser IR MPD of BCl_3 molecules in a mixture with an optically active sensitizer and SF_6 radical acceptor [1, 2] and isotope-selective IR MPD of 2-chloroethyldichloroborane molecules [10, 11]. Sections 7.2–10 present a detailed examination of the results obtained in these studies.

7.2 Spectral and energy characteristics of isotope-selective IR multiphoton dissociation of BCl_3 molecules

The basic parameters of laser isotope separation are the yields and selectivities of dissociation of the isotopologues under study. Therefore, it is of primary importance to measure these parameters under specific experimental conditions and examine their dependence on the parameters of the exciting laser radiation (frequency, energy density, duration, and number of exciting pulses) and the parameters of the irradiated gas (pressure, temperature, and presence of acceptors and/or buffer gases). It is precisely such studies, carried out with BCl_3 molecules, that we discuss in this section.

The dependences of the yields and selectivities of dissociation of $^{10}BCl_3$ and $^{11}BCl_3$ molecules on the frequency and energy density of the exciting pulse were measured in detail in [156, 157]. The yields and selectivities of dissociation of molecules were determined using Eqns (3) and (4). The experiments were conducted using focused laser beams. Therefore, the integral molecular dissociation yields over the cell volume were measured, and in most cases they are presented in relative units. In study [156], the laser radiation pulse was focused by a lens with focal length $f = 20$ cm into a cell containing 0.25 Torr of BCl_3 and 4 Torr of dried air. The diameter of the laser beam spot at the lens focus was 0.8 mm. With a laser pulse duration of 85 ns, the power density at the lens focus was about 8×10^8 W cm^{-2}. The duration of the irradiation process was selected so that the amount of gas produced did not exceed 20%.

The dependence of the dissociation yield β_{11} of $^{11}BCl_3$ molecules on the excitation radiation frequency obtained in [156] is displayed in Fig. 7a. The linear absorption spectrum of a natural mixture of $^{11}BCl_3$ and $^{10}BCl_3$ isotopologues is also shown in this plot. The figure shows the resonance nature of the dissociation of molecules. It is clearly seen that the spectral dependence of the dissociation yield $\beta_{11}(\nu)$ is shifted relative to the linear absorption spectrum of $^{11}BCl_3$ molecules towards longer wavelengths, which is explained by the anharmonicity of the vibrations of the molecules [72]. The magnitude of the shift in the position of the maxima of these curves is about 17 cm^{-1}. The measured shift of the maximum of the dissociation yield curve of $^{11}BCl_3$ molecules relative to that of the linear absorption spectrum significantly exceeds the shift of the levels of the ν_3 mode due to the anharmonicity of the vibrations ($\Delta\nu_{\mathrm{anh}} = 3.3$ cm^{-1} [131, 173]). This observation, which characterizes the collisionless excitation of high vibrational states of molecules (as a result of which the 'effect of accumulation of anharmonic level shift' takes place), is a general feature upon excitation and dissociation of molecules in a strong IR laser field [72].

Figure 7b shows the dependence of the selectivity of the dissociation of BCl_3 molecules on the exciting radiation frequency. It is evident that there is no selectivity (it is approximately one) in the frequency range of about 956 cm^{-1}. In the lower frequency range, $^{11}BCl_3$ molecules predominantly dissociate, while in the higher frequency range, $^{10}BCl_3$ molecules do. Higher selectivity ($\beta_{10} \approx 4$) is observed upon excitation of $^{10}BCl_3$ molecules. This is due to the fact that, during the excitation pulse, some of the excited molecules have sufficient time to collide with unexcited molecules, which leads, due to vibrational-vibrational (V–V) energy exchange, to the excitation and dissociation of molecules that were not initially irradiated by the laser. The probability of such a process upon excitation of the heavy isotopologue ($^{11}BCl_3$) is higher due to its higher concentration than upon excitation of the light isotopologue ($^{10}BCl_3$).

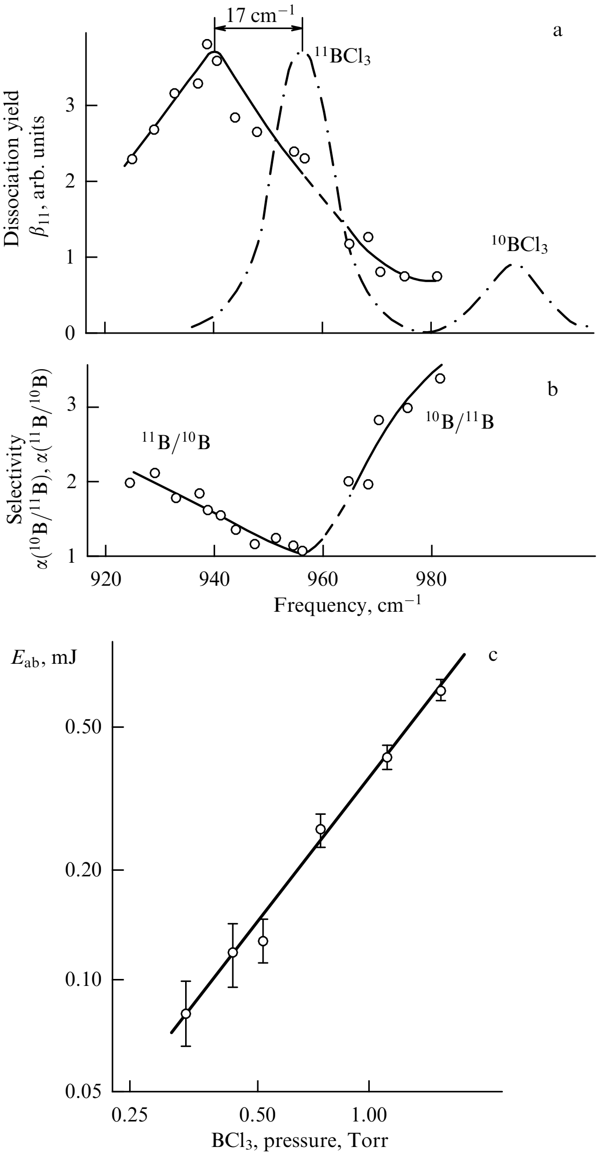

Figure 7. Frequency dependences of yield (a) and selectivity (b) of dissociation of $^{11}BCl_3$ molecules at a power density of 8×10^8 W cm^{-2}. Dashed line shows linear absorption spectrum of BCI_3 molecules. (c) Specific energy absorbed by BCl_3 molecules from an unfocused CO_2 laser beam as a function of gas pressure. Power density of laser radiation is 10^6 W cm^{-2} [156].

If focused laser beams are used for dissociation of molecules, it is virtually impossible to obtain the dependences of the yields and selectivity of BCl_3 dissociation on the energy density of the exciting laser radiation. Suchlike data are presented in Section 8, which presents the results of experiments on the dissociation of BCl_3 molecules by an unfocused laser beam using a sensitizer and an acceptor of SF_6 radicals. In the study under consideration [156], the dependence of the energy absorbed by BCl_3 molecules on the pressure of the gas itself was measured using an unfocused laser beam geometry at a laser radiation intensity of 10^6 W cm^{-2} (Fig. 7c). The measurements were carried out at a radiation frequency of 979.7 cm^{-1} (laser generation line 10R(26)) using a 50-cm-long cuvette. The laser beam diameter

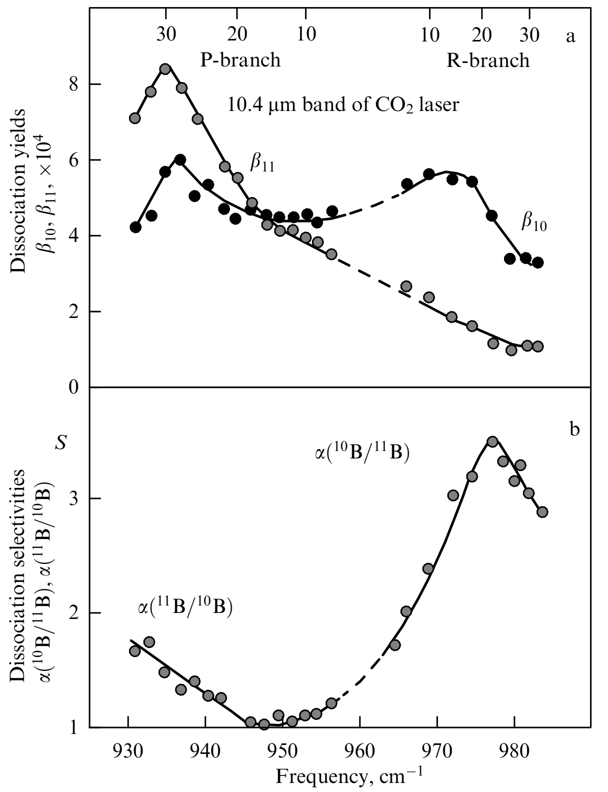

Figure 8. Yields (a) and selectivities (b) of dissociation of $^{10}BCl_3$ and $^{11}BCl_3$ molecules as functions of frequency of exciting laser radiation. BCl_3 pressure is 0.5 Torr; dry air pressure is 5.5 Torr. Exciting pulse energy is 1 J [157].

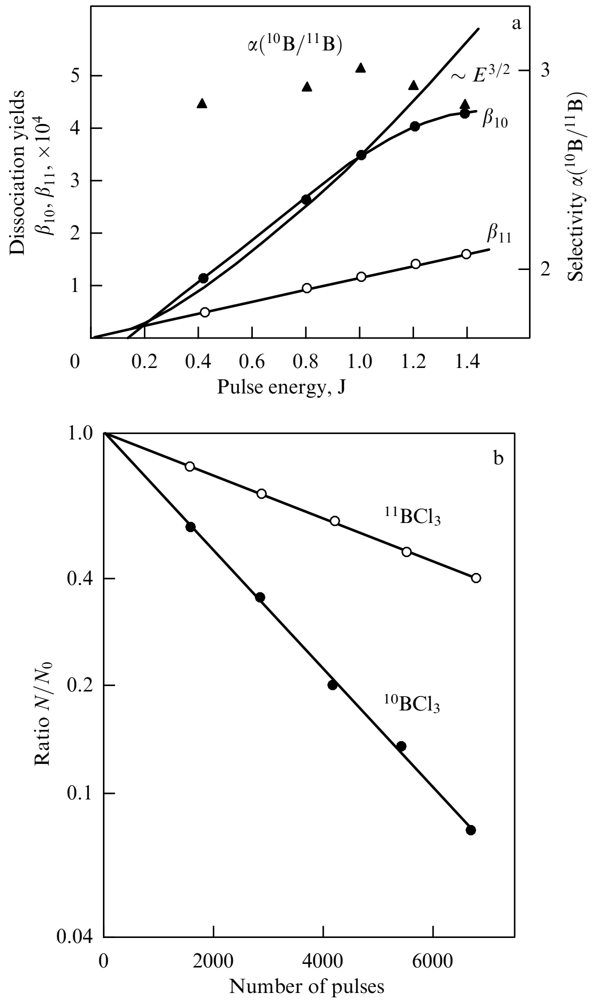

Figure 9. (a) Dissociation yields of β_{10} and β_{11} and dissociation selectivity of $\alpha(^{10}B/^{11}B)$ as functions of exciting radiation energy at frequency of 979.7cm^{-1} (laser 10R(26) generation line). (b) Change in concentrations of $^{10}BCl_3$ and $^{11}BCl_3$ molecules as function of number of irradiation pulses at a frequency of 974.6 cm^{-1} (laser 10R(18) generation line) at energy per pulse of 1 J. BCl_3 pressure is 0.5 Torr, and dry air pressure is 5.5 Torr [157].

was 13 mm. The BCl_3 pressure varied from 0.3 to 1.6 Torr. The obtained dependence is close to linear. This implies that the number of absorbed photons per molecule is virtually independent of the pressure in this range and is ≈ 0.45 photon mol^{-1} at the specified power density. The result obtained confirms that, under the experimental conditions, the molecules acquire energy in collisions.

The spectral and energy characteristics of the yield and selectivity of dissociation of BCl_3 molecules were studied in more detail in [157]. The frequency dependences of these parameters were measured in a wide range upon excitation of both $^{10}BCl_3$ and $^{11}BCl_3$ molecules using the P and R lines of the 10.6-μm generation band of a CO_2 laser. The laser pulse consisted of a peak with a half-maximum duration of about 85 ns and a tail with a duration of ≈ 2 μs, which contained approximately half the pulse energy. A glass cell 16 cm long and 1.6 cm in diameter with KCl windows was used in the experiments. The laser beam was focused into a cuvette with an NaCl lens with focal length $f = 20$ cm. A mixture of BCl_3 molecules (8.3%) and dried air (91.7%) was irradiated at a total pressure of 6 Torr.

Figure 8a, b shows the yields and selectivities of dissociation of $^{10}BCl_3$ and $^{11}BCl_3$ molecules as functions of the frequency of the exciting laser radiation at a pulse energy of 1 J. It should be noted that the dissociation yields (values integrated over the entire volume of the cuvette) are presented in absolute units. It is evident that, at the excitation energy used, the dissociation yields are small. The curves of the dissociation yields β_{10} and β_{11} are shifted relative to the IR absorption bands of the $^{10}BCl_3$ and $^{11}BCl_3$ molecules, respectively, by approximately 23 and 20 cm^{-1}. The maxima of the curves β_{10} and β_{11} are observed at frequencies of approximately 972 and 935 cm^{-1}. The dissociation selectivity is equal to unity at the intersection of the curves of the dissociation yields β_{10} and β_{11} at a frequency of approximately 947 cm^{-1}. The selectivity $\alpha(^{10}B/^{11}B)$ depends more sharply on frequency than $\alpha(^{11}B/^{10}B)$ and has a maximum in the region of 977.2 cm^{-1} (generation line of the 10R(22) laser). The maximum obtained selectivity $\alpha(^{10}B/^{11}B) \approx 3.6$.

Figure 9a shows the dissociation yields β_{10} and β_{11} and the dissociation selectivity $\alpha(^{10}B/^{11}B)$ as functions of the excitation radiation energy in the range from 0.2 to 1.4 J found in [157] when irradiating molecules at a frequency of 979.7 cm^{-1} (the 10R(26) laser generation line). It is apparent that, in the energy range E up to approximately 1 J, the dissociation yield of resonantly excited $^{10}BCl_3$ molecules is fairly well described by the dependence $\beta_{10} \sim E^{3/2}$, which is typical when using a focused laser beam [72]. At an excitation energy $E > 1$ J, the dependence $\beta_{10}(E)$ shows a tendency toward saturation, while the dissociation β_{11} yield continues to increase linearly with energy. This leads to a decrease in the selectivity of dissociation $\alpha(^{10}B/^{11}B)$ with an increase in the excitation energy in the region $E > 1$ J. It should be noted that, if a lens with a focal length of $f = 20$ cm is used to focus the laser beam, the energy density at the lens focus is approximately two orders of magnitude higher than the numerical value of the energy in the pulse. The dependence of the dissociation yield on the energy $\beta_{10}(E)$ crosses the abscissa axis in the region of 0.15 J. Therefore, based on these data, it can be assumed that the dissociation threshold of BCl_3 molecules is about 15 J cm^{-2}.

An important result obtained in [157] is the dependence of the change in the concentrations of $^{10}BCl_3$ and $^{11}BCl_3$ molecules on the number of irradiation pulses. Figure 9b presents such dependences in the case of irradiation of molecules at a frequency of 974.6 cm^{-1} (laser generation line 10R(18)) at an energy per pulse of 1 J. The slopes of the obtained dependences represent the dissociation rates of β_{10} and β_{11} of $^{10}BCl_3$ and $^{11}BCl_3$ molecules at this frequency. Thus, the results presented show that, during the irradiation of BCl_3, the dissociation yields remain virtually unaltered when the number of irradiation pulses is varied. The selectivity of dissociation (the ratio of the slopes of the two dependences) is also virtually independent of the number of irradiation pulses up to significant ($\geqslant 92\%$) gas production. This result is of great importance in terms of practical implementation of the laser method for separating boron isotopes.

The parameters of isotope-selective IR multiphoton dissociation of BCl_3 molecules were studied in detail in [158]. There, selective dissociation of separate isotopologues $^{10}BCl_3$ and $^{11}BCl_3$ and BCl_3 of natural isotopic composition in a mixture with oxygen was examined upon interaction with radiation from a pulsed CO_2 laser. Molecules were irradiated with a focused ($f = 7.5$ cm or $f = 128$ cm) laser beam at a frequency of 944.2 cm^{-1} (laser generation line 10P(20)), resonant with the absorption band of $^{11}BCl_3$ molecules. The laser energy was about 0.5 J per pulse. The dissociation yield of $^{11}BCl_3$ molecules and the intensity of visible luminescence arising during irradiation of molecules vs. the energy density of the exciting radiation in the lens focus were obtained (Fig. 10a). The dependences of the yields β_{10} and β_{11} and selectivity of dissociation $\alpha(^{11}B/^{10}B)$ of $^{10}BCl_3$ and $^{11}BCl_3$ molecules on the oxygen pressure were measured for irradiation of BCl_3 of natural isotopic composition (Fig. 10b). The dependences displayed in Fig. 10a show that visible luminescence is only observable when dissociation of molecules begins, i.e., when oxygen interacts with the molecular dissociation products. The yields of dissociation of molecules in a mixture with a natural content of isotopologues (Fig. 10b) initially increase with an increase in the oxygen pressure acting as an acceptor of radicals in the region up to approximately 10–12 Torr. They decrease with a further increase in the oxygen pressure, which is associated with the deactivation of excited molecules as a result of an increase in the rate of vibrational-translational relaxation with oxygen molecules.

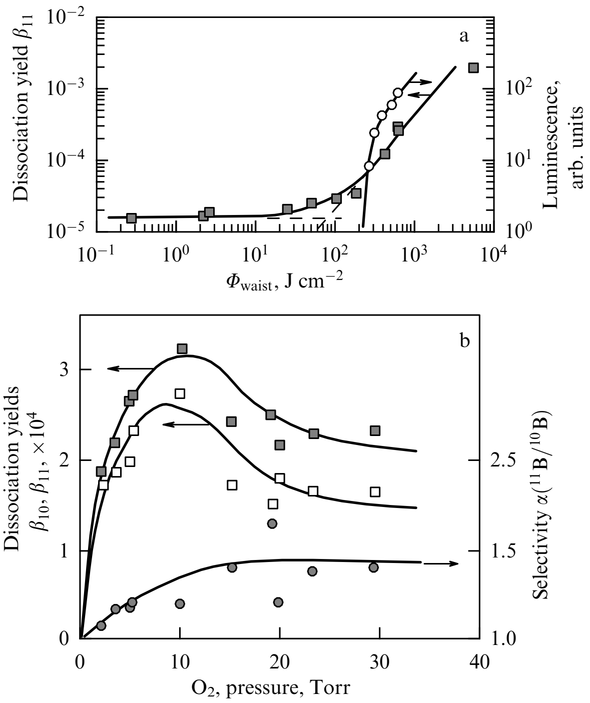

Figure 10. (a) Dependences of dissociation yield of $^{11}BCl_3$ molecules (■) and intensity of visible luminescence (○) arising during irradiation of molecules on energy density of exciting radiation at lens focus. (b) Dependences of dissociation yields β_{10} (□) and β_{11} (■) and selectivity $\alpha(^{11}B/^{10}B)$ (●) of $^{10}BCl_3$ and $^{11}BCl_3$ molecules on oxygen pressure in the case of irradiation of BCl_3 of natural isotopic composition. In both cases, BCl_3 pressure = 1 Torr [158].

It was found in [158] that the ratio of the dissociation yields obtained separately with $^{10}BCl_3$ molecules (with a content of 98%) and $^{11}BCl_3$ molecules (97%) under the same experimental conditions is 4.7 ± 1.3, while the same ratio obtained with BCl_3 molecules of natural isotopic composition is 1.3. In the opinion of the authors, such a sharp difference in the indicated ratio observed in these two cases is due to the fact that, when a natural mixture of isotopologues is irradiated, an effective vibrational-vibrational (V–V) exchange of energy occurs between highly excited $^{11}BCl_3$ and $^{10}BCl_3$ molecules, which leads to a significant decrease in the selectivity of dissociation of molecules.

The yields and selectivity of IR MPD of BCl_3 molecules were also measured in [5, 159]. In [159], the isotope-selective dissociation of $^{10}BCl_3$ and $^{11}BCl_3$ molecules was investigated using a CO_2 laser at a low temperature of the irradiated gas. Higher enrichment factors were observed than in the case of irradiation of molecules at room temperature; however, specific values of the parameters were not reported. In [5], during the irradiation of BCl_3 molecules in a mixture with an oxygen acceptor on the 10P(20) generation line of a CO_2 laser (at a frequency of 944.2 cm^{-1}), the gas residual after irradiation was enriched with ^{10}B. The enrichment factor in the residual BCl_3 gas was $K_{enr}^{res} \approx 1.17$. It should be noted that the main reason for the small selectivities of $^{11}BCl_3$ molecule dissociation observed in [5, 159] is that the molecules were irradiated at frequencies near which the selectivity of $^{11}BCl_3$ dissociation is minimal (Figs 7b and 8b).

7.3 Effect of radical acceptors and buffer gases on selectivity and yield of BCl_3 dissociation. Identification of final products

7.3.1 Effect of pressure of gas itself on selectivity and yield of BCl_3 dissociation. The dependences of the enrichment factors in the residual BCl_3 gas after irradiation and in the resulting products on the pressure of the gas itself and that of acceptor gases were already investigated in the first studies on isotope-selective IR MPD of BCl_3 [108, 109] (Fig. 11a, b).

Dry air was used as a radical acceptor in these studies. The dependences of the yields and selectivity of dissocia-

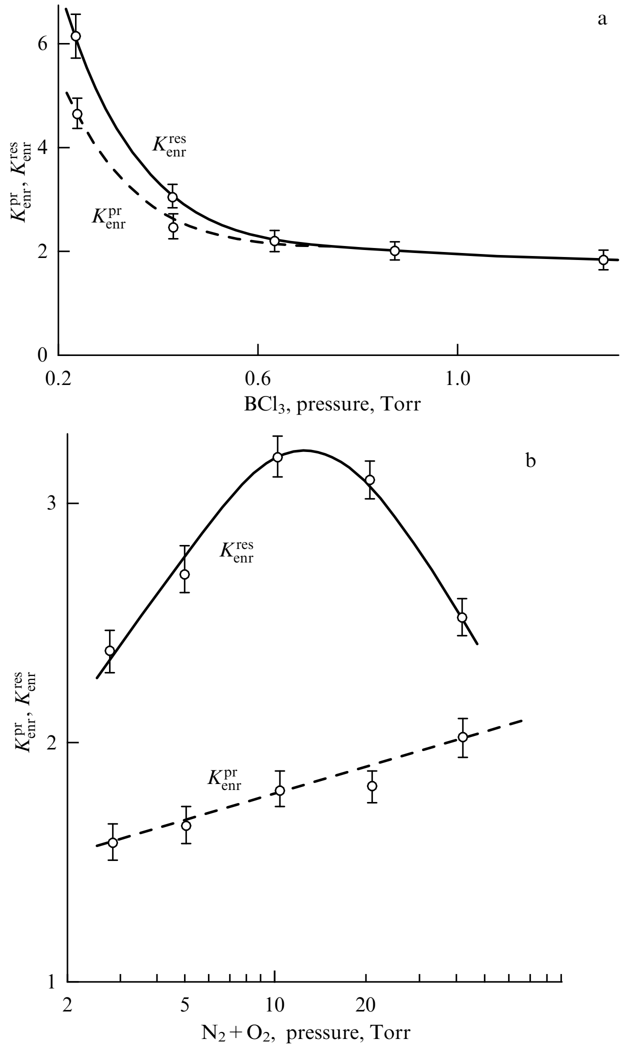

Figure 11. (a) Dependences of enrichment factors in residual gas after irradiation and in resulting products on BCl_3 pressure. Acceptor (dried air) pressure is 10 Torr. Irradiation time is 30 min. (b) Dependences of enrichment factors in residual gas after irradiation and in resulting products on pressure of dried air. BCl_3 pressure is 1 Torr. Irradiation time is 1 h [108].

tion of $^{10}BCl_3$ and $^{11}BCl_3$ molecules in a natural mixture of isotopologues on the pressure of BCl_3 itself were examined in detail in [158] using oxygen as an acceptor. The results obtained are shown in Fig. 12a and b, respectively.

The O_2 acceptor pressure in both cases is 5 Torr. Figure 12 shows that, with an increase in the BCl_3 pressure, both the dissociation yield of laser-excited $^{11}BCl_3$ molecules and the dissociation selectivity decrease. The decrease in the dissociation yield of $^{11}BCl_3$ molecules is primarily associated with vibrational-translational relaxation of excited molecules, while the decrease in selectivity is associated with vibrational-vibrational V–V energy exchange between the isotopologues. It should be noted that the dissociation yield of $^{11}BCl_3$ molecules (Fig. 12a) decreases with an increase in pressure somewhat more slowly than the dissociation selectivity (Fig. 12b). The time constants for these two processes (vibrational-translational and vibrational-vibrational energy relaxation in BCl_3) are $p\tau_{V\text{–}T} \approx 5.8$ μs Torr [111] and $p\tau_{V\text{–}V} \approx 0.5$ μs Torr [111], respectively.

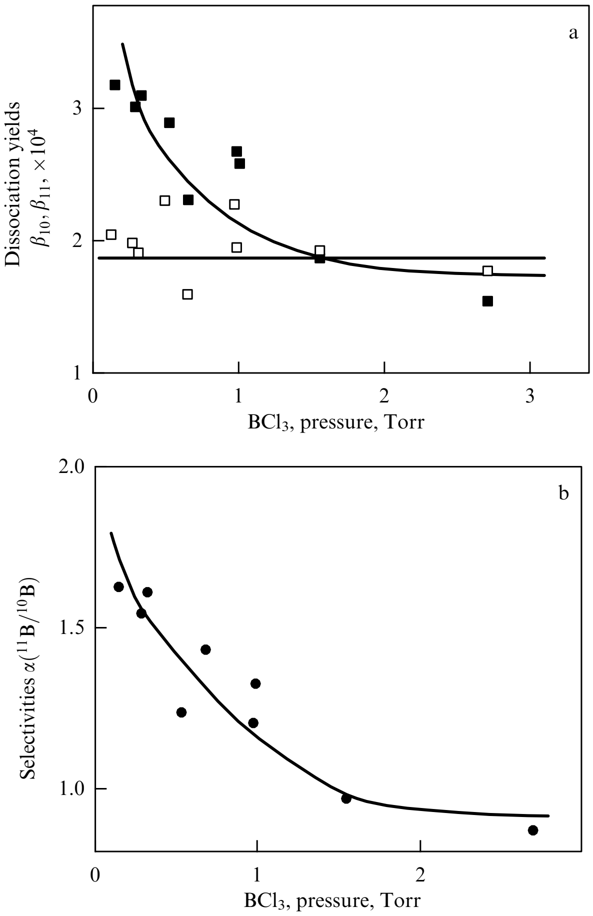

Figure 12. Dependences of dissociation yields of $^{11}BCl_3$ (■) and $^{10}BCl_3$ (□) molecules (a) and dissociation selectivity $\alpha(^{11}B/^{10}B)$ (●) (b) in natural mixture of isotopologues on pressure of BCl_3 itself. Pressure of acceptor, O_2, in both cases is equal to 5 Torr [158].

7.3.2 Effect of acceptor gases on selectivity and yield of BCl_3 dissociation.

Already the first studies [108, 109] on isotope-selective laser IR MPD of BCl_3 molecules showed that radicals formed during the dissociation of molecules associate with the formation of the initial substance. Therefore, to accumulate the effect of molecular dissociation and to obtain the final products, it is necessary to use radical acceptors. In most cases, it is desirable that the final products formed as a result of molecular dissociation and subsequent chemical reactions be gaseous. They are easier to detect, for example, using IR absorption spectra, and also to separate from the initial substance. The type and pressure of the acceptor used can greatly affect the efficiency of the molecular dissociation process — the yields and selectivity of dissociation (see Tables 2 and 3).

In the first studies [108, 109] and in many subsequent studies [156–160], oxygen or oxygen-containing dry air was used as a radical acceptor. The final products of BCl_3 molecule dissociation and subsequent chemical reactions are B_2O_3 and Cl_2 [108, 109]. Acceptor gases also perform as buffer gases, the main effect of which is to involve more molecules in the interaction with laser radiation in experiments with low BCl_3 pressures, when the rotational relaxation time of molecules is longer than the duration of the exciting laser pulse.

The effect of the oxygen radical acceptor pressure on the selectivity and dissociation yield of BCl_3 molecules with natural isotopologue content was investigated in [108, 109, 159]. The results are presented in Figs 10b and 11b. The dissociation yields of BCl_3 molecules initially increase with increasing pressure of oxygen as a radical acceptor in the region up to approximately 10–15 Torr and decrease with a further increase in oxygen pressure, which is associated with the deactivation of excited molecules as a result of an increase in their vibrational-translational relaxation rate. The dissociation selectivity $\alpha(^{11}B/^{10}B)$ of $^{11}BCl_3$ molecules increases from approximately unity to ≈ 1.4 at oxygen pressures up to ≈ 15 Torr and reaches a plateau extending to a pressure of ≈ 30 Torr (Fig. 10b).

In what regards investigating the influence of radical acceptors on the efficiency of laser IR MPD of BCl_3 molecules, of great interest is study [160], in which the kinetics of the reaction of multiphoton excited BCl_3 molecules with H_2S molecules were examined. Two types of experiments were carried out: a parallel laser beam and a focused beam were used to excite the molecules. The experiments of the first type showed that the activation energy of the reaction is significantly lower than the binding energy in the BCl_3 molecule. In the experiments of the second type, it was found that the isotopic selectivity of dissociation increases with increasing excitation pulse energy. These results differ from typical results on MPD of BCl_3 molecules and exhibit their own characteristics of the occurring processes. In the opinion of the authors, the results obtained show that the primary reaction is based on a mechanism that includes collisions of vibrationally excited BCl_3 molecules with an H_2S acceptor and a reaction between them.

7.3.3 Effect of catalysts on selectivity and dissociation yield of BCl_3. Studies [163, 164] investigated the photochemical separation of boron isotopes by the IR MPD BCl_3 method using catalysts. In [163], a mixture of BCl_3 molecules of natural isotopic composition (at a pressure of 10 Torr) and H_2 molecules (at a pressure of 20 Torr) with the addition of a catalyst — 1 g of Ti powder — was irradiated with pulsed CO_2 laser radiation at a frequency of 947.7 cm^{-1} (the 10P(16) laser line), resonant with the absorption band of $^{11}BCl_3$ molecules. A glass cuvette 50 cm long and 2.5 cm in diameter with KBr windows was used as a reactor for irradiating the gas. The laser radiation was input into the cuvette without focusing. The laser pulse repetition frequency was 5 Hz, and the average radiation power was about 7 W. After 1.5 h of irradiation, a 10% enrichment of the residual BCl_3 gas with the ^{10}B isotope relative to the ^{11}B isotope was detected, i.e., an enrichment factor $K_{enr}^{res}(^{10}B/^{11}B) \approx 1.1$ was obtained. In the opinion of the authors, the observed effect can be explained by two mechanisms: (1) the metal acts as a catalyst predominantly on excited molecules and (2) $^{11}BCl_3$ molecules dissociate selectively more efficiently due to better resonance of the laser generation line with their IR absorption band. The authors concluded that the efficiency of isotopic enrichment depends on the type of metal used as a catalyst.

In a subsequent study [164], a mixture of the natural isotopic composition of $BCl_3 + H_2$ molecules (1 Torr + 2 Torr) with the addition of various catalysts — 1 g of Ti or Pb powder — was irradiated. The main difference between these two catalysts is that chemical adsorption occurs when hydrogen molecules interact with the titanium surface, while, when they interact with the lead surface, the adsorption is physical. The molecules were irradiated on the same laser generation line, 10P(16). The laser operated with a pulse repetition frequency of 3 Hz. The laser radiation was focused into the reactor center with a GaAs lens with focal length $f = 5$ cm. It was found that products formed using these catalysts were different. When Ti was used, the reaction products were $^{10}B^{11}BH_2Cl_4$, $^{11}B^{11}BH_2Cl_4$, and HCl, while, when Pb was employed, the products were $^{10}B^{11}BCl_4$, $^{11}B^{11}BCl_4$, and HCl. It was also found that the concentration of $^{10}BCl_3$ molecules in the residual gas increased from 20% to 37% after irradiation with 360 laser pulses. However, isotopic enrichment in the formed products was not observed.

7.3.4 Selective IR multiphoton dissociation of $BCl_3 \bullet CH_3SH$ complex. Isotope-selective IR MPD of the $BCl_3 \bullet CH_3SH$ molecular complex was studied in [166]. The authors found that the IR absorption spectrum of a mixture of BCl_3 and CH_3SH (methyl mercaptan) molecules in the gas phase has three peaks in the 1000 cm^{-1} region. This absorption was tentatively attributed to the $BCl_3 \bullet CH_3SH$ complex. Experiments were carried out on the dissociation of the complex with a pulsed CO_2 laser at several radiation frequencies coinciding with the absorption bands of the complex. Mixtures prepared using monoisotopologues $^{10}BCl_3$ and $^{11}BCl_3$ and BCl_3 with a natural content of isotopologues were irradiated. The threshold energy density for the dissociation of this complex was found to be about 0.5 J cm^{-2}, which is significantly less than that for the dissociation of BCl_3 molecules. At an irradiation frequency of 944.2 cm^{-1} (generation line of the 10P(20) laser), the dissociation yield of the $^{10}BCl_3 \bullet CH_3SH$ complex was approximately 10 times greater than the dissociation yield of the $^{11}BCl_3 \bullet CH_3SH$ complex. Based on the obtained dependence of the dissociation yield of the complex on the absorbed energy, the authors concluded that, as a result of irradiation of the complex, two reaction channels with different dissociation energies are realized: one with the detachment of the Cl atom from the vibrationally excited complex and the other in which the HCl molecule is detached.

The obtained dependence of the dissociation yield of the $^{10}BCl_3 \bullet CH_3SH$ complex on the absorbed energy coincides with a similar dependence revealed by the authors earlier in experiments on the irradiation of a $BCl_3 + H_2S$ mixture [160]. Based on this observation, the authors suggested that vibrationally excited BCl_3 molecules lead to the formation of a transient $BCl_3 \bullet H_2S$ complex, which undergoes dissociation through the same channels as the $BCl_3 \bullet CH_3SH$ complex.

Although this complex features a low dissociation threshold and fairly high dissociation yields (approximately an order of magnitude higher than with BCl_3) were obtained, the measured dissociation selectivity is comparable to that found upon irradiation of BCl_3 molecules using O_2 or the H_2S radical as acceptors. The authors believe that the low selectivity of the process is due to the fact that the laser-induced reactions lead to nonselective decomposition of the complex due to the low dissociation energy.

7.3.5 Products of laser IR multiphoton dissociation of BCl_3. The composition and amount of the final products formed as a result of laser IR MPD of BCl_3 molecules and subsequent chemical reactions depend on the type of radical acceptor used and the degree of production of the irradiated gas (number of irradiation pulses). The resulting products are usually identified based on their IR absorption spectra and by a chromatograph or mass spectrometer. As noted in

Table 4. Products formed during irradiation of BCl_3 molecules with various acceptors.

Irradiated molecules	Acceptors	Products formed	References
BCl_3	O_2	B_2O_3, Cl_2	[64, 108]
BCl_3	H_2	$HBCl_2$, HCl	[155, 161]
BCl_3	D_2	$DBCl_2$, DCl	[155]
BCl_3	CH_4	$HBCl_2$, HCl, CH_3Cl	[10]
BCl_3	H_2S	$HBSCl_2$, HCl	[153, 154, 160]
BCl_3	D_2S	$DBSCl_2$, DCl	[153, 154]
BCl_3	SF_6	$BFCl_2$, BF_2Cl, SF_5Cl	[1, 2]

Section 7.1, when BCl_3 is irradiated with oxygen, the final products are B_2O_3 and Cl_2 [108, 109]. If BCl_3 is irradiated with hydrogen or deuterium, the final products are dichloroboranes $HBCl_2$ or $DBCl_2$ and HCl or DCl, respectively [155].

If more complex molecules are used as a radical acceptor and the BCl_3 production degree is deeper, the range of final products may be broader (see Section 8 below). For example, when irradiating BCl_3 with hydrogen or methane, the final products may contain, in addition to $HBCl_2$ and HCl, boranes di- or tri-substituted with hydrogen — H_2BCl and BH_3. If BCl_3 is irradiated with methane, chloromethane (CH_3Cl) and dichloromethane (CH_2Cl_2) are also formed as a result of the replacement of hydrogen in methane with chlorine. In the case of BCl_3 irradiated with H_2S or D_2S, the final products are $HBSCl_2$ or $DBSCl_2$ and HCl or DCl, respectively [153, 154, 165]. When BCl_3 molecules are irradiated with SF_6, mono- or difluorinated boron chlorides ($BFCl_2$ or BF_2Cl) and SF_5Cl are formed [1, 2] (Table 4, see also Section 8).

7.4 Two-frequency isotope-selective IR multiphoton dissociation of BCl_3

As shown in Sections 7.1–7.3, isotope-selective laser IR MPD of BCl_3 molecules with single-frequency laser radiation is characterized by a fairly high threshold energy density for dissociation (≈ 20 J cm^{-2}) and comparatively low yields ($\beta \leqslant 5 \times 10^{-4}$) and selectivities ($\alpha \leqslant 2-4$). This leads to low efficiency of the laser IR MPD of BCl_3 and is a challenge for practical application of the method for separating boron isotopes. The efficiency of laser IR MPD of BCl_3 molecules can be enhanced (the yield and selectivity of dissociation increase and the threshold dissociation energy densities decrease) if two-frequency laser IR multiphoton dissociation of molecules is applied [66, 67] (see also Section 3.1). In [167, 168], IR MPD of BCl_3 molecules by two-frequency laser IR radiation was examined. We now consider the main results of these studies.

In [167], the spectral dependences of the yield and selectivity of IR MPD of BCl_3 molecules were measured. In the experiments, a mixture of 0.1–1.0 Torr BCl_3 with a natural content of isotopologues and 4.5 Torr O_2 was irradiated in a stainless steel cuvette 11.2 cm long and 1.2 cm in diameter. Oxygen was added to bind the dissociation products. The energy density of the first, exciting, laser radiation was 3.7 J cm^{-2}, and that of the second, dissociating, one was 3.0 J cm^{-2}. The delay between pulses was $\Delta\tau = 100 \pm 50$ ns. The main results are displayed in Fig. 13a, b, where the dissociation yield β_{10} of $^{10}BCl_3$ molecules and the dissociation selectivity $\alpha(^{10}B/^{11}B)$ are plotted as functions of the radiation frequency ν_2 of the dissociating laser (a) and the radiation frequency ν_1 of the exciting laser (b). The BCl_3 pressure was 0.1 Torr.

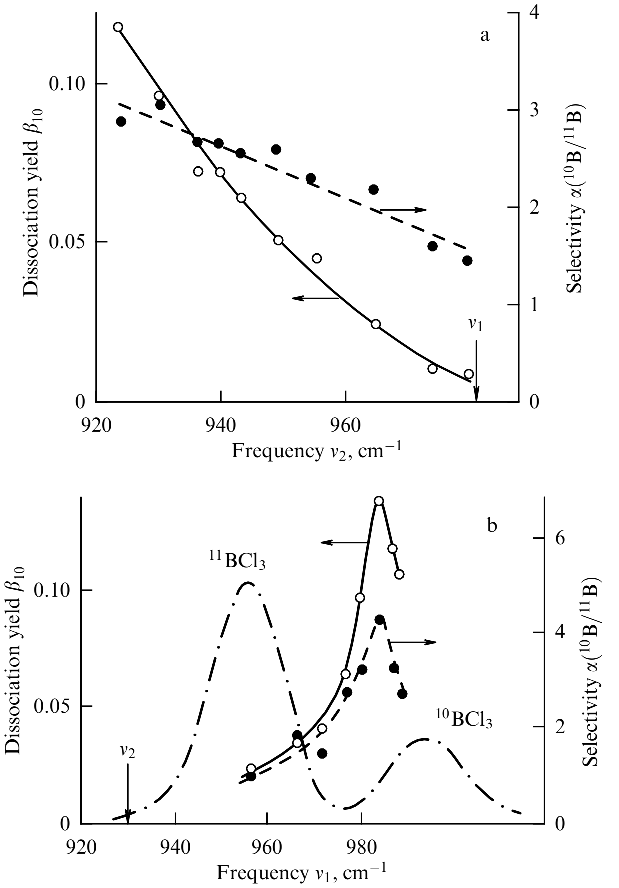

Figure 13. (a) Dependences of selectivity $\alpha(^{10}B/^{11}B)$ (black dots) and dissociation yield β_{10} of $^{10}BCl_3$ molecules (circles) on frequency ν_2 of dissociating laser radiation. Excitation radiation frequency $\nu_1 = 980.9$ cm^{-1} (line 10R(28) of the CO_2 laser). (b) Dependences of selectivity $\alpha(^{10}B/^{11}B)$ (black dots) and dissociation yield of β_{10} $^{10}BCl_3$ molecules (circles) on frequency ν_1 of exciting laser radiation. Frequency of dissociating radiation $\nu_2 = 931.0$ cm^{-1} (line 10P(34) of CO_2 laser). BCl_3 pressure is 0.1 Torr in both cases. Dashed-dotted line in panel b represents linear IR absorption spectrum of BCl_3 molecules [167].

Figure 13a shows that, as the frequency of the dissociating laser shifts toward the red from the fixed 980.9-cm^{-1} (line 10R(28) of the CO_2 laser) frequency of the exciting laser, the dissociation yields of both isotopologues increase. This increase reaches a factor of ≈ 15 for $^{10}BCl_3$ and ≈ 8 for $^{11}BCl_3$ when the frequency of the dissociating laser decreases to $\nu_2 = 924.97$ cm^{-1} (line 10P(40) of the CO_2 laser). The selectivity of $\alpha(^{10}B/^{11}B)$ dissociation increases from approximately 1.5 to 3.0.

When varying the frequency ν_1 of the exciting laser with a fixed frequency ($\nu_2 = 931$ cm^{-1}, line 10P(34)) of the dissociating laser, a maximum at a frequency $\nu_1 = 985.5$ cm^{-1} (line 10R(36) of the CO_2 laser) is observed for the dependences β_{10} and $\alpha(^{10}B/^{11}B)$. The dissociation yield of $^{10}BCl_3$ molecules and selectivity reaches values of $\beta_{10} \approx 0.14$ and $\alpha(^{10}B/^{11}B) \approx 4.2$. Thus, in the study under consideration [167], a comparatively high yield of dissociation of $^{10}BCl_3$ molecules ($\approx 15\%$ with a selectivity of ≈ 4.2) was obtained with a significant decrease in the total energy density of the laser radiation compared to the single-frequency version.

In what regards isotope separation, the use of the two-frequency multiphoton dissociation of BCl_3 made it possible to significantly reduce the total energy density of laser radiation and switch from strong focusing to quasi-parallel beams, and, consequently, to larger irradiated volumes. To enhance the productivity of the process, the BCl_3 pressure can be increased from 0.1 to 1.0 Torr. As shown in [167], the molecular dissociation yield decreases slightly (by about 1.5 times), while selectivity is maintained at the same level. It may be expected that, by optimizing the excitation conditions (selecting the frequency and duration of laser pulses, temperature, and type and pressure of the acceptor), it will be possible to further enhance the selectivity of the process.

Study [168] was devoted to clarifying the processes that affect selectivity and, ultimately, to obtaining the maximum possible selectivity of dissociation. The multiphoton absorption coefficients in BCl_3 were also measured, which made it possible to determine such an important parameter as the laser energy consumption for the separation process. The experimental conditions were similar to those described in [167]. In [168], the dependences of the selectivity and dissociation yield of BCl_3 molecules on the energy densities of the exciting and dissociating lasers and on the pressure of the gas itself and that of the buffer gas were studied.

Figure 14a shows the yield β_{10} and selectivity $\alpha(^{10}B/^{11}B)$ of $^{10}BCl_3$ dissociation as functions of the energy densities of the exciting Φ_1 and dissociating Φ_2 laser radiation. Oxygen performed as the radical acceptor in these experiments.

The dependences of the yields have a power-law character, but the powers for different isotopic components differ: for $\beta_{10}(\Phi_1)$ and $\beta_{10}(\Phi_2)$, the dependence is approximately quadratic, while for $\beta_{11}(\Phi_1)$ and $\beta_{11}(\Phi_2)$, it is close to linear. This difference leads to a rather unusual behavior of the dissociation selectivity, which, unlike most previously obtained results (see, for example, Section 7.2 and [72]), increases with both Φ_1 and Φ_2 approximately linearly to saturate in the range from 3 to 4 J cm^{-2}. Notably, the authors refer to this fact to explain the choice of optimal values of the energy densities Φ_1 and Φ_2 for the dissociation of molecules (3.7 and 3.0 J cm^{-2}, respectively).

A possible channel where the selectivity of multiphoton dissociation is lost may be secondary chemical reactions following the primary act of dissociation of BCl_3 molecules. In [168], experiments were also carried out with other radical acceptors: NO and CO. The dissociation yield β_{10} of the target isotopic component $^{10}BCl_3$ and the selectivity $\alpha(^{10}B/^{11}B)$, depending on the acceptor type (A), under the conditions $\Phi_1 = 3.7$ J cm^{-2} and $\Phi_2 = 3.0$ J cm^{-2}, BCl_3 pressure of 0.2 Torr, acceptor pressure of 4.5 Torr, and delay between pulses of 150 ns are displayed in Table 5.

It is apparent that the parameters of multiphoton dissociation of $^{10}BCl_3$ molecules strongly depend on the acceptor type. The maximum dissociation yield $\beta_{10} = 0.15$ was observed with the O_2 acceptor, and the maximum selectivity $\alpha(^{10}B/^{11}B) = 7.0$, with the NO acceptor.

Figure 14b shows the dependences of the dissociation yields and selectivity on the BCl_3 pressure. With an increase in the BCl_3 pressure from 0.1 to ≈ 0.3 Torr, the yield β_{10} of the target isotopologue $^{10}BCl_3$ remains almost unaltered, but, with a further increase in pressure (to 2 Torr), it quickly decreases from 0.08 to 1.8×10^{-2}. The dependence of β_{11} on the BCl_3 pressure behaves differently: the yield of the

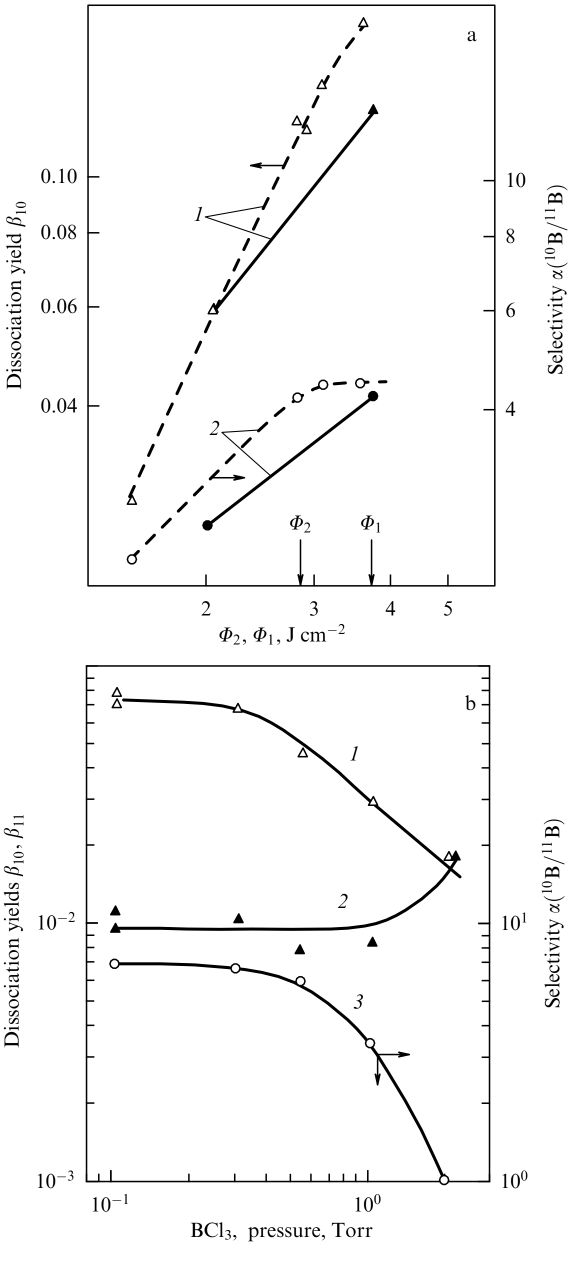

Figure 14. (a) Dependences of β_{10} yield (*1*) and dissociation selectivity (*2*) of BCl_3 molecules on energy density of first Φ_1 (solid line) and second Φ_2 (dashed line) laser fields. Fixed values of second and first fields, respectively, are indicated by arrows. BCl_3 pressure is 0.1 Torr; O_2 pressure is 4.5 Torr; delay between pulses $\Delta\tau = 150$ ns. (b) Dependences of β_{10} (*1*) and β_{11} (*2*) yields and $\alpha(^{10}B/^{11}B)$ dissociation selectivity (*3*) on BCl_3 pressure. NO pressure is 4.5 Torr, $\Delta\tau = 150$ ns [168].

Table 5. Dissociation yield β_{10} of target isotopic component $^{10}BCl_3$ and selectivity $\alpha(^{10}B/^{11}B)$, depending on acceptor type at excitation energy densities $\Phi_1 = 3.7$ J cm^{-2}, $\Phi_2 = 3.0$ J cm^{-2}. BCl_3 pressure is 0.2 Torr, acceptor pressure is 4.5 Torr. Time delay between pulses $\Delta\tau = 150$ ns [168].

Acceptor	NO	O_2	CO
β_{10}	0.08	0.15	0.13
$\alpha(^{10}B/^{11}B)$	7.0	4.5	3.4

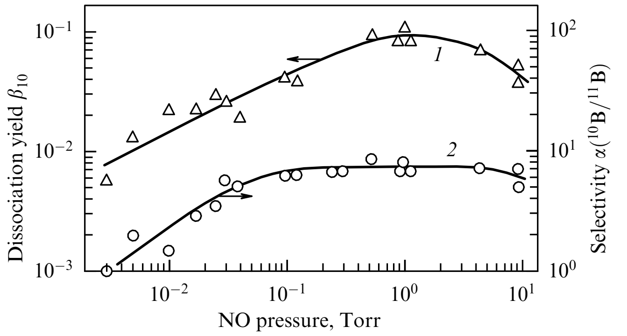

Figure 15. Dependences of β_{10} (*1*) dissociation yield and $\alpha(^{10}B/^{11}B)$ dissociation selectivity (*2*) on NO pressure. BCl_3 pressure is 0.3 Torr, and delay time between pulses $\Delta\tau = 150$ ns [168].

isotopologue $^{11}BCl_3$ remains almost unchanged up to a pressure of ≈ 1 Torr and then increases with an increase in the BCl_3 pressure to 2 Torr. The dependence of the selectivity $\alpha(^{10}B/^{11}B)$ on the BCl_3 pressure is similar to the dependence of β_{10} on the BCl_3 pressure: it is initially constant with a change in pressure from 0.1 to 0.3 Torr and sharply decreases to unity at a BCl_3 pressure of 2 Torr. The main reason for the rapid decrease in selectivity with increasing BCl_3 pressure is the short time of vibrational-vibrational (V–V) energy exchange between the isotopologues $^{10}BCl_3$ and $^{11}BCl_3$ ($p\tau_{\text{V–V}} \approx 0.5$ μs Torr [111]).

Figure 15 shows the yield β_{10} and selectivity $\alpha(^{10}B/^{11}B)$ of $^{10}BCl_3$ dissociation as functions of the pressure of the buffer gas NO. When NO is added, the dissociation yield increases and reaches a maximum at a pressure of ≈ 1 Torr. A further increase in the buffer gas pressure leads to a decrease in the dissociation yield. The dissociation selectivity also depends on the NO pressure but is almost constant in the range from about 0.1 to 10 Torr. At NO pressures NO $\geqslant 10$ Torr and $\leqslant 0.1$ Torr, the selectivity decreases to unity [168]. The selectivity achieved in the experiments turned out to be relatively low ($\alpha(^{10}B/^{11}B) = 7$).

The authors of [168] examined the main reasons leading to the limitation of the selectivity of the process: spectral features of multiphoton excitation, secondary chemical reactions, and the short time of vibrational-vibrational (V–V) interisotopic energy exchange between excited and unexcited molecules. The selectivity of IR MPD of BCl_3 was found to be significantly affected by secondary chemical reactions of the dissociation products (BCl_2 or BCl radicals) with the BCl_3 molecules themselves and with radical acceptors. However, the authors did not rule out other mechanisms that limit the selectivity of molecule dissociation. The conditions were determined under which secondary chemical processes do not affect the parameters of isotope-selective dissociation of molecules: a BCl_3 pressure of $\leqslant 0.3$ Torr, NO pressure from 0.3 to 5 Torr, and time delay between pulses of $\Delta\tau = 150$ ns. The authors of [168] also estimated the energy costs for obtaining one ^{10}B atom using the method of two-frequency dissociation of molecules. This value turned out to be fairly high: $\geqslant 1.5$ keV per ^{10}B atom at a BCl_3 pressure of 0.3 Torr.

The authors analyzed the results obtained in [167, 168] in what regards the feasibility of implementing a technological process for separating boron isotopes based on two-frequency dissociation of BCl_3. Energy costs were high ($\geqslant 1.5$ keV per ^{10}B atom). The selectivity of dissociation $\alpha(^{10}B/^{11}B) \approx 7$ corresponds to enrichment in products with ^{10}B of up to 62%. Consequently, if a two-stage separation process is applied, enrichment at the level of 92% can be achieved. These parameters turn out to be worse than those obtained with single-frequency isotope-selective dissociation of $HClC{=}CHBCl_2$ molecules [11, 169] (see Section 9.2). However, in the opinion of the authors, to compare the competitiveness of these two approaches, it is necessary to take into account the economics of the separation process as a whole.

7.5 Selective dissociation of BCl_3 molecules by a free electron laser

In [165], the isotope-selective IR MPD of BCl_3 molecules by a free electron laser (FEL) was investigated. To compare the results obtained with the data on the dissociation of molecules by a CO_2 laser, the authors also conducted experiments on irradiating molecules with pulsed CO_2 laser radiation. We now analyze the results of these studies.

The dependences of the yields and selectivity of the dissociation of BCl_3 molecules on the intensity, frequency, and number of irradiation pulses and on the mode of irradiation by a free electron laser — micro- or macropulses — were obtained. The FEL generated in the frequency range of 5.5 – 12.5 μm. The generation linewidth was $\Delta\nu/\nu = 0.6\%$, and the average laser radiation power was 50 mW. The laser pulse consisted of a macropulse and micropulses. The pulse parameters are presented in Table 6. Each macropulse contained 268 micropulses.

BCl_3 molecules (at a pressure of 2 Torr) were irradiated in a mixture with H_2S molecules (at a pressure of 10 Torr) in a stainless steel cuvette 6 cm in length and 38 cm^3 in volume with KCl windows. The laser radiation was focused into the cuvette using a ZnSe lens with focal length $f = 30$ mm. Using H_2S as an acceptor resulted in the formation of the final product $HSBCl_2$ in the liquid phase. The FEL spot diameter in the focal region was 400 μm. The maximum radiation intensity was ≈ 1.5 GW cm^{-2}. The laser linewidth was about 6 cm^{-1}, which is significantly smaller than the isotopic shift (≈ 39.5 cm^{-1} [116]) between the absorption bands of the ν_3 vibrations of $^{10}BCl_3$ and $^{11}BCl_3$ molecules. This circumstance made it possible to study the selectivity of the molecular dissociation process. The fraction of dissociated molecules was determined from the intensity of the IR absorption bands of the molecules measured using a Fourier spectrometer before and after irradiation. The CO_2 laser energy was varied in the range from 50 to 600 mJ, while the laser radiation power was in the range from 5.5×10^8 to 6.5×10^9 W cm^{-2}.

It was found that the dissociation yield of molecules in the case of FEL excitation reached almost unity in the irradiated region where the radiation intensity exceeded the dissociation threshold. Figure 16a shows a decrease in the concentrations of $^{10}BCl_3$ and $^{11}BCl_3$ molecules upon their irradiation with the FEL at a frequency of 944 cm^{-1}. The current concentration N of molecules is normalized to their initial concentra-

Table 6. Characteristics of generation pulses of a free electron laser [165].

Parameters	Micropulse	Macropulse
Energy	18 μJ	5 mJ
Pulse duration	10 ps	12 μs
Pulse repetition frequency	22.3 MHz	10 Hz

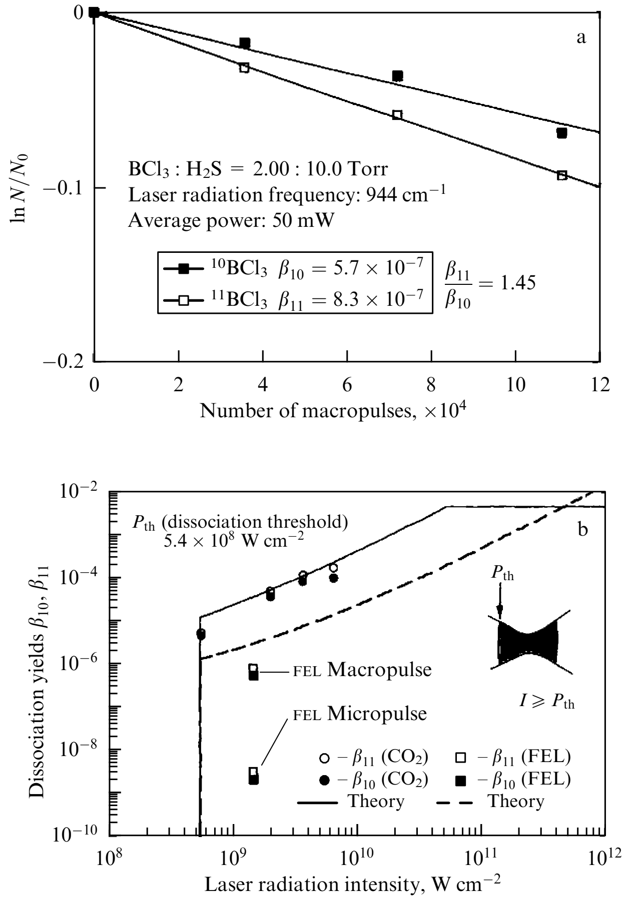

Figure 16. (a) Multiphoton dissociation of BCl_3 by a free-electron laser. (b) Dissociation yields of BCl_3 molecules depending on radiation intensity during irradiation with a free-electron laser and a CO_2 laser at a frequency of 944 cm^{-1}. Solid and dashed curves are dissociation yields for CO_2 laser and free-electron laser, respectively, calculated under the assumption that, in region where radiation intensity exceeds dissociation threshold ($I \geqslant P_{th}$), all BCl_3 molecules dissociate in one laser pulse or in one FEL macropulse. In calculations, it is assumed that $P_{th} = 540$ MW cm^{-2} [165].

tion N_0. Solid lines were obtained using the formula

$$N = N_0 \exp(-\beta_i S), \tag{7}$$

where S is the number of laser pulses and β_i is the dissociation yield of the ith BCl_3 isotopologue ($i = 10, 11$), averaged over the entire volume of the cuvette. In the described experiments, the dissociation yield per macropulse was 5.7×10^{-7} and 8.3×10^{-7} for $^{10}BCl_3$ and $^{11}BCl_3$, respectively. The isotopic selectivity was $\alpha(^{11}B/^{10}B) \approx 1.45$, which is comparable to the values obtained earlier in [156, 157]. The small values of selectivity are explained by the fast process of vibrational-vibrational (V–V) exchange between $^{11}BCl_3$ and $^{10}BCl_3$ molecules ($p\tau_{V\text{–}V} \approx 0.5$ µs Torr [111]) and the comparatively long duration (≈ 12 µs) of the exciting FEL macropulse. Under the conditions of the experiment, the duration of the exciting pulse was approximately two orders of magnitude longer than the time of V–V exchange between the molecules. The duration of the CO_2 laser pulse was comparable to the time of vibrational-vibrational energy exchange between the molecules.

Of interest is a comparison of the dissociation yields of BCl_3 molecules upon their irradiation with an FEL and a CO_2 laser. Figure 16b shows the dependences of the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules on the exciting radiation power upon their irradiation with an FEL (light and dark squares) and a CO_2 laser (light and dark circles). The molecules were irradiated at a frequency of 944 cm^{-1} (the 10P(20) generation line in the case of the CO_2 laser). The abscissa axis in Fig. 16b shows the intensity of the laser radiation in the focal region of the lens. The solid and dashed curves are the calculated dissociation yields when the molecules were irradiated with the CO_2 laser and the FEL, respectively. It was assumed in the calculations that, in the region where the laser intensity exceeded the dissociation threshold ($I \geqslant P_{th}$), all BCl_3 molecules dissociated during one CO_2 laser pulse or one FEL macropulse. The value $P_{th} = 540$ MW cm^{-2} was used in the calculations. Some studies [156–158] reported that the dissociation threshold for BCl_3 molecules due to pulsed CO_2 laser radiation is in the range of $10^8 - 10^9$ W cm^{-2}.

The results displayed in Fig. 16b show fairly good agreement between the experimental and calculated data for the case BCl_3 molecules excited by pulsed CO_2 laser radiation. When BCl_3 molecules were excited by an FEL macropulse, the experimental values of the dissociation yields were approximately 4–5 times lower than the calculated values. In the opinion of the authors, the dissociation of molecules occurs primarily during each exciting micropulse. The experimental result for the case of excitation of molecules by an FEL micropulse shown in Fig. 16b represents the lower limit, since the dissociation yield for a single micropulse could not be measured.

Finally, the study [165] under discussion showed that the selectivity of dissociation of BCl_3 molecules using the FEL is comparable to that by pulsed radiation from the CO_2 laser, while the dissociation yields under irradiation of molecules from the FEL are approximately 30–50 times lower than those under irradiation by the CO_2 laser. In the opinion of the authors of [165], the FEL can be used in a two-frequency BCl_3 dissociation scheme at the first stage for selective excitation of molecules, while the CO_2 laser can be employed for dissociation of excited particles, which will enhance the efficiency of isotope-selective dissociation of molecules.

7.6 Isotope-selective suppression of condensation of BCl_3 molecules by an IR laser

7.6.1 Early experiments. Condensation of BCl_3 molecules on a cold surface. Low-energy LIS methods have been experimentally investigated as applied to boron isotopes in only a few studies, in contrast to SF_6 molecules, which have been used in quite a lot of research [80–93] (see also reviews [78, 79] and references therein). However, already at the early stage of using IR lasers for isotope separation, methods were proposed for selecting molecules using heterogeneous processes that occur during the interaction of molecules with a cold surface. These methods are based on the difference in the probability of physical adsorption (or desorption) of excited and unexcited molecules incident on a cold surface covered with a condensed-phase layer. In the case of physical adsorption, the energies of adsorption E_{ad} and desorption E_{des} are the same, $E_{ad} = E_{des}$ [174]. The energies of adsorption of molecules on a surface covered with molecules (or clusters) are comparable to those of van der Waals interaction (0.1–0.5 eV [175]), i.e., are significantly less than the energy of dissociation of molecules ($\approx 3-5$ eV [49, 50]). Therefore, heterogeneous selective processes of adsorption and desorption are of great interest in what regards developing low-energy methods of molecular laser isotope separation.

Theoretical [176–179] and experimental [179–181] studies investigated various mechanisms leading to differences in the coefficients of adhesion (adsorption) to the surface for vibrationally excited and unexcited molecules. For example, it was assumed in [176] that the coefficient S of sticking of a polyatomic molecule to a surface can be represented by the formula

$$S = 1 - \exp\left(\frac{E_{\mathrm{ad}}}{E_{\mathrm{tot}}}\right), \tag{8}$$

where E_{tot} is the total energy of the incident molecule (the sum of translational, vibrational, and rotational energies)

$$E_{\mathrm{tot}} = E_{\mathrm{trans}} + E_{\mathrm{vib}} + E_{\mathrm{rot}}\,. \tag{9}$$

It follows from Eqn (8) that, due to the difference between the sticking coefficients (and, consequently, reflection) for selectively excited and unexcited molecules, it is possible to select molecules by isotopic and/or component composition. However, the description the complex processes of energy transfer during the interaction of molecules with a surface is this model is oversimplified. In [177–179], alternative mechanisms and factors affecting the reflection (sticking) of molecules to a cold surface were analyzed (see review [78] and references therein).

The models presented in [176–179] do indeed predict that the excitation of the internal degrees of freedom of molecules should hinder the condensation process. As for the experimental results, they contain many inconsistencies regarding the influence of the internal energy of molecules on physical adsorption. For example, experiments carried in [179, 180] (see also [181]) with CO and CO_2 molecules excited in an electric discharge [179] and with BCl_3 molecules excited by a laser [180] showed a fairly strong dependence of the condensation rate of molecules on their vibrational temperature. However, subsequent studies [182] failed to reproduce the results obtained in [180] and detect any noticeable influence of the internal energy of laser-excited BCl_3 molecules on the condensation process. At the same time, in the opinion of the authors of [182], the dependence of the condensation rate on the vibrational energy of molecules should not be excluded from consideration.

The influence of vibrational and translational energies of molecules on the probability of condensation (adsorption) during their collision with the condensed phase on a cold surface was studied in detail in [183] for CF_4 and SF_6 molecules using an effusion molecular beam (see also [184] and review [78]). It is worth noting that a slowdown in the condensation of molecules during their vibrational excitation was observed for $^{235}UF_6$ [185] and $CHCl_3$ [186] (see also review [78]).

In the quoted studies [176–186], selective heterogeneous processes were examined using continuous CO_2 lasers to excite molecules, when excitation of high vibrational states of molecules is unlikely. Molecules were predominantly excited to the first vibrational level with an energy of about 0.12 eV. Similar studies using powerful pulsed CO_2 lasers to excite molecules, when high vibrational states of molecules are excited, were carried out in [187–190]. These studies investigated the passage of vibrationally highly excited and unexcited SF_6 [187–189] and CF_3I [73, 190] molecules in a gas-dynamically cooled molecular beam through cooled multichannel plates and converging cones, and reflections from a cold surface covered with molecular (cluster) layers.

It has been shown [187–190] that molecules excited in a beam by intense laser IR radiation to high vibrational states with an energy in the range of $0.3 \leqslant E_{\mathrm{vib}} \leqslant 2.0$ eV pass through multichannel plates and cones cooled to $T_{\mathrm{s}} \approx 80-85$ K and are reflected from the surface significantly (by a factor of 3–5) more efficiently than unexcited molecules.

It has been found that the probabilities of molecules passing through a plate and cone and reflecting from the surface strongly depend on the energy density and on the frequency of the exciting laser radiation. This observation indicates that such processes can be used for laser selection of molecules in a beam by isotopic and/or component composition. However, the selectivity of the processes was not determined in the experiments [187–190]. Therefore, further studies are needed to clarify the selectivity and efficiency of the processes under consideration.

7.6.2 Isotope-selective suppression by an IR laser of clustering of BCl_3 molecules during gas-dynamic expansion at nozzle exit. To the best of our knowledge, isotope-selective suppression (slowing down) of the clustering of BCl_3 molecules with each other or with atoms (molecules) of the carrier gas during gas-dynamic expansion at the nozzle exit has not been experimentally studied in the context of laser separation of boron isotopes. However, many theoretical studies [3, 4, 6–9, 96–99] discuss in detail challenges and problems associated with separating boron isotopes using this particular method. Explored in these studies were various options for implementing the LIS method investigated by Jeff W. Eerkens for the case of SF_6 and UF_6 molecules [191, 192] using the slowdown of the condensation of BCl_3 molecules during gas-dynamic expansion at the nozzle exit.

In particular, in [96, 97], a statistical model of a two-step iterative scheme for separating boron isotopes by slowing down condensation (the SILARC method) has been developed. The combined effect of all important parameters of the setup and the irradiated gas and the relationship between them on the separation of boron isotopes was analyzed. These parameters include carrier gas, the degree of dilution of BCl_3 molecules in the carrier gas, laser pulse intensity, gas pulse duration, gas pressure and temperature in the irradiation chamber, optimal dimensions of the skimmer and irradiation chamber, and nozzle throughput. A method for finding the optimal values of these parameters was proposed, which is based on finding the global minimum of a certain objective function introduced by the authors. The minimum of this function is shown to be directly related to the minimum of the total energy consumed and the total volume of the setup.

Two types of industrial-scale setups for the LIS of boron are compared. The first contains a gas irradiation chamber with one large, high-capacity slot nozzle, while the second one has a chamber with many small nozzles arranged in parallel to provide better overlap with the laser beam (Fig. 17). The second type is shown to be preferable. It is asserted that NO_2 is the carrier gas, which provides the best efficiency for separating boron isotopes, while Ar is the best with regard to the compactness of the setup.

A new design of the setup for separating isotopes using the laser method is proposed in [98]. The setup parameters are determined using the separation optimization criterion based on the transport model of the rarefied gas flow dynamics. The limitations imposed by the condensation dynamics lead to the

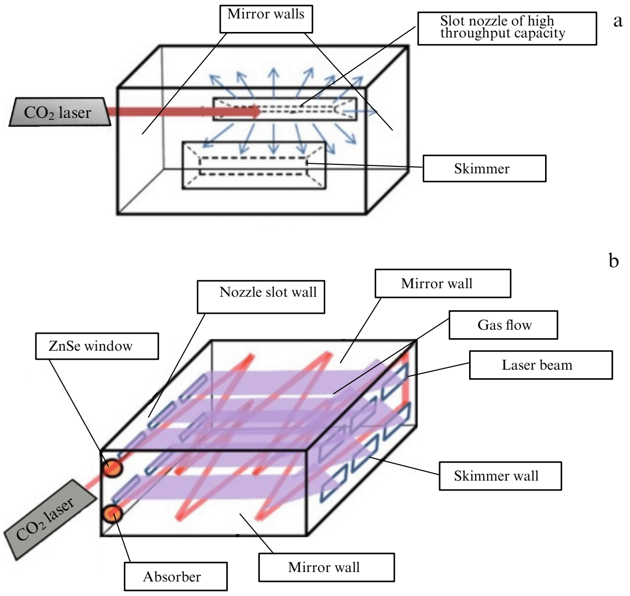

Figure 17. Schematic diagram of an industrial setup for separating boron isotopes with one nozzle (a) and many nozzles (b) [96].

conclusion that, since the yields and selectivities of molecule dissociation are small, enriched isotopes in this setup should be obtained in an iterative way. These iterations must be repeated until the desired level of enrichment of the separation gas flow is obtained. It is asserted that the method for calculating the optimal parameters of the experimental setup proposed by the authors can also be applied to separating isotopes of other elements. The optimal arrangement of the experimental setup is illustrated using the example of separating sulfur isotopes.

A new experimental setup for implementing isotope separation by slowing down condensation is proposed in [99]. The fundamental difference from other setups intended for isotope separation by this method is a specially designed CO$_2$ laser cavity into which a cell with the irradiated gas is placed. This arrangement allows expensive laser photons to be used more efficiently [193]. The case of continuous irradiation of a stationary gas flow is considered. It is shown that continuous gas irradiation with an irradiation cell located inside the cavity provides a significant (by a factor of 4.2–4.6) reduction in energy consumption.

The issues related to the development of a large industrial-scale setup for separating boron isotopes using the method of slowing down condensation are analyzed in [6]. A design of an industrial setup with a modular structure is proposed. Each module contains a gas irradiation chamber with a nozzle and a skimmer, which are installed on opposite sides. Using BCl$_3$ as a target gas in a mixture with an Ar carrier gas is considered. It is shown that irradiation of a gas flow with continuous radiation from a CO$_2$ laser is preferable to pulsed irradiation. Energy costs during continuous irradiation of a gas are approximately one third those using separation of boron isotopes by IR multiphoton dissociation of BCl$_3$ molecules.

Studies [7, 8] presented and described a scheme of an industrial installation for separation of boron isotopes by slowing down condensation of BCl$_3$ molecules (Fig. 18). A variant of multi-frequency irradiation of BCl$_3$ molecules with pulsed radiation from a CO$_2$ laser was examined. Resonant excitation of all four isotopologues (relative to chlorine isotopes) ^{11}BCl$_3$ by one pulsed laser was analyzed. In the pulsed mode, it is possible to obtain generation of a CO$_2$ laser on four different lines; therefore, excitation of all four isotopologues $^{11}\mathrm{B}^{35}\mathrm{Cl}_n^{37}\mathrm{Cl}_{3-n}$ $(n = 1, 2, 3)$ is possible, in principle. A formula for the rate of multilinear excitation of ^{11}BCl$_3$ molecules was derived. The total number of photons absorbed by the target gas was compared for the cases of multilinear pulsed irradiation and irradiation with a continuous laser. It was found that the efficiency of the pulsed mode is approximately 20.6 times lower than that of the continuous mode, mainly due to an increase in the duration of laser pulses of different frequencies during multilinear generation and the spread of the time delay (phase mismatch) between them. Calculations made in [8] showed that three-linear (three-frequency) excitation of molecules is more efficient. The main physical limitations on the laser intensity and its spectral properties were considered in [9]. The effect of laser generation frequencies and BCl$_3$ spectral properties at various temperatures and pressures on the efficiency of the SILARC method was discussed. The relationship between the gas flow properties, nozzle design, and the rate of irradiation chamber pumping was also determined.

Thus, in theoretical studies [6–9, 96–99], several models for describing the LIS of boron using the method of slowing down condensation were developed, and several schemes for the experimental implementation of this method in practice, including at a large-scale industrial facility, were proposed and analyzed. However, it should be noted that the results obtained in these studies are not associated with any experimental data obtained by this method (there are none for BCl$_3$ molecules). Using the example of SF$_6$ molecules, studies [85–91] (see also reviews [78, 79] and references cited therein) showed that slowing down condensation due to vibrational excitation of molecules by an IR laser is only realized in a small spatial region localized near the nozzle, in which dimers and small van der Waals molecules are formed. Outside this zone, the jet primarily contains already-formed dimers and larger clusters, and their IR absorption spectra differ significantly from those of the monomers. Therefore, isotope-selective dissociation of larger dimers and clusters requires laser radiation of a different wavelength.

Studies [3, 4] analyzed laser excitation of BCl$_3$ molecules mixed with carrier gases (He, N$_2$, Ar, Xe) and subsequent interaction of excited molecules with carrier gas particles using the Lennard–Jones parameters for both molecules and carrier gases in the calculations. The processes of energy transfer between particles due to vibrational-vibrational (V–V) and vibrational-translational (V–T) relaxation and dimer formation and dissociation are considered. It is shown that the highest enrichment factors in the products during excitation of cooled BCl$_3$ molecules with a carrier in the jet can be obtained using Xe atoms ($K_{\mathrm{enr}}^{\mathrm{pr}}(^{10}\mathrm{B}/^{11}\mathrm{B}) \approx 2$) or N$_2$ molecules ($K_{\mathrm{enr}}^{\mathrm{pr}}(^{10}\mathrm{B}/^{11}\mathrm{B}) \approx 1.7$) as a carrier, and the lowest, with He atoms ($K_{\mathrm{enr}}^{\mathrm{pr}}(^{10}\mathrm{B}/^{11}\mathrm{B}) \leqslant 1.2$). The results obtained in [3] are of importance for understanding the mechanism of transport of excited BCl$_3$ molecules in a mixture with carrier gases and for estimating the enrichment factors (selectivity) and the yield of enriched products. In study [4], the analytical equations and methods of theoretical calculations proposed in [191, 192] are used to investigate the transport of excited BCl$_3$ molecules taking into account such parameters as the gas pressure in the source, the nozzle throat radius, and the

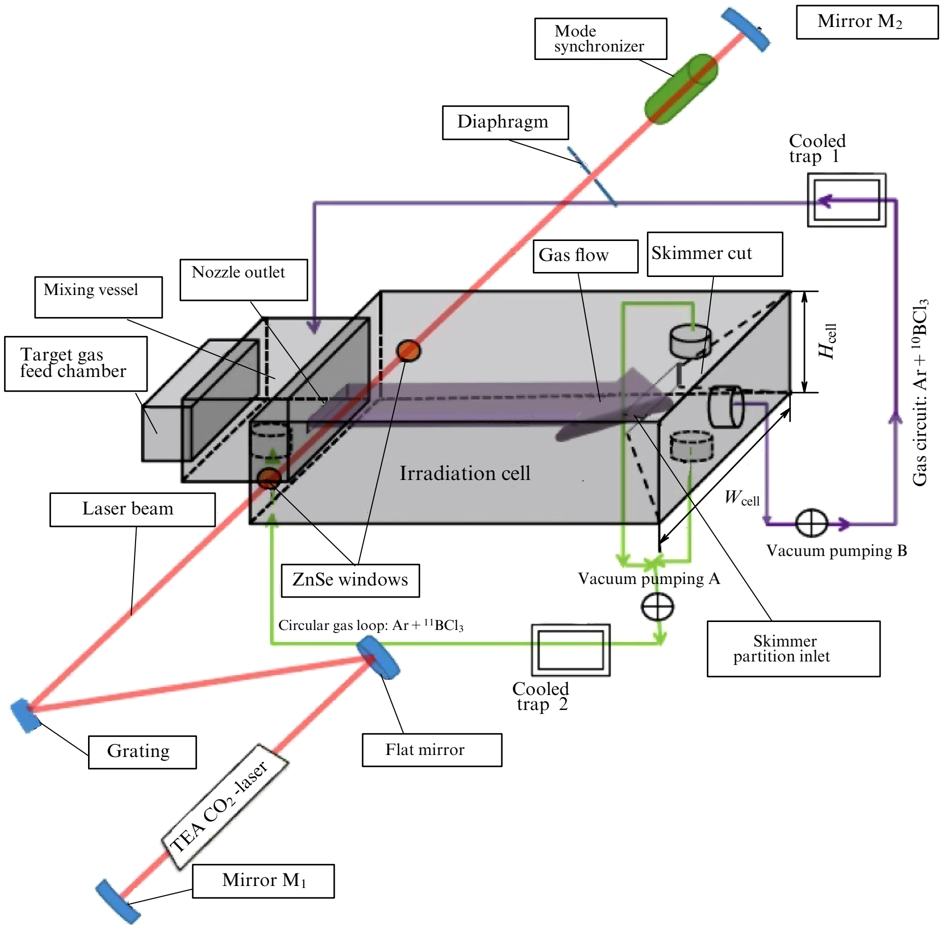

Figure 18. Schematic diagram of boron isotope enrichment setup (angles, lines, and details that are not visible from the front are shown in dotted lines). Laser beam passes through a semitransparent window and crosses molecular flow in perpendicular direction. To enhance excitation efficiency, laser beam intersects molecular flow many times, propagating inside a multipass cavity between mirror walls to irradiate entire molecular flow. With selective laser excitation of $^{11}BCl_3$ molecules, central part (core) of gas flow is enriched with $^{10}BCl_3$ isotopologue. Gas circulates from mixing tank also in opposite direction to compensate for pressure drop and to obtain a higher degree of enrichment with target isotope. Radius of curvature of mirrors M_1 and M_2 is assumed to be 2500 mm [8].

minimum jet temperature. It is shown that, the higher the jet temperature, the higher the product yield; and the higher the pressure, the lower the product yield and the higher the enrichment factor. Therefore, to optimize the isotope separation process, it is necessary to select the appropriate values of parameters.

7.7 Selective laser IR dissociation of van der Waals Ar-BCl_3 molecules

Study [162] investigated the isotope-selective IR dissociation of van der Waals Ar-BCl_3 molecules in a molecular beam (Fig. 19a) using a tunable continuous CO_2 laser. A quadrupole mass spectrometer was used to detect and determine the composition of the molecular beam. Ar-BCl_3 clusters were formed by supersonic expansion of a mixture of Ar and BCl_3 gases in the presence of a large amount of He through a continuous nozzle with a diameter of 50 μm [162]. To avoid the formation of $(BCl_3)_2$ dimers or larger clusters, the concentration of BCl_3 molecules in the gas above the nozzle did not exceed 1%.

Homogeneous irradiation of the beam was ensured by directing the CO_2 laser radiation (at a power density of up to 10 W cm^{-2}) without focusing towards the molecular beam through a mass spectrometer ionizer. The laser beam was modulated by a chopper; the intensity of a selected ion peak in the mass spectrum of the molecular beam was measured in the experiments, both with and without laser irradiation.

The variations in the ion peak intensities due to the dissociation of van der Waals Ar-BCl_3 molecules were measured as a function of the laser power and wavelength. The obtained photodissociation spectra of Ar-BCl_3 molecules are displayed in Fig. 19b. It is shown that homogeneous broadening dominates in the spectra, and the predissociation time is in the range of 1–3 ps. Options for applying the method under consideration for isotope separation in practice are discussed in terms of the process efficiency and selectivity (see also Section 10.1).

Figure 19b shows that the half-width of the photodissociation spectrum of $^{11}BCl_3$ molecules (and $^{10}BCl_3$ molecules) is $\leqslant 5\ cm^{-1}$, which is significantly less than the isotopic shift in the laser-excited vibration of $^{10}BCl_3$and $^{11}BCl_3$ molecules ($\Delta\nu_{is} \approx 39.5\ cm^{-1}$ [116]).

Consequently, isotope-selective IR vibrational predissociation of van der Waals Ar-BCl_3 molecules can, in principle, be used for laser separation of boron isotopes.

As regards the practical application of this method for isotope separation, its comparatively low efficiency should be noted, which is due to the inherent properties of the method

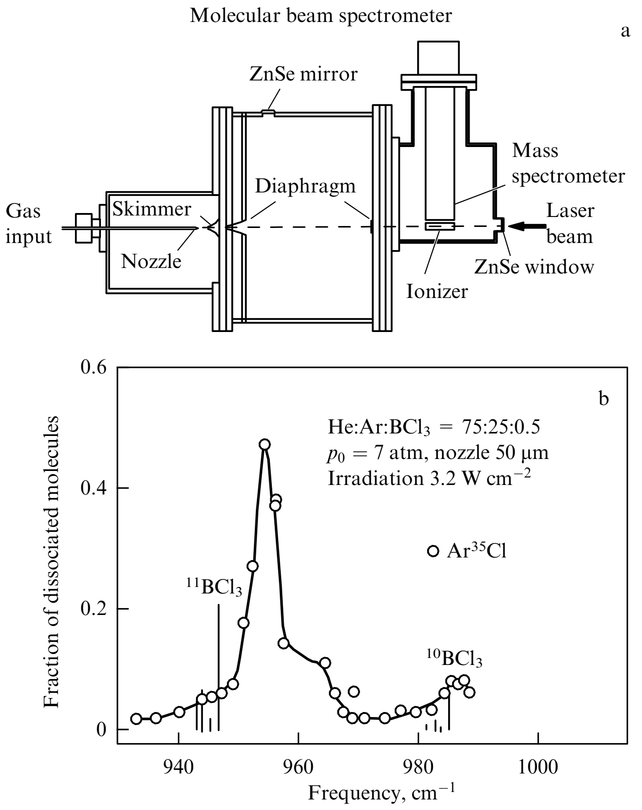

Figure 19. (a) Schematic diagram of molecular beam spectrometer. (b) IR photodissociation spectrum of Ar-BCl$_3$. Ar-BCl$_3$ dimers were detected as Ar^{35}Cl$^+$ ions. Line spectrum represents absorption of BCl$_3$ molecules dissolved in solid argon at a temperature of 75.8 K. Width of BCl$_3$ absorption lines in matrix is less than 0.1 cm^{-1} [162].

under consideration, in particular, its low productivity. For example, estimates made in [162] show that, although about 70% of Ar-^{10}BCl$_3$ molecules can be removed from a molecular beam, this is only a small fraction of the total number of ^{10}BCl$_3$ molecules in the beam. The concentration of van der Waals dimers in the beam is only a few percent of the total concentration of BCl$_3$ gas above the nozzle. Therefore, under the conditions of the experimental setup described above (nozzle diameter of 50 μm, total gas pressure above the nozzle of about 7 atm), several years of continuous irradiation, gas recirculation, and product collection would be required to separate 1 mole of ^{10}BCl$_3$ from the natural mixture of isotopologues. However, the productivity of such a setup can easily be increased, for example, by a factor of 100, if large vacuum pumps and nozzles with large-diameter holes are used. This would reduce the required time to several days [162].

8. Efficient isotope-selective IR multiphoton dissociation of BCl$_3$ molecules mixed with a sensitizer and SF$_6$ radical acceptor

It is shown in Sections 7.1–7.5 that efficient IR MPD of BCl$_3$ molecules requires fairly high energy densities of the exciting laser radiation ($\Phi \geqslant 20$ J cm^{-2}) [157, 158], which is primarily due to the high binding energy of the molecule (≈ 110 kcal mol^{-1} [49, 50]). Therefore, IR dissociation of molecules is only possible with focused laser beams. However, the use of focused laser beams usually leads to a decrease in the isotope selectivity of the molecular dissociation and the irradiated gas volume [72–77]. The best parameters are realized with isotope-selective dissociation of BCl$_3$ molecules in a two-frequency IR laser field [167, 168].

Recently, it has been found in [1, 2] that, if SF$_6$ molecules are used as an acceptor of radicals in isotope-selective laser IR multiphoton dissociation, which are also effective sensitizers for BCl$_3$ molecules, a significant increase in the selectivity and yield of ^{11}BCl$_3$ molecule dissociation along with a significant decrease in the threshold energy density of dissociation by single-frequency IR radiation occur. As a result, it becomes possible to carry out single-frequency isotope-selective dissociation of ^{11}BCl$_3$ molecules in unfocused laser beams at a moderate ($\approx 3-5$ J cm^{-2}) excitation energy density, which is very important in the practical implementation of the technological process of laser separation of boron isotopes. We now consider the results obtained in these studies.

8.1 Experimental setup and research method

The experimental setup (Fig. 20) included a tunable pulsed CO$_2$ laser, forming optics, a stainless steel gas cell (for irradiating the molecules under study) 112 mm long, 24.2 cm^3 in volume, with KBr windows, and radiation receivers for measuring the energy incident on and transmitted through the cell. The CO$_2$ laser radiation pulse consisted of a leading peak with a duration of about 80 ns at half-maximum and a tail with a duration of $\approx$ 750 ns, which contained approximately one third of the laser pulse energy. The laser beam was collimated into the irradiated cell by a long-focus ($f = 100$ cm) lens. Due to the small length of the cell, the size of the laser spot and the energy density of the laser radiation were approximately the same along its entire length. The laser radiation energy in a pulse varied from 0.7 to 3.0 J, depending on the generation frequency and the partial composition of the laser mixture. The laser radiation frequency was tuned in the range of $\approx 929.0-985.5$ cm^{-1}. An optical-acoustic receiver with an NH$_3$ reference gas was used to reference the frequency of the CO$_2$ laser radiation lines. The transverse distribution of the energy density and the cross-sectional area of the laser beam were determined using a microprobe by scanning it across the laser beam in mutually perpendicular directions at the input and output of the cuvette.

Most experiments on isotope-selective dissociation of BCl$_3$ molecules in a mixture with SF$_6$ were carried out [1, 2] with the CO$_2$ laser radiation frequency tuned to the 10P(32) line (frequency 932.96 cm^{-1}), which coincides with the long-wavelength wing of the absorption band of the ν_3 vibrations of ^{11}BCl$_3$ molecules (≈ 954.2 cm^{-1} [116]). The absorption

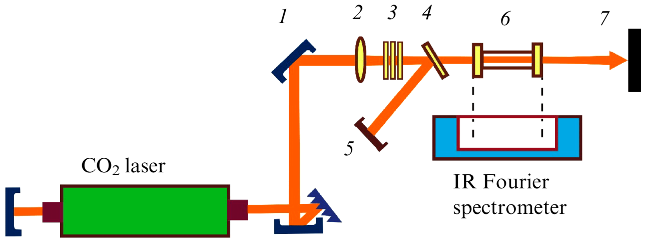

Figure 20. Schematic diagram of experimental setup. *1* — mirror, *2* — long-focus lens, *3* — laser radiation attenuators, *4* — splitting plate, *5* — radiation receiver, *6* — cuvette with irradiated gas, *7* — radiation absorber [1, 2].

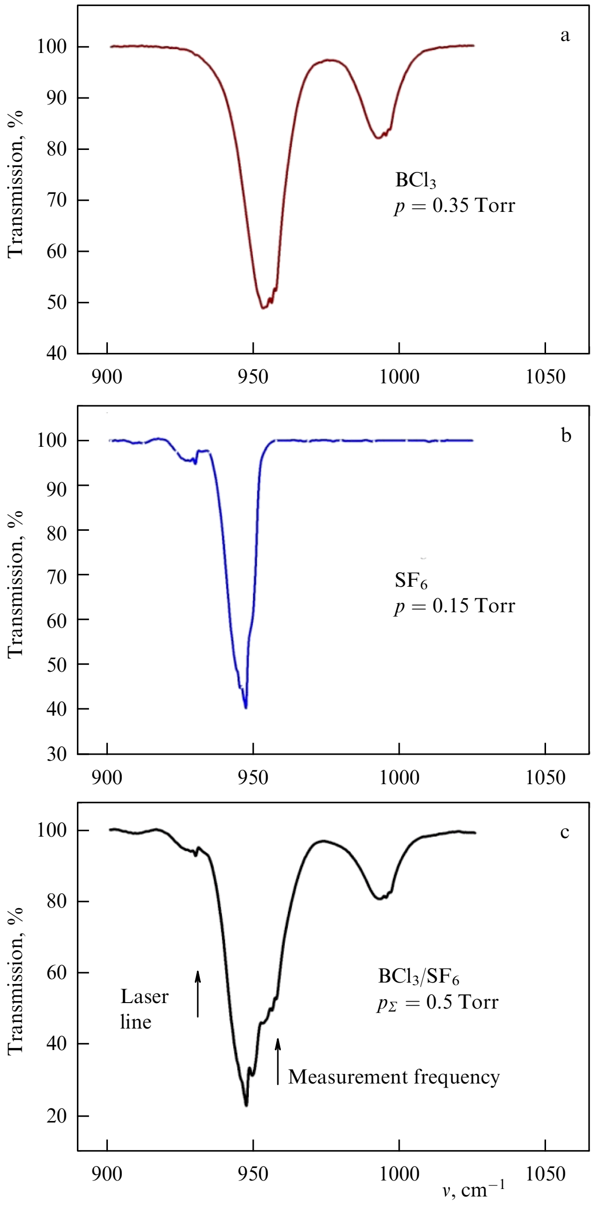

Figure 21. (a) IR absorption bands of ν_3 vibrations of ^{11}BCl$_3$ and ^{10}BCl$_3$ molecules. BCl$_3$ pressure in cuvette is 0.35 Torr; cuvette length is 11.2 cm. (b) IR absorption band of SF$_6$ vibrations of ν_3 molecules. SF$_6$ pressure in cuvette is 0.15 Torr. (c) IR absorption bands of vibrations of ν_3 molecules ^{11}BCl$_3$, ^{10}BCl$_3$, and SF$_6$. BCl$_3$ pressure in cuvette is 0.35 Torr; SF$_6$ pressure is 0.15 Torr [1, 2].

band of the ν_3 vibrations of SF$_6$ molecules (≈ 948 cm^{-1} [194]) is shifted by approximately 6.2 cm^{-1} to the low-frequency side from the center of the absorption band of ^{11}BCl$_3$ molecules (Fig. 21a–c).

During laser IR multiphoton excitation of ^{11}BCl$_3$ and SF$_6$ molecules, their IR absorption bands are shifted to the red side (towards the laser radiation frequency) due to the anharmonicity of the vibrations and come into optimal resonance with the laser field [195–199]. An efficient IR multiphoton excitation of both types of molecules, including SF$_6$ molecules, occurs, the absorbed energy from which is transferred to ^{11}BCl$_3$ molecules. Since the absorption bands of SF$_6$ and ^{11}BCl$_3$ molecules almost coincide, vibrational-vibrational (V–V) energy exchange between them has a resonant character and proceeds very efficiently [199–201]. This leads to an increase in the dissociation yield of ^{11}BCl$_3$ molecules. The mechanisms and probability of vibrational energy transfer during simultaneous laser IR multiphoton excitation of molecules in a two-component molecular medium are investigated in more detail (using the example of a mixture of CF$_2$HCl/CF$_3$Br molecules) in recent studies [197, 198]. It should be noted that, since the dissociation energy of SF$_6$ molecules (≈ 92 kcal mol^{-1} [202]) is less than that of BCl$_3$ molecules, at high excitation energy densities, dissociation of SF$_6$ molecules also occurs.

The dissociation yields β_{11} and β_{10} were determined based on the changes in the intensity of the bands in the IR absorption spectra for each of the isotopic components of BCl$_3$ using Eqn (3), where $\Gamma \approx 0.083$ is the ratio of the irradiated volume ($V_{\rm irr} \approx 2.0$ cm^3) to the volume of the cuvette ($V_{\rm cell} = 24.2$ cm^3), and N is the number of irradiation pulses. The absorption spectra were measured using an FT-801 IR Fourier spectrometer. Since the IR absorption bands of ^{11}BCl$_3$ and SF$_6$ molecules overlap (Fig. 21c), measuring the ^{11}BCl$_3$ gas flow rate using the IR absorption spectrum required special attention. The absorption band intensity of ^{11}BCl$_3$ molecules before and after irradiation was measured at a frequency of ≈ 954.2 cm^{-1} (at approximately the maximum of the ^{11}BCl$_3$ absorption band), at which there was virtually no contribution from the absorption of SF$_6$ molecules at the pressures used in the experiment (Fig. 21b, c). The selectivity $\alpha(^{11}\mathrm{B}/^{10}\mathrm{B})$ was determined as the ratio of the dissociation yields of ^{11}BCl$_3$ and ^{10}BCl$_3$ molecules using Eqn (4).

Experiments [1, 2] measured the main parameters of isotope-selective laser IR MPD of BCl$_3$ molecules: dissociation yields of ^{11}BCl$_3$ (β_{11}) and ^{10}BCl$_3$ (β_{11}) molecules and the dissociation selectivity of ^{11}BCl$_3$ molecules with respect to ^{10}BCl$_3$ molecules, ($\alpha(^{11}\mathrm{B}/^{10}\mathrm{B})$). The dependences of these parameters on the pressures of the irradiated BCl$_3$ and SF$_6$ gases and the energy density and frequency of the exciting laser radiation were obtained. The main products formed were identified.

8.2 Results of studies of parameters of isotope-selective dissociation of BCl$_3$

8.2.1 Dependences of yields and selectivity of BCl$_3$ dissociation on SF$_6$ pressure.

Figure 22 shows the results representing the measurement technique. The IR absorption bands of the ν_3 vibrations of ^{11}BCl$_3$, ^{10}BCl$_3$, and SF$_6$ molecules before (*1*) and after (*2*) laser irradiation are displayed. Also shown are the IR absorption bands of the ν_1 (≈ 851.4 cm^{-1}) and ν_8 (≈ 909.1 cm^{-1}) vibrations of the SF$_5$Cl product being formed. The initial pressure of BCl$_3$ in the cuvette is 0.35 Torr, and that of 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$_5$Cl, the molecules of BCl$_2$F, BClF$_2$, and BF$_3$ were also detected in the products being formed (the IR absorption spectra of other products are not shown in Fig. 22).

The dissociation yields β_{11} and β_{10}, respectively, of ^{11}BCl$_3$ and ^{10}BCl$_3$ molecules and the selectivity of dissociation of ^{11}BCl$_3$ molecules with respect to ^{10}BCl$_3$ molecules, $\alpha(^{11}\mathrm{B}/^{10}\mathrm{B})$ as functions of the SF$_6$ pressure in the range of 0.05–2.0 Torr at a fixed BCl$_3$ pressure of 0.35 Torr and an excitation radiation energy density of $\Phi \approx 2.1$ J cm^{-2} are presented in Fig. 23a, b. It is apparent that, in the studied range of SF$_6$ pressures, the dissociation yields of ^{11}BCl$_3$ and ^{10}BCl$_3$ molecules increase, respectively, from $\beta_{11} \approx$

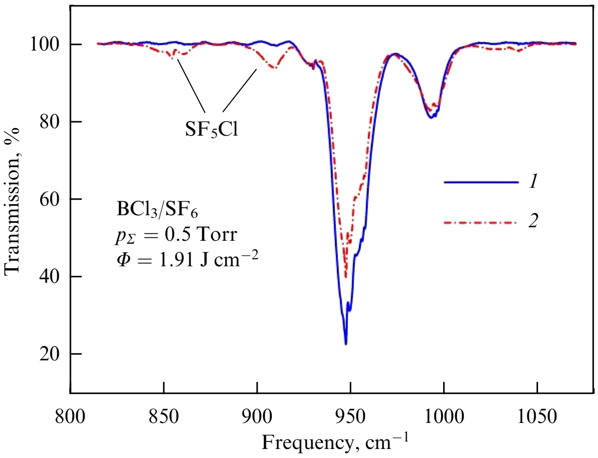

Figure 22. IR absorption bands of ν_3 vibrations of $^{11}BCl_3$, $^{10}BCl_3$, and SF_6 molecules before (*1*) and after (*2*) laser irradiation. IR absorption bands of resulting SF_5Cl product with band centers at frequencies of 851.4 cm^{-1} (vibration ν_1) and 909.1 cm^{-1} (vibration ν_8) are also displayed. Initial pressure of BCl_3 in cuvette is 0.35 Torr; SF_6 pressure is 0.15 Torr. Energy density of exciting laser radiation is 1.91 J cm^{-1}. Number of irradiation pulses $N = 1800$ [1, 2].

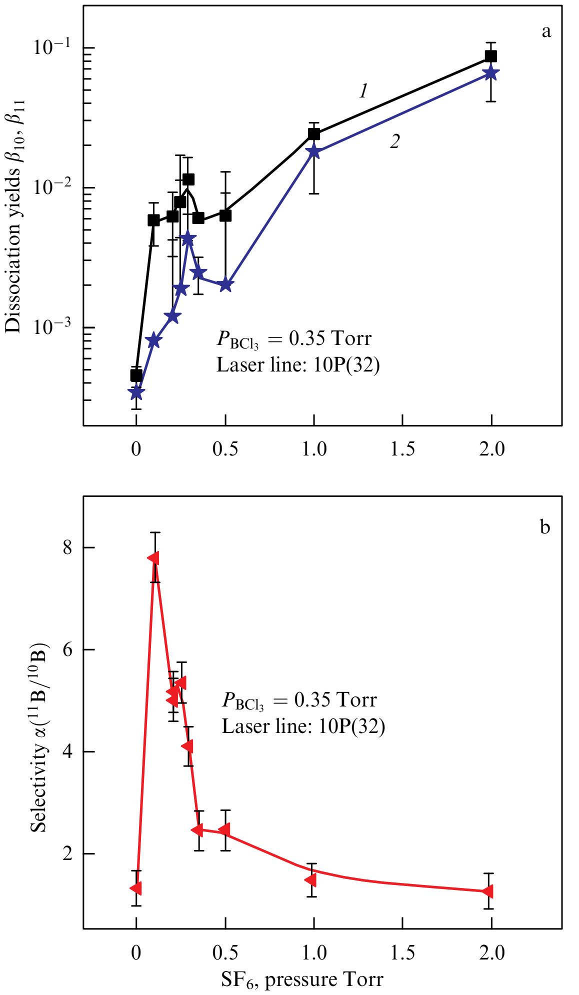

Figure 23. Dependences of (a) dissociation yields β_{11} (curve *1*) and β_{10} (curve *2*) and (b) dissociation selectivity $\alpha(^{11}B/^{10}B)$ on SF_6 pressure at fixed BCl_3 pressure of 0.35 Torr and exciting radiation energy density of 2.1 J cm^{-1} [2].

4.5×10^{-4} and $\beta_{10} \approx 3.4 \times 10^{-4}$ when BCl_3 molecules are irradiated without SF_6 to $\beta_{11} \approx 8.5 \times 10^{-2}$ and $\beta_{10} \approx 7.2 \times 10^{-2}$ when BCl_3 molecules are irradiated with SF_6 at a pressure of 2.0 Torr.

The results presented in Fig. 23a show that, when irradiating BCl_3 molecules mixed with SF_6, the dissociation yields of BCl_3 molecules increase by more than two orders of magnitude. Note the sharp increase (by more than an order of magnitude) in the dissociation yield of $^{11}BCl_3$ molecules when only 0.1 Torr of SF_6 is added to 0.35 Torr of BCl_3. This also implies that the threshold energy density of dissociation of $^{11}BCl_3$ molecules decreases significantly due to the addition of SF_6. The increase in the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules with increasing SF_6 pressure in the range of $\approx 0.5-0.2$ Torr is monotonic and reflects the increase in the amount of energy transferred to BCl_3 molecules from SF_6 molecules excited by the laser.

The selectivity of dissociation of $^{11}BCl_3$ molecules with respect to $^{10}BCl_3$ molecules (Fig. 23b) increases sharply from $\alpha(^{11}B/^{10}B) \approx 1.3$ in the case of molecules irradiated without SF_6 to $\alpha(^{11}B/^{10}B) \approx 7-8$ when molecules are irradiated with SF_6 at a pressure of $\approx 0.15-0.2$ Torr. With a further increase in the SF_6 pressure to ≈ 0.4 Torr, the selectivity rapidly falls to $\alpha(^{11}B/^{10}B) \approx 3.0$ and then slowly decreases to $\alpha(^{11}B/^{10}B) \approx 1.0$ at an SF_6 pressure of $\geqslant 1.5$ Torr. The rapid drop in the selectivity $\alpha(^{11}B/^{10}B)$ in the region of $\approx 0.15-0.4$ Torr is probably associated with a sharp decrease in the amount of energy transferred to the $^{11}BCl_3$ molecules from the SF_6 molecules. The main reason for this behavior may be the 'escape' of energy from the laser-excited ν_3 SF_6 mode (resonant with the vibration of $^{11}BCl_3$ molecules) to other modes of the molecule as a result of intramolecular intermode vibrational-vibrational (V–V) energy relaxation.

The decrease in the selectivity of $^{11}BCl_3$ molecule dissociation with increasing SF_6 pressure at high pressure values is associated with the acceleration of the vibrational-vibrational energy exchange between the 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 selectivity of $\alpha(^{11}B/^{10}B)$ dissociation are achieved at an SF_6 pressure in the range of 0.15–0.25 Torr. 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 BCl_3 molecules irradiated without SF_6.

8.2.2 Dependences of yields and dissociation selectivity of BCl_3 on energy density of exciting laser radiation. It should be noted that the dependences of the yields and dissociation selectivity of BCl_3 molecules on the energy density of the exciting laser radiation using unfocused irradiation geometry with single-frequency excitation, which are of great interest in terms of practical applications, have not been previously studied. This situation is due to the fact that high energy densities required for efficient dissociation of molecules are difficult to achieve without radiation focusing, since they lead to the destruction of the windows of the cuvette in which the molecules are irradiated. Such dependences with the unfocused geometry of BCl_3 irradiation were obtained in [1, 2] precisely due to a significant increase in the efficiency of BCl_3 molecule dissociation due to the use of a sensitizer and radical acceptor, SF_6 molecules. Figure 24a, b shows the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules and the dissociation selectivity $\alpha(^{11}B/^{10}B)$ as functions of

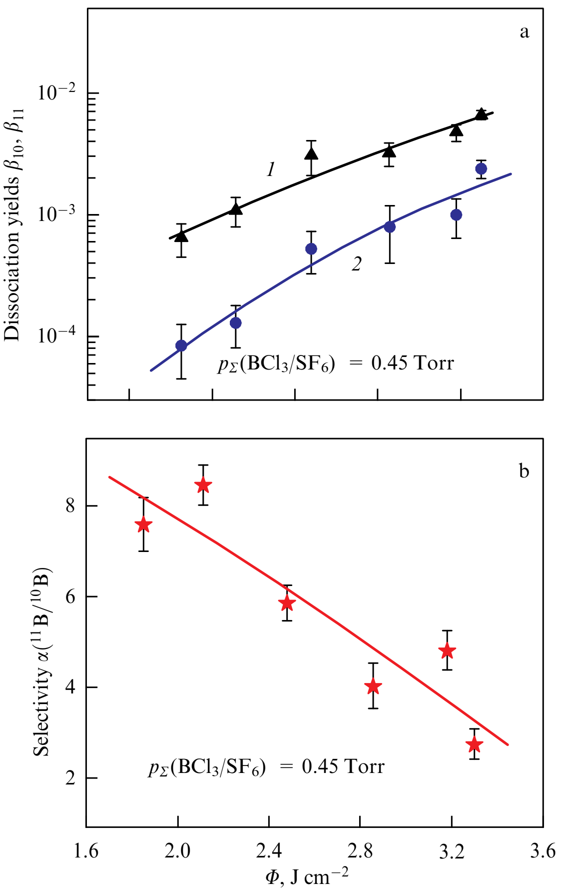

Figure 24. Dependences of (a) dissociation yields β_{11} (curve *1*) and β_{10} (curve *2*) and (b) dissociation selectivity $\alpha(^{11}B/^{10}B)$ on energy density of exciting laser radiation. Gas pressure in cuvette: 0.35-Torr BCl_3 + 0.1-Torr SF_6 [2].

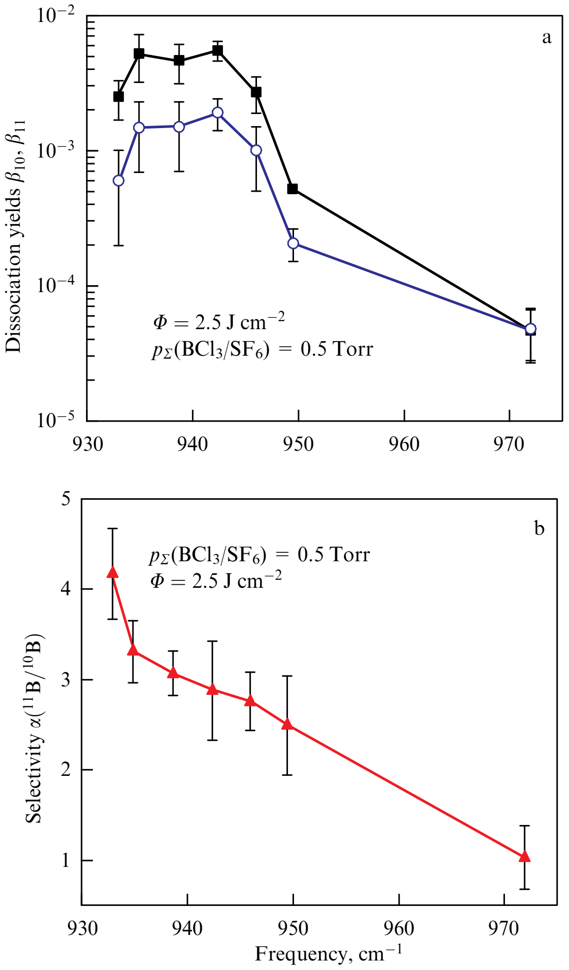

Figure 25. Dependences of (a) dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules and (b) dissociation selectivity $\alpha(^{11}B/^{10}B)$ on frequency of exciting laser radiation. Mixture of 0.35-Torr BCl_3 + 0.15-Torr SF_6 molecules was irradiated at excitation radiation energy density of 2.5 J cm^{-1} [2].

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 $^{11}BCl_3$ + 0.1-Torr SF_6 molecules was irradiated. It is apparent that the dissociation yields of BCl_3 molecules rapidly increase with increasing excitation energy density. Such a rapid increase in dissociation yields is explained by the fact [72, 76, 77] that, due to the high binding energy of molecules at such laser radiation energy densities, dissociation occurs above the threshold and is comparatively far from saturation.

The selectivity of dissociation of $^{11}BCl_3$ $\alpha(^{11}B/^{10}B)$ molecules, on the contrary, decreases sharply with increasing excitation energy density. At the same time, at all studied excitation energy densities, the selectivity of dissociation using SF_6 is significantly (2 to 5 times) higher than that without SF_6. The observed behavior of the dependences of dissociation yields and selectivity on the energy density of excitation laser radiation (a sharp increase in the dissociation yield and a decrease in selectivity with increasing excitation energy density) is characteristic of isotope-selective IR MPD of a large number of molecules [72, 76, 77].

8.2.3 Dependences of BCl_3 dissociation yields and selectivity on frequency of excitation laser radiation. Figure 25a, b shows the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules and the dissociation selectivity $\alpha(^{11}B/^{10}B)$ as functions of the frequency of the exciting laser radiation in the region of the P branch 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 region of the R branch of the CO_2 laser radiation (at a frequency of ≈ 971.9 cm^{-1}, the 9R(14) laser line) are also presented. A mixture of 0.35 Torr BCl_3 + 0.15 Torr SF_6 molecules was irradiated at an exciting radiation energy density of 2.5 J cm^{-2}. It is apparent that the maximum dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules are observed in the frequency range of ≈ 935 – 948 cm^{-1}, while the maximum selectivity is in the region of ≈ 932.96 cm^{-1} (on the 10P(32) laser generation line).

The dependences of the dissociation yields of BCl_3 molecules on the frequency of the exciting laser radiation obtained in [1, 2] correlate fairly well with similar data from [156, 157], where the geometry of irradiation of molecules with focused laser radiation was used. The significant difference between these data and those of [156, 157] is that both the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules and the dissociation selectivity of $^{11}BCl_3$ molecules reported in [1, 2], are notably greater than the similar quantities observed in [156, 157].

If BCl_3 molecules are irradiated in a mixture with SF_6, a very large contribution to the increase in the yield and selectivity of $^{11}BCl_3$ dissociation is made by resonant vibrational-vibrational (V–V) energy exchange between BCl_3 and SF_6 molecules, which occurs under conditions of a comparatively high density of the irradiated gas (total pressure of 0.5–1.5 Torr). The role of vibrational-vibrational energy exchange between molecules, including those of different types, is especially great if almost resonant vibrational levels of molecules are available [201] (see also [203]), which was realized in our experiments.

The frequency dependences of the dissociation yields of $^{11}BCl_3$ and $^{10}BCl_3$ molecules and the dissociation selectivity of $^{11}BCl_3$ molecules show that it is precisely due to the resonance energy transfer from SF_6 molecules (the IR absorption band of which coincides well with that of $^{11}BCl_3$ molecules) to $^{11}BCl_3$ molecules that the efficiency of isotope-selective dissociation of $^{11}BCl_3$ molecules is strongly enhanced. This is exhibited by a significant increase in the yield and selectivity of dissociation of molecules and a decrease in the threshold energy density of their dissociation.

8.2.4 Identification of formed products. The gaseous products formed as a result of laser IR MPD of BCl_3 molecules mixed with SF_6 and subsequent chemical reactions were identified by their IR absorption spectra in the spectral region from approximately 750 to 3600 cm^{-1}. In most of the experiments, the partial pressures of the irradiated BCl_3 and SF_6 gases in the cuvette were in the range of 0.1–1.0 Torr, and the BCl_3/SF_6 pressure ratio was approximately 5/1 to 1/10. It was found in [1, 2] that the composition and amount of the formed products depend on the ratio of the partial pressures of the initial BCl_3 and SF_6 gases and on the degree of their production during irradiation.

At small $^{11}BCl_3$ production yields ($\leqslant 15-20\%$), the main end products were SF_5Cl and $^{11}BCl_2F$ (Fig. 26). At $^{11}BCl_3$ consumption levels exceeding 20–30% and at partial pressures of SF_6 significantly exceeding the partial pressure of BCl_3, the composition of the formed products was much broader: SF_5Cl, $^{11}BCl_2F$, and $^{10}BCl_2F$, $^{11}BClF_2$ and $^{10}BClF_2$. At even higher BCl_3 consumption levels ($\geqslant 35-40\%$), the main final products were SF_5Cl, $^{11}BF_3$, 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, at a high temperature of the mixture at the moments of irradiation with a laser pulse and the presence of fluorine atoms in the reaction volume (in the composition of the SF_6 acceptor), the latter effectively substitute chlorine atoms in the BCl_2F and $BClF_2$ molecules [1, 2].

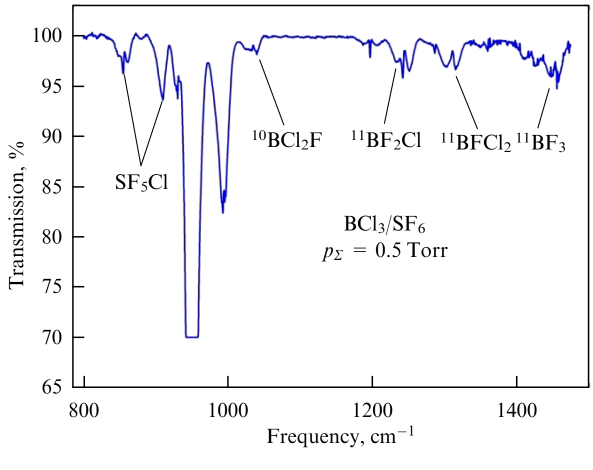

Figure 26. IR absorption bands of products formed as a result of laser IR multiphoton dissociation of BCl_3 molecules in a mixture with SF_6 and subsequent chemical reactions. A mixture of 0.35-Torr BCl_3 + 0.15-Torr SF_6 molecules was irradiated [2].

8.2.5 Conclusions. The studies conducted in [1, 2] showed that the efficiency of isotope-selective dissociation of $^{11}BCl_3$ molecules in a mixture with a gas that resonantly absorbs laser radiation (an optically active sensitizer) and an acceptor of radicals, SF_6, greatly increases due to the resonant energy transfer from SF_6 molecules to $^{11}BCl_3$ molecules. The main products that form 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 has been shown that irradiation of BCl_3 in a mixture with SF_6 results in a significant increase in the dissociation yield of $^{11}BCl_3$ molecules (by 1–2 orders of magnitude) and dissociation selectivity (by 2–5 times) and a significant decrease in the threshold energy density of dissociation (by about an order of magnitude) compared to BCl_3 irradiation without SF_6. This provides new options for implementing single-frequency isotope-selective laser IR dissociation of $^{11}BCl_3$ molecules in unfocused laser beams at a moderate ($\leqslant 4-5$ J cm^{-2}) excitation energy density.

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

9. Results of studies on laser separation of boron isotopes using $HClC{=}CHBCl_2$ molecules

As noted in Section 6, due to the good coincidence of the IR absorption bands of BCl_3 molecules with the 10.6-μm generation band of the CO_2 laser, strong absorption of the molecules, and the commercial availability of this product, at the initial stage of the development of boron LIS, almost all experimental studies were carried out using BCl_3 molecules. About a decade later, in 1980, Jensen et al. reported in [110] that 2-chloroethenyldichloroborane ($HClC{=}CHBCl_2$) was obtained and experiments on isotope-selective IR MPD of molecules and separation of boron isotopes were carried out with this substance. Somewhat later, the isotope-selective dissociation of this molecule was studied in [169–172] and, more recently, in [10, 11]. It should be noted that, in the case of 2-chloroethenyldichloroborane molecules, as in the case of BCl_3, there is a very good coincidence of its intense IR absorption bands with the 10.6-μm generation band of a CO_2 laser (see Section 4.2). The physical and chemical properties of this compound are described in [118–122]. In subsequent Sections 9.1 and 9.2, we consider the results of studies on isotope-selective dissociation of $HClC{=}CHBCl_2$ molecules.

9.1 First experiments: demonstration of isotope selectivity of a process

In study [110], experiments on isotope-selective dissociation of $HClC{=}CHBCl_2$ molecules with a CO_2 laser were carried out using a reaction cell made of a brass cylinder with an internal diameter of 2.5 cm, a length of 7.5 cm, and windows made of NaCl. The laser energy was less than 1 J per pulse. The cross section of the laser beam inside the cuvette was 1.0 × 1.5 cm. The studies showed that, when 2-chloroethyldichloroborane is irradiated (at a pressure of 1–10 Torr) with a CO_2 laser tuned to the absorption bands of molecules in the spectral region of 950–1000 cm^{-1}, BCl_3 and C_2H_2 are formed, i.e., the same compounds from which it was synthesized. The resulting BCl_3 gas absorbs laser radiation at virtually the same frequencies as those of the asymmetric stretching vibration of the B–Cl bond of $HClC{=}CHBCl_2$ molecules. The absorption of BCl_3 molecules at these frequencies is much stronger than that of $HClC{=}CHBCl_2$ molecules. Consequently, during the irradiation of molecules, the absorption at frequencies in the region of 960 and 990 cm^{-1} will increase as the concentrations of $^{11}BCl_3$ and $^{10}BCl_3$ molecules increase. The relative changes in the intensities of these bands will reflect enrichment in the dissociation products. Conversely, the absorption in the region of the stretching vibration of the B–C bond of the $HClC{=}CHBCl_2$ molecules will decrease, since the concentration of these molecules decreases as a result of their dissociation. The relative changes in these peaks can be used to determine the isotopic enrichment in the starting product. These expected changes in the intensities of the IR absorption peaks during irradiation of the molecules are summarized in the last column of Table 1.

Figure 27 shows the IR absorption spectra obtained (using a Beckman IR-7 spectrophotometer) before and after irradiation of $HClC{=}CHBCl_2$ molecules with sixteen pulses of a CO_2 laser with a pulse energy of 0.9 J at a generation frequency of 934.9 cm^{-1} (the 10P(30) laser line). Spectrum (*1*) was obtained with an empty cuvette, spectrum (*2*), with $HClC{=}CHBCl_2$ gas in the cuvette at a pressure of 2.9 Torr before irradiation, and spectrum (*3*), after irradiation of the gas. The absorption at a frequency of about 1060 cm^{-1} is atmospheric. In the described experiments, the authors observed predominant dissociation of $HClC{=}CHBCl_2$ molecules containing the ^{11}B isotope. The relative proportions of the dissociated $HClC{=}CH^{10}BCl_2$ and $HClC{=}CH^{11}BCl_2$ molecules were 0.56 ± 0.04 and 0.68 ± 0.02, respectively. The selectivity of the dissociation process in these experiments was $\alpha(^{11}B/^{10}B) = 1.21$.

If 2-chloroethenyldichloroborane molecules are irradiated at a frequency of 986.6 cm^{-1} (generation line of the 10R(38) CO_2 laser), resonant with the absorption band of molecules containing the ^{10}B isotope, predominant dissociation of $HClC{=}CH^{10}BCl_2$ occurs, the dissociation selectivity being $\alpha(^{10}B/^{11}B) = 1.58$.

According to the authors, the obtained small values of the dissociation selectivities are due to the following reasons. First, nonselective thermal decomposition of some molecules may have occurred due to the high temperature during irradiation. Second, the optimal frequencies for gas irradiation were not selected. Third, highly reactive fragments (e.g., hydrogen atoms) could have formed during the dissociation of molecules, which could have interacted in a nonselective way with the initial molecules. It should be added that the use of a comparatively high pressure (3 Torr) of the irradiated gas in the first experiments [110] also led to a decrease in selectivity.

Finally, the authors of [110] synthesized a gaseous boron-containing product suitable for conducting experiments on the separation of boron isotopes using powerful CO_2 lasers and demonstrated the isotopic selectivity of its dissociation. Selective dissociation of this molecule was shown to occur at significantly lower energy densities of the exciting laser radiation than the dissociation of BCl_3 molecules. As a result, unfocused laser beams can be used for the dissociation of molecules, which is especially important in terms of practical applications of the method for separating boron isotopes.

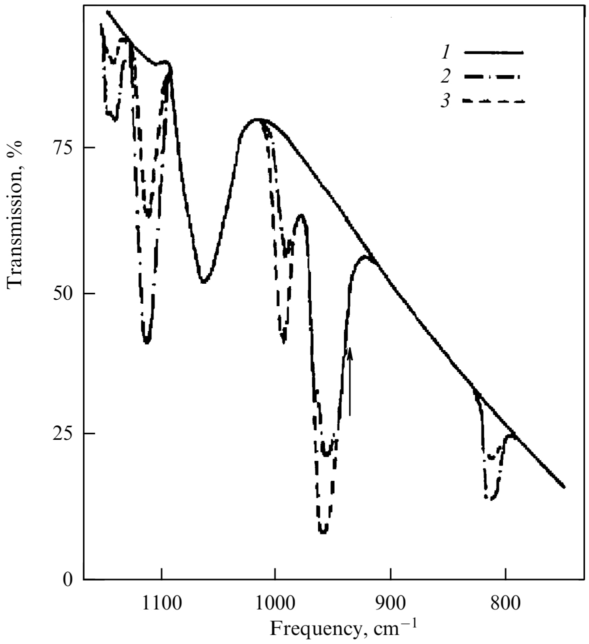

Figure 27. IR absorption spectra of $C_2H_2BCl_3$ molecules: (*1*) absorption spectrum of evacuated cuvette, (*2*) absorption spectrum of 2.9-Torr $C_2H_2BCl_3$ before irradiation, (*3*) absorption spectrum of sample after irradiation with 16 pulses of CO_2 laser with energy of 0.9 J. Arrow shows laser generation frequency [110].

9.2 Spectral and energy characteristics of isotope-selective laser IR multiphoton dissociation of $HClC{=}CHBCl_2$ molecules

The main characteristics of isotope-selective laser IR MPD of 2-chloroethenyldichloroborane molecules were examined in more detail in [11, 169–171]. In these studies, selective dissociation of molecules was carried out at various gas pressures and various laser generation frequencies. As a result, these studies determined the conditions under which the main parameters of isotope-selective dissociation of molecules (dissociation yields and selectivities) were significantly higher than those obtained in [110]. We now consider the results of these studies.

9.2.1 Dependences of yields and selectivity of dissociation of $HClC{=}CHBCl_2$ molecules on pressure of the gas itself. Such dependences were investigated in [11, 169] by varying the pressure of the irradiated gas in a range from about 0.5 to 5.0 Torr. More detailed studies were carried out in recent paper [11]. The experiments were conducted on a setup whose schematic diagram is shown in Fig. 20. The molecules were irradiated at a frequency of 985.5 cm^{-1} (line 10R(36) of the laser), which coincides with the low-frequency wing of the linear absorption band of $HClC{=}CH^{10}BCl_2$ molecules containing the ^{10}B isotope (Fig. 4b).

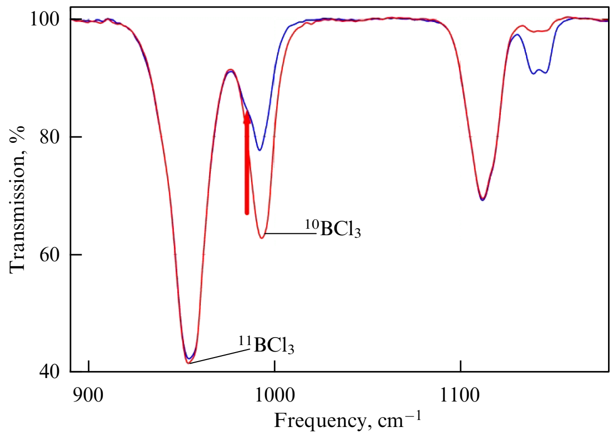

Figure 28. IR absorption spectra of 2-chloroethenyldichloroborane molecules before and after irradiation. Blue/red line shows spectrum before/after irradiation. Pressure of $HClC{=}CHBCl_2$ is 1 Torr; cuvette length is 11.2 cm. Energy density of laser radiation $\Phi = 2.5$ J cm^{-2}. Radiation frequency of 985.5 cm^{-1} (line 10R(36) of CO_2 laser) is shown in spectrum by red arrow. Number of irradiation pulses $N = 420$ [11].

Figure 28 displays the IR absorption spectra of 2-chloroethenyldichloroborane molecules at a pressure in the cuvette of 1 Torr before (blue line) and after (red line) irradiation of the molecules with 420 pulses of a CO_2 laser. The figure shows that irradiation results in a significantly more noticeable decrease in the absorption peak of $HClC{=}CH^{10}BCl_2$ molecules (at a frequency of 1143 cm^{-1}) that the absorption peak of $HClC{=}CH^{11}BCl_2$ molecules (at a frequency of 1112 cm^{-1}). This indicates a high isotopic selectivity of the molecule dissociation, which is further confirmed by the change in the intensity of the peaks at frequencies of 953 and 992 cm^{-1}. As mentioned in Section 4.2, two bands from the dissociation product (boron trichloride) with frequencies of 993.7 cm^{-1} ($^{10}BCl_3$) and 954.2 cm^{-1} ($^{11}BCl_3$) are superimposed on the absorption bands of 2-chloroethenyldichloroborane [116]. Therefore, the intensity of the absorption band at 992 cm^{-1} significantly increases, which is associated with the enrichment of the BCl_3 dissociation product with boron-10, while the intensity of the peak at a frequency of 953 cm^{-1} increases slightly due to the low concentration of the formed $^{11}BCl_3$ molecules.

The dependences of the dissociation yields of $HClC{=}CH^{10}BCl_2$ (*1*) and $HClC{=}CH^{11}BCl_2$ (*2*) molecules on the pressure of the gas itself in the range from 0.5 to ≈ 2.5 Torr are presented in Fig. 29a. Note the fairly large (about 6–9%) dissociation yield of β_{10} selectively excited $HClC{=}CH^{10}BCl_2$ molecules at pressures below 1 Torr. With an increase in pressure to ≈ 2.5 Torr, the yield β_{10} decreases to $\approx 1.5\%$. In the studied pressure range of 2-chloroethenyldichloroborane, a constant decrease in the dissociation yield β_{10} is observed. The dissociation yield β_{11} of $HClC{=}CH^{11}BCl_2$ molecules at pressures below 1.5 Torr has an almost constant value of about 0.1–0.05% with a weak tendency to decrease. With an increase in the gas pressure in the region above 1.5 Torr, the dissociation yield increases to β_{11} 0.6%. This leads to a rapid drop (by about an order of magnitude) in the dissociation selectivity $\alpha(^{10}B/^{11}B)$ (Fig. 29b). Similar behavior of the dissociation yields, which was observed earlier for some molecules, is explained by the action of vibrational-vibrational (V–V) exchange between highly excited $HClC{=}CH^{10}BCl_2$ molecules and a 'reservoir' of unexcited and weakly excited $HClC{=}CH^{11}BCl_2$ molecules (see, for example, [18, 72, 204]). We also note that, in the pressure range of 0.5–2.5 Torr, the selectivity values are still quite high: $\alpha(^{10}B/^{11}B) = 40-100$, which makes it possible to achieve a ^{10}B concentration in the BCl_3 dissociation product of about 88–95% with a half-exhausted $HClC{=}CH^{10}BCl_2$ component [11].

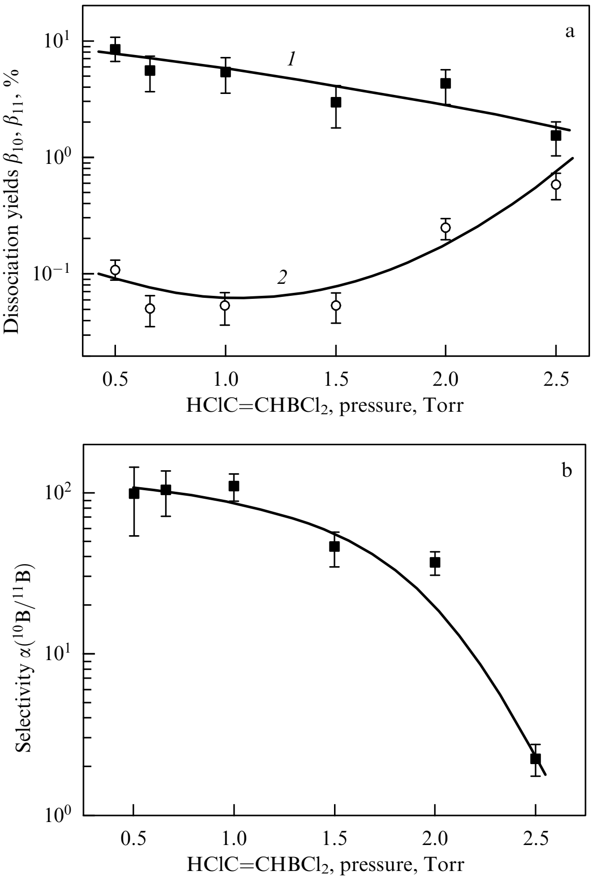

Figure 29. (a) Dependences of dissociation yields of $HClC{=}CH^{10}BCl_2$ β_{10} (*1*) and $HClC{=}CH^{11}BCl_2$ β_{11} (*2*) molecules on pressure of 2-chloroethenyldichloroborane itself. (b) Dependence of dissociation selectivity of $HClC{=}CH^{10}BCl_2$ $\alpha(^{10}B/^{11}B)$ molecules on pressure of 2-chloroethenyldichloroborane itself. In both cases, laser radiation energy density $\Phi = 2.5$ J cm^{-2}; radiation frequency is 985.5 cm^{-1} (line 10R(36) of CO_2 laser) [11].

9.2.2 Dependences of yields and selectivity of $HClC{=}CHBCl_2$ dissociation on energy density of exciting radiation. The dependences of the dissociation yields β_{10} and β_{11} of $HClC{=}CH^{10}BCl_2$ and $HClC{=}CH^{11}BCl_2$ molecules on the energy density of the exciting laser radiation were studied in [11, 170] at pressures of 0.5 Torr [11] and 1 Torr [170]. They are basically similar. Such dependences obtained in [11] in the range of energy densities from 0.9 to 3.2 J cm^{-1} are displayed in Fig. 30a. Note that, at comparatively low energy densities of CO_2 laser radiation ($\Phi \geqslant 2$ J cm^{-2}), the dissociation yield of $HClC{=}CH^{10}BCl_2$ molecules is already quite high, $\beta_{10} \geqslant 5\%$, and the dissociation selectivity remains fairly large ($\alpha(^{10}B/^{11}B) \geqslant 20-25$) even at higher energy density $\Phi = 3.2$ J cm^{-2}. In the studied range, the dissociation yields β_{10} and β_{11} feature a strong power-law dependence on the energy density: $\beta_{10} \sim \Phi^5$ and $\beta_{11} \sim \Phi^6$.

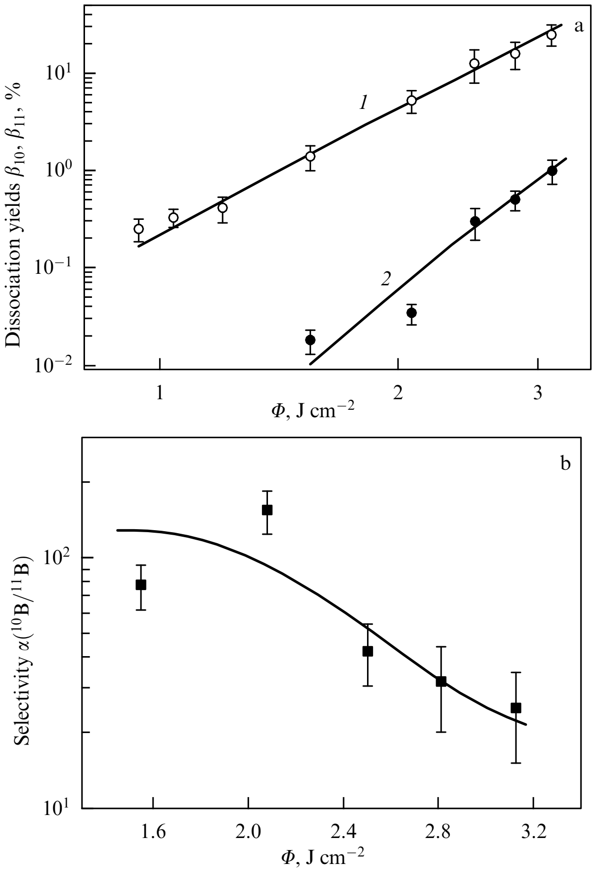

Figure 30. (a) Dependences of dissociation yields of $HClC{=}CH^{10}BCl_2$ β_{10} (*1*) and $HClC{=}CH^{11}BCl_2$ β_{11} (*2*) molecules on laser radiation energy density. Radiation frequency is 985.5 cm^{-1} (line 10R(36) of CO_2 laser); pressure of gas itself is 0.5 Torr. (b) Dependence of dissociation selectivity of $HClC{=}CH^{10}BCl_2$ $\alpha(^{10}B/^{11}B)$ molecules on laser radiation energy density. In both cases, exciting radiation frequency is 985.5 cm^{-1} (line 10R(36) of CO_2 laser); pressure of gas itself is 0.5 Torr [11].

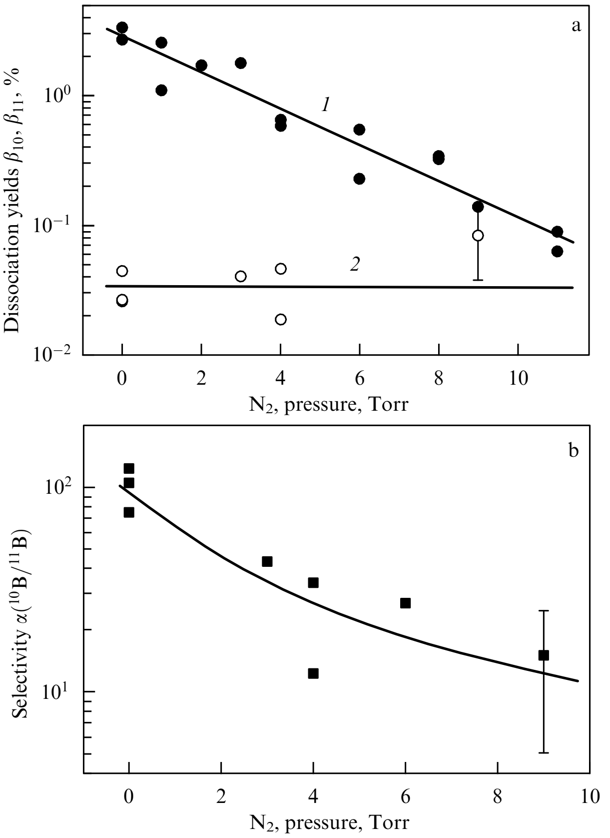

Figure 31. (a) Dependences of dissociation yields of $HClC{=}CH^{10}BCl_2$ β_{10} (*1*) and $HClC{=}CH^{11}BCl_2$ β_{11} (*2*) molecules on pressure of nitrogen buffer gas. (b) Dependence of selectivity of dissociation of $HClC{=}CH^{10}BCl_2$ $\alpha(^{10}B/^{11}B)$ molecules on pressure of nitrogen buffer gas. In both cases, laser radiation energy density $\Phi = 2.1$ J cm^{-2}. Radiation frequency is 985.5 cm^{-1} (line 10R(36) of the CO_2 laser). Pressure of gas itself is 1.0 Torr [11].

Since the degree of increase in the yield of β_{10} is less than that of β_{11}, this leads to a decrease in the selectivity of dissociation of $HClC{=}CHBCl_2$ molecules $\alpha(^{10}B/^{11}B)$ from ≈ 100 to 20–25 when the energy density of laser radiation increases from 1.6 to 3.2 J cm^{-1} (Fig. 30b). A decrease in the isotopic selectivity of MPD molecules with an increase in the density/intensity of laser radiation was observed in experiments many times, and it is explained primarily by the field broadening of the spectrum of vibrational transitions in molecules [18, 72].

9.2.3 Dependences of yields and selectivity of dissociation of $HClC{=}CHBCl_2$ on pressure of buffer gas.

Such dependences were investigated in [11]. Figure 31a presents the dissociation yields of β_{10} and β_{11} and $HClC{=}CH^{10}BCl_2$ and $HClC{=}CH^{11}BCl_2$ molecules as functions of the pressure of a nitrogen buffer gas in the range from 0 to ≈ 9 Torr. The addition of buffer gas results in an exponential decrease in the dissociation yield β_{10} (curve *1*). At a nitrogen pressure of about 9 Torr, the dissociation yield decreases to almost 20 times from ≈ 3 to 0.14%. The dissociation yield β_{11} of $HClC{=}CH^{11}BCl_2$ molecules (curve *2*) remains virtually constant within the spread of experimental values. An increase in nitrogen pressure results in an exponential decrease in the isotopic selectivity $\alpha(^{10}B/^{11}B)$ of the dissociation of $HClC{=}CH^{10}BCl_2$ molecules, which is mainly due to a decrease in the dissociation yield β_{10} and the virtually constant yield β_{11} (Fig. 31b).

The decrease in the dissociation yield β_{10} upon addition of buffer gas is explained by the deactivation of excited $HClC{=}CH^{10}BCl_2$ molecules as a result of collisions with nitrogen molecules due to vibrational-translational (V–T) relaxation [205].

9.2.4 Dependences of yields and selectivity of dissociation of $HClC{=}CHBCl_2$ on exciting radiation frequency.

Such dependences were investigated in [11, 170] at various gas pressures and various energy densities of the exciting laser radiation at a pressure of 0.1 Torr and an energy density of 2.5 J cm^{-1} in [170] and at a pressure of 1 Torr and an energy density of 2.1 J cm^{-1} in [11]. These dependences were studied in more detail in [170]. The results recently obtained in [11] significantly complement the data of [170]. Figure 32a presents the dependences of the dissociation yields β_{10} and β_{11} of $HClC{=}CH^{10}BCl_2$ and $HClC{=}CH^{11}BCl_2$ molecules on the frequency of the exciting radiation of a CO_2 laser obtained in [11].

Note that, with an increase in the excitation radiation frequency to ≈ 975 cm^{-1}, the dissociation yields of both isotopic components of 2-chloroethenyldichloroborane decrease almost exponentially, but the rate of decrease in the dissociation yield β_{10} of $HClC{=}CH^{10}BCl_2$ molecules is

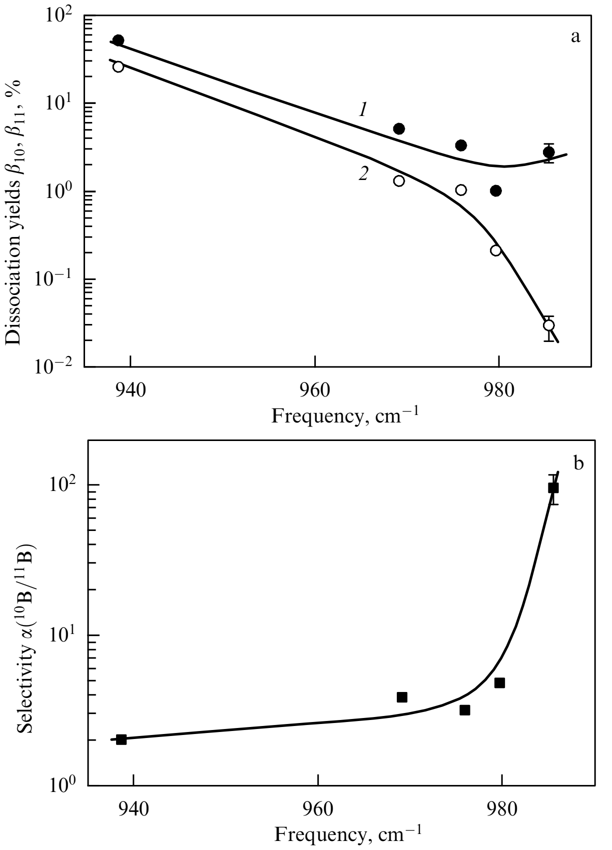

Figure 32. (a) Dependences of dissociation yields of $HClC{=}CH^{10}BCl_2$ β_{10} (*1*) and $HClC{=}CH^{11}BCl_2$ β_{11} (*2*) molecules on laser radiation frequency. (b) Dependence of dissociation selectivity of $HClC{=}CH^{10}BCl_2$ $\alpha(^{10}B/^{11}B)$ molecules on laser radiation frequency. In both cases, laser radiation energy density $\Phi = 2.1$ J cm^{-2}; pressure of gas itself is 1.0 Torr [11].

slightly less than that in the dissociation yield β_{11}. With a further increase in the radiation frequency (from ≈ 975 to 985.5 cm^{-1}), the decrease in the dissociation yields β_{11} is enhanced significantly, while the dissociation yield β_{10} almost stabilizes at a level of several percent. The different behavior of the dependences of the dissociation yields β_{10} and β_{11} on the laser radiation frequency determines the behavior of frequency dependence of the dissociation selectivity $\alpha(^{10}B/^{11}B)$ of $HClC{=}CHBCl_2$ molecules displayed in Fig. 32b. In the frequency range from 938.7 to ≈ 975 cm^{-1}, the dissociation selectivity increases slightly from 2 to 4 (see also [170]). With a further increase in frequency, the increase in $\alpha(^{10}B/^{11}B)$ sharply increases, and the selectivity increases from 4 to ≈ 100 at a frequency of 985.5 cm^{-1} (line 10R(36) of the CO_2 laser). The frequency dependences of the dissociation yields and selectivity of $HClC{=}CHBCl_2$ are associated with the resonance properties of the MPD effect. When the laser radiation frequency is shifted to the 'red' side, the resonance character of the effect weakens for $HClC{=}CH^{10}BCl_2$ molecules, while the radiation frequency enters into resonance with the $HClC{=}CH^{11}BCl_2$ molecules, which is manifested in an increase in the dissociation yield of these molecules.

9.2.5 Conclusions. We now briefly list the main results of studies [11, 169, 170]. The dependences of the dissociation yields of $HClC{=}CH^{10}BCl_2$ and $HClC{=}CH^{11}BCl_2$ molecules on the pressure of the gas itself in the range from 0.5 to 5 Torr were obtained. It should be noted that the dissociation yield β_{10} of selectively excited $HClC{=}CH^{10}BCl_2$ molecules is fairly large (about 6–9%) at pressures less than 1 Torr. In the pressure range of 0.5–2.0 Torr, the selectivity is quite high: $\alpha(^{10}B/^{11}B) = 40-100$, which makes it possible to obtain ^{10}B concentrations of 88–95% in the BCl_3 dissociation product with the $HClC{=}CH^{10}BCl_2$ component exhausted by a half.

The yields and selectivity of molecule dissociation were measured as functions of the energy density of the exciting laser radiation in the range from $\Phi = 0.9$ to $\Phi = 3.2$ J cm^{-2}. It should be noted that a fairly high yield of $HClC{=}CH^{10}BCl_2$ molecule dissociation ($\beta_{10} \geqslant 5\%$) is already observed at comparatively low energy densities of the exciting laser radiation, $\Phi \geqslant 2$ J cm^{-2}, and the dissociation selectivity remains fairly high ($\alpha(^{10}B/^{11}B) \geqslant 20-25$) even at larger energy density $\Phi \approx 3.2$ J cm^{-2}.

It is shown that the addition of nitrogen buffer gas to 2-chloroethenyldichloroborane results in a significant (by approximately an order of magnitude) decrease in both the dissociation yield and selectivity of $HClC{=}C^{10}BCl_2$ β_{10} molecules compared to irradiation of pure gas. Such behavior of the dependences of β_{10} and $\alpha(^{10}B/^{11}B)$ on the buffer gas pressure is associated with the deactivation of excited $HClC{=}CH^{10}BCl_2$ molecules as a result of collisions with nitrogen molecules due to vibrational-translational (V–T) relaxation.

The yields (β_{10} and β_{11}) and selectivity ($\alpha(^{10}B/^{11}B)$) of dissociation of $HClC = CHBCl_2$ molecules were measured as functions of the exciting CO_2 laser radiation frequency in the range of 938.7–985.5 cm^{-1}. At a frequency of 985.5 cm^{-1}, the maximum value of dissociation selectivity ($\alpha(^{10}B/^{11}B) \approx 100$) is achieved with an acceptable ($\beta_{10} \approx 3\%$) value of the dissociation yield of the $HClC{=}C^{10}BCl_2$ component.

Thus, the experiments conducted with 2-chloroethenyldichloroborane have shown that high parameters of selective IR MPD of these molecules can be achieved, including dissociation yields β_{10} of up to 6–9% and selectivity from 30 to 100, which are realized at a fairly high pressure of $HClC{=}CHBCl_2$ itself (from 0.5 to 2.0 Torr) and low energy density of laser radiation (2–3 J cm^{-1}). The results obtained show that 2-chloroethenyldichloroborane is currently the most promising compound to be used as a working substance in an efficient laser process for separating boron isotopes.

In concluding this section, we note that the products that are formed, along with BCl_3 and C_2H_2, during laser IR dissociation of 2-chloroethenyldichloroborane molecules in a strong IR field were investigated in [171, 172]. It was found in [171] that, when large quantities of $HClC{=}CHBCl_2$ gas are irradiated in a flow passing through a cuvette at a comparatively high excitation energy density of ≈ 2.5 J cm^{-2}, some molecules disintegrate to elemental boron enriched in the ^{10}B isotope to 80%. It was shown in [172] that the resulting elemental boron, which precipitates in the reactor in the form of powder, is deposited as a film on the cuvette windows. A theoretical model is proposed to describe the multi-stage disintegration of the molecule and the formation of the free elemental boron. In the opinion of the authors, the most probable channel for the formation of elemental boron is the reaction between the molecules and fragments formed, strongly excited by laser radiation, namely the reaction $BCl_2^* + C_2H_2^* \rightarrow HClC{=}CHCl + B$.

10. Options for technological implementation of laser separation of boron isotopes

10.1 General remarks

Note that, despite the existing well-developed and advanced approaches to laser separation of uranium isotopes (see, for example, reviews [34, 78] and the references therein), to date, no clearly defined and sufficiently developed schemes are available for the technological application of laser methods for separating boron isotopes. However, some proposals and obtained research results (including those referring to other molecules that do not contain boron) make it possible to identify several of the most optimal and relatively simple schemes for the technological implementation of boron LIS using boron trichloride or 2-chloroethenyldichloroborane as the starting material.

Based on the results presented and analyzed above, we can conclude that some methods of boron isotope separation are either ineffective or poorly studied and/or rather challenging for technological implementation in practice. For example, low-energy boron LIS methods (isotope-selective processes of suppressing molecule clustering and cluster dissociation in gas-dynamic jets) are ineffective and insufficiently well studied using BCl_3 molecules as an example, and are also quite difficult for technical implementation. These methods were investigated and developed primarily for their application in laser separation of isotopes in molecules characterized by small isotopic shifts in the IR absorption spectra, mainly for the separation of uranium isotopes [34, 35, 78]. IR laser-induced isotope-selective processes of slowing down the condensation of molecules on the cooled walls of a cuvette have also been insufficiently studied, and they are characterized by low productivity and low selectivity ($\alpha \leqslant 1.03-1.2$) [78, 79, 185, 186].

Studies [34, 78, 206] assessed the productivity of some methods of molecular laser isotope separation. Molecules $^{10}BCl_3$, $^{34}SF_6$, and $^{235}UF_6$ were used as examples to show that isotope-selective IR MPD of molecules under nonequilibrium thermodynamic conditions of a compression shock exhibits a comparatively high productivity. It should be noted that, in the shock wave that forms in front of a solid surface when an intense pulsed gas-dynamically cooled molecular jet hits it, the conditions created are such that the vibrational temperature of the molecules in the jet is comparable to the low vibrational temperature of the molecules in the gas-dynamically cooled molecular flow incident on the surface [73, 78]. In this case, high selectivity of molecular dissociation is realized in the shock wave. This method was studied in detail in [207–214] using the example of separating sulfur and carbon isotopes employing SF_6 [207–213] and CF_3I [73, 214] molecules. It has been found that, when molecules are excited in a compression shock and in a flow incident on the surface, a significant increase (in the incident flow by a factor of 2 to 3, and in the compression shock by more than an order of magnitude) occurs in the yield of products compared to that occurring when molecules are excited in an unperturbed flow. However, the dissociation selectivity is only slightly (by no more than 25–30%) less than that in an unperturbed flow.

Similar results have been obtained recently in experiments on isotope-selective laser IR dissociation of CF_3Br and CF_2HCl molecules [195–197, 215]. These molecules are characterized by small isotopic shifts in the IR absorption spectra with respect to bromine and chlorine isotopes (≈ 0.25 cm^{-1} [216] with respect to bromine isotopes and ≈ 0.05 cm^{-1} [217] with respect to chlorine isotopes) in laser-excited molecular vibrations. These experiments were also primarily aimed at developing laser methods for separating uranium isotopes (see, for example, recent study [218]). Methods using molecular jets and flows are rather challenging for technical implementation. In addition, if boron isotopes are separated using BCl_3 molecules, which feature a large isotopic shift in the IR absorption spectra (≈ 39.5 cm^{-1} [116]), there is no need to deeply cool the gas in the jets or flows. Experimental studies on the separation of boron isotopes with this method have not been carried out to date.

Based on the obtained results of experimental studies, at least three options for the technological implementation of laser separation of boron isotopes can be proposed, which seem to be the most studied, most effective, and/or simplest today. All three options involve the use of isotope-selective laser IR MPD of molecules by radiation from a pulse-periodic CO_2 laser [219] with the placement of a separation reactor inside the laser cavity, by analogy with the previously implemented method of laser separation of carbon isotopes [36–38, 193]. These options include dissociation of:

(1) $HClC=CHBCl_2$ molecules with single-frequency radiation;

(2) BCl_3 molecules with two-frequency radiation;

(3) BCl_3 molecules in a mixture with a sensitizer and an acceptor of radicals, SF_6, with single-frequency radiation.

We now discuss these approaches in more detail.

10.2 Isotope-selective IR multiphoton dissociation of $HClC=CHBCl_2$ molecules

The results presented in this review (see Section 9) enable hypothesizing that the technique for laser separation of boron isotopes currently considered the most effective and simplest for practical implementation is IR multiphoton dissociation of 2-chloroethenyldichloroborane molecules. The fairly high parameters of the elementary act of separation-dissociation yields and selectivity of molecules along with the very simple IR photochemistry (the formation of simple products (BCl_3 and C_2H_2) as a result of laser IR dissociation of molecules) are very attractive factors for the industrial implementation of this method.

Experiments conducted with $HClC=CHBCl_2$ molecules showed that fairly high parameters of selective multiphoton dissociation can be achieved — yields β_{10} up to 6–9% and dissociation selectivity $\alpha(^{10}B/^{11}B)$ in a range from 30 to 100 at a fairly high intrinsic pressure of $HClC=CHBCl_2$ (0.5–2.0 Torr) and low density of laser radiation energy ($\approx 2-3$ J cm^{-2}). The results obtained enable asserting that 2-chloroethenyldichloroborane is currently the most promising compound to be used as a working substance in the boron LIS. High values of the parameters of the elementary act of separation provide high efficiency of the method, especially in comparison with the use of boron trichloride [11].

Another favorable factor in the industrial implementation of laser separation of boron isotopes using the IR MPD method of $HClC=CHBCl_2$ molecules is that, upon selective excitation of any of the isotopologues, the resulting product BCl_3 (at low pressures of $\approx 0.3-0.4$ Torr) will perform as an optically active sensitizer and promote an increase in the selectivity of $HClC=CHBCl_2$ dissociation [11, 170]. For example, during isotope-selective dissociation of $HClC=CH^{10}BCl_2$ molecules, $^{10}BCl_3$ molecules are formed whose IR absorption band virtually coincides with the

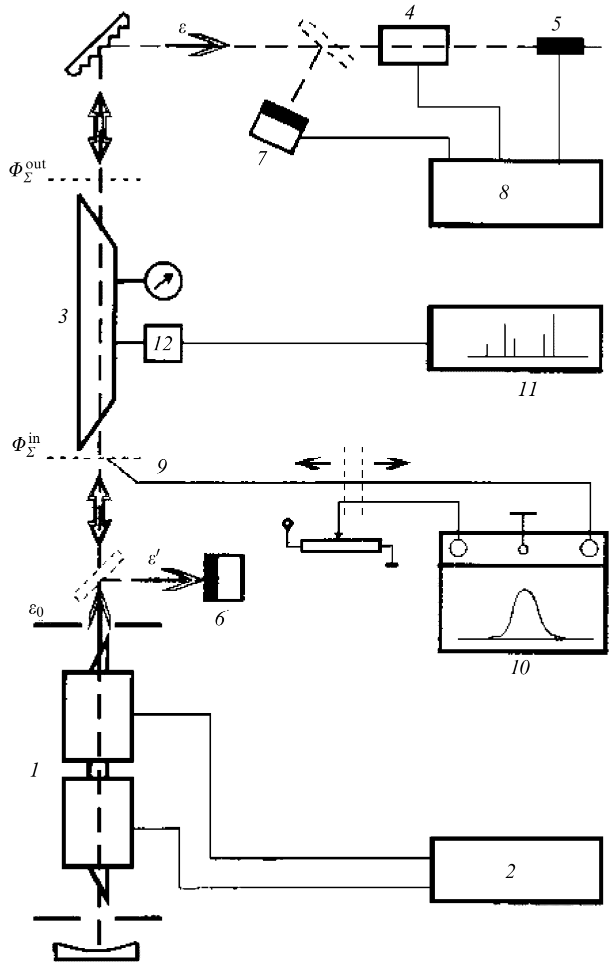

Figure 33. Schematic diagram of experimental setup: *1* — laser cuvettes; *2* — laser power supplies; *3* — laser separation reactor; *4* — optoacoustic receiver; *5* — fast IR photodetector (GeAu); *6, 7* — calorimeters; *8* — detection system; *9* — microprobe; *10* — data recorder; *11* — mass spectrometer; *12* — mass spectrometric sensor. Symbols ε_0, ε and $\Phi_{\Sigma}^{\rm in}$, $\Phi_{\Sigma}^{\rm out}$ denote locations for measuring input (into separation reactor) and output energies and laser energy densities, respectively [193].

absorption band of $HClC=CH^{10}BCl_2$ molecules, and $^{10}BCl_3$ molecules will act as an optically active sensitizer. Since unfocused laser beams and the comparatively low energy densities of the exciting radiation are used for the dissociation of $HClC=CHBCl_2$ molecules, BCl_3 molecules will not undergo dissociation.

An important factor limiting the industrial implementation of the boron LIS, based on the use of 2-chloroethenyl dichloroborane as the starting material, is the lack of industrial technology for its production. However, there are reasons to believe that its production is not a complex technological problem and can be realized. Should the industrial production of 2-chloroethenyldichloroborane be undertaken, the optimal approach for laser enrichment of bromine isotopes will be the IR MPD of $HClC=CHBCl_2$ molecules.

The technological implementation of the laser IR MPD of molecules has been well studied, developed, and tested via the example of carbon isotope separation using CF_2HCl (freon-22) molecules [36–38], and its effectiveness has been proven. In the technological process, a separation reactor with CF_2HCl gas was placed inside the laser cavity. If $HClC=CHBCl_2$ molecules are used, the separation reactor is also supposed to be placed inside the laser cavity. The separation reactor being located inside the cavity enables obtainment of higher parameters of the elementary act of isotope separation than those with the resonator located outside the cavity, achievement of a high energy density of laser radiation in large volumes, and the use of laser radiation in a more efficient way. A simplified schematic diagram of the laser part of the proposed setup is displayed in Fig. 33 [193]. Since IR absorption bands of $HClC=CHBCl_2$ molecules are stronger than those of CF_2HCl molecules, $HClC=CHBCl_2$ should be irradiated at lower gas pressures in the reactor. Similar to the case of CF_2HCl molecules, nitrogen can be used as a carrier in the technological process.

10.3 Isotope-selective dissociation of BCl_3 molecules in a two-frequency IR field

An alternative approach to the practical implementation of boron LIS process is isotope-selective dissociation of BCl_3 molecules in a two-frequency IR laser field. As shown in [167, 168], when dissociating molecules with two-frequency radiation, in contrast to dissociating molecules with a single-frequency IR field, fairly high parameters of the elementary act of separation — yields and selectivity of molecule dissociation — are obtained. Moreover, these parameters are achieved with a significantly lower total energy density for molecule dissociation than in the single-frequency case.

For example, in [167], upon excitation of BCl_3 molecules at a frequency of $\nu_1 = 985.5$ cm^{-1} (line 10R(36) of a CO_2 laser) and dissociation of excited molecules at a frequency of $\nu_2 = 931$ cm^{-1} (line 10P(34) of a laser), the yield and selectivity of dissociation of $^{10}BCl_3$ molecules was as high as $\beta_{10} \approx 0.14$ and $\alpha(^{10}B/^{11}B) \approx 4.2$, respectively. Thus, in this study, a comparatively high yield of $^{10}BCl_3$ molecule dissociation was obtained ($\approx 15\%$ with a selectivity of ≈ 4.2) with a significant decrease in the total energy density of laser radiation ($\leqslant 8.0$ J cm^{-2}) compared to the single-frequency version, where fairly high energy densities ($\geqslant 20$ J cm^{-2}) are required for the dissociation of molecules [158, 167].

The use of the two-frequency multiphoton dissociation of BCl_3 makes it possible to significantly reduce the total energy density of laser radiation and to switch from strong focusing to quasi-parallel laser beams and, consequently, to larger irradiated volumes. To enhance the productivity of the process, the BCl_3 pressure can be increased from 0.1 to 1.0 Torr. As shown in [168], the yield of molecule dissociation decreases insignificantly (by about 1.5 times), and the selectivity is preserved. Therefore, it can be assumed that by optimizing the excitation conditions (frequency and duration of laser radiation pulses, temperature, type and pressure of the acceptor) the process selectivity can be further enhanced. For example, experiments using NO as an acceptor showed in [168] that, in if the NO acceptor is added to BCl_3 molecules, the dissociation yield of $^{10}BCl_3$ molecules increases and reaches a maximum at a pressure of ≈ 1 Torr. The selectivity achieved in these experiments turned out to be higher ($\alpha(^{10}B/^{11}B) = 7$). Two-frequency dissociation of BCl_3 molecules can be realized using one pulse-periodic CO_2 laser generating at two frequencies [220].

The authors analyzed the results obtained in [167, 168] in terms of the feasibility of their use for the development of a technological process for boron LIS based on two-frequency MPD BCl_3. It was found that the energy costs for dissociation of BCl_3 molecules in a two-frequency laser field are comparatively high ($\geqslant 1.5$ keV per ^{10}B atom). The dissociation selectivity ($\alpha(^{10}B/^{11}B) \approx 7$) corresponds to enrichment in products of up to 62%. Consequently, in a two-stage separation process, enrichment with respect to the ^{10}B isotope of up to 92% can be achieved. These parameters are inferior to those obtained with single-frequency isotope-selective dissociation of $HClC{=}CHBCl_2$ molecules (see Section 9 and Refs [11, 169]). However, when comparing the competitiveness of these two approaches, the economics of the entire separation process as a whole should be taken into account.

10.4 Isotope-selective dissociation of BCl_3 molecules in a mixture with a sensitizer and SF_6 radical acceptor

The results of the isotope-selective laser IR MPD studies of $^{11}BCl_3$ molecules in a natural mixture with $^{10}BCl_3$ presented in Section 8 in the case of their irradiation with a sensitizer resonantly absorbing laser radiation and SF_6 radical acceptor, which were obtained in [1, 2], can also be the basis for the practical application of this method for the enrichment of boron isotopes. In these studies, a strong increase in the efficiency of dissociation of $^{11}BCl_3$ molecules in a natural mixture of BCl_3 isotopologues was revealed under irradiation with SF_6 compared to the case of irradiation without SF_6. The obtained dependences of the main parameters of $^{11}BCl_3$ molecule dissociation (dissociation yields and selectivity) on the SF_6 pressure and on the energy density and frequency of the exciting laser radiation confirm the high efficiency of the isotope-selective dissociation of $^{11}BCl_3$ molecules.

It is shown that, when BCl_3 is irradiated in a mixture with SF_6, the dissociation yield of $^{11}BCl_3$ molecules increases by 1–2 orders of magnitude and the dissociation selectivity increases by a factor of 2 to 5, while the threshold density of dissociation energy decreases significantly (by approximately an order of magnitude) compared to the case of irradiating BCl_3 without SF_6. A strong increase in the efficiency of isotope-selective dissociation of $^{11}BCl_3$ molecules is found to occur due to the resonant energy transfer from SF_6 molecules to $^{11}BCl_3$ molecules.

The main products formed as a result of laser IR dissociation of BCl_3 molecules in a mixture with SF_6 and subsequent chemical reactions were identified. A strong increase in the efficiency of $^{11}BCl_3$ molecule dissociation and a significant decrease in the threshold density of energy for molecule dissociation provide an option to implement single-frequency isotope-selective laser IR dissociation of $^{11}BCl_3$ molecules in unfocused laser beams at a moderate ($\leqslant 3-4$ J cm^{-2}) excitation energy density and, as a consequence, irradiation of large volumes of gas. As a result, it is now possible to obtain a molecular BCl_3 gas highly enriched in the ^{10}B isotope due to the dissociation of $^{11}BCl_3$ molecules in a natural mixture with $^{10}BCl_3$.

In addition, it may be hypothesized that the process studied using an optically active sensitizer is also applicable to $^{10}BCl_3$ molecules. In the case of isotope-selective IR MPD of $^{10}BCl_3$ molecules, it is probably possible to use CH_3F, C_2H_4, SiH_4, or SiH_3F molecules, which feature strong IR absorption bands near the absorption band of $^{10}BCl_3$ molecules, as both a sensitizer and a radical acceptor [221].

At the end of this section, we note that, for successful industrial implementation of any of the proposed options for laser separation of boron isotopes in practice, preliminary studies of this process on a semi-industrial laboratory setup are necessary to identify and resolve emerging problems and optimize the entire process as a whole.

11. Conclusions

The considered studies experimentally investigated in detail the laser separation of boron isotopes using IR multiphoton dissociation of BCl_3 and $HClC{=}CHBCl_2$ molecules and the $BCl_3 \bullet CH_3SH$ complex. Schemes were proposed and model calculations were carried out for the separation of boron isotopes using low-energy isotope-selective suppression of BCl_3 molecule condensation in a gas-dynamically cooled molecular flow with a carrier gas. Experiments were conducted to study the isotope-selective dissociation of van der Waals Ar-BCl_3 clusters. Isotope-selective dissociation of BCl_3 molecules in a two-frequency IR laser field and in the case of molecule excitation by a free-electron laser was explored. Selective dissociation of BCl_3 was investigated with various radical acceptors and in the presence of catalysts. Experiments were carried out on isotope-selective IR multiphoton dissociation of BCl_3 molecules in a mixture with an optically active sensitizer and SF_6 radical acceptor.

Spectral and energy characteristics of isotope-selective laser IR multiphoton dissociation of BCl_3 and $HClC = CHBCl_2$ molecules were examined in detail. Dependences of the yields and selectivity of molecule dissociation on the parameters of exciting laser radiation (frequency and energy density) and the parameters of the irradiated gas (pressure of the gas itself and the acceptor and buffer gases) were obtained. It is shown that the best parameters of isotope-selective laser IR multiphoton dissociation of molecules (dissociation yields and selectivity) are achieved when 2-chloroethyldichloroborane is used as the starting material for laser separation of boron isotopes. It is found that, in the case of isotope-selective dissociation of BCl_3 molecules in a two-frequency IR laser field, the achieved parameters of the elementary act of boron isotope separation (dissociation yield and selectivity) are significantly higher than with single-frequency dissociation. Using two-frequency dissociation, it is also possible to irradiate large volumes of gas.

It is shown that the efficiency of isotope-selective laser IR multiphoton dissociation of $^{11}BCl_3$ molecules can be significantly enhanced by using SF_6 as a sensitizer and acceptor of radicals. In this case, the yield of $^{11}BCl_3$ molecule dissociation increases significantly (by 1–2 orders of magnitude) and the dissociation selectivity (by 2–5 times), while the threshold density of dissociation energy notably decreases (by about an order of magnitude) compared to the case of BCl_3 irradiation without SF_6. This provides an option to implement single-frequency isotope-selective laser IR dissociation of $^{11}BCl_3$ molecules in unfocused laser beams at a moderate ($\leqslant 4-5$ J cm^{-2}) excitation energy density. The results obtained are of importance and relevance in terms of applying the described method for the development of laser technology for separating boron isotopes, since they enable obtainment of a molecular BCl_3 gas highly enriched in the ^{10}B isotope due to the dissociation of $^{11}BCl_3$ molecules in a natural mixture with $^{10}BCl_3$.

Proposed and substantiated are variants for the technological application of laser methods for separating boron isotopes in practice, including isotope-selective dissociation of (1) $HClC{=}CHBCl_2$ molecules, (2) BCl_3 molecules in a two-frequency IR laser field, and (3) BCl_3 molecules mixed with a sensitizer and SF_6 radical acceptor by single-frequency

IR radiation. All the methods proposed involve the use of unfocused (or weakly focused) laser beams. Based on the experimental results obtained, it can be argued that the first of the proposed methods is currently the optimal one.

In conclusion, it should be emphasized that the development of an effective technology for separating boron isotopes is an urgent task. The availability of powerful and efficient pulse-periodic CO_2 lasers and the exact coincidence of their generation frequencies with intense IR absorption bands of BCl_3 and $HClC=CHBCl_2$ molecules provide a reliable basis for the development of laser technology for the separation (enrichment) of boron isotopes.

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