Towards molecular laser separation of uranium isotopes

G N Makarov

Contents

Abstract. About half a century ago, active research began on the use of lasers for the separation of isotopes, including uranium isotopes. In a number of highly developed countries, projects on laser separation of uranium isotopes were initiated. However, in the late 1990s, these projects were closed. At the same time, research on laser separation of uranium isotopes is being carried out in a number of countries at the present time. Research today is mainly focused on the development of low energy methods. A review of the results of studies on molecular laser isotope separation (MLIS) of uranium is presented. MLIS methods, including low-energy methods, as well as the physicochemical processes underlying them, are considered. The infrared and ultraviolet absorption spectra of UF$_6$ molecules, which form the basis of uranium MLIS methods, are presented and discussed. Lasers that have been developed and used to excite and dissociate UF$_6$ molecules are briefly described. The results of studies on laser dissociation of UF$_6$ molecules using different excitation schemes and laser separation of uranium isotopes are presented and analyzed. Applications of low-energy MLIS methods, including SILEX technology, for the separation of uranium isotopes are considered. In the context of molecular laser separation of uranium isotopes using low-energy methods, the recently obtained results on the separation of isotopes in SF$_6$ and CF$_3$Br molecules, which are close analogs of UF$_6$ molecules in a number of spectroscopic properties, are presented and analyzed. Approaches that can be a promising alternative to low-energy MLIS methods are discussed. Data on the efficiency of some laser methods and their comparison with each other are given. A brief historical excursion into research on laser separation of uranium isotopes is given.

G N Makarov
Institute of Spectroscopy, Russian Academy of Sciences,
ul. Fizicheskaya 5, 108840 Troitsk, Moscow, Russian Federation
E-mail: gmakarov@isan.troitsk.ru

1. Introduction

One of the important applications of lasers almost at once after their invention became their use in selective photophysics and photochemistry. About 50 years ago, lasers came into active use to study the separation of isotopes, including uranium isotopes. In the early 1970s, under the supervision of V S Letokhov at the Institute of Spectroscopy, USSR Academy of Sciences, the first experiments on the selective laser photoionization of rubidium atoms [1] and separation of nitrogen isotopes were performed using the method of selective two-step (IR + UV) photodissociation of ammonia molecules [2]. Shortly thereafter, the laser separation of boron [3], sulfur [4], and osmium [5] isotopes via IR multiphoton dissociation (MPD) of BCl_3, SF_6, and OsO_4 molecules was achieved. The results of these studies clearly demonstrated the great possibility of laser separation of isotopes of various elements and stimulated the development of projects on laser separation of uranium isotopes. The use of lasers for isotope separation is of interest both for fundamental studies and practical applications. In the 1970s–1980s, closed projects on the laser separation of uranium isotopes were initiated in a number of highly developed countries (USA, Germany, England, France, Japan, Australia) [6–25] (see also Section 7). It was expected that lasers could be used to develop cheaper and more efficient laser technology for uranium enrichment than did centrifugation. Studies were developed in two directions using the atomic vapor of metal uranium as an initial substance (AVLIS method: Atomic Vapor Laser Isotope Separation) [6, 7, 12, 13, 18, 24–26] or a molecular UF_6 gas (MLIS method: Molecular Laser Isotope Separation) [8–11, 18, 22, 23, 27].

These studies gave many interesting and important scientific results and demonstrated the capabilities of lasers to obtain enriched uranium, including in amounts required for semi-industrial facilities. However, in the late 1990s, most projects on laser separation of uranium isotopes were terminated for a number of reasons. In many cases, this was explained by economic factors. It was assumed that laser technology at that stage of its development was unprofitable for building industrial modules for laser separation of uranium isotopes [23] (see also Section 7). At the same time, it was shown in some projects [6, 7, 12, 13, 27] that the economic efficiency of laser methods for uranium enrichment per unit separation work was comparable to that for the most developed centrifugation methods. Projects on the laser separation of uranium isotopes were terminated mainly for politically economic reasons. This was the result of the HEU–LEU (High-Enriched Uranium–Low-Enriched Uranium) Intergovernmental Agreement between Russia and the USA in 1993 (Megatons to Megawatts Program) [28, 29]. According to this agreement, in effect for 20 years (until 2013), the USA purchased from Russia low-enriched uranium obtained from weapons-grade uranium for their atomic electric stations. This decelerated the development of technologies for uranium isotope separation in the USA. At the same time, studies on the laser separation of uranium isotopes are still performed in many countries at present. Today they are mainly directed at the development of low-energy MLIS methods for uranium [30–34]. In the USA and Australia, the SILEX (Separation of Isotopes by Laser Excitation) technol-

ogy is being developed [35–39]. Laser separation of uranium isotopes is also being studied in Japan, South Korea, India, Iran, China, and South Africa (see Section 7).

Fundamental interest in laser isotope separation, in particular, uranium isotopes, is explained first of all by a desire to understand physicochemical processes underlying molecular and atomic methods of isotope separation, whose main aspects are related to the general problem of interaction of laser radiation with matter. In practice, laser separation of uranium isotopes is important for the production of enriched uranium for nuclear energy production. Today, almost 200 atomic electric stations in more than thirty countries are working with enriched uranium [40]. They produce in some countries about 20% of the consumable electric energy (USA, Great Britain, Russia) and in some others more than 50% (France, Ukraine, Slovakia) [40]. Natural uranium contains three isotopes: ^{238}U (99.2745%), ^{235}U (0.7200%), and ^{234}U (0.0055%). Atomic reactors cooled with usual water require uranium containing the ^{235}U isotope in the range from 3 to 5%. Uranium enrichment is a rather energy-consuming and expensive process. Thus, the uranium enrichment process costs about one third of the general cost of enriched uranium for nuclear reactors produced by the most advanced gas centrifugation technology today [41]. Uranium enrichment is the most large-scale market in the field of nuclear energy production.

This review considers the results of MLIS studies of uranium using high-energy separation methods based on the laser-induced isotope-selective dissociation of UF_6 molecules, which were extensively performed at many laboratories around the world for the last three decades of the 20th century. In addition, the results of recent investigations devoted to the development of low-energy MLIS methods were considered using, along with UF_6 molecules, SF_6 and CF_3Br molecules with some spectroscopic properties similar to those of the UF_6 molecule.

The aim of the review is to attract the attention of a new generation of researches to the field considered here and to the development of lasers and laser technologies for uranium isotope separation. In this connection, the main problems and tasks encountered by researchers in the study of laser separation of uranium isotopes are presented, the achieved successes are pointed out, the most important results on the MLIS of uranium are given, the current state of the problem is considered, and the main directions of further studies are formulated.

The review is structured as follows. In Section 2, the general concept of laser isotope separation is considered, and conditions required for the development of laser methods are described. Section 3 is devoted to a discussion of various methods for laser isotope separation, including low-energy MLIS methods, and of the physicochemical methods underlying them. The AVLIS method is also briefly considered. In Section 4, the IR and UV absorption spectra of UF_6 molecules playing a key role in the MLIS of uranium are examined. In Section 5, the motivation for applications, advantages, and basic parameters of laser methods for separating uranium isotopes are discussed. Section 6 contains a description of IR lasers that were developed and used for the excitation and dissociation of UF_6 molecules. Section 7 presents a brief historical excursus on the laser separation of uranium isotopes. In Section 8, the results of studies on the excitation and dissociation of UF_6 molecules with the help of sensitizers are discussed and the results of isotope-selective

dissociation of complex uranium-containing molecules are considered. Data on the laser separation of uranium isotopes and dissociation of UF_6 molecules using various excitation schemes are presented and analyzed. In Section 9, applications of low-energy MLIS methods, including SILEX technology, for separating uranium isotopes are analyzed. Recent results on the separation of isotopes in SF_6 and CF_3Br molecules by low-energy methods are presented and briefly discussed. In Section 10, the selective dissociation of molecules under nonequilibrium thermodynamic conditions of a pressure shock is described, which is an alternative approach to MLIS methods for uranium. The efficiencies of some MLIS methods are compared with each other. In Section 11, the main results of the study and conclusions are presented.

2. Basic concept of laser isotope separation and necessary conditions for realizing laser methods

2.1 Fundamentals of laser isotope separation

Laser isotope separation is based on the selective action of laser radiation on chosen isotopes (or isotopomers) in the initial substance for changing their physical or chemical properties without affecting other isotopes (or isotopomers) (Fig. 1) [42, 43]. When two types of atoms or molecules with different isotopic compositions (A and B) have, at least, one non-overlapping absorption line, it is possible to excite selectively by laser radiation an atom or a molecule of the chosen isotopic composition (for example, particle A). The excitation of particles A changes their chemical and physical properties and, therefore, this can be used to separate a mixture of particles by different methods based on difference of characteristics of excited and unexcited particles.

Using a photochemical approach, one can induce a chemical reaction of excited particles A^* with a suitable reagent and obtain products (AR in Fig. 1) before excited particles begin to relax to the ground state or almost resonantly transfer their energy to particles B in collisions, producing excited particles B^* (see Fig. 1). On the other hand, a photophysical approach is based on laser-induced dissociation or ionization of preliminary selectively excited particles. In both approaches, new products enriched with a chosen isotope are obtained, which can be separated from the mixture by standard methods. Thus, the common feature of all the methods of laser isotope separation is the isotopically selective excitation of an electronic or vibrational level of a molecule (or an atom) on a quantum transition having a distinct isotopic shift.

A disadvantage of the photochemical approach is the necessity of choosing a reaction with an appropriate activation barrier E_a, and the most important drawback is the requirement that the reaction rate K_{A^*R} between the excited particle and reagent greatly exceed the rate Q_{A^*B} of resonance energy transfer from the excited to unexcited particle ($K_{A^*R} \gg Q_{A^*B}$). This condition is rather difficult to fulfill, and this approach has not found wide application despite a number of demonstrations. For this reason, in most cases, the first stage of selective excitation is 'fixed' by performing dissociation or ionization of excited particles, thereby transforming them into a different chemical state (forming radicals or ions). The rate W of this additional excitation can be readily made high enough, greatly exceeding the rate of collisional excitation transfer to another isotope ($W \gg Q_{A^*B}$).
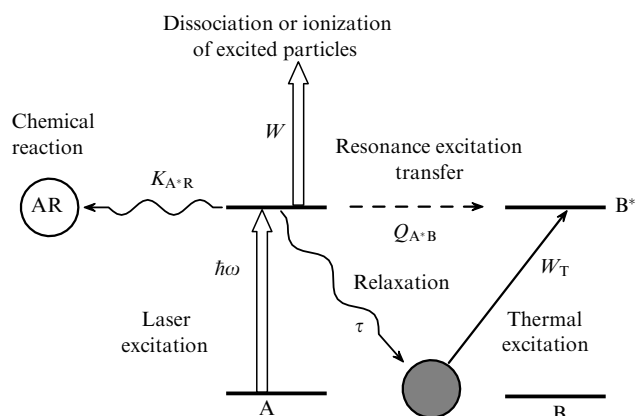
Figure 1. General scheme of isotope-selective laser excitation of particles A (atoms, molecules) in a mixture with particles B of different isotopic composition and of related processes. Details are presented in the text.

This approach much more simply provides the selectivity of initial excitation followed by the extraction of the required isotope.

2.2 Conditions for realization of laser methods

To use laser methods for isotope separation, the following conditions must be fulfilled [16, 42, 43]:

(i) Isotopomers of atoms or molecules containing isotopes being separated must be in a gaseous state and should have allowed isotopic shifts in electronic or vibrational absorption spectra. Isotopic shifts in electronic absorption spectra of atoms are usually small, their relative value being $10^{-5} - 10^{-8}$ of the transition energy. Isotopic shifts in vibrational molecular spectra are $10^{-2} - 10^{-4}$ of the vibrational transition energy.

(ii) Lasers used in studies must emit a narrow enough and tunable spectral line providing the predominant excitation of atoms or molecules before of the chosen isotopic composition.

(iii) It is necessary to realize the efficient separation of a required (target) isotope, which acts only on excited atoms or molecules before their relaxation or energy exchange with unexcited particles.

There are several schemes for the isotopically selective excitation of atoms and molecules by laser radiation using single-, two-, and multiphoton processes. The separation of a required isotope in a photochemical process has not found wide application because of the complexity of searching for a suitable chemical reaction with the rate considerably exceeding the relaxation rate of preliminarily excited particles and the rate of near-resonance energy transfer to particles containing other isotopes. At the same time, using intense UV, visible, or IR laser radiation, it was possible to develop a number of methods for isotopically selective excitation of atoms and molecules. These methods are considered in Section 3.

3. Methods of laser isotope separation

3.1 Methods of molecular laser isotope separation

3.1.1 High-energy methods. Methods of isotope-selective dissociation of molecules and selective ionization of atoms are high-energy methods, because their activation energies
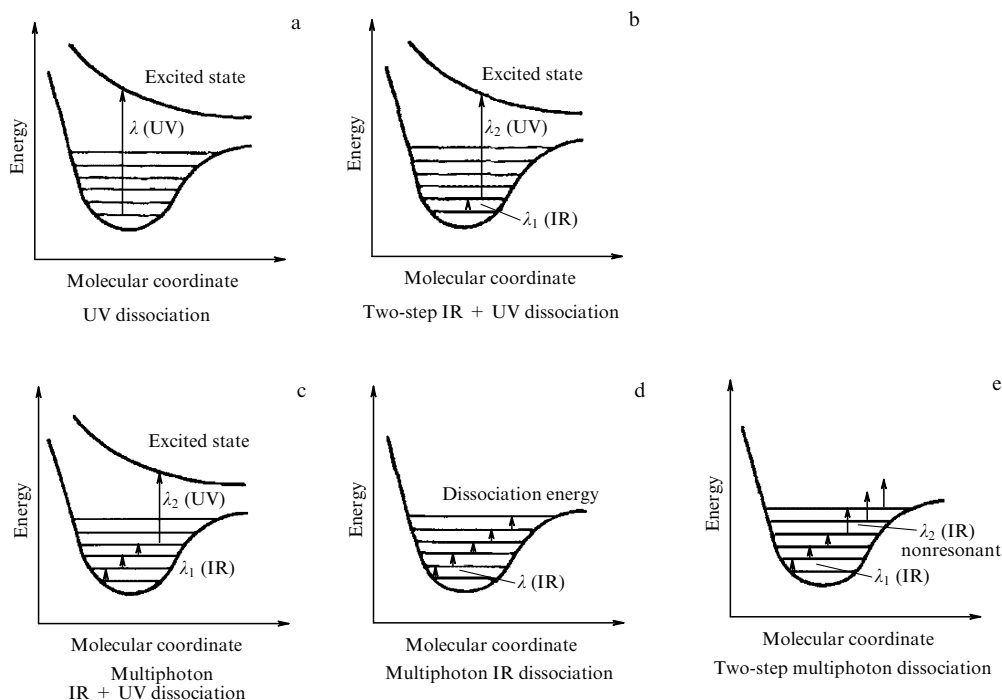
Figure 2. Single- and two-frequency processes in molecular laser isotope separation [9, 47].

are rather high ($\geqslant 3-6$ eV). To perform the dissociation of a molecule, it is necessary to spend energy comparable to the dissociation energy (from about 2.5 to 5.0 eV [44, 45]) or even exceeding it. The ionization of atoms requires even more energy (from about 5 to 10 eV [44, 45]). The dissociation energy of UF_6 molecules is about 3.2 eV [45, 46], while the ionization energy of uranium atoms is ≈ 6.2 eV [44, 45]. High-energy MLIS methods include (Fig. 2) [9, 47]: (a) single-photon UV dissociation of molecules, (b) two-step IR + UV dissociation of molecules, (c) multiphoton IR + UV dissociation, (d) single-frequency multiphoton IR dissociation of molecules, and (e) two- or three-frequency multiphoton IR dissociation of molecules. The sequence of schemata in Fig. 2 approximately reflects the historical sequence of application and development of the corresponding methods of selective dissociation of molecules. Methods (a) and (d) are based on single-frequency dissociation of molecules, while methods (b), (c), and (e) use two-frequency dissociation.

UV dissociation of molecules. In the method shown in Fig. 2a, the isotope-selective UV dissociation occurs due to absorption of laser radiation at the transition from the ground electronic state to the excited predissociation state. The selective process is realized if an isotopic shift exists between vibrational levels of isotopomers in the ground electronic state from which molecules are excited. The separation of isotopomers by the method of selective laser photopredissociation of molecules was first considered in papers [48, 49] (see also review [50]). In [48], the separation of H and D isotopes was performed using the photopredissociation of formaldehyde molecules (H_2CO).

Two-step IR + UV dissociation of molecules. In the method of two-step IR + UV dissociation of molecules (Fig. 2b), molecules of the chosen isotopic composition (target molecules) are selectively excited to the first vibrational level of the ground electronic state by IR laser radiation at a wavelength of λ_1. At the second stage, UV laser radiation

at λ_2 causes the dissociation of vibrationally excited molecules by exciting them from the electronic ground state to a predissociation electronic state. In this case, molecules that have not been excited by IR radiation do not absorb UV radiation at λ_2 and do not dissociate. This method was first used in papers [51, 52] for the two-step IR + UV dissociation of ammonia molecules and the separation of nitrogen isotopes [2, 53].

Multiphoton IR + UV dissociation of molecules. The method of multiphoton IR + UV dissociation of molecules (Fig. 2c) is a development of the method of IR + UV dissociation for polyatomic molecules capable of absorbing several photons from an intense IR laser field. As a result, unlike method (b), not only is the first vibrational level populated, but so are the higher vibrational levels of the ground electronic state. This leads to a considerable increase in the UV absorption cross section for selectively excited molecules, which was first observed for OsO_4 [5] and CF_3I [54] molecules (Fig. 3a, b). The long-wavelength wing of the UV absorption spectrum seemingly shifts to the red. The increase in the UV absorption cross section was also observed upon vibrational excitation of UF_6 molecules [55–57]. In this method, the isotopic selectivity of the dissociation of molecules is achieved due to the difference in UV absorption cross sections between vibrationally excited and unexcited molecules.

IR multiphoton dissociation of molecules. The IR-MPD of molecules (Fig. 2d) is based on the fact that, in an intense laser field, a molecule, despite the anharmonicity of its vibrations, absorbs purely radiatively (without collisions) many IR photons (several tens) from the laser pulse field, reaches the dissociation limit, and decomposes into fragments. The collisionless IR-MPD of molecules was first observed in papers [58, 59] for SiF_4 and BCl_3 molecules, respectively, while isotopically selective IR-MPD was first performed in [3, 4] for BCl_3 and SF_6 molecules, respectively. Results analo-

gous to data on the separation of sulfur isotopes obtained at the Institute of Spectroscopy [4] were soon obtained at the Los Alamos National Laboratory [60]. After these experiments, the extensive development of isotope-selective IR-MPD studies of molecules began in many countries [61–64].

The isotope-selective IR-MPD method was developed for practical applications. In 1988–2005, a plant was built in Kaliningrad for the separation of ^{13}C isotopes based on the isotope-selective dissociation of CF_2HCl (freon-22) molecules by a periodically pulsed CO_2 laser [65–68].

Two-frequency IR multiphoton dissociation of molecules. In this method (Fig. 2e), molecules are resonantly excited to lower vibrational levels by weak IR laser radiation at λ_1. The subsequent dissociation of previously excited molecules is performed by a stronger IR laser field at λ_2 detuned from the resonance with lower-level transitions. A pulse from a second laser is usually time-delayed by 0.5–1.0 μs. Thus, this method allows separation of the functions of the IR field into the selective excitation of molecules in the region of the lower vibrational levels and excitation in the region of higher levels and the dissociation of molecules. Because at the resonance stage a weak laser field is used, the dynamic broadening of molecular absorption lines by the laser pulse field is small. This allows the isotopic selectivity of the dissociation process to be increased considerably [69–72]. The red shift of the dissociation-stage frequency relatively to the linear absorption spectrum of unexcited molecules provides the best resonance with vibrationally excited molecules, because their absorption spectrum shifts to the red due to anharmonicity [73]. As a result, the dissociation yield of molecules considerably increases [71, 72, 74]. Thus, this method significantly increases both the isotopic selectivity and the dissociation yield, which is very important for its application for isotope separation in practice. This method was discovered in papers [69, 70] and was later widely used for isotopically selective dissociation of molecules [61–64], including OsO_4 [71, 72, 75–77] and UF_6 molecules (see Sections 8.3 and 8.4), which have small isotopic shifts in IR absorption spectra.

3.1.2 Low-energy methods. In the case of low-energy methods, the activation energies of processes underlying them are approximately an order of magnitude smaller than those for high-energy methods. They are $\leqslant 0.3 - 0.5$ eV. Such activation energies are typical for physicochemical processes of adsorption and desorption of molecules on surfaces, in particular, those covered by molecules or clusters, as well as on the surface of large clusters, and for dissociation and fragmentation of weakly bound van der Waals molecules. The MLIS of uranium has been studied quite extensively by low-energy methods in recent years [30–34]. Among many low-energy methods proposed at present, two [33, 34] are studied most of all and are of interest for practical realization, namely, the isotope-selective suppression of molecular clustering and the isotope-selective IR vibrational predissociation of weakly bound van der Waals clusters.

3.1.2.1 Method of isotope-selective repression of molecular clustering. This process in jets and flows with the use of IR lasers [33, 34, 78–82] is based on the preliminary (before the beginning of clustering) selective vibrational excitation of molecules during hydrodynamic expansion at the nozzle exit (Fig. 4a). As a result, during the subsequent condensation, the stored vibrational energy suppresses the clustering of excited
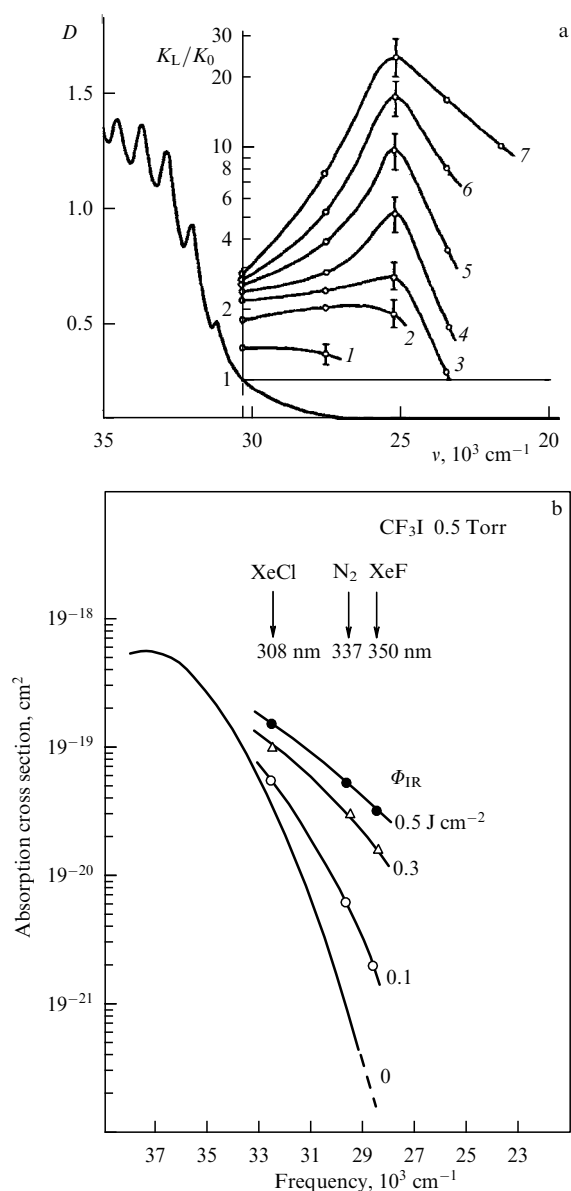
Figure 3. (a) Changes in the electronic absorption spectrum of OsO_4 molecules for excitation radiation intensities of 2, 4, 6, 7, 8, 9, and 10 MW cm^{-2} (curves *1–7*, respectively); K_L is the absorption coefficient of excited molecules, K_0 is the absorption coefficient of unexcited molecules. On the left, the long-wavelength wing of the electronic absorption band of OsO_4 is shown (D is the optical density) [5], (b) UV absorption cross sections of CF_3I molecules previously vibrationally excited by a CO_2 laser at different energy densities [54[.

molecules. In addition, molecular clustering can be controlled due to dissociation of small clusters (dimers) near the nozzle in the region of their formation [83–91]. In this case, it is necessary to ensure (for example, by the choice of suitable conditions for gas expansion) the predominant formation of dimers in the absence of larger clusters.

The method was proposed and studied in detail in papers [78, 80–82] using the example of clustering of SF_6 molecules with each other and with argon atoms. Today, this method is considered one of the viable and most promising methods for laser isotope separation [31–34]. The possibilities of its application for uranium isotope separation were considered in [31, 32] (see Section 9.1). In this method, a cluster beam is depleted with selectively excited molecules and is enriched
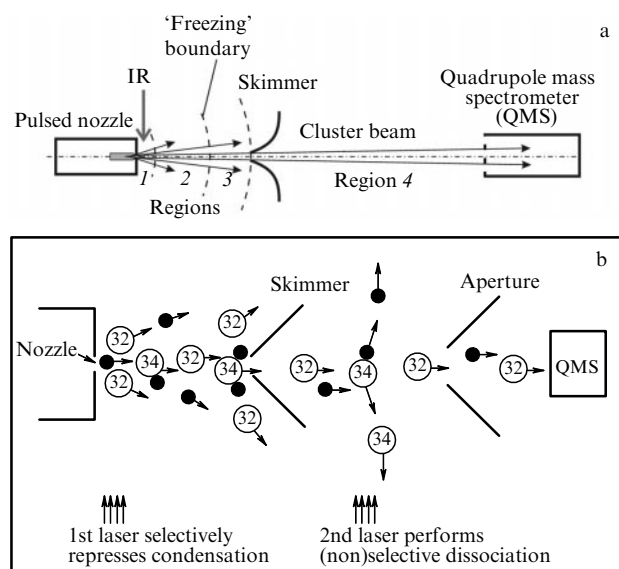
Figure 4. (a) Formation of a cluster beam in a pulsed jet. *1–4* — regions with different beam clustering degrees (*1* — beginning of clustering, *2* — growth of clusters, *3* — further growth and stabilization of clusters, *4* — free flight of clusters) [87]. (b) Two-step laser separation of sulfur isotopes. At the first step, selective repression of clustering is used, while at the second step, selective or nonselective dissociation of SF_6 clusters is performed. Circles with numbers 32 and 34 denote $^{32}SF_6$ and $^{34}SF_6$ molecules, black dots denote argon atoms.

with molecules which are not excited, because free molecules propagate within a considerably wider solid angle than the cluster beam does [92].

The method of molecular clustering (condensation) repression is sometimes called in the literature SILARC (Separation of Isotopes by Laser-Assisted Retardation of Condensation) [31, 32] or CRISLA (Chemical Reaction by Isotope-Selective Laser Activation or Condensation Repression by Isotope Selective Laser Activation (after 1995)).

3.1.2.2 Method of isotope-selective IR dissociation of van der Waals clusters. The method of isotope-selective dissociation of weakly bound van der Waals clusters (molecules), in particular, dimers, is based on their vibrational IR predissociation. The bond (dissociation) energy E_b of van der Waals molecules consisting of polyatomic molecules lies in the range $0.1 \leqslant E_b \leqslant 0.5$ eV, while the dissociation energy of van der Waals molecules consisting of a polyatomic molecule and a noble gas atom is $E_b \leqslant 0.1$ eV [93–97]. The absorption by a molecule of one or several IR photons at a wavelength of about 10 μm, for example, radiation from a CO_2 laser, leads to its dissociation over a weak bond. This method was patented in [98] by Y T Lee, a Nobel Prize winner in chemistry 1986, as a new method for separating isotopes of various elements. The method was recently investigated in detail for application to laser separation of uranium isotopes via the example of isotope-selective dissociation of small van der Waals SF_6 and CF_3Br clusters [34, 88–91].

In a number of cases, the IR absorption spectra of dimers and small homogeneous or mixed clusters are considerably narrower than those of free molecules and consist of rather narrow bands localized near vibrational frequencies of monomer molecules contained in the composition of clusters [93–96, 99]. This makes possible the selective excitation and dissociation of clusters.

During the dissociation of clusters due to recoil processes, fragments (monomers) 'fly out' of the beam. As a result, in a laboratory coordinate system, target molecules (dissociation products) propagate within a comparatively large solid angle determined by the mass and velocity of the molecules, while non-target molecules remain in the axial region of the cluster beam. The spatial separation of different isotopic components can be performed using specially chosen apertures (skimmers).

3.1.2.3. Combination of methods of molecular clustering repression and cluster dissociation. A combination of the two methods described above can also be used. Figure 4 shows via the example of SF_6 molecules the scheme of such a two-step separation process, in which the selective repression of molecular clustering is used at the first stage and the selective dissociation of clusters is used at the second stage. The first laser in a low-pressure chamber selectively excites $^{32}SF_6$ molecules at the nozzle exit, thereby repressing their clustering with argon atoms. The second laser in a high-pressure chamber then performs the selective (or nonselective) dissociation of clusters containing $^{34}SF_6$ molecules, which fly out of the beam due to the recoil process. The $^{32}SF_6$ molecules found in this region, even if they absorb IR radiation, do not in fact leave the beam. Therefore, even the nonselective excitation of clusters by broadband laser radiation in this scheme with two lasers can be used in principle for isotope separation.

3.2 Atomic vapor laser isotope separation method
To give a more complete idea of laser uranium isotope separation methods, consider briefly some important aspects of the atomic method [12, 13, 18, 24, 100]. It is based on the selective multiphoton ionization of uranium atoms (Fig. 5a). The ionization is performed by tunable dye lasers pumped by high-power copper vapor lasers. This method is well developed and widely used in practice (see, e.g., [18, 22, 24–26, 42]). The method is based on the fact that the absorption spectra of ^{235}U and ^{238}U atoms contain intense and rather narrow lines at frequencies coinciding with those of available laser lines.

The electronic absorption spectrum of uranium atoms contains many lines (about 3×10^5 [18]). The isotope-selective ionization of uranium is possible only by exciting atoms from the ground state using multifrequency radiation. Although the relative isotopic frequency shift in electronic spectra of uranium atoms is small ($\Delta v/v \sim 10^{-5}$), the selective excitation of atoms is no problem because of rather narrow laser lines. Therefore, rather high selectivity ($\alpha \geqslant 10^2$) can be achieved upon ionization of uranium atoms, which provides the production of enriched ^{235}U for nuclear reactors in one technological stage.

One of the most complicated processes in the technology of separation of uranium isotopes using atomic vapor is the evaporation of metal uranium. The pressure of uranium vapors is low, even at very high temperatures (about 10^{-4} Torr at 2000 K [18]). At the same time, both melted and evaporated uranium are very strong reagents [101]. In the AVLIS method, uranium vapors were obtained by the innovative method of metal uranium evaporation with an electron beam.

An important factor which should be taken into account in the AVLIS of uranium is that the fraction of uranium atoms in the ground state is only 47% at a temperature of 2800 K. About 27% of the atoms are at the level lying
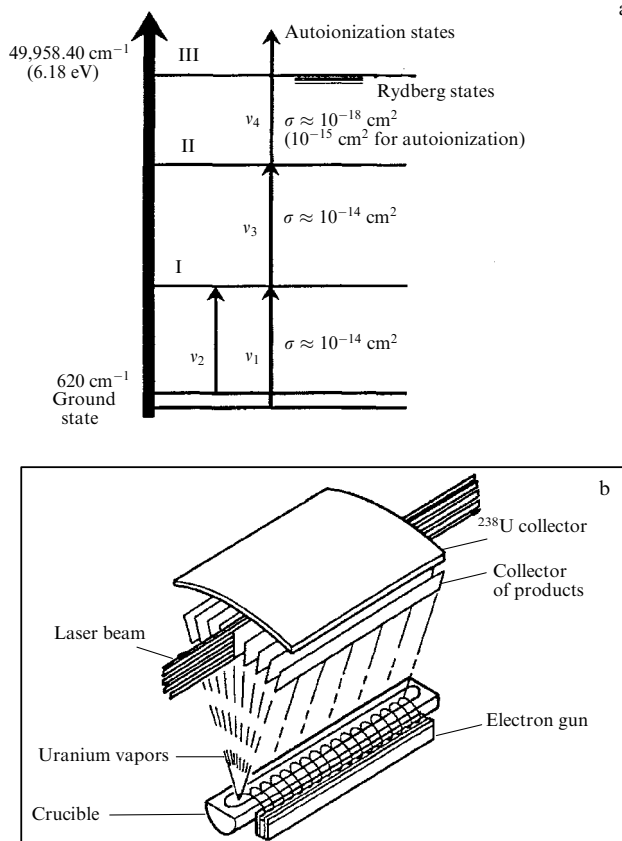
Figure 5. (a) Four-frequency scheme for uranium isotope separation by the selective ionization of atoms proposed for use in a pilot setup [100, 103]. (b) Separator model for laser uranium isotope separation by the method of selective ionization of atoms (AVLIS) [11].

620 cm^{-1} above the ground state, and the rest of them occupy the higher levels [102]. Therefore, to ionize at least half of the chosen kind of uranium atoms, two lasers are needed already at the first excitation step: the first one, to excite uranium atoms from the ground state to the first excited state, and the second, to excite them from the state lying only 620 cm^{-1} higher than the ground state.

Figure 5a shows uranium isotope separation proposed for a pilot setup in the Exxon-Avco project [103]. A similar scheme was used in projects on atomic laser separation of uranium isotopes in France, India, and Brazil. In this scheme using two dye lasers emitting at frequencies v_1 and v_2, about 75% of the uranium isotope can be transferred to the excited electronic state (I), from which they are excited by a laser at frequency v_3 to the second excited electronic state (II). Finally, the uranium atoms are excited from this state by a laser with frequency v_4 up to the ionization threshold (6.187 eV) and are ionized.

A concept model of a separator for the laser separation of uranium isotopes by the AVLIS method is shown in Fig. 5b. Metal uranium is evaporated with an electron beam in the lower part of a separator and uranium atoms fly at a velocity of $\approx 4 \times 10^4 \text{ cm s}^{-1}$ upwards into the region of the collector plates. Uranium vapors are irradiated by a laser between the plates. The $^{235}U^+$ ions produced in this way are extracted by electromagnetic fields and are deposited on the collector plates. ^{238}U atoms are collected on the separator cover [11]. Processes during selective multiphoton ionization of atoms

are described theoretically in detail in papers [24, 42, 104]. Detailed information on the atomic separation of uranium isotopes can be found in Refs [18, 22, 24–26].

4. Vibrational and electronic absorption spectra of UF$_6$
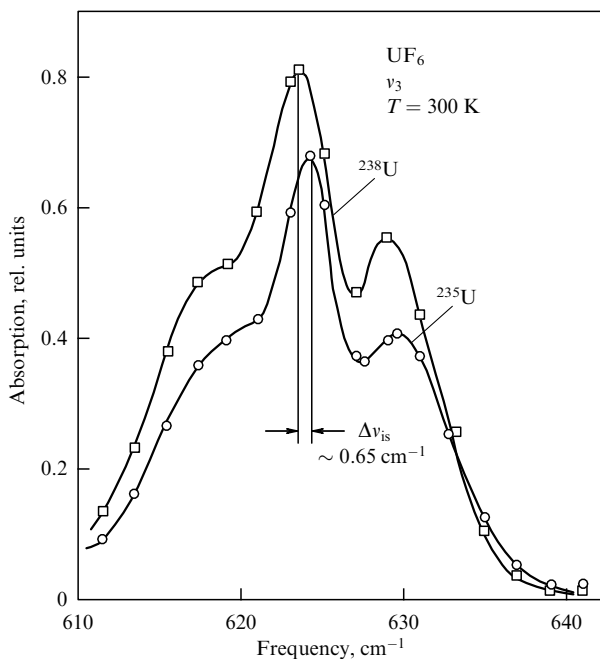
4.1 IR absorption spectra of UF$_6$ molecules

Uranium hexafluoride is the most suitable gas for molecular laser separation of uranium isotopes. The advantage of UF_6 is a comparatively high vapor pressure at room temperature and the absence of isotopes of a fluorine atom, which considerably simplifies the IR and UV absorption spectra of the molecule. In addition, the wide use of UF_6 in uranium enrichment technology makes it possible to purchase and store it.

The spectroscopic properties of the UF_6 molecule are analogous to those of the SF_6 molecule well studied in the aspect of selective IR laser dissociation. Both molecules belong to the O_h symmetry group and each has 15 degrees of freedom distributed between one nondegenerate Raman active mode, one doubly degenerate Raman active mode, and four triply degenerate modes, of which two are IR active, one is Raman active, and one is inactive [105, 106]. Vibrations at v_3 ($\approx 627.7 \text{ cm}^{-1}$) and v_4 ($\approx 146.7 \text{ cm}^{-1}$) are modes active in the IR absorption of the UF_6 molecule [105, 107]. Valence vibrations v_3 of UF_6 and SF_6 molecules have the maximum absorption cross sections as well as the largest isotopic shifts in IR absorption spectra.

The vibrational frequency v_3 ($\approx 948 \text{ cm}^{-1}$ [106]) of the SF_6 molecule coincides with the 10.6-μm emission line of a CO_2 laser. This facilitated numerous studies on the excitation of SF_6 molecules by IR radiation from CO_2 lasers, including the isotope-selective IR dissociation of SF_6 and laser separation of sulfur isotopes [4, 108–111]. In particular, the laser separation of isotopes at macroscopic scales with high enrichment coefficients was first demonstrated namely by the example of SF_6 molecules [4, 108]. Later, the mechanisms of multiphoton excitation (MPE) and many parameters of the isotope-selective laser IR dissociation of molecules were investigated based on the example of the SF_6 molecule [108–111].

Unlike this, in the spectral region of vibration v_3 of UF_6 ($\approx 627.7 \text{ cm}^{-1}$ [107]), lasers that are efficient and simple in operation were not available for a long time, which considerably hindered studies on the isotope-selective laser IR dissociation of UF_6 molecules. Some projects on the MLIS of uranium were initiated when lasers tunable in the 16-μm region required for the vibrational excitation of UF_6 molecules were not available yet. However, soon a 16-μm CF_4 laser pumped by a CO_2 laser was developed, as was a laser based on the shift of the CO_2 laser line in parahydrogen due to Raman scattering at rotational transitions in hydrogen molecules (see Section 6).

Because of a small isotopic shift in the absorption spectrum of UF_6 molecules at v_3 ($\Delta v_{is} \approx 0.604 \text{ cm}^{-1}$ for $^{235}UF_6$ and $^{238}UF_6$ [107]) and a comparatively large width (about 20 cm^{-1}) of IR absorption bands of these molecules (Fig. 6), a high selectivity of the IR dissociation of UF_6 at room temperature cannot be achieved. The laser IR dissociation of UF_6 molecules with a comparatively high selectivity can be achieved only at low temperatures when the IR absorption spectra of isotopomers of UF_6 are considerably
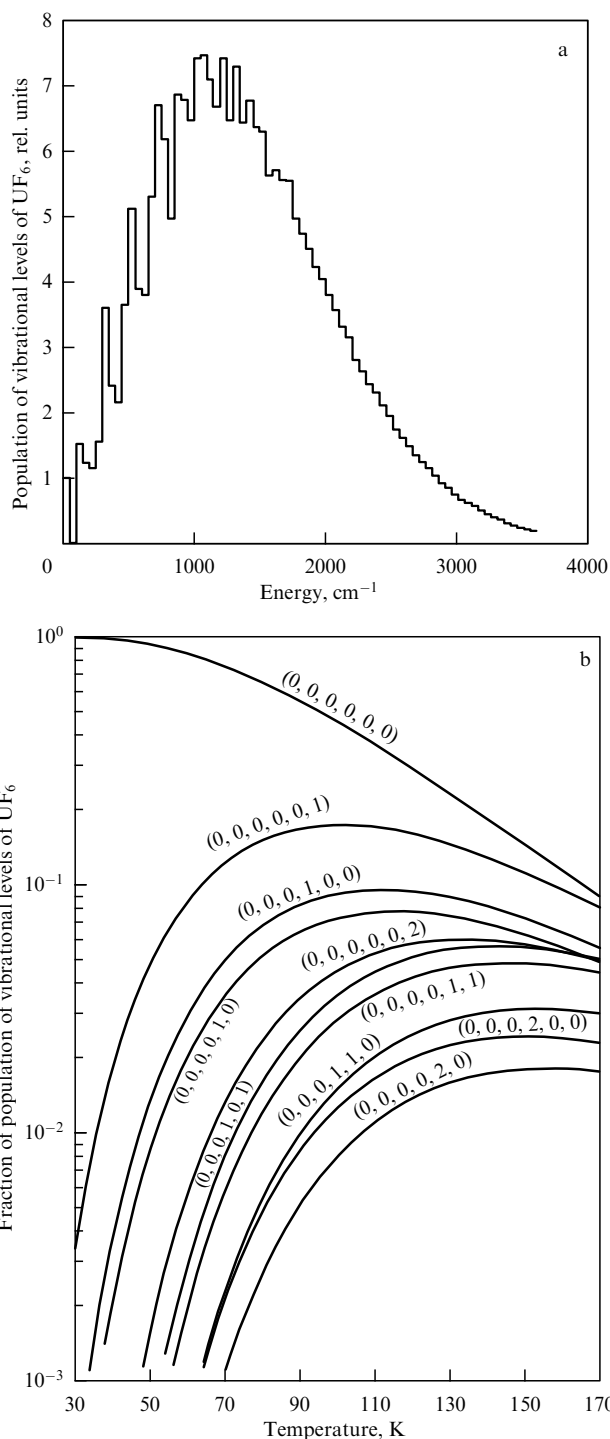
Figure 6. v_3 vibrational absorption spectra of $^{235}UF_6$ and $^{238}UF_6$ molecules in the ≈ 625-cm^{-1} region. Because of a small difference ($\approx 1\%$) in masses of uranium atoms, the isotopic shift is only about 0.65 cm^{-1} [101].

narrowed. At room temperature, UF$_6$ molecules are distributed among many vibrational and rotational states. Less than 1% of molecules (~ 0.004) (Fig. 7) occupy the ground vibrational level; the remaining molecules occupy higher levels. For this reason, the IR absorption spectrum of the v_3 vibration of the UF$_6$ molecule at room temperature mainly contains 'hot bands,' i.e., the absorption bands of molecules occupying not the ground level but higher vibrational levels. This and the high rotational temperature of the gas at room temperature cause the broadening of the IR absorption band of UF$_6$ molecules. To perform isotope-selective IR dissociation of UF$_6$, a strong cooling of the gas is required in order to obtain narrow IR absorption lines.

A strong cooling of UF$_6$ under static conditions is impossible due to gas condensation, and it is necessary to use gas-dynamic cooling in jets or flows. More efficient cooling of UF$_6$ is achieved using carrier gases, for example, Ar, H$_2$, and CH$_4$. Molecular gases H$_2$, CH$_4$, etc. serve simultaneously as acceptors of radicals (fluorine atoms) produced due to laser IR dissociation of UF$_6$ molecules. The gas cooling that can be achieved is determined by the ratio of pressures at the nozzle entrance (p_0) and exit (p) and by the ratio of thermal capacities $\gamma = C_p/C_v$ of the carrier gas [112]

$$T = T_0 \left(\frac{p}{p_0} \right)^{(\gamma-1)/\gamma}, \tag{1}$$

where T_0 and T are gas temperatures over the nozzle and in the flow, respectively. The gas-dynamic cooling of UF$_6$ results in a strong simplification of the IR absorption spectrum of molecule at v_3 (Fig. 8). This makes possible the laser isotope-selective IR excitation and dissociation of UF$_6$. By selecting the optimal laser emission frequency and intensity for exciting molecules, one can obtain a comparatively high dissociation selectivity (see Section 8.4).

Figure 7. (a) Dependence of the relative population of vibrational levels of UF$_6$ on energy at a temperature of 300 K [10]. (b) Calculated populations of the ten lowest vibrational levels of UF$_6$ as functions of temperature [10].

4.2 IR absorption spectra of homogeneous and mixed UF$_6$ clusters

Sometimes, isotope separation can be achieved by the method of isotope-selective dissociation of homogeneous or mixed clusters [81, 82, 87–90]. The IR absorption spectra of homogeneous UF$_6$ clusters and clusters mixed with argon atoms were investigated in detail by IR Fourier spectroscopy at the Institute of Chemical and Physical Studies (RIKEN) in Japan [113–115]. A mixture of UF$_6$ with inert carrier gas argon expanded through a continuous plane symmetric Laval
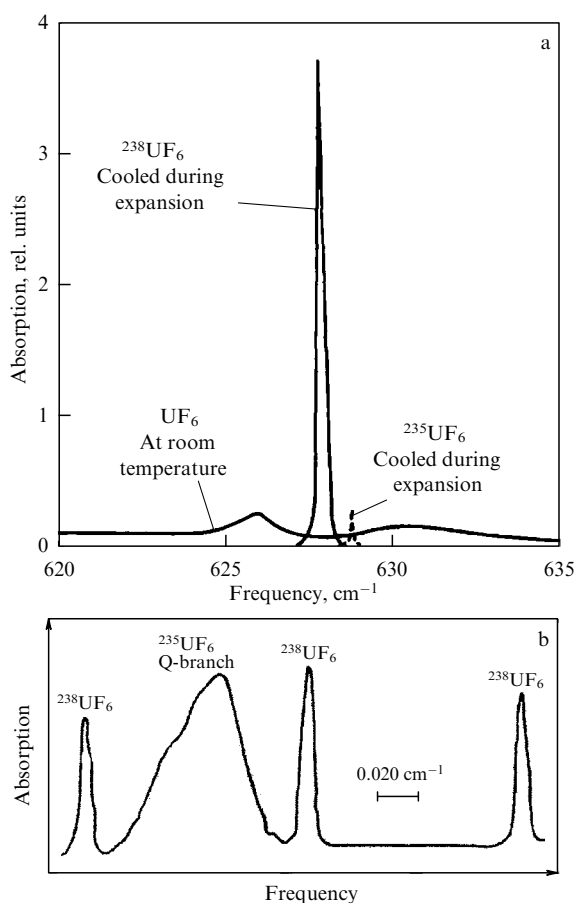
Figure 8. (a) v_3 vibrational absorption spectrum of UF_6 molecules cooled in a gas-dynamic jet to $T = 80$ K and the absorption spectrum at room temperature [8, 10]. (b) Small part of the v_3 vibrational absorption band of UF_6 molecules cooled in a gas-dynamic jet to below 100 K recorded at high resolution with a tunable diode laser. Sharp peaks are the R(5), R(6), and R(7) absorption lines (from left to right) of $^{238}UF_6$ molecules [8, 10].

Figure 9. IR Fourier spectra of UF_6 molecules and clusters obtained in a supersonic molecular jet of UF_6 molecules with argon at the molar fraction of 0.08 at a distance of 30 mm from a Laval nozzle exit [115]. See the text.

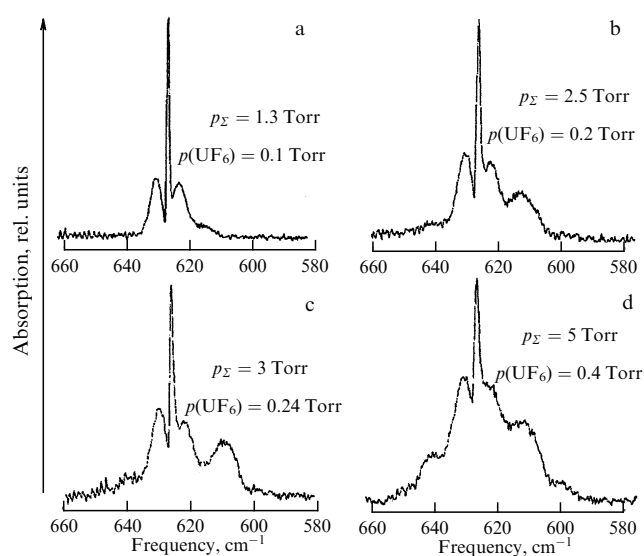nozzle restricted on both sides with KCl windows transparent to radiation at 16 μm. The nozzle provided the optical path in a gas-dynamic jet equal to 10 mm. The cluster formation process as a function of the UF_6 partial pressure was studied in paper [113]. The resolution of the IR Fourier spectrometer was 0.5 cm^{-1}. At the temperature of a molecular flow $\leqslant 130$ K, homogeneous UF_6/UF_6 were detected in the spectral region of about 600–650 cm^{-1}. The dissociation of clusters was studied in [114] using a Raman parahydrogen laser (see Section 6.3) emitting at 614.8 cm^{-1}, which was tuned to the vibrational absorption spectrum of UF_6 clusters.

In paper [115], the IR absorption spectra of UF_6 were measured in a jet with argon at a molar fraction of 0.08 at a distance of 30 mm from the nozzle exit at a temperature $\leqslant 130$ K. Figure 9 shows typical spectra at relatively high total mixture pressures. In the region of 620–635 cm^{-1}, the P, Q, and R branches of UF_6 molecules are observed. On the low-frequency side of monomer peaks in the region of 610–615 cm^{-1}, distinct peaks are present, while in the high-energy region (about 640 cm^{-1}), relatively weak peaks are observed. As the total pressure is increased, peaks in both regions increase, while the relative intensity of monomer peaks decreases. Peaks appearing upon increasing the total pressure of the mixture are the absorption peaks of homogeneous UF_6 clusters. Mixed clusters $(UF_6)_m Ar_n$ (where m and n

are the numbers of molecules and atoms in a cluster, respectively) were not formed under these experimental conditions, because the gas temperature was higher than the boiling temperature of argon (87 K) at a pressure of 1 atm. This is also confirmed by the fact that the shape of the peaks was the same as in experiments with argon or neon used as carrier gases. At a total gas pressure over $\leqslant 0.95$ Torr, no peaks, except monomer peaks, were observed.

One can see from Fig. 9 that the width of absorption bands of UF_6 dimers is about (FWHM) 10 cm^{-1} (see, for example, the 615-cm^{-1} absorption peak in Fig. 9c). For the isotopic shift Δv_{is} between $^{235}U^{238}U$ and $^{238}U^{238}U$ clusters of about 0.604 cm^{-1} (as for UF_6 molecules [107]), it is impossible to obtain high enough selectivity values by the cluster dissociation method. The absorption spectra of mixed $(UF_6)_m Ar_n$ clusters are also rather broad [116, 117]. Data on the width of absorption spectra of small van der Waals molecules including the UF_6 molecule and atoms of inert gases (for example, $UF_6 - Ar$ dimers) are absent in the literature. Note that isotope-selective dissociation of mixed $CF_3Br - Ar$ clusters was observed in [89] for CF_3Br molecules characterized by a very small ($\leqslant 0.25$ cm^{-1}) isotopic shift (with respect to bromine isotopes) in IR absorption spectra (see Section 9.3).

4.3 UV absorption spectrum of UF_6

The UV absorption spectrum of UF_6 molecules (Fig. 10) was studied in papers [19, 118–120]. It contains two bands, $X \rightarrow A$ and $X \rightarrow B$, caused by transitions from the ground electronic state X to excited states A and B located between 400–360 nm and 340–200 nm, respectively. Both transitions are predissociation transitions. The absorption of radiation in these bands causes the dissociation of molecules with the detachment of a fluorine atom [121]. The long-wavelength wing of the absorption spectrum is located in the region $\lambda_{UV} \approx 250 - 350$ nm (see Fig. 10). Therefore, the UV dissociation of UF_6 molecules selectively excited by an IR laser can be performed by $Xe - F$ excimer lasers emitting at $\lambda_{UV} \approx 353$ nm or by $Xe - Cl$ lasers emitting at $\lambda_{UV} \approx 308$ nm. Upon the UV
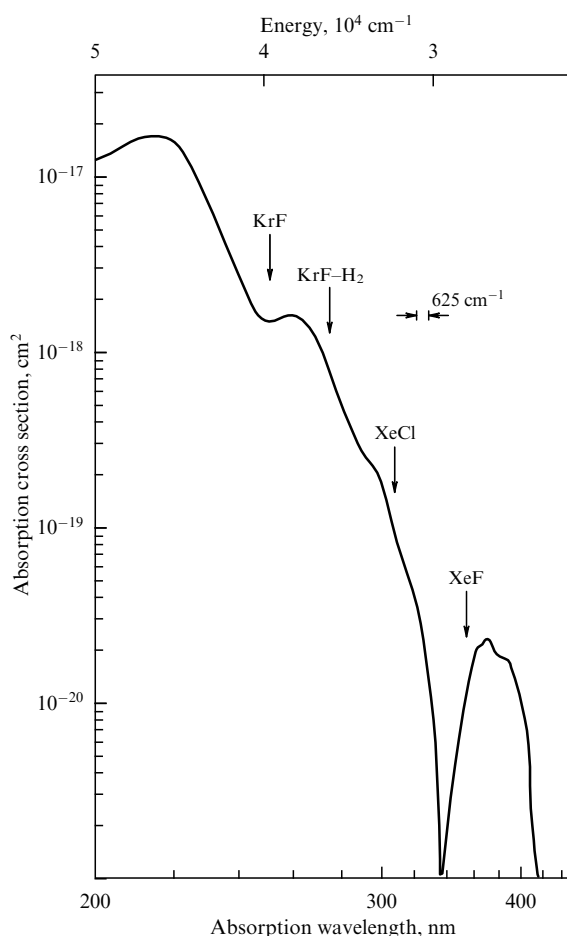
Figure 10. Electronic absorption spectrum of UF_6 in the visible (above 380 nm) and UV regions at room temperature. Arrows show the emission frequencies of corresponding excimer lasers [19, 118].

dissociation of UF_6 molecules, the same primary products (UF_5 and F radicals) are formed as upon their IR dissociation. The isotope-selective laser IR + UV dissociation of UF_6 molecules was performed in papers [19, 120] (see Section 8.3).

5. Basic parameters of laser methods for the separation of uranium isotopes

5.1 Motivation for applications of laser methods
The development of laser methods for uranium isotope separation in the mid-1970s was stimulated by at least two factors: the increasing demand for enriched uranium and the high selectivity of laser isotope separation methods. Demand in the West at that time was mainly satisfied by diffusion facilities. Centrifuges looked attractive and promising, but were still at the development stage. Along with the diffusion method and centrifuging, methods using a separation nozzle (Germany and Brazil), a vortex tube (South Africa), chemical exchange processes (France), a plasma centrifuge, cyclotron resonance, and lasers were also applied. However, these methods did not find large-scale applications for a number of reasons. The high selectivity of laser methods makes possible the extraction of a considerable fraction of the remaining 0.2–0.4% of ^{235}U in ^{235}U-depleted uranium hexafluoride, which was accumulated in large amounts in uranium-enrichment plants. During the 1990s, all these

Table 1. Selectivity of uranium isotope separation processes [27].

Method	Selectivity
Diffusion	1.003
Centrifuging	$\geqslant 1.5$
Mass spectrometry (electromagnetic process)	$10 - 10{,}000$
Separation nozzle (vortex process)	$1.015 - 1.05$
Laser AVLIS	$\leqslant 20{,}000$
Laser MLIS (IR MPD)	$\geqslant 5 - 10$
Laser MLIS (SILEX)	$2 - 20$

methods were discarded in favor of centrifuges, except the SILEX method.

In 2013, the last plant for diffusion uranium enrichment in Paducah (USA) was closed. Since then, enriched uranium has been produced by the centrifugation method. In recent years, at least two new motivations [27] for developing laser methods have appeared: (1) the SILEX company is actively discussing the question of using depleted uranium [38, 39] (see Section 9.2) and (2) in the USA, the necessity of replacing or even expanding separation output is observed, demonstrated by the import of enriched uranium from Europe and Russia [27, 122].

5.2 Advantages of laser technologies for separation of uranium isotopes
The potential advantages of laser isotope-separation methods over traditional methods are as follows [16, 47]:

(i) The high selectivity of the elementary separation event (Table 1). The separation coefficient (selectivity) α in one step in many traditional methods is very small, close to unity, and therefore, to achieve the high enrichment degree K, a great number ($n \gg 1$) of separation steps have to be used: $K = \alpha^n \gg 1$. At the same time, laser processes of the isotope-selective ionization of atoms and dissociation of molecules provide the separation coefficient $\alpha \gg 1$. This allows considerably reducing the number of separation steps and is only one step in a number of cases.

(ii) The possibility of separating required isotopes without strongly affecting other isotopes of the same elements, even in atomic or molecular gases containing several isotopomers. This can be achieved by properly tuning laser radiation.

(iii) Low energy consumption. The energy consumption per atom of the target isotope in traditional methods is considerably higher (by approximately an order of magnitude) than for laser methods.

(iv) Universality. With rare exceptions, laser methods can be efficiently used to separate isotopes of any elements with light, medium, and heavy masses, unlike traditional methods whose efficiency depends on the isotope mass.

(v) Short technology startup time. In the case of laser methods, a separation facility begins to work in the operation regime in fact at once, whereas the startup time for traditional methods can be a few months.

5.3 IR and UV photochemistry of UF_6
Upon laser IR multiphoton dissociation, UF_6 molecules are decomposed according to the formula

$$UF_6 + nh\nu \rightarrow UF_5 + F. \tag{2}$$

UF_5 radicals produced in the reaction precipitate and are polymerized. To couple fluorine atoms and suppress the recombination reaction of radicals, acceptors are used, commonly hydrogen-containing molecules, for example, H_2 or CH_4. The reaction of F atoms with acceptor molecules gives HF.

Upon UV irradiation of UF_6 in the long-wavelength segment of the electronic absorption spectrum (see Fig. 10), molecules are dissociated with the formation of radicals UF_5 and F. It was also found in [123] that UV irradiation both of pure UF_6 gas and in a mixture with H_2 leads to the production of a solid deposit consisting of a UF_3 and UF_4 mixture.

5.4 Basic parameters
of the laser isotope separation process
The basic standard parameters characterizing the laser isotope separation process are the dissociation (or ionization) yield β, the selectivity α, and the enrichment coefficient K in products and in a residual gas (in landfills). Let us define these parameters applied to UF_6 molecules.

The **dissociation yield**, for example, for $^{235}UF_6$ molecules (β_{235}) irradiated by a laser is described by the relation

$$N_L(235) = N_0(235)(1 - \beta_{235}\Gamma), \tag{3}$$

where $N_0(235)$ and $N_L(235)$ are concentrations of unexcited and excited $^{235}UF_6$ molecules, respectively, and Γ is the ratio of the irradiated volume to the total volume of a molecular flow (or gas in a cell). In experiments, the conditions are often realized when $\Gamma = 1$ (see Section 10).

The **selectivity** of dissociation of $^{235}UF_6$ molecules with respect to $^{238}UF_6$ molecules is defined as the ratio of the dissociation yields of these molecules:

$$\alpha = \frac{\beta_{235}}{\beta_{238}}. \tag{4}$$

The ^{235}U isotope **enrichment coefficient** of the $(UF_5)_n$ product formed with respect to the ^{238}U isotope is defined as the R_L/R_0 ratio, where R_L is the ratio of concentrations of these isotopes in the $(UF_5)_n$ product to the concentration ratio R_0 in the initial UF_6 gas:

$$K_{enr}^{pr}\left(\frac{^{235}U}{^{238}U}\right) = \frac{R_L}{R_0} = \frac{(^{235}U/^{238}U)_{in\,UF_5}}{(^{235}U/^{238}U)_{in\,UF_6}}. \tag{5}$$

The ^{235}U isotope **enrichment** (depletion) **coefficient** in the UF_6 residual gas with respect to the ^{238}U isotope, taking into account (3), is defined as

$$K_{enr}^{res}\left(\frac{^{235}U}{^{238}U}\right) = \frac{1 - \beta_{235}}{1 - \beta_{238}}. \tag{6}$$

We will also use relations similar to (3)–(5) by considering the results obtained for SF_6 and CF_3Br molecules.

6. IR lasers for vibrational excitation and dissociation of UF_6 molecules

6.1 Some remarks
One of the most important problems in the fulfillment of projects on laser uranium isotope separation was the development and application of efficient modern lasers with the required emission linewidth and energy. In the case of the

uranium MLIS using UF_6, the problem was the absence of a high-power IR laser tunable in the 16-µm region required for selective vibrational excitation of molecules. Initially, many studies on the IR dissociation and photochemistry of UF_6 molecules were performed using sensitizers (see Section 8.2). As sensitizers, molecules efficiently excited by high-power CO_2 lasers were used. The subsequent energy transfer from molecular sensitizers to UF_6 molecules resulted in their vibrational excitation and dissociation.

The absence of high-power lasers in the 16-µm region stimulated extensive investigations in this direction. The first proposals [10, 18] were the generation of laser emission tunable in lines in the 16-µm region due to the difference in emission frequencies between CO and CO_2 lasers, the frequency shift of the bending vibration of CO_2 (~ 667 cm^{-1}) in a nonlinear optical CdTe crystal, the use of stimulated Raman scattering at electronic transitions, and the use of an optical parametric oscillator (OPO) pumped by an HF laser [124].

Lasers for experiments on the isotope-selective dissociation of UF_6 should satisfy certain requirements concerning the emission power, frequency tuning, and the pulse repetition rate. Lasers emitting 0.01–0.1-J pulses about 10^{-7} s in duration with a pulse repletion rate above 0.1 Hz, tunable in the 610–640-cm^{-1} region, are required [18]. Later, two lasers tunable in the 16-µm region were rapidly developed: a molecular CF_4 laser pumped by a high-power CO_2 laser and a CO_2 laser tunable in the 16-µm region due to the stimulated Raman scattering of light by rotational transitions in parahydrogen.

6.2 Molecular CF_4 laser
The development of a CF_4 laser was first reported in paper [125]. The optical scheme of the laser is shown in Fig. 11a by the example of the most intense emission line at 615.2 cm^{-1} [126], while one of the first experimental schemes of a CF_4 laser is presented in Fig. 11b [127]. The laser emits at the $v_2 + v_4 \rightarrow v_2$ transition. A CF_4 molecule has the $v_2 + v_4$ combination band (~ 1067 cm^{-1}) overlapping with emission frequencies of a CO_2 laser. The excitation of this combination band by a high-power CO_2 laser results in stimulated emission in the 16-µm region due to the $v_2 + v_4 \rightarrow v_2$ transition. Detailed high-resolution spectral studies of the $(v_0 \rightarrow v_2 + v_4)$ absorption band and the $(v_2 + v_4 \rightarrow v_2)$ emission band were carried out by researchers at Los Alamos [126], the Prokhorov Institute of General Physics, RAS (IOFAN) [128], and the Institute of Spectroscopy, RAS [129, 130].

The authors of paper [125] used a CO_2 laser operating at the 9R(12) line with a pulsed energy of about 1 J to pump a CF_4 laser and obtained an output energy up to 4 mJ at a frequency of 615 cm^{-1}. The energy conversion efficiency was about 3%. Later, upon pumping by CO_2 lasers with different isotopic modifications of CO_2 [128, 131, 132] and CF_4 [133] molecules, more than 100 emission lines of a CF_4 laser were observed in the spectral region from 605 to 655 cm^{-1}. Extensive information on emission lines of a CF_4 laser is presented in paper [126].

The CF_4 laser was studied and developed in many papers [126–137]. The tuning range of the laser was investigated [126, 129–133], and the dependence of the emission energy on the gas composition, pressure, and temperature [126–130] (Fig. 12) and also on the spectrum and width of the emission line of a CO_2 laser exciting CF_4 molecules was considered (see, for example, reviews [129, 130, 136] and references therein). It was found that the laser emission can be tuned in
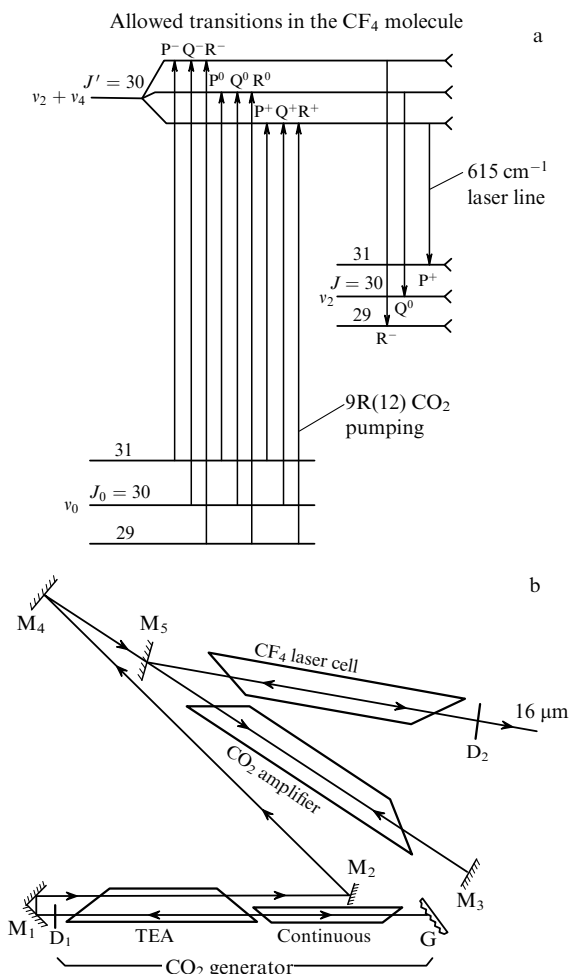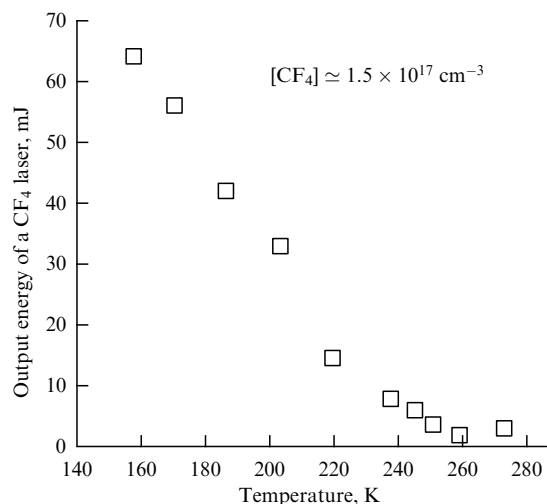
Figure 11. (a) Typical energy level diagram of a CF_4 laser with quantum numbers of the total angular momentum in the ground vibrational state and $v_2 + v_4$ and v_2 states denoted by J_0, J', and J, respectively. Arrows show allowed transitions to three $J' = 30$ Coriolis sublevels of the $v_2 + v_4$ state and allowed laser transitions to the v_2 state. Pumping of $^{12}C^{16}O_2$ molecules by the 9R(12) laser line at the $R^+(29)$ transition leads to the population of the $J' = 30$ level. Stimulated emission occurs from this level to the $J = 31$ level of the v_2 state. As a result, the CF_4 laser emits an intense P(31) line at 615 cm^{-1} [126]. (b) Experimental scheme of a CF_4 laser. ($M_1 - M_5$): mirrors, G: diffraction grating, D_1, D_2: apertures [127].

Figure 12. Dependence of the output energy of a CF_4 laser on the gas temperature in a cell [127].

the region of 612–645 cm^{-1} [126, 128–131]. The laser energy can reach 0.4–0.5 J per pulse [129, 130, 136] and the pulse repetition rate can be up to 10 Hz [129, 130, 136]. The continuous operation regime of the laser was also obtained [137].

Due to a rich spectral substructure of molecular transitions, the CF_4 laser allows us to perform potentially a precise tuning of the emission frequency with a discreteness of $\leqslant 0.1$ cm^{-1} [130, 138]. To provide a more precise tuning of the CF_4 laser line to the absorption lines of UF_6 molecules, pumping was also done by continuously tuned high-pressure CO_2 lasers [138, 139]. Laser pulses were obtained with energies exceeding 100 mJ with an energy conversion coefficient up to 10% [129, 130]. The average emission power of the CF_4 laser reached 2.5 W at the optimal pulse repetition rate of 80 Hz [140] and 2 mW in the continuous-wave mode [137].

The tuning characteristics of the CF_4 laser considerably depend on the overlap of its emission band with the absorption band of the molecule at the $v_0 \rightarrow v_4$ transition. Because of the low CF_4 absorption cross section at the pumped transition and a small gas operating pressure (due to overlap of the laser emission band with the absorption band), to obtain efficient lasing, it is necessary to use narrow-band pumping resonantly with absorption lines of CF_4 molecules. The characteristics of the CF_4 laser are considerably improved when a low-pressure CO_2 laser is used in the resonator of a high-power pump laser to narrow its emission spectrum [134, 141]. To obtain energy-stable lasing, it is necessary to stabilize the pump laser frequency with an accuracy of up to 5 MHz [142, 143]. Low absorption coefficients for the pump radiation and the low-lying lower laser level require the use of long cryogen cells in order to obtain efficient lasing. Commonly, CF_4 laser cells are cooled with liquid nitrogen vapors to 110–150 K [129, 130, 136].

Significant disadvantages of the CF_4 laser in application to the uranium isotope separation, other than its comparatively complicated use in experiments, is the discreteness of its tuning over individual lines and the absence of strong and tunable emission lines in the region of the vibrational Q-band v_3 of $^{235}UF_6$ molecules (628.3 cm^{-1} [107]). It seems that, for this reason, the isotope-selective dissociation of UF_6 molecules was not achieved using this laser. However, CF_4 lasers were used in experiments on two-frequency excitation and dissociation of UF_6 molecules, in particular, together with a CO_2 laser to study various aspects of the IR-MPD of UF_6 not related to the isotopic selectivity of the process (see Section 8.4).

6.3 Parahydrogen Raman laser

To date, the only efficient IR radiation source with acceptable energy characteristics that can provide the selective excitation of $^{235}UF_6$ molecules is a para-H_2 laser that can be used both in the MLIS and SILEX technology. A scheme for obtaining a potentially efficient radiation source emitting a comparatively high energy in the 16-μm region was first proposed by Byer [144]. Upon pumping a para-H_2 gas by 8.5-MW pulses from a CO_2 laser, a weak signal gain was observed at a level of above 80 dB for the transverse TEM_{00} mode. In experiments with parahydrogen, a multipass cell (15 passages) cooled to the liquid nitrogen temperature was used. Gas cooling is

necessary for transferring parahydrogen particles from excited rotational states to the ground rotational sublevel.

This scheme is based on stimulated Raman scattering of radiation from a high-power CO_2 laser by rotational transitions in H_2 molecules. The author of [144] assumes that this scheme for generating 16-μm radiation can provide a conversion of about 10% of the CO_2 laser energy to a Stokes wave. The remaining 10.2-μm photons of the CO_2 laser can be used for multiphoton excitation and dissociation of selectively excited $^{235}UF_6$ molecules. Using high-power CO_2 lasers available at present, this method can be applied to generate 16-μm pulses with an energy exceeding 1 J and a pulse repetition rate above 1 Hz. Moreover, the author of [144] believes that the further development of CO_2 lasers will provide the generation of 16-μm pulses with a pulse repetition rate of about 1 kHz required for efficient isotope separation in commercial projects.

The operation principle of such a laser is presented in Fig. 13a. High-power CO_2 laser radiation is scattered by rotational levels of molecular hydrogen. As a rule, the H_2 para-component is used (where the nuclear spins of two atoms are parallel). Due to this inelastic scattering, the emission frequency of the CO_2 laser decreases by the rotational quantum frequency ≈ 354.3 cm^{-1} of the H_2 molecule and falls into the 16-μm range. The tuning of the CO_2 laser automatically causes the tuning of the para-H_2 laser emission. To obtain the required gain and a comparatively high conversion efficiency, a special multipass cell is used [145]. Figure 13b shows an experimental scheme using a para-H_2 laser [146].

Mirrors of a multipass cell should provide the required pump-radiation focusing. The energy conversion to 16-μm emission in such a device can reach 25% [147]. For industrial applications, the device should operate at a high pulse repetition rate of at least ~ 1 kHz to irradiate a considerable part of the UF_6 flow. This required a considerable amount of work for the development of an industrial prototype of such a laser, including the development of an optical scheme, the choice of the optimal pressure of H_2, gas cooling, etc. [18]. To obtain a high conversion efficiency, the pump power (Fig. 14) [148] and the optical quality of pump radiation (the homogeneity of the transverse spatial distribution, low divergence, energy stability, etc.) [145, 146] should be high. The operation of a para-H_2 laser at room temperature was demonstrated in [149]. The photon conversion efficiency was 60% for the 10.6-μm CO_2 laser pump energy of 4.3 J, which gave 0.85 J in the first Stokes pulse at 17.0 μm.

Note that the emission lines of the para-H_2 laser do not exactly coincide with the center of the Q-branch of the ν_3 absorption band of $^{235}UF_6$ at ≈ 628.3 cm^{-1} [107]. To provide such a coincidence, a high-pressure CO_2 laser can be used by replacing the carbon and oxygen isotopic composition of its active medium and continuously tuning its emission frequency to the required value. In this laser based on Raman scattering, the D_2 ortho-component can also be used as an active medium [144].

7. Brief historical excursus into studies on the laser separation of uranium isotopes

Consider briefly studies performed in projects on laser separation of uranium isotopes in countries where the greatest progress has been achieved and the most significant results have been obtained.
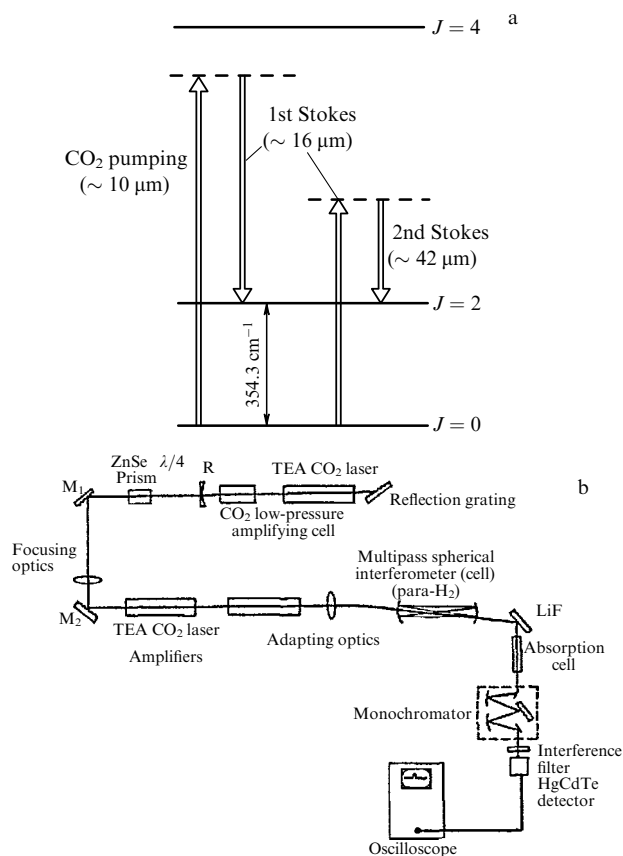
Figure 13. (a) Operation principle [144] and (b) experimental scheme with a para-H_2 laser [146].
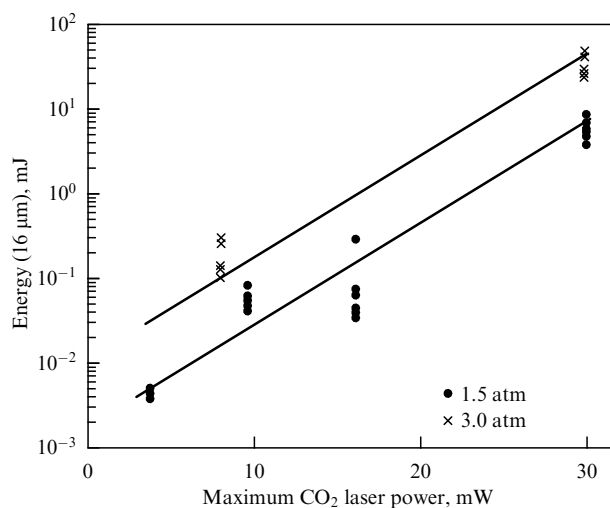
Figure 14. Output emission energy at 16.95 μm as a function of the peak CO_2 laser pump power [148].

USA

In the USA, laser studies on uranium isotope separation were most extensively performed at two classified laboratories of the US Department of Energy: Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL). In addition, the AVCO Everett Research Laboratory (AERL), Aerospace Industry, in cooperation with the Jersey Nuclear Company (now the Exxon Nuclear Company), were involved in this research. Studies at LLNL and AERL used the AVLIS method, while at LANL the MLIS

method was used. Projects on the laser separation of isotopes began at LANL [8–11] and LLNL [6, 7, 150] in 1972.

In the first half of the 1980s, researches at LLNL built an experimental facility with a potential productivity of about 10^3 kg of low-enriched uranium per year. The production of a few kilograms was reported. Uranium was enriched by ionizing uranium vapors in the scheme shown in Fig. 5a. Metal uranium was evaporated by an electron beam in a separator unit located in a vacuum chamber and expanded at a velocity of about 5.9×10^4 cm s^{-1} to a region irradiated by lasers (see Section 3.2 and Fig. 5a, b). ^{235}U vapors were excited and ionized by dye lasers pumped by copper vapor lasers. The laser pulse duration was 20–30 ns and the pulse repetition rate was about 10^4 Hz.

This project received an investment of about 2 billion dollars. Researchers at the Livermore Laboratory planned to develop a technology and demonstrate the separation of uranium isotopes using a large-scale pilot facility. The first stage of work on separating uranium isotopes was fulfilled in the early 1990s, and in the late 1990s the technology of uranium isotope separation was developed for commercial applications. The production of uranium enriched to 3–5% with ^{235}U was worked out and it was shown that a comparatively small compact system consisting of one separator can give a result equivalent to that obtained using several thousands of centrifuges. However, in 1999, the United States Enrichment Corporation (USEC) suspended project funding.

The AERL project on the laser isotope separation by the AVLIS method was developed quite successfully at the first stage. This was considerably facilitated by competition with the LLNL. Here, many studies on uranium atom spectroscopy, the development of schemes for multiphoton excitation and ionization of atoms, and the development of lasers were performed [6, 7, 150]. The isotope-selective dissociation of uranium-containing volatile organic compounds was investigated [151, 152] (see also Section 8.1). However, stable funding for the research at the LLNL by the US Government provided a more successful development of these studies namely at this laboratory. In 1981, the project on the laser separation of uranium isotopes at the AERL was suspended.

Researchers at the LANL performed extensive MLIS studies of uranium [8–11]. In 1972, a new scientific Department of Applied Chemistry was created here [153] for the laser separation of uranium isotopes by the method of isotope-selective dissociation of UF$_6$ molecules. This method seemed to be promising, and the program was rapidly developed [153]. Numerous investigations were performed, especially on the spectroscopy of UF$_6$ and SF$_6$ molecules [8–10, 107, 154–159], the development of optimal schemes of two-frequency IR and IR + UV excitation and dissociation of molecules [9, 10], and the development of lasers for isotope-selective dissociation of UF$_6$ [125–127].

The macroscopic separation of sulfur isotopes was performed on a pilot setup using the recirculation of irradiated gas [9, 10]. Experimental and pilot setups were developed with gas-dynamic cooling and UF$_6$ gas recirculation with a carrier for the isotope-selective dissociation of UF$_6$ molecules and uranium isotope separation. In 1976, milligrams of weakly enriched uranium were obtained by the MLIS method using a laboratory setup with a pulsed molecular flow. The dependences of the parameters of the isotope-selective dissociation of UF$_6$ molecules (selectivity and dissociation yield) on those of the molecular flow and

exciting lasers were studied to obtain optimal parameters for enrichment of uranium on a pilot setup [9, 10]. However, beginning in 1983, project funding was reduced: the US Government preferred the AVLIS project performed at the LLNL.

After the termination of the project on the laser separation of uranium isotopes, researchers at the LANL began MLIS studies for plutonium. However, "because of the abundance of the reactor uranium in the world market," the plutonium project was also suspended in the late 1980s [153]. A number of results of MLIS studies for uranium performed at the LANL are considered in Sections 3.1, 6.2, 8.3, and 8.4.

USSR–Russia
In the USSR, laser methods for uranium isotope separation were initiated in the 1970s at the Kurchatov Institute of Atomic Energy (IAE) and its branch (FIAE) in Troitsk, the General Physics Institute, USSR Academy of Sciences (IOFAN), the Lebedev Physical Institute, USSR Academy of Sciences (FIAN), and the Institute of Spectroscopy, USSR Academy of Sciences (ISAN) [14, 23, 24, 26, 128–131] (see also Sections 8.3 and 8.4). At IAE and FIAN, both molecular and atomic uranium isotope separation were studied, while researches at FIAE, IOFAN, and ISAN investigated the molecular case. This activity was developed within the framework of small projects and mainly had a fragmentary character [134, 138–140, 160–168]. Individual problems related to the separation of uranium isotopes were studied, including the development of lasers [128–131, 140, 167] and excitation schemes for atoms and molecules [160, 161, 165], spectroscopic investigations of molecules and lasers [128, 165,166], measurements of the absorption of laser radiation by UF$_6$ molecules [160–163], multiphoton ionization of a uranium atom [24, 26], and dissociation of UF$_6$ molecules [160, 161, 164, 165, 168].

At the same time, many studies at these scientific centers, especially at ISAN, involved the SF$_6$ molecule [4, 61, 64], which is similar in its spectroscopic and some chemical properties to the UF$_6$ molecule. Some other molecules were also investigated [61, 169–172], including BCl$_3$ molecules [3, 4, 61, 172], OsO$_4$ [5, 61, 75–77], CF$_3$I [61, 173], and CF$_2$HCl [61, 65–68, 174]. Note that many investigations were devoted to the separation of uranium isotopes in UF$_6$ molecules. A significant difference between SF$_6$ molecules and UF$_6$ molecules in the MLIS aspect is the former's comparatively large isotopic shift for the molecular vibration v_3 excited by laser radiation ($\Delta v_{is} \approx 17$ cm^{-1} for ^{32}SF$_6$ and ^{34}SF$_6$ molecules [175, 176] and $\Delta v_{is} \approx 0.604$ cm^{-1} for ^{238}UF$_6$ and ^{235}UF$_6$ molecules [107]).

Many characteristics of the isotope-selective IR MPD of molecules were studied via the example of SF$_6$ at ISAN and other scientific centers [61, 64, 177–181] (see also Sections 3.1, 8.3, and 8.4). The isotope-selective IR multiphoton dissociation of OsO$_4$ molecules was studied in [5, 75, 76]. This molecule, like the UF$_6$ molecule, has a small isotopic shift of ≈ 0.262 cm^{-1} per atomic mass unit in the IR absorption spectrum of the v_3 vibration excited by laser radiation [182, 183]. Note that the selective dissociation of molecules was performed both by single-frequency [5, 71] and two-frequency [72, 75, 76] methods. It was shown that the two-frequency method can significantly increase the selectivity and the dissociation yield of molecules.

A combined project of FIAE and ISAN performed in the late 1970s resulted in the development of a semi-industrial

facility for the laser separation of sulfur isotopes by the IR MPD of SF_6 molecules by a repetitively pulsed CO_2 laser [184]. Weighed amounts of SF_4 enriched with the ^{34}S isotope were produced [185–187]. In 1979, a semi-industrial facility was started in Tbilisi (Georgia) for the separation of carbon isotopes using the method of IR MPD of CF_3I and CF_3Br molecules developed in a combined project involving ISAN, FIAE, and the Research Institute of Stable Isotopes (Tbilisi) [188].

Later, in 1998–1999, researchers at ISAN and FIAE developed and started in Kaliningrad [65–68] a semi-industrial pilot setup for separating carbon isotopes by the method of selective IR MPD of CF_2HCl molecules (freon-22). This setup produced carbon dioxide enriched with the C^{13} isotope (containing up to 30–35% of C^{13}). It operated successfully until 2005.

Based on the IR multiphoton excitation of molecules, at ISAN, the laser spectroscopy of highly excited vibrational molecular states was developed and the spectra of transitions between excited molecular states were studies in detail. In addition, the dynamics of intermolecular and intramolecular redistributions of the vibrational energy during the IR MPD of molecules was investigated [61, 189–191].

The development of the MLIS methods for uranium and other heavy elements at ISAN includes recent investigations of low-energy MLIS methods with the use of molecular and cluster beams [33, 34, 64, 181] and of alternative methods [33, 181]. Some results are considered in Sections 3.1, 9.3, 9.4, and 10.

Studies on the development of methods for the laser separation of uranium isotopes, including UF_6 spectroscopy and the development of lasers and laser technologies, are also being performed at present in a number of other scientific centers in Russia. Thus, in [192], the $v_1 + v_3$ vibrational absorption spectra of $^{238}UF_6$ and $^{235}UF_6$ molecules in the mid-IR region of ≈ 7.68 μm were studied with a high spectral resolution using a tunable diode laser. The efficient generation of the difference radiation frequencies of CO and CO_2 lasers in the 16-μm region in a nonlinear optical $AgGaSe_2$ crystal was demonstrated in [193]. In [194], the generation and amplification of high-power nanosecond pulses was obtained from a CO laser in the active mode-locking regime. High-power ($\approx 2-3$ kW) CO lasers emitting in the 5.3-μm region are being developed [195, 196], which can be used to separate uranium isotopes by exciting UF_6 into the $3v_3$ absorption band (≈ 1875.5 cm^{-1}) [156] (the isotopic shift is about 1.8 cm^{-1} [107, 156]). Projects are being developed on the intracavity laser separation of uranium isotopes by suppressing the condensation of UF_6 molecules with the help of an actively mode-locked CO laser [196].

France

Studies on the laser separation of uranium isotopes began in France in 1985 [12, 13]. They were based on the SILVA method (Séparation Isotopique par Laser de la Vapeur Atomique d'uranium — French version of AVLIS). The research was performed at Saclay and Pierrelatte in close cooperation with the Atomic Energy Commission, CEA (Commissariat a l'Energie Atomique) and the COGEMA company, the world leader in the nuclear energy industry (at present, it is joining the AREVA holding). The SILVA program included the development and creation of laser systems, a separator, the required equipment and components, and the development of methods for testing materials and equipment used in the research. Three sets of 100-W copper vapor lasers (with amplifiers) and four sets of dye lasers (also with amplifiers) pumped by copper lasers were created for the MPE of ^{235}U atoms. A separator was made in which uranium was evaporated to obtain an atomic vapor, uranium atoms were selectively irradiated by laser radiation, liquid flows of enriched and depleted uranium atoms were collected, and nonirradiated uranium vapors were recirculated.

In addition, a plan for a pilot facility was developed for testing an extractor/collector system under physicochemical conditions and on a scale typical of a large-scale technological process. The facility was built, and laser systems and a separator were created. The uranium isotope separation achieved in it showed a comparatively high enrichment of the product (up to 5.5% of ^{235}U). The efficiency of the facility was 1–10 g h^{-1}. A technical and economical analysis of the results of the project gave strong confidence to researchers and investors in the potential success of this innovation process. The project was directed to the building of an industrial facility by 2010.

In late 1996, successful tests of the enrichment characteristics were performed at the pilot facility. Researchers planned to deplete residual natural uranium down to a level of 0.2% of ^{235}U. The result obtained exceeded all their expectations: the depletion reached 0.13% of ^{235}U per cycle. A computer code, LACAN, was developed for simulating the characteristics of the separator, evaporator, and lasers.

In 1997, characteristics of the technological process (productivity, composition of products and landfills, enrichment degree), the state of operation with uranium flows in the separator, the operation lifetime of the laser system, and the reliability of individual components and materials under operation conditions were estimated as a whole. The economic efficiency of the industrial application of the method under development was also estimated. A date to build a completely integrated industrial pilot facility was determined and a plan for the step-by-step development of the SILVA project was formulated.

The program was terminated in 2003. It seems that, at present, it is assumed the SILVA method is being used for the laser separation of plutonium ^{242}Pu isotopes, which are applied, in particular, in atomic reactors of power systems in ships and submarines [197].

India

Programs on the laser separation of uranium isotopes in India were initiated in the early 1980s at the Bhabha Atomic Research Centre (BARC) in Bombay (now Mumbai), the leading interdisciplinary nuclear research center in India. Both molecular [15, 16, 198] and atomic [16] methods of separation of uranium isotopes were used. Laboratory studies were extensively performed in both areas. In 1993, a large-scale pilot facility for AVLIS investigations was built [15, 16].

Three approaches to the problem were considered: a molecular approach using a CO_2 laser and specially selected uranium-containing molecules, another molecular approach using UF_6 and a 16-μm laser, and an atomic approach using uranium vapors and tunable dye lasers. In all three approaches, the infrastructure was created for studies.

The isotope-selective dissociation of volatile organic molecular uranium compounds was performed using a CO_2 laser [15, 16, 198–200] (see also Section 8.1). Studies on the

laser IR dissociation of UF_6 molecules were initiated and actively carried out using sensitizers — polyatomic molecules that strongly absorb CO_2 laser radiation and transfer energy to UF_6 molecules due to a vibrational–rotational $V-V$ exchange [15, 16, 201, 202] (see Section 8.2).

Later, both molecular approaches were suspended and attention was focused on the AVLIS method. The ^{235}U enrichment obtained in laboratory setups within the framework of this project was between 2.5 and 3% [16]. Studies on the laser separation of uranium isotopes are being performed in India at present as well [15, 16, 203–205].

Great Britain, Germany, Netherlands

Studies on the laser enrichment of uranium in Great Britain, Germany, and the Netherlands were carried out from the 1970s and were supported by the British company Urenco Group, which produced the nuclear fuel. In Great Britain, the atomic method was used, in Germany, molecular, while in the Netherlands, some particular aspects of both processes were studied. Thus, Urenco had the unique opportunity to compare the costs, risks, and potential of the laser and centrifugal enrichment technologies. The results achieved by the partners of Urenco and the reasons for a political solution to terminate further studies on laser uranium enrichment methods are considered in detail in paper [17].

In **Great Britain**, research on laser uranium enrichment began in 1974 at the United Kingdom Atomic Energy Authority (UKAEA). Initially, both the molecular and atomic methods were studied. In 1983, the decision was adopted to focus attention on the atomic method as more economical. In 1986, an agreement was signed about collaboration between British Nuclear Fuels (the British partner of Urenco) and UKAEA. Later, partners of Urenco in all three countries agreed to expand the combined activity on laser uranium enrichment.

By 1987, multiphoton (three-step, 3×2 eV) isotope-selective ionization of uranium atoms was observed in UKAEA experiments in Harwell. The experimental setup included copper vapor lasers and dye lasers. Metal uranium was evaporated in a small electron-beam vaporizer (EBV1). Later, the decision was made to develop new experimental setups, including an LPDF setup for laser equipment testing to estimate the possibility of technical realization and the economic attractiveness of the method [206].

From 1986 till the 1990s, the LPDF setup was designed, built, and put into operation. It included copper vapor lasers (CVLs) with amplifiers and three chains of dye lasers (MOPA). The possibility of CVL operation for 10^5 h was demonstrated. However, although the possibility of building the required laser system was confirmed (ignoring economic considerations), the conclusion was made that the main problems in using the atomic method concern metal uranium evaporation technology, the collection of $^{235}U^+$ ions, and the processing of the product obtained and tail flows in the amount of several hundred tons per year.

To evaluate electron-beam uranium evaporation technology, an EBV2 experimental setup with a 250-kW electron gun was built and put into operation from 1986 through the 1990s. It was also used to develop and test methods for collecting ions at densities typical of a plant and studying characteristics of the metal uranium evaporation process and the corrosion of materials used. It was found how the uranium evaporation efficiency can be improved, how to solve the problems of liquid uranium handling, and how to prevent the corrosion of

materials. Also, an efficient method for the collection of ions was developed.

In **the Netherlands**, materials and coverings to use with liquid uranium were studied in detail. The most promising of them were tested in operation in the EBV2 setup. The results were analyzed and estimated in late 1992. The conclusion was reached that it is unlikely that technology based on the CVL/dye laser system and three-photon excitation of uranium atoms can compete with advanced centrifuging technology. At the same time, the project was continued for an additional two years in order to estimate the long-run prospects of laser technology based on two-photon excitation using solid-state lasers. This decision stimulated extensive spectroscopic studies of uranium atoms in Almelo and the development of excimer lasers at the Nederlands Centrum voor Laser Research (NCLR) [206].

In **Germany**, MLIS studies were carried out starting in 1971 within the framework of a research institute [18, 27, 207, 208]. Since 1975, this research has been concentrated at the Uranit company (Urenco Deutschland at present) in Jülich. The aim of the research was the demonstration of the possibility of uranium enrichment with the ^{235}U isotope required for atomic reactors in a single-stage process at reasonable UF_6 gas densities and reasonable laser energies. These conditions dictated the requirement that the UF_6 gas density in the MLIS method exceed uranium vapor densities used in the atomic method by approximately two orders of magnitude, the laser pulse energy being no more than 1 J. The main tasks of the program were to determine the dependence of the isotope separation efficiency on the UF_6 density and laser parameters; the optimization of the nozzle construction capable of providing the required temperatures and UF_6 concentrations in a flow; and the development of laser systems emitting 16-μm pulses at a high pulse repetition rate.

Molecular-beam studies, in which UF_6 gas enriched with the ^{235}U isotope up to 50% in a mixture with a carrier gas expanded from a circular nozzle, demonstrated that the requirements for a single-stage process can be fulfilled. Then, experiments were carried out using a pulsed slit nozzle 20 cm in width in a closed circuit containing a photolysis chamber and a section for separating the UF_5 product. The duration of a typical experiment was less than 1 h at a laser pulse repetition rate of 2 Hz. As a result, milligrams of the solid UF_5 product enriched with the ^{235}U isotope were obtained. The UF_6 dissociation selectivity in Uranit experiments was $\alpha \geqslant 10$ [27].

Along with uranium enrichment experiments, the parameters of slit nozzles and their operation were studied and new lasers were developed. It was shown that slit nozzles can provide the UF_6 gas parameters (temperature and concentration) required for uranium enrichment, which are comparable to parameters obtained with usual nozzles. Requirements for the laser system were satisfied due to the proprietary development of a 16-μm system based on pulsed CO_2 lasers and multibeam Raman cells containing parahydrogen cooled to $T \approx 77$ K [18, 208]. This system emitted laser pulses with an energy exceeding 1 J at a pulse repetition rate of about 3–5 Hz. At the same time, it was assumed that the pulse repetition rate in an industrial plant should be about 10^4 Hz.

By 1992, a CO_2 laser was built with a pulse repetition rate above 1 kHz and a pulse energy of a few joules. In addition, a para-H_2 Raman frequency converter was created operating at room temperature at a pulse repetition rate of 1 kHz [18, 208]. As with the atomic approach, considerable efforts were made

to estimate the applicability of the MLIS method and its technological advantages at the industrial scale. The main conclusions of this research are as follows: the single-stage laser enrichment of uranium can be fulfilled, the requirements on the laser system can be achieved, and the construction of the setup created ensures costs per separation operation unit much lower than for advanced centrifuging technology. Nevertheless, a great deal of work still needs to be done and considerable uncertainties exist, which greatly affect the economic prospects. The MLIS project was terminated in Uranit in 1992. After that, the AVLIS project in Great Britain was also terminated.

Brazil

Research on laser isotope separation in Brazil was initiated in 1973. In 1974, an isotope separation program of the National Nuclear Energy Commission (CNEN) and the Centro Tecnico Aeroespacial (CTA) was approved [209]. At the same time, a research contract was signed between CTA and the Campinas State University (Unicamp). Such cooperation was successfully used to study many problems related to the laser separation of nitrogen and bromine isotopes. Interest in these studies was mainly related to laser uranium enrichment. After some preliminary experiments carried out at Unicamp using the molecular approach and at the Institute of Atomic Energy (IEA) using the atomic method, a new research institute was founded in São José dos Campos city, state of São Paulo. Since then, experiments on laser isotope separation were concentrated at the Instituto de Estudos Avancados.

Research on uranium isotope separation was based on the atomic method [210]. During the development of this project, copper vapor lasers with an average output power of up to 40 W were built and three-photon, two-frequency photoionization of uranium atoms was studied (in hollow-cathode lamps and in a furnace [211, 212]). It was found that the photoionization of atoms has a very high selectivity (about 100%), which deteriorates during the extraction and collection of ions, so that the content of ^{235}U in the mixture of products is usually 5–60% [210]. Uranium evaporation was investigated, and special heat resistant materials for crucibles stable against uranium action were selected. A new setup was built for more detailed uranium evaporation studies and the photoionization spectroscopy of atoms [212].

South Africa

Studies on laser uranium isotope separation in South Africa was initiated in 1983. They were performed at the Atomic Energy Corporation (AEC) at Pelindaba near Pretoria, the main nuclear research center in South Africa. The research was directed at the technological realization of the molecular laser isotope separation (MLIS) of uranium. The project was performed in close collaboration with the French branch of the COGEMA company. The main goal of the combined AEC–COGEMA program, which was equally funded by both sides, was to estimate the MLIS technology for uranium enrichment using an experimental setup and to consider its future industrial applications. In South Africa, technological CO_2 lasers with high repetition rates [213, 214] and 16-μm Raman para-H_2 lasers emitting 1-J pulses were developed. Slit Laval nozzles 50 cm in length were constructed for the gas-dynamic cooling of UF_6/carrier mixtures with a closed gas-circulation cycle. Gas cooling and circulation processes and the absorption of laser radiation by UF_6 and SF_6 in a cooled flow were extensively studied [215, 216]. The productivity and efficiency of the technology developed in the project were estimated.

In late 1997, COGEMA and South Africa Atomic Energy Corporation decided to stop their combined program on laser uranium enrichment. The announcement published by the AEC reported that the termination of the three-year collaboration agreement was caused "first of all by its inability to satisfy the increasing financial requirements of the program." In the opinion of a representative of the COGEMA company, this decision meant that the program would be gradually dismantled by both partners. At the same time, it was noted that France would continue its own SILVA program. After the termination of the project at the AEC, MLIS studies in South Africa began at the Klydon Pty Ltd. Company using the aerodynamic process [217–219].

Iran, China, South Korea, Japan

Studies on the laser separation of uranium isotopes began in these countries in the 1970s and continue today. In Iran, the research is carried out in three directions [220–222]: by the AVLIS method, the high-energy MLIS method based on the dissociation of UF_6 molecules, and the MLIS method based on low-energy processes, similarly to the SILEX technology.

In China, studies are based on the AVLIS and MLIS methods [223–225]. In the molecular method, the chemical reaction of vibrationally excited UF_6 molecules with HCl molecules proposed in [226] is used. UF_6 molecules are excited by a 5.33-μm CO laser into the ≈ 1876-cm^{-1} $3v_3$ vibrational band [156] in which the isotopic shift is about 1.8 cm^{-1}. Because of a weak absorption at frequency $3v_3$, molecules are excited in an intracavity cooled cell. The separation of uranium isotopes is performed due to the difference in the rates of reactions between HCl molecules with vibrationally excited and unexcited UF_6 molecules. Thus, separation selectivity $\alpha = 1.2$ was achieved for uranium isotopes in [224].

Some results on the laser separation of uranium isotopes by the MLIS method obtained in South Korea [30–32, 227, 228] and Japan [229–233] are presented in Sections 8.4 and 9.1.

## 8. Laser dissociation of UF_6 and separation of uranium isotopes

8.1 Isotope-selective IR dissociation of volatile uranium compounds

In addition to the laser separation of uranium isotopes in UF_6 molecules, uranium-containing molecules absorbing CO_2 laser radiation in the region from 9.2 to 10.8 μm were also studied within the framework of the molecular uranium isotope separation project. These studies were motivated by the advantages of using technological CO_2 lasers for the isotope-selective IR MPD of chosen molecules. In this case, an important scientific problem was the synthesis of a suitable uranium-containing molecular compound. The search for such a compound was restricted by the requirements of a high enough vapor pressure and chemical stability. Works in this area were carried out at the Exxon Mobil Corporation (USA) and at BARC (India). The most interesting results were obtained with the organic compound uranyl-(hexafluoroacetylacetonate)$_2$ ($UO_2[(CF_3CO)_2CH]_2$) [16, 18], which was used either in a coordination compound with tetrahydrofuran
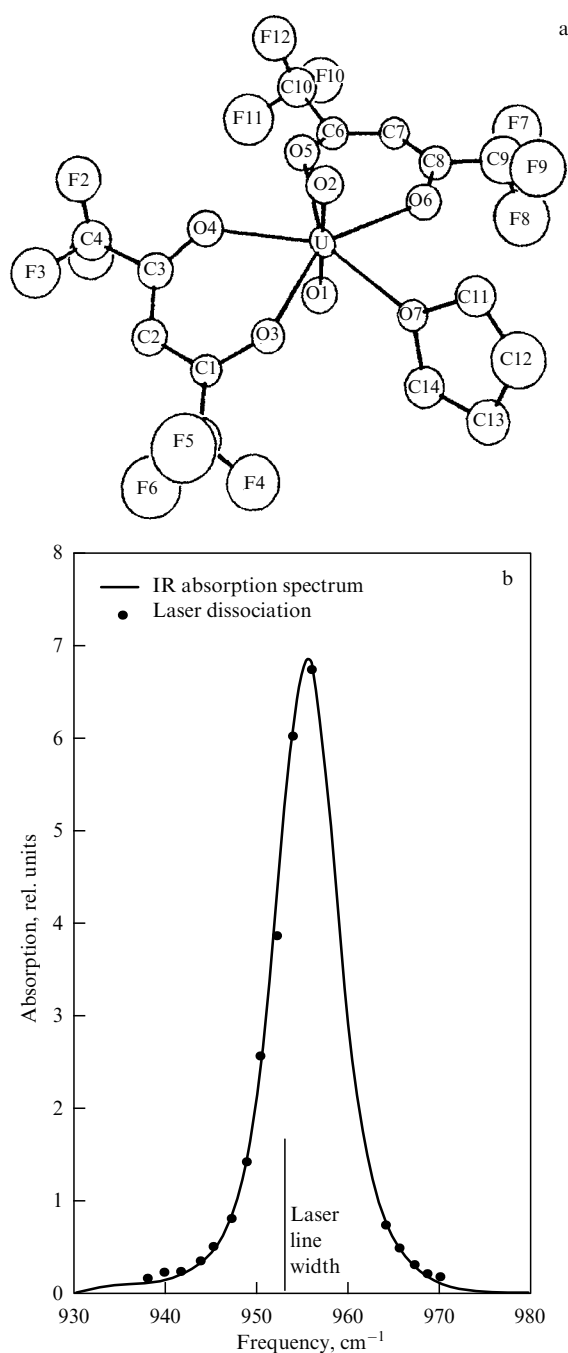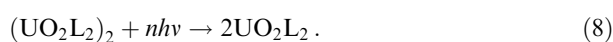
Figure 15. (a) Spatial structure of the volatile organometallic compound bis-(hexafluoroacetylacetonate)-uranyl-tetrahydrofuran (UO_2L_2B), which was used in experiments on uranium isotope separation by radiation from a CO_2 laser [16, 18]. (b) Frequency dependences of the absorption of weak IR radiation (curve) and the dissociation yield (points) for the UO_2L_2B compound [236].

[151, 154, 234–236] (containing 44 atoms) or in a dimer form [237, 238]. Using notations L (for hexafluoroacetylacetonate) and B (for tetrahydrofuran), these two compounds can be written as UO_2L_2B and $(UO_2L_2)_2$, respectively. Upon laser IR dissociation of the first compound, tetrahydrofuran is detached from it:

$$UO_2L_2B + nh\nu \rightarrow UO_2L_2 + B\,, \qquad (7)$$
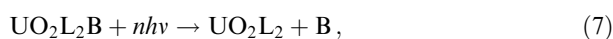
while the second compound is decomposed into monomers:

$$(UO_2L_2)_2 + nh\nu \rightarrow 2UO_2L_2\,. \qquad (8)$$

The study of process (7) gave many results [151, 152, 234–239]. Qualitatively analogous results were obtained in the study of process (8). Figure 15a shows the spatial structure of the UO_2L_2B compound. The pressure of UO_2L_2B vapors is ~ 0.7 Torr at a temperature of $100\,^{\circ}$C [234]. A decisive factor in the separation of uranium isotopes using these compounds is that in both cases the laser excites the asymmetric stretching vibration of the central uranyl UO_2 group. The very intense absorption band corresponding to this vibration of this well coincides with the emission band of the CO_2 laser. The use of this vibration allows us to study the isotope-selective dissociation of these compounds both with respect to oxygen isotopes (the isotopic shift is $\sim 17\ \mathrm{cm}^{-1}$ for $U^{16}O_2/U^{16}O^{18}O$) and with respect to uranium isotopes (the isotopic shift is $\sim 0.7\ \mathrm{cm}^{-1}$) [151].

Figure 15b shows the dissociation curve for UO_2L_2B obtained with a CO_2 laser and the linear absorption spectrum of this molecule. One can see that these curves well coincide [236]. Experiments on the isotope-selective dissociation of these compounds were performed using molecular beams with a quadrupole mass spectrometer as a detector. It was unexpectedly found that the frequency dependence of the dissociation yield (for yields $\leqslant 50\%$) coincided with the absorption spectrum of a weak signal. A red shift of the spectral dependence of the dissociation yield with respect to the linear absorption spectrum of the molecules, taking place, for example, during the laser IR MPD of SF_6 molecules [73, 110] due to the anharmonicity of molecular vibrations, was not observed.

As would be expected, oxygen isotopes were completely separated in these experiments. The maximum enrichment coefficient for uranium isotopes $K_{enr}(^{238}U/^{235}U) \approx 1.9$ was obtained using a mixture of molecules with a pressure ratio of $1/1$. This is in good agreement with values calculated based on the frequency shift of the linear absorption spectra of UO_2L_2B molecules by the isotopic shift value. The effects observed can be explained assuming that the dissociation of UO_2L_2B is initiated only by *one* photon of a CO_2 laser. This is probably related to the small chemical stability of the compound under study [18], which is already unstable at temperatures $> 120\,^{\circ}$C. Therefore, the absorption of even one IR radiation photon can cause the dissociation of a molecule. The detachment of the ligand from the active center can also be caused by the accidental concentration of the absorbed energy on its bond with the molecular core.

The isotopic selectivity measured in experiments increased with decreasing temperature. Thus, the selectivity measured at temperatures of 120 and 65 °C was ≈ 1.2 and ≈ 1.9, respectively [152]. This occurs partly due to the narrowing of the absorption band of molecules and probably because the dissipation of molecules requires only a few IR radiation photons.

The isotopic selectivity in process (7) under static conditions of gas in a cell was not observed. The UO_2L_2B compound was studied under static conditions at a gas pressure of 1 Torr. The instant concentration of an initial compound in experiments was determined by the fluorescent method using a dye laser. It was shown that, although the irradiation of UO_2L_2B molecules by a CO_2 laser pulse leads to the almost instant dissociation of molecules, a constant decrease in the fluorescence signal was not observed, even after 1000 pulses (i.e., the dissociation yield of molecules did not decrease), which is related to the reversibility of

reaction (7). Analogous results were probably also obtained with reaction (8).

These compounds and some other volatile organic uranium compounds were also studied at BARC in India [15, 16]. Online experiments were carried out using a molecular beam and a quadrupole mass spectrometer for detecting molecules and their dissociation products. The process selectivity was measured with a mass spectrometer detecting the most intense ion peaks of initial molecules $^{238}UO_2LB^+$ ($m/z = 549$) and $^{235}UO_2LB^+$ ($m/z = 546$) irradiated by a laser pulse. UO_2L_2B molecules were irradiated by the 10P(6) line of the CO_2 laser with the energy density of 85 mJ cm^{-2}. Thirty percent of molecules containing ^{238}U were decomposed and only 5% of molecules containing ^{235}U were decomposed. Therefore, the enrichment coefficient in dissociation fragments was $K_{enr}(^{238}U/^{235}U) = 3.4$, while the residual gas was enriched with ^{235}U atoms with the coefficient $K_{enr}(^{235}U/^{238}U) = 1.3$. In experiments with gas in a cell, isotopic selectivity was not observed.

8.2 Dissociation of UF_6 molecules with the help of sensitizers

Because of the absence of efficient lasers for vibrational excitation of UF_6 molecules, many studies on the dissociation of UF_6 at the first stage of research were performed using sensitizers [201, 202, 240–242]. As sensitizers, polyatomic molecules with a high vibrational heat capacity were most often used, which efficiently absorb high-power CO_2 laser radiation in the region of 9.2–10.8 μm and have vibrational frequencies close to the vibrational frequency v_3 (≈ 627 cm^{-1}) of UF_6 molecules [107]. The role of sensitizing molecules was to transfer efficiently the CO_2 laser energy absorbed by them to UF_6 molecules. This resulted in strong vibrational excitation and dissociation of UF_6 molecules.

Although molecular sensitizers (mainly SF_6 molecules and methane halogenides CF_4, CF_3Cl, CF_2Cl_2) can be excited by intense CO_2 laser pulses up to the dissociation threshold and decompose, in the case of comparatively low pump energy densities, the excitation and dissociation of UF_6 molecules can be performed without the dissociation of sensitizers themselves. Under almost resonance conditions, the excitation energy of molecular sensitizers can transfer to other molecules, which are not excited by the laser directly.

At room temperature, UF_6 molecules barely absorb CO_2 laser radiation, even due hot bands [243]. However, the IR photochemistry of UF_6 can be comparatively readily investigated using a CO_2 laser. The CO_2 laser-induced dissociation of UF_6 with the help of sensitizers was first observed in [201] and was later studied in papers [202, 240–242]. In [201], SF_6 molecules were used as sensitizers. The excitation and dissociation of UF_6 molecules using sensitizers were investigated in detail in paper [202] where sensitizers were methane halogenides CF_4, CF_3Cl, and CF_2Cl_2.

The choice of these molecules as sensitizers was based on the following criteria: different levels of absorption of the CO_2 laser radiation (depending on excitation of the fundamental or composite vibration), the presence of suitable vibrational levels for energy transfer to UF_6 molecules, the dissociation energy exceeding that of UF_6, and inertness with respect to UF_6 (Table 2). The choice of different molecules allowed the authors to study the influence of various experimental parameters such as the frequency and density of excitation energy [202, 241], the number of laser pulses [240], the sensitizer and UF_6 pressures [202, 240, 241], and the

pressure of the acceptor of radicals (H_2) [202, 240, 241] on the dissociation of UF_6 molecules. Thus, for example, the dependence of the dissociation yield of UF_6 molecules on the excitation frequency of CF_2Cl_2 molecules studied in a CF_2Cl_2/UF_6 mixture showed that, independently of the excitation frequency, the UF_6 dissociation yield is the same for the same absorbed energy. It was shown that the UF_6 dissociation yield rapidly increased with increasing partial pressure of the sensitizer SF_6 (Fig. 16a) [240] or CF_2Cl_2 (Fig. 16b) [202]. The efficiency of energy transfer from molecular sensitizers to UF_6 donor molecules was considered in [202] within the framework of the long-range dipole–dipole interaction.

This interaction is described assuming that the role of vibrational–vibrational energy exchange between molecules, in particular, of different types, is especially large when vibrational levels of different molecules are almost in resonance [244]. As a result, long-range dipole–dipole interactions can induce almost resonance processes of the $V-V$ energy exchange leading to efficient energy transfer between colliding molecules (see, e.g., [202] and references therein). The probabilities of vibrational energy transfer in UF_6/sensitizer systems were estimated in paper [202] within the framework of the accepted procedure. The results obtained for the transfer of a single energy quantum are presented in Table 2. These data show that energy transfer from CF_2Cl_2 and SF_6 molecules to UF_6 molecules can occur very efficiently.

8.3 Results of studies on IR and UV dissociation of UF_6

As noted in Section 3.1, the vibrational excitation of molecules increases their absorption cross sections at electronic transitions [5, 54], which can be used for the isotope-selective dissociation of molecules [2, 53, 54]. It was shown in one of the first papers [55] that the UV absorption of UF_6 molecules in the 420–550-nm region increased approximately 50-fold upon excitation of the composite $v_2 + v_3$ vibration by an 8.6-μm IR laser. The authors of [56] studied changes in the UV absorption spectrum of UF_6 molecules in the range from 220 to 250 nm due to their vibrational excitation caused by the vibrational energy transfer from SF_6 sensitizers excited by a high-power CO_2 laser. Experiments were performed with molecules cooled to $T \leqslant 100$ K in a supersonic jet with an argon gas carrier. It was found that laser-induced changes in the UV absorption spectrum of UF_6 molecules depend on the wavelength, i.e., on the level of their vibrational excitation. Excitation of UF_6 molecules due to energy transfer from SF_6 molecules resulted in most cases in an increase in the UV absorption cross section. Thus, upon irradiation of an $SF_6 : UF_6 : Ar = 2 : 2 : 8$ mixture by a 400-mJ CO_2 laser at the 947.74-cm^{-1} 10P(16) line, the UV absorption of UF_6 in the region of 235–245 nm increased by a factor of 1.7–2.0.

Changes in the UV absorption cross sections of UF_6 molecules caused by their vibrational excitation were studied in detail in a project on uranium isotope separation in [57]. The vibrational excitation of molecules was performed with an Nd:YAG laser-pumped lithium niobate parametric oscillator tunable in the 16-μm region. Measurements were carried out under conditions of the adiabatic expansion of gas in a jet with the N_2 carrier at two temperatures: 293 and 106 K. The dependences of the UV absorption cross sections of molecules on the frequency and energy density of laser radiation and the gas temperature were studied. At low energy densities (0.4 mJ cm^{-2}), a distinct UV absorption peak was observed
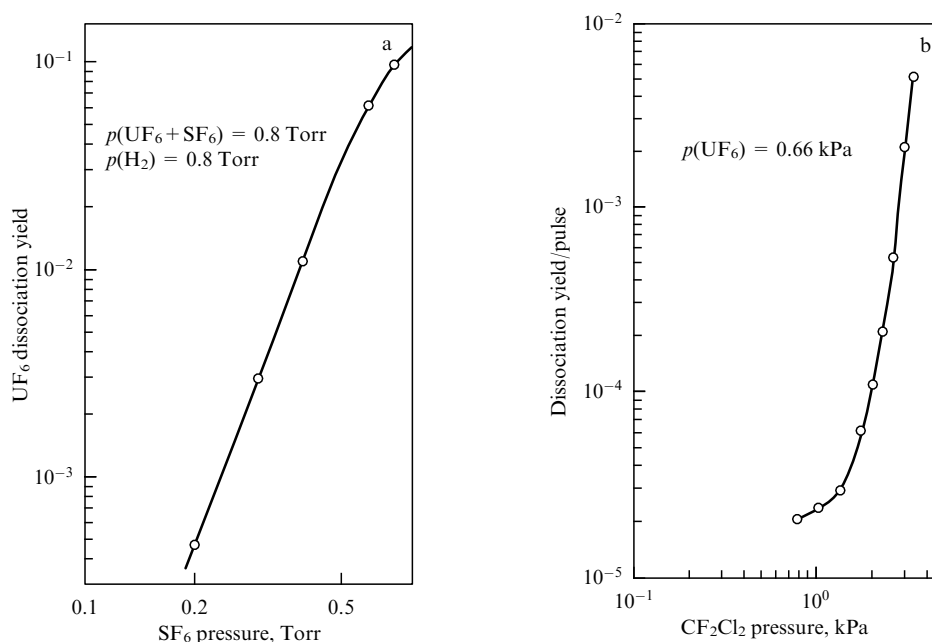
Figure 16. (a) Dependence of the fraction of dissociated UF_6 molecules per pulse on SF_6 pressures in a UF_6/SF_6 mixture. Gas pressure in a cell: $p(UF_6 + SF_6) = 0.80$ Torr; $p(H_2) = 0.80$ Torr. Molecules were excited by 5-J, 944.2-cm^{-1} 10P(20) CO_2 laser line [240]. (b) Dependence of dissociation yield of UF_6 molecules per pulse on CF_2Cl_2 pressure in the UF_6/CF_2Cl_2 mixture. UF_6 pressure was maintained constant and equal to 0.66 kPa. Molecules were excited by 0.5-J cm^{-2}, 1084.63-cm^{-1} CO_2 laser line [202].

Table 2. Molecular parameters for sensitizers and probabilities of vibrational energy transfer [202].

Molecule	Excited vibration, cm^{-1}	Laser line, cm^{-1}	Transferring vibration near v_3 UF_6	Bond energy, kcal mol^{-1}	Vibration energy transfer probability
CF_4	$v_2 + v_4$, 1067	2R(12), 1073	v_4, 630	$D(R-F) = 100$ [44, 45]	0.0276
CF_3Cl	v_3, 1105	9R(30), 1084	v_2, 781	$D(R-Cl) = 81$ [44, 45]	0.0062
CF_2Cl_2	v_1, 1101	9R(30), 1084	v_2, 667	$D(R-Cl) = 76$ [44, 45]	0.369
SF_6	v_3, 948	10P(20), 944	v_4, 615	$D(S-F) = 92$ [44, 45]	0.239
UF_6			v_3, 625	$D(U-F) = 68$ [46]	

when the excitation laser frequency coincided with the Q-branch frequency ≈ 627.7 cm^{-1} of $^{238}UF_6$ molecules [107].

It was shown that changes in the electronic absorption spectrum of UF_6 induced by IR radiation considerably exceed changes caused by the increase in the gas temperature. The results of measurements of IR absorption were used in the model of the IR + UV dissociation of molecules developed by the authors. It was found in [57] that experimental measurements of changes in the UV absorption were in good agreement with model calculations and give the maximum selectivity $\alpha \approx 2$ for the IR + UV dissociation of molecules.

8.4 IR laser multiphoton dissociation of UF_6 and separation of uranium isotopes

8.4.1 Some results on nonselective IR dissociation of UF_6 molecules.
The IR multiphoton excitation and dissociation of UF_6 molecules have been studied in many papers (see, e.g., reviews [22, 23] and references therein). In earlier papers, the nonselective dissociation of UF_6 was studied because of the absence of efficient tunable lasers in the 16-μm region. For excitation and dissociation of UF_6 molecules, CF_4 and CO_2 lasers were used. In the case of two-frequency UF_6 dissociation, CF_4 lasers were mainly used to excite molecules in the

region of lower vibrational levels, while high-power CO_2 lasers performed the dissociation of excited molecules. Such experiments were used to study many characteristics of the multiphoton IR excitation and dissociation of UF_6 molecules.

The absorbed energy and multiphoton absorption cross sections of molecules were studied as functions of the laser radiation energy in single-frequency and two-frequency excitation regimes [168, 245–248]. The dependences of the dissociation yield of UF_6 molecules on the frequency and density of exciting radiation were obtained. The IR-MPD thresholds of UF_6 were measured (Fig. 17a) [249]. The dependences of the dissociation yield of UF_6 molecules on the gas temperature and pressure were studied and the role of different acceptors added for binding fluorine atoms was elucidated [23]. Most of the experiments were performed at room temperature of the gas. It was found that two-frequency CF_4 laser + CO_2 laser excitation resulted in an increase of more than an order of magnitude in the dissociation yield [168, 245, 250].

In [245], two-frequency UF_6 dissociation was studied using a CF_4 laser emitting at a frequency of 615.2 cm^{-1} (at the strongest transition) and a CO_2 laser. It was found that, when a low-energy 5-mJ CF_4 laser was used for preliminary

excitation, the dissociation yield of UF_6 molecules increased 10–100 times upon irradiation by a 0.7-J CO_2 laser at 1077 cm^{-1}. The dissociation was observed only when molecules were excited by two lasers. Similar studies were performed in paper [250]. In two-frequency experiments, the CF_4 laser-induced absorption of the 9.3-μm emission from a CO_2 laser by UF_6 molecules was studied. It was found that preliminarily vibrationally excited UF_6 molecules absorbed from 1 to 2.8 eV of energy from the CO_2 laser depending on the excitation energy. The authors assumed that the total absorbed energy was sufficient for the dissociation of molecules observed in experiments.

In [168], UF_6 dissociation was studied at room temperature of the gas in a cell irradiated only by a CF_4 laser. Also, the two-frequency dissociation of UF_6 molecules irradiated by CF_4 and CO_2 lasers was investigated. Spectral and energy characteristics of the dissociation yield of UF_6 molecules were obtained and a considerable increase in the dissociation yield was observed by irradiating UF_6 molecules by two lasers. It was shown that the influence of a CO_2 laser on the dissociation yield was most efficient when the laser radiation frequency approached the composite vibration frequency $v_2 + v_3$ (1157 cm^{-1}) of UF_6 (Fig. 17b).

The cross sections of multiphoton absorption of radiation from a para-H_2 laser by $^{238}UF_6$ molecules cooled to $T \approx 90$ K in a supersonic jet (the nozzle-slit width was 50 cm) at frequencies of 625–629 cm^{-1} were measured in papers [247, 248] at different excitation energy densities in the range of 50–500 mJ cm^{-2}. It was found that the absorption cross section decreased from $\sigma \approx 3 \times 10^{-17}$ to $\approx 1.2 \times 10^{-18}$ with increasing energy density.

In concluding this section, we also note rather important spectroscopic papers [107, 156, 251]. In paper [251] performed at the Uranit company, anharmonicity constants for vibration v_3 of UF_6 were measured. Measurements were carried out using a supersonic jet of UF_6 molecules at a concentration of $\sim 10^{14}$ cm^{-3} with a carrier gas at $T \leqslant 60$ K. The supersonic jet was formed in a 5-cm slit nozzle. The pump–probe method with a para-H_2 laser exciting UF_6 molecules and a tunable diode laser for probing excited molecules was used to measure with a high resolution the vibration absorption spectra v_3 of UF_6 molecules and to determine anharmonicity constants. Detailed measurements and analysis of the fundamental IR vibration v_3 of UF_6 molecules were performed in [107], and of the $3v_3$ vibration in [156].

8.4.2 Isotope-selective IR multiphoton dissociation of UF_6 and separation of uranium isotopes.

Because of the broad v_3 vibrational band (≈ 20 cm^{-1}) of UF_6 and a comparatively large width of the Q band (≈ 3.5 cm^{-1}), as well as a small isotopic shift in the v_3 vibrational band (≈ 0.604 cm^{-1} [107, 233]), the absorption spectra of molecules $^{235}UF_6$ and $^{238}UF_6$ at room temperature almost completely overlap [8, 101] (see Fig. 6 and Section 3.1). In the case of UF_6 dissociation in a cell at room temperature [165], isotopic selectivity was not observed. A comparatively high isotopic selectivity can be obtained only in cooled gases in jets or flows using the two-frequency or three-frequency excitation methods. Note that studies in this field are classified and the number of publications in the open literature is small.

The IR absorption spectra of $^{235}UF_6$ and $^{238}UF_6$ at room temperature were measured in one of the earlier papers [252] by the Fourier spectroscopy method with a resolution of about 1 cm^{-1}. The ratio α of linear absorption coefficients for
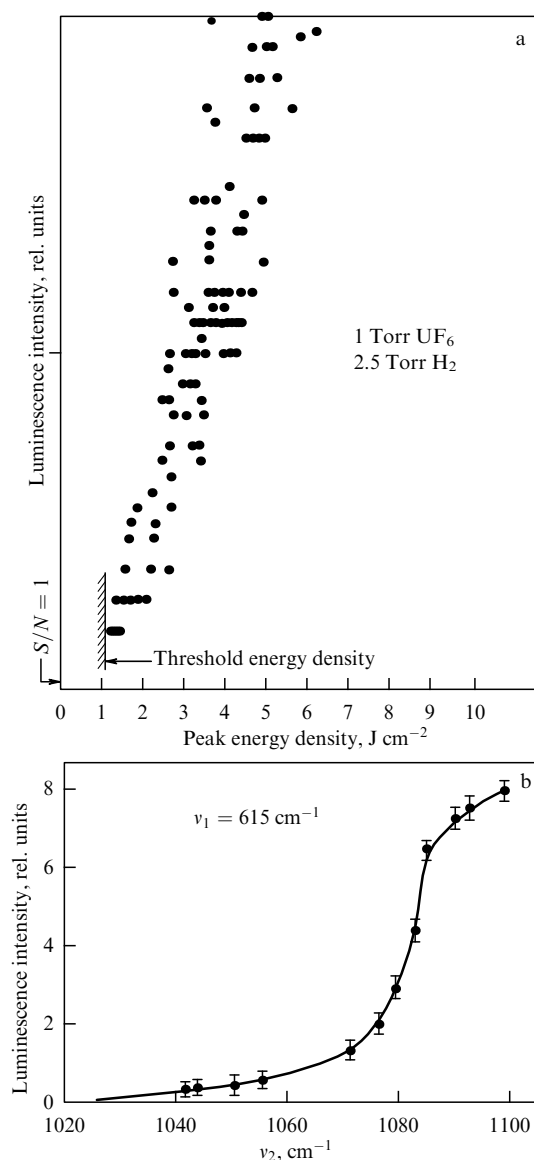
Figure 17. (a) Dependence of the dissociation yield of UF_6 molecules (the yield is proportional to the luminescence intensity) on the peak density of the excitation energy density. Molecules were irradiated by focused radiation from a CF_4 laser. Each point is the result of the action of one pulse with energy changing from pulse to pulse. S/N is the signal-to-noise ratio [249]. (b) Dependence of the dissociation yield of UF_6 molecules on the frequency of v_2 of a CO_2 laser dissociating radiation upon two-frequency UF_6 dissociation. Exciting radiation frequency $v_1 = 615.3$ cm^{-1} is fixed. Exciting and dissociating radiation energy densities are 100 mJ cm^{-2} and 60 J cm^{-2}, respectively. UF_6 pressure is 0.2 Torr [168].

two isotopomers gives the value of the expected selectivity in the case of excitation of molecules by weak radiation (in the linear regime) with a spectral width of about 1 cm^{-1}. Samples enriched with the ^{235}U isotope of uranium hexafluoride contained 97.6% of $^{235}UF_6$ and 2.4% of $^{238}UF_6$. The results of measurements are presented in Fig. 18a. The isotopic shift of the v_3 absorption band was measured to be $\Delta v_{is} = 0.65 \pm 0.1$ cm^{-1}. The maximum value of the single-step excitation selectivity obtained from the frequency dependence of the ratio $\alpha(235)/\alpha(238)$ was 1.57 at frequency 627.5 cm^{-1} on the high-frequency side of Q-branches. Obviously, comparatively high selectivity can be obtained in

Table 3. Selectivity of the IR dissociation of UF_6 molecules calculated from v_3 linear vibrational absorption spectra [252].

| Frequency v, cm^{-1}	Selectivity $\alpha(^{235}UF_6/^{238}UF_6)$
$\leqslant 616$	$\leqslant 0.9$
$\geqslant 633$	$\geqslant 1.1$
627.5	1.57
$623.5 \leqslant v \leqslant 625.5$	< 0.9
629	~ 0.9
Frequencies v at which $\alpha(^{235}UF_6/^{238}UF_6) = 1$: 622, 626, 628.5, 631.7 cm^{-1}.	

the wings of both the P- and R-branches of IR absorption bands, but with lower values. Selectivities calculated for a number of frequencies are presented in Table 3.

The first successful experiments on the isotope-selective dissociation of UF_6 were performed in [253] (see also paper [254] of the same group). Experiments were carried out using an effusive molecular beam formed during the flowing out of the equimolar mixture of UF_6 isotopomers through a hole 25 μm in diameter. Molecules in the beam were excited by two para-H_2 lasers at different frequencies. One laser, scanned in the range from 613.4 to 628.9 cm^{-1}, selectively excited molecules, while the other, with a fixed frequency 596.8 cm^{-1}, performed the dissociation of excited molecules (Fig. 18b). After irradiation, the isotopic composition of molecules in the beam was analyzed. The selectivity was determined by the ratio of the beam depletion by $^{235}UF_6$ to the depletion by $^{238}UF_6$ molecules. Obviously, the higher the deviation of this ratio from unity, the higher the selectivity. Maximum deviations from unity (1.2 and 0.73) were observed at excitation frequencies of 627.8 and 613.4 cm^{-1}, respectively (Table 4). These results agree well with data in [252].

In [255], the selective dissociation of UF_6 was observed by irradiating gas simultaneously with a CF_4 laser at 615.2 cm^{-1} and a pulsed CO_2 laser at 1073.3 cm^{-1} using different energy densities at different gas pressures. In experiments, the fractions D_{235} and D_{238} of molecules $^{235}UF_6$ and $^{238}UF_6$ subjected to dissociation were measured. The gas was analyzed before and after irradiation by the precision nuclear method of gamma spectrometry. In experiments, the content of uranium isotope nuclei in the initial and irradiated gas was measured. Under particular experimental conditions, when the UF_6 pressure was 0.47 Torr, the energy densities of CF_4 and CO_2 lasers were 20 mJ cm^{-2} and 1 J cm^{-2}, respectively, and the $^{238}UF_6$ dissociation level was $41 \pm 1\%$, with the enrichment coefficient reaching $K_{enr}(^{235}UF_6/^{238}UF_6) = 1.049 \pm 0.016$.

The influence of H_2, CH_4, and C_2H_6 on the dissociation selectivity of UF_6 molecules cooled to $-35\,°C$ in a cell was studied in [229, 230] upon irradiation by 0.1–0.16-J para-H_2 laser pulses at the uranium hexafluoride pressure of 0.2–0.4 Torr and pressure of additional gases of 1 Torr. The maximum selectivity of 1.043 was obtained by irradiating UF_6 without additions and UF_6 in a mixture with CH_4, while the selectivity in UF_6/H_2 and UF_6/C_2H_6 mixtures was 1.028 and 1.024, respectively.

Papers [231, 232] present the results of experiments on the two-frequency irradiation of supercooled UF_6, CH_4, Ar, or
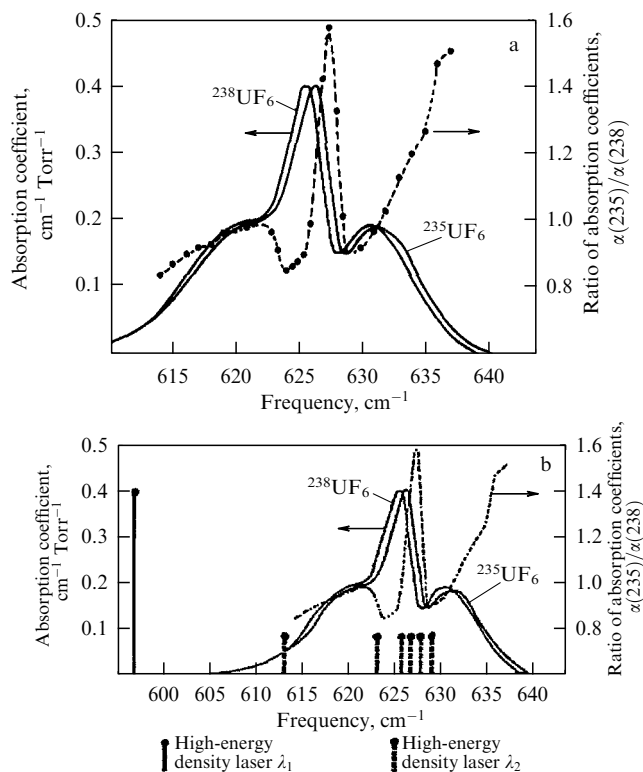
Figure 18. (a) Absorption coefficients of UF_6 molecules measured in the v_3 vibrational band at room temperature [252]. (b) Positions of radiation frequencies of exciting and dissociating lasers with respect to linear IR absorption spectra of $^{235}UF_6$ and $^{238}UF_6$ molecules. See the text [253].

Kr mixtures at the exit of a supersonic nozzle at temperatures $T \leqslant 100$ K. Excitation was performed with a continuously tunable para-H_2 laser. Selectivity $\alpha \approx 4$ was obtained (Table 5). Close selectivities were obtained upon three-frequency excitation and dissociation of UF_6 molecules in [256]. According to recent data, the maximum selectivity (enrichment in products) $\alpha \approx 5$ was achieved under the same conditions at the Institute of Physical and Chemical Research (RIKEN, Japan) upon three-frequency irradiation. Such a selectivity is sufficient for the enrichment of natural uranium with the ^{235}U isotope up to 3–3.5%, which is necessary for its use as a fuel for atomic power stations.

According to some reports [27], researchers at the Uranit company (German branch of the Urenco company) achieved the selectivity $\alpha > 15$ upon the laser IR MPD of UF_6 molecules, albeit at low dissociation yields. For dissociation yields of practical interest, the selectivity was $\alpha \approx 9$. It was also reported that researchers at the AEC (South Africa) obtained selectivities $\alpha \approx 6-8$.

Note, however, that the creation of industrial modules for the laser separation of uranium isotopes by the IR MPD of UF_6 molecules is assumed unprofitable (at the current level of laser technology) [23]. This quite complicated process should be optimized at all its steps, including the selective excitation and multiphoton dissociation of UF_6 molecules, in particu-

Table 4. Measured averaged selectivities of two-frequency UF_6 dissociation [253].

v_1, cm^{-1}	628.9	627.8	626.6	625.4	622.9	613.4
$\alpha(^{235}UF_6/^{238}UF_6)$	1.03 ± 0.13	1.20 ± 0.03	1.15 ± 0.02	1.11 ± 0.04	1.03 ± 0.10	0.73 ± 0.09
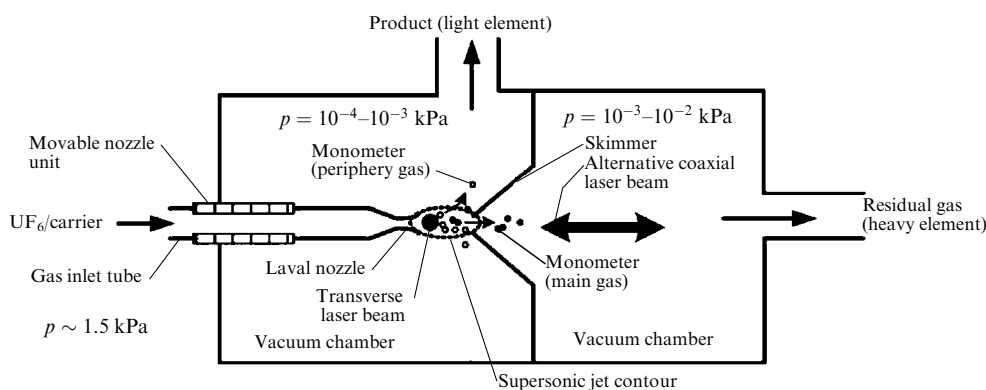
Figure 19. Diagram of uranium isotope separation process using a Becker nozzle + IR laser combination [32].

lar, laser and gas jet parameters. In this connection, low-energy MLIS methods and alternative methods have been extensively studied in recent years.

9. Application of low-energy methods for laser separation of uranium isotopes

Low-energy MLIS methods using IR lasers are described in many papers (see, e.g., reviews [33, 34] and references therein). Many of these methods (isotope separation due to the capture of low-energy electrons by molecules, selection of molecules introduced into helium nanodrops, isotope separation involving clusters and nanoparticles) are poorly studied and (or) are difficult to realize in practice [33]. The method of isotope-selective suppression of molecular clustering using IR lasers during the gas-dynamic expansion at the exit of a nozzle, the method of isotope-selective IR dissociation of small molecular van der Waals clusters [33, 34, 78–82], and the method of IR laser control of the condensation of molecules on a cold surface [33, 257–259] are the most investigated and promising. These studies attract great interest due to the possibility of their application to uranium isotope separation.

9.1 Separation Becker nozzle–IR laser combination

The application of low-energy MLIS methods for uranium isotope separation, in particular, in the SILEX process, was considered in papers [31, 32], where some methods were compared, including low-energy IR MPD, SILEX, and CRISLA (Condensation Repression by Isotope Selective Laser Activation) methods. The method of isotope-selective repression of clustering of UF_6 molecules with each other and with carrier gas atoms and the method of isotope-selective dissociation of clusters are considered most extensively. In [32], the method of repression of molecular clustering was studied in combination with a separation Becker nozzle [260]. The nozzle scheme and the principle of isotope separation are presented in Fig. 19 [32]. The Becker nozzle operation is based on the difference in radial diffusions of isotopomers at the nozzle exit due to their different masses: light particles tend to concentrate in the peripheral region of the jet, while heavy particles concentrate in the axial region.

A combination of a separation Becker nozzle and an IR laser considerably increases the isotope separation efficiency. The isotope-selective repression of UF_6 clustering at the nozzle exit is performed with a laser. The $^{235}UF_6$ molecules selectively excited by a laser do not condense and do not form clusters, whereas unexcited $^{238}UF_6$ molecules form clusters, combining together or with carrier gas atoms. As a result, clusters containing $^{238}UF_6$ molecules remain predominantly in the axial region (core) of the jet, whereas the lighter free $^{235}UF_6$ molecules diffuse from the jet core outside. The spatial separation of isotopomers is achieved using skimmers and apertures located in certain places.

To increase the selectivity and efficiency of this method, it is desirable to use atoms or molecules with a large mass as a gas carrier (Xe, SF_6). During the dissociation (clustering repression) of mixed UF_6/G clusters (G is a carrier gas particle) containing heavier carrier gas particles, the recoil energy is greater than in the case of light carrier gases. As a result, selectively excited $^{235}UF_6$ molecules will fly out of the axial part of a jet more efficiently, thereby increasing the selectivity. To minimize the undesirable energy transfer between isotopomers due to the $V-V$ exchange, the concentration of UF_6 molecules diluted in a carrier should not exceed 1–5%.

9.2 SILEX technology

Detailed information on the SILEX company and its technology is presented in review [33]. Here, we note only some important details of the SILEX technology and the current state of the company's activity in the field of uranium enrichment known from open sources.

The SILEX technology is being developed in a collaboration between Australia and the USA [35–39]. Project authors believe that SILEX has a number of advantages over other uranium enrichment processes [35]: (i) a much higher efficiency, (ii) relatively low operating costs, (iii) and a considerably lower capital cost than that of centrifugation technology. Plus, which is very important, the SILEX technology is the only laser uranium enrichment technology being extensively developed at present, the third generation technology.

Table 5. Typical selectivities of UF_6 dissociation under various irradiation conditions [232].

UF_6 temperature, K	IR laser for excitation	IR laser for dissociation	Selectivity, $\alpha(^{235}UF_6/^{238}UF_6)$
160	Tunable in lines	Tunable in lines	1.6 (1.7)
100	Tunable in lines	Tunable in lines	2.1 (2.3)
70	Continuously tunable	Tunable in lines	4.2 (4.7)

According to SILEX Systems information [35, 37], the enrichment efficiency of this technology greatly exceeds (by 1.6–16 times) the efficiency of operating centrifuges. It requires lower energies and smaller areas compared to existing technologies. According to SILEX supporters [35, 37], the cheaper and more efficient uranium enrichment technology will reduce electricity costs and make atomic power production a more competitive industry.

Although particular details of the SILEX technology are strictly classified, the analysis of publicly available information about it [35, 37] and existing laser uranium enrichment methods (AVLIS and MLIS based on the IR MPD of UF_6 molecules) allows one to establish some details of the SILEX technology. The AVLIS method is based on the selective ionization of uranium atom vapors [22, 24–26]. The ionization energy of uranium atoms is about 6.2 eV [44, 45]. In this process, the initial material and product have the same chemical composition.

In the MLIS process based on the isotope-selective dissociation of UF_6 molecules, the selective vibrational excitation of molecules by an IR laser and their subsequent dissociation by an IR or UV laser are used [8–11, 22]. The excitation and dissociation of molecules are performed in a gas-dynamic cooled molecular jet. The UF_6 dissociation products are UF_5 and F. In this process, the UF_6 gas is mixed with a suitable carrier gas (usually inert gas) and an acceptor of fluorine atoms (as an acceptor, methane or hydrogen are often used). The selective vibrational excitation of $^{235}UF_6$ molecules is performed by tunable lasers emitting in the 16-μm region in resonance with the v_3 vibration of molecules. Solid particles enriched with the $^{235}UF_5$ isotope produced after the dissociation of molecules are collected on corrugated plates [22, 24–26]. Chemical compositions of the initial material and dissociation products are different.

The SILEX technology also uses UF_6 molecules in a gas-dynamic flow with a carrier gas as the initial material. At the same time, it is known [261] that all three flows, the initial gas, products, and residual gas, are UF_6 molecules. Therefore, we can assume that this method does not use the dissociation of molecules and is based on intermolecular interaction forces. This means that [261]: (i) the mechanism of excitation of molecules is similar to that used in the MLIS method, namely, the increase in the vibrational energy of molecules and (ii) the required energy level in the SILEX method is considerably lower than in the MLIS method based on the dissociation of molecules. This is distinctly affirmed by people promoting and advertising the SILEX technology [262]. Probably, the SILEX technology is based either on the isotope-selective repression of clustering of UF_6 molecules or on the isotope-selective dissociation of dimers or small clusters of UF_6 molecules themselves or UF_6 molecules with a carrier gas (see Section 9.3). It is also possible that the SILEX technology includes both processes (see Section 3.1.2).

According to [35, 37, 263], a gas-dynamically cooled flow with a mixture of UF_6 molecules with a gas carrier is irradiated by a tunable pulsed laser in the 16-μm region. This emission falls in resonance with the v_3 vibration of UF_6 molecules. Emission in the 16-μm region is obtained due to stimulated Raman scattering of the 10.6-μm emission from a pulsed CO_2 laser in parahydrogen. It is also possible to use a tunable diode laser emitting at 16 μm. A 16-μm laser selectively excites mainly $^{235}UF_6$ molecules, thereby producing a difference between the relative amounts if isotopomers

in the flow of products enriched with the ^{235}U isotope and in the carrier gas flow in which the fraction of the ^{238}U isotope is greater (see Section 3.1.2). The SILEX method can be used to enrich chlorine, molybdenum, and uranium isotopes, as well as carbon and silicon [35].

SILEX's spheres of activity on uranium enrichment changes significantly each year, depending on the market conditions, first of all on the supply and demand of enriched uranium. Note that the problem of SILEX uranium enrichment is developed at the GLE (Global Laser Enrichment) Corporation, created in 2007 [35]. In May 2013, in Wilmington, USA, the first stage of the test cycle was ended after a demonstration of the advantages of the SILEX technology [35]. It was assumed in [35, 36] that the GLE would construct a new enterprise for SILEX uranium enrichment on the territory of the plant for diffusion uranium isotope separation in Paducah, Kentucky, which was closed in 2013. The main goal of this project was the enrichment of a great reserve (several hundred thousand tons) of industrial waste uranium accumulated here, which was depleted with the ^{235}U isotope. The enrichment assumed the production of uranium with a natural concentration of isotopes or with the isotope concentration at which uranium can be used in the atomic industry. In 2014, the United State Department of Energy (DOE) chose the GLE for future work at this enterprise.

As noted in a 2020 report by SILEX, because of the uncertainty related to the GLE restructuring for several years, after GE-Hitachi declared its intention to leave this project, and due to a continuing depressive nuclear fuel market situation, plans for the commercial introduction of the SILEX technology are considerably postponed and remain under threat. Thus, the future of the SILEX technology is rather uncertain and any plans for its commercial application are speculative [38, 39].

At the same time, the developers of the third-generation SILEX technology still believe that SILEX's potential as a key component of the nuclear fuel cycle is considerable [38]. In their opinion, the prospects of the SILEX technology are supported by the possibility of building a commercial plant in Paducah according the agreement signed in 2016 between the DOE and GLE for enriching great reserves of uranium waste depleted with the ^{235}U isotope. This agreement assumes the purchase of about 300,000 tons of uranium waste for its repeated use after SILEX enrichment.

9.3 Results of studies with SF_6 and CF_3Br molecules

The efficient laser repression of molecular clustering in free jets was first demonstrated by van den Bergh's group at École Polytechnique Fédérale de Lausanne (EPFL) [78, 81, 82]. The clustering repression was studied for SF_6 molecules highly dissolved in argon (pressure ratios were 1:100 and 1:200), which were irradiated by a 24-W cw CO_2 laser at the exit of a sonic nozzle with a hole 100 μm in diameter [78, 81]. The gas temperature and pressure over the nozzle were $T_0 = 233$ K and $p_0 = 1.5$ atm, respectively.

It was shown that the formation of $(SF_6)_2$ clusters was strongly repressed upon excitation of SF_6 monomers by a few kilowatts of resonance laser radiation in the collision region directly at the nozzle exit. With increasing distance from the nozzle to the irradiation region, along with clustering repression, vibrational predissociation of clusters begins. Upon irradiation of the jet at large distances from the nozzle, the predissociation of clusters occurs. A strong dilution of SF_6 in argon increases the efficiency of gas-

dynamic cooling of molecules, facilitates clustering and the formation of mixed SF_6Ar_n clusters, and prevents the energy exchange between molecules with different isotopic compositions.

It was shown that the selective excitation of $^iSF_6$ isotopomers ($i = 32, 33, 34$) in the gas expansion region (at a distance of 0.2 mm from the nozzle cut) resulted in a considerable decrease in the concentration of $^iSF_6Ar_n$ clusters in a beam. Enrichment coefficients $K_{enr} \approx 2$ were obtained. A strong dependence of the enrichment coefficient on the dilution degree of SF_6 in argon was found [78]. As the concentration of SF_6 molecules was decreased, the enrichment coefficient increased due to a decrease in the rate of $V-V$ energy exchange between molecules. Thus, as the partial pressure of SF_6 in argon was increased from 0.5 to 3%, the enrichment coefficient decreased from approximately 2 to 1 [78].

The vibrational predissociation of van der Waals molecules was studied for applications for isotope separation in papers [79–82] using the example of $(SF_6)_mAr_n$ complexes (where $1 \leqslant m \leqslant 3$, $1 \leqslant n \leqslant 9$ are the numbers of molecules and atoms in clusters, respectively). The isotopic selectivity of the dissociation process was observed in experiments. Upon irradiation of the natural mixture of SF_6 isotopomers diluted in argon by a 20-W cw CO_2 laser, the $^iSF_6$ ($i = 32, 34$) enrichment coefficient $K_{enr} \approx 1.2$ was obtained [79, 82]. The dependences of enrichment coefficients on the laser excitation frequency were studied. It was shown that, by selecting the laser emission wavelength, both the enrichment and depletion of a beam with a required isotopomer can be obtained.

Thus, it was shown in [78–82] that both methods considered above give comparatively low selectivities and enrichment coefficients ($K_{enr} \leqslant 1.5-2.0$). Note that SF_6 molecules are characterized by a rather large isotopic shift in the v_3 vibrational absorption spectra ($\Delta v_{is} \approx 17$ cm^{-1} with respect to $^{32}SF_6$ and $^{34}SF_6$ isotopomers [175, 176]). In contrast, the v_3 isotopic shift of UF_6 molecules is much smaller ($\Delta v_{is} \approx 0.604$ cm^{-1} with respect to $^{235}UF_6$ and $^{238}SF_6$ isotopomers [107, 233]). Therefore, similar studies with molecules having a small isotopic shift in vibrational spectra excited by lasers are quite important.

The isotope-selective dissociation of clusters and isotope-selective clustering repression were recently studied in detail for CF_3Br and SF_6 molecules [84–90]. CF_3Br molecules were chosen for studies because they have a very small isotopic shift (≈ 0.248 cm^{-1} [264]) for $CF_3{}^{79}Br$ and $CF_3{}^{81}Br$ isotopomers in the v_1 (≈ 1085 cm^{-1} [264]) vibrational spectrum (Fig. 20). Therefore, the results obtained for CF_3Br molecules are of interest for elucidating the possibility of using these methods for isotope separation in UF_6 molecules.

The SF_6 molecule was studied because it can be treated as a prototype of the UF_6 molecule in its structure and spectra. In addition, the IR absorption spectra of small $(SF_6)_m$ ($m \leqslant 6$) clusters were measured near the v_3 (948 cm^{-1}) absorption band excited by a laser [265–267]. Low-resolution IR absorption spectra were obtained (from IR dissociation measurements) for small mixed $(SF_6)_mAr_n$ complexes [80]. This molecule was also chosen for studying the possibility of obtaining in these processes higher selectivities than those observed in experiments [78–82].

The results obtained in [84–90], the experimental setup, and the research method are considered in recent review [34]. Here, we briefly consider only the main results to compare them with data presented in early papers [78–82]. In papers
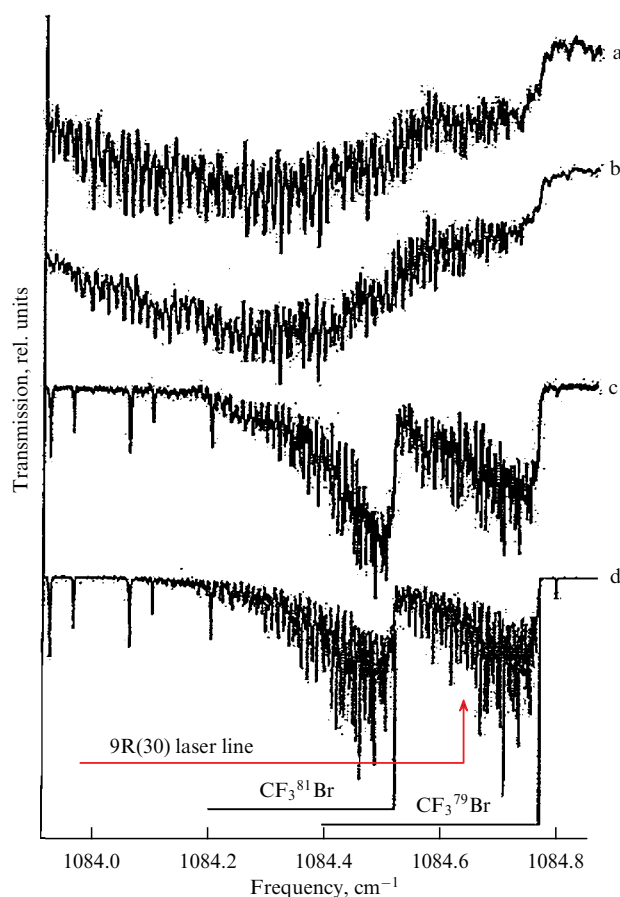

Figure 20. Q-branch v_1 vibrational spectra of CF_3Br molecules. (a) Room-temperature gas spectrum in a cell, (b) at gas temperature 200 K, (c) cooled gas in a free jet (averaged over 32 scans), (d) calculated spectrum ($T = 50$ K, FWHM is 0.002 cm^{-1}) [264].

[84–90], a molecular cluster beam and a quadrupole mass spectrometer were used, and molecules and clusters were excited by cw and pulsed CO_2 lasers.

The clustering repression selectivity of SF_6 molecules with argon atoms was studied [87] for mixed $(SF_6)_mAr_n$ clusters. Measurements were performed by SF_5Ar^+ ion peaks. An SF_6/Ar mixture was used at a pressure ratio of 1:200 and total gas pressure over the nozzle of 2 atm. The jet was irradiated by the 947.74-cm^{-1} 10P(16) laser line at a distance of 1.25 mm from the nozzle. This laser line is in resonance with $^{32}SF_6$ molecules [175]. The results obtained are presented in Fig. 21. The $^{32}SF_5Ar^+$ and $^{34}SF_5Ar^+$ ion signals are shown without irradiation of the jet (curve *1*) and for a jet irradiated by a laser (curve *2*). Curves *3–5* in Fig. 21 show model signals calculated taking into account the relation between sulfur isotopes normalized to the natural content (presented in parentheses). It was found in [87] that the control of clustering of SF_6 molecules with argon atoms provides the rather high selectivity $\alpha(^{32}SF_6/^{34}SF_6) \geqslant 25-30$ (see also Table 6). The rather high selectivity $\alpha(^{81}Br/^{79}Br) \geqslant 2.3-4$ was also observed in experiments on clustering repression for CF_3Br molecules with argon atoms (Table 7).

High selectivities were also obtained for the dissociation of homogeneous SF_6 clusters. Thus, it was shown in [88] that the dissociation selectivity of $(^{32}SF_6)_2$ dimers with respect to $^{34}SF_6{}^{32}SF_6$ dimers was $\alpha \geqslant 20-25$. In paper [89], during
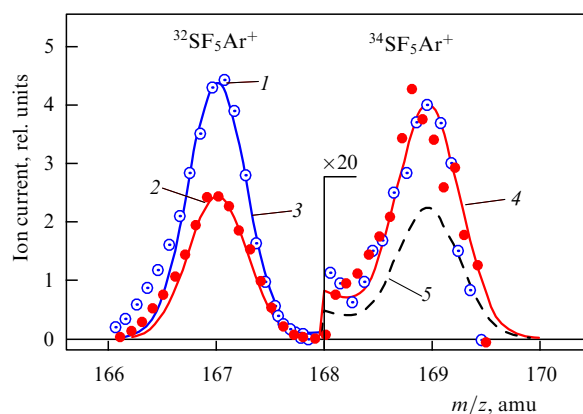
Figure 21. $Ar^{32}SF_5^+$ and $Ar^{34}SF_5^+$ ion peaks. Curve *1*: initial signal without irradiation of particles; *2*: after irradiation of particles; *3, 4, 5*: model signals for $ArSF_5^+$ ions containing ^{32}S, ^{33}S, and ^{34}S sulfur isotopes with relative concentrations of $(1, 1, 1)$, $(0.56, 1, 1)$, and $(0.56, 0.56, 0.56)$, where $(1, 1, 1)$ is the natural isotope relation. Molecules were irradiated by the 7.2-W, 947.74-cm^{-1} 10P(16) laser line. Total pressure of the SF_6/Ar gas mixture over the nozzle was 2 atm with a 1/200 pressure ratio. Nozzle pulse duration was 1.6 ms [87].

the dissociation of mixed CF_3Br-Ar clusters, which have a rather broad IR absorption band (the FWHM exceeds 3 cm^{-1}) and a small isotopic shift (smaller than 0.25 cm^{-1}), the selectivity was also demonstrated. Upon irradiation of clusters by the 1083.48-cm^{-1}, 0.054-J-cm^{-2}, 9R(28) laser line (CF_3Br/Ar pressure ratio is 1:200, total gas pressure over the nozzle is 3 atm), the enrichment coefficient $K_{enr}(^{79}Br/^{81}Br) = 0.88$ was obtained. In this case, the cluster dissociation selectivity was $\alpha(^{79}Br/^{81}Br) = 1.15$ [89].

Thus, experiments with SF_6 molecules gave considerably higher enrichment coefficients and selectivities than those obtained in early papers [78–82] using the methods of isotope-selective molecular clustering repression and of the isotope-selective IR dissociation of clusters. It was also found that a rather high selectivity was achieved by repressing the clustering of CF_3Br molecules with argon atoms. Studies performed in [84–90] showed that the methods described can be used for isotope separation in molecules with a small isotopic shift in IR absorption spectra, including UF_6.

9.4 Isotope-selective IR laser control of condensation of molecules on a surface

The method is based on the fact that the probability of desorption of vibrationally excited molecules from a cold surface exceeds the desorption probability for unexcited molecules (see review [33] and references therein). Studies of the interaction of atoms and molecules with surfaces have shown that, in most cases of physical adsorption on a cold pure surface or a surface covered with particles, a potential barrier for capturing particles does not exist [268, 269]. Therefore, the capturing probability decreases upon increasing the energy of atoms or molecules. The probability P_{des} of desorption of a molecule from the surface depends on the bond energy E_b of the molecule with the surface and the surface temperature T_s [268, 269]:

$$P_{des} \sim \exp\left(-\frac{E_b}{kT_s}\right). \tag{9}$$

In the absence of a potential barrier for adsorption, the bond energy and the desorption energy are equal, $E_b = E_{des}$ [269].

If a surface is covered with molecules, then E_b is the bond energy with molecules on the surface or the bond energy of molecules in clusters. Therefore, if the total energy of a molecule falling on a cold surface is smaller than the bond energy of molecules in clusters and the bond energy of the molecule with the surface, then the molecule will be captured by the potential interaction and will remain on the surface. However, if the total energy of the molecule exceeds these quantities, the molecule can be reflected from the surface. Therefore, one can assume that the probability of reflection of vibrationally excited molecules from molecular (cluster) layers condensed on a surface will considerably exceed the reflection probability of unexcited molecules.

This method was used in [270] for uranium isotope separation in UF_6 molecules. In experiments, a tube cell 2.6 m in length at a temperature of $-33\,°C$ located in the cavity of a CO laser was filled with a mixture of $UF_6/HBr/Ar$ (1.5 : 20 : 20) gases at a total pressure of 41.5 Torr. The laser emission frequency was tuned in the region of 1876.3–1876.6 cm^{-1}, exciting mainly the $3\nu_3$ vibration of $^{235}UF_6$ molecules. An increase in the concentration of $^{235}UF_6$ molecules in the cell was observed from 0.712% (natural content) up to 0.727%. The enrichment coefficient was $K_{enr} \approx 1.021$.

Table 6. Selective repression of clustering of SF_6 molecules with each other and with argon atoms (in bold) during the gas-dynamic expansion of an SF_6/Ar mixture under different experimental conditions. Particles were irradiated by the 947.74-cm^{-1} 10P(16) laser line. Total gas pressure over the nozzle was 2 atm [87].

Gas composition over the nozzle	Laser power, W	Selectivity of the repression of clustering of SF_6 molecules with each other, $\alpha(^{32,32}S/^{34,32}S)$	Selectivity of the repression of clustering of SF_6 molecules with argon atoms, $\alpha(^{32}S/^{34}S)$	Nozzle pulse duration, ms	Distance from the region of irradiated particles to the nozzle cut, mm
$SF_6/Ar = 1:200$	2	≈ 20		1.2	0.25
$SF_6/Ar/CH_4 = 1:195:4$	4	$\geqslant 15$		1.2	0.1
$SF_6/Ar = 1:200$	**7.2**		**$\geqslant 25-30$**	**1.6**	**1.25**

Table 7. Selective repression of clustering of CF_3Br molecules with argon atoms during gas-dynamic expansion of a CF_3Br/Ar mixture. Jet was irradiated by the 1084.635-cm^{-1} 9R(30) CO_2 laser line. Total gas pressure over the nozzle was 1.5 atm. Nozzle pulse duration was 600 µs. Distance from the region of irradiated particles to the nozzle was 0.45 mm (line 1) and 0.3 mm (line 2) [86].

$\dfrac{p_{CF_3Br}}{p_{Ar}}$	Laser power, W	Measured ion peak	Mass number m/z, amu	Residual signal	Enrichment coefficient, $K_{enr}(^{79}Br/^{81}Br)$	Selectivity, $\alpha(^{81}Br/^{79}Br)$
1:100	4.6	$BrAr^+$	(119), (121)	0.62 ± 0.07	0.67 ± 0.05	4.02 ± 0.19
1:200	3.8	$BrAr^+$	(119), (121)	0.67 ± 0.09	0.77 ± 0.09	2.31 ± 0.11

Table 8. Estimates of productivity for some methods of molecular laser isotope separation in particular experiments [272].

Method	Molecules	Operation regime and laser pulse repetition rate	Estimated productivity, $mg\ h^{-1}$
Selective vibrational predissociation of van der Waals molecules	$^{10}BCl_3$	CW CO_2 laser	$\approx 1-1.5$
Selective IR MPD of molecules in a gas-dynamically cooled molecular flow	$^{235}UF_6$	Pulsed 500-Hz CO_2 laser	$\approx 1-2$
Selective IR MPD of molecules in nonequilibrium conditions of a pressure shock	$^{34}SF_6$	Pulsed 100-Hz CO_2 laser	$\approx 50-100$

In [271], the separation of carbon isotopes was studied by the method of slowing the condensation of $CHCl_3$ molecules in a mixture with He or N_2. The gas mixture propagated at a subsonic velocity through a coaxial cylindrical chamber with cold walls and was irradiated by lines of a cw CO_2 laser in the frequency range from 934.9 to 929.0 cm^{-1}. When using a mixture of $CHCl_3$ with nitrogen, the concentration of excited molecules in the gas phase in the chamber increased more than 15% compared to their concentration in the natural mixture of isotopomers. Upon selective vibrational excitation of molecules, the separation of $^{12}CHCl_3$ and $^{13}CHCl_3$ isotopomers was observed with an enrichment coefficient from 1.01 to 1.15. When a mixture of $CHCl_3$ with helium was irradiated, no isotope separation was observed.

In papers [257–259], the interaction of intense beams of vibrationally excited SF_6 and CF_3I molecules with molecules (clusters) condensed on a cold surface ($T_s \approx 80-85$ K) was studied. The probability of reflection of molecules excited by high-power IR laser radiation to high vibrational states ($E_{vib} \approx 0.3-2.0$ eV) was studied, as was the reflection of unexcited molecules from a cold metal surface covered with molecules (clusters), as well as the probability of propagation of excited and unexcited molecules through cooled metal multichannel plates and cones mounted at an angle to the beam axis. It was shown that vibrationally excited molecules propagated through plates and cones and reflected from the surface with much greater probabilities than unexcited molecules. These results [33] suggest that this method can be used for the isotopic separation of molecules.

10. Separation of isotopes under nonequilibrium thermodynamic conditions of a pressure shock as an alternative to low-energy methods of uranium isotope separation

10.1 Some remarks
It was shown in papers [33, 272] that an alternative to low-energy MLIS methods can be an approach in which the isotope-selective dissociation of molecules is performed under nonequilibrium thermodynamic conditions of a pressure shock formed in front of a solid surface under the action of an incident intense pulsed gas-dynamically cooled molecular steam (beam). Estimates made in these papers show that this method offers a much higher efficiency (productivity) than do existing MLIS methods (Table 8). This approach was developed in papers [273–278], where the selective IR dissociation of SF_6 [273–277] and CF_3I [278] molecules was studied under nonequilibrium thermodynamic conditions (see also review [181]).

It was found in [273–278] that, upon excitation of SF_6 [273–277] and CF_3I [181, 278] molecules under nonequilibrium conditions of a pressure shock formed in front of a surface and also in a flow incident on the surface, a high yield of products and high selectivity are achieved at a comparatively low excitation energy density (smaller than 1.5–2.0 J cm^{-2}). Such energy densities are considerably lower (3–5 times) than energy densities required for the dissociation of molecules in unperturbed jets and flows. Therefore, although the approach developed in [273–278] is based on the dissociation of molecules, because of a moderate required energy density, this approach can be considered an alternative to low-energy MLIS methods [33, 272].

In the case of SF_6 and CF_3I molecules, isotopic shifts in the IR absorption spectra of v_3 (SF_6) and v_1 (CF_3I) vibrations excited by a laser are, respectively, $\Delta v_{is} \approx 17$ cm^{-1} (with respect to ^{32}S and ^{34}S isotopes) [175, 176] and ≈ 27 cm^{-1} (with respect to ^{12}C and ^{13}C isotopes) [279]. These values considerably exceed the widths of IR absorption bands of molecules in a cooled molecular flow. The situation is fundamentally different in the case of molecules with a small isotopic shift, when the absorption spectra of different isotopomers almost completely overlap. A small isotopic shift in the IR absorption spectra of molecules containing heavy-element isotopes is one of the main problems preventing the achievement of high selectivity in the laser isotope separation by the method of IR dissociation of molecules.

Recently, experiments were performed in [280–283] on the isotope-selective IR dissociation of other molecules under nonequilibrium thermodynamic conditions of a pressure shock, namely, CF_3Br and CF_2HCl molecules, which were studied well with multiphoton IR excitation [61]. In our opinion, the results obtained are important for the uranium MLIS. These molecules, like UF_6, are characterized by very small (< 0.25 cm^{-1}) isotopic shifts in the IR absorption spectra of vibrations excited by a CO_2 laser with respect to bromine and chlorine isotopes, respectively. Thus, the isotopic shift in the v_1 (≈ 1085 cm^{-1} [264]) absorption spectrum of CF_3Br molecules is $\Delta v_{is} \approx 0.248$ cm^{-1} [264], while in the v_3 (≈ 1109 cm^{-1} [284]) absorption spectrum of CF_2HCl molecules, this shift is $\Delta v_{is} \approx 0.048$ cm^{-1} [284]. Therefore, these results are of special interest for elucidating the possibility of using this approach for isotope separation in molecules with a small isotopic shift in the spectra of excited vibrations, which is typical of molecules containing heavy-element isotopes, including uranium isotopes.

10.2 Nonequilibrium thermodynamic conditions in a pressure shock
As a molecular gas is rapidly cooled during its expansion from a nozzle, the thermodynamic equilibrium between different

degrees of freedom of molecules is violated due to the difference among the times of translational, rotational, and vibrational relaxations: $\tau_{tr} \leqslant \tau_{rot} \leqslant \tau_{vib}$. The degree of deviation from local equilibrium depends on the number of collisions z_{col} required for the relaxation of the given degree of freedom. For polyatomic molecules, the relation $z_{tr} \leqslant z_{rot} \leqslant z_{vib}$ is usually fulfilled. Therefore, the effective temperatures in a flow satisfy the condition [112]

$$T_{1,\,tr} \leqslant T_{1,\,rot} \leqslant T_{1,\,vib} \, . \tag{10}$$

In a pressure shock [285–287] formed in the interaction of an intense pulsed gas-dynamically cooled molecular flow with a surface, the difference among the rates of translational, rotational, and vibrational relaxation [288] leads to non-equilibrium conditions opposite to (10), namely,

$$T_{2,\,tr} \geqslant T_{2,\,rot} \geqslant T_{2,\,vib} \, . \tag{11}$$

In this case, because of a long vibrational–translational relaxation time (for example, $p\tau_{V-T} \approx 135$ μs Torr [289] for CF_3Br and $p\tau_{V-T} \approx 65$ μs Torr for CF_2HCl [290]), the vibrational temperature of molecules in a pressure shock in a pulsed flow of a rarefied gas can be approximately equal to the vibrational temperature of molecules in the incident flow ($T_{2,\,vib} \approx T_{1,\,vib}$), while the translational and rotational temperatures of molecules in the pressure shock greatly exceed those in the unperturbed flow:

$$T_{2,\,tr} > T_{1,\,tr} \, , \quad T_{2,\,rot} > T_{1,\,rot} \, . \tag{12}$$

Thus, new nonequilibrium conditions are produced in the pressure shock in which the vibrational temperature of molecules is considerably lower than are the translational and rotational temperatures. The isotope-selective dissociation of CF_3Br and CF_2HCl molecules was studied namely in these conditions in papers [280–283]. Earlier, it was shown in [277] by the example of SF_6 that the vibrational temperature much more strongly affects the dissociation selectivity of molecules than the rotational temperature does.

10.3 Experiment and the investigation method

10.3.1 Experimental setup. Experiments in [280–283] were performed using an intense pulsed gas-dynamically cooled molecular beam (flow), a quadrupole mass spectrometer for detecting particles of the beam, and a tunable pulsed CO_2 laser emitting 100-ns (FWHM) exciting pulses with an energy up to 4 J (Fig. 22). Chambers for the molecular beam source and the quadrupole mass spectrometer were evacuated with turbomolecular pumps down to pressures $\leqslant 10^{-5}$ and $\sim 10^{-7}$ Torr, respectively. The isotope-selective laser IR dissociation of CF_3Br and CF_2HCl molecules was studied both separately and in a mixture.

A molecular CF_3Br (either CF_2HCl or CF_2HCl/CF_3Br mixture) beam was generated in the source chamber during the supersonic expansion of gases through a pulsed nozzle with an output hole 0.8 mm in diameter. The molecular beam intensity was increased with the help of a diverging cone 20 mm in length with a cone angle of $15°$. The mass spectrometer chamber was separated from the source chamber with a skimmer (cone aperture) 1.05 mm in diameter located at a distance of 150 mm from the nozzle. A beam formed in this way fell into the ionization chamber of the mass spectrometer. The distance from the nozzle cut to the ionization chamber was 350 mm.

The CO_2 laser beam crossed a molecular beam at an angle of about $90°$. The laser beam size in the molecular-beam
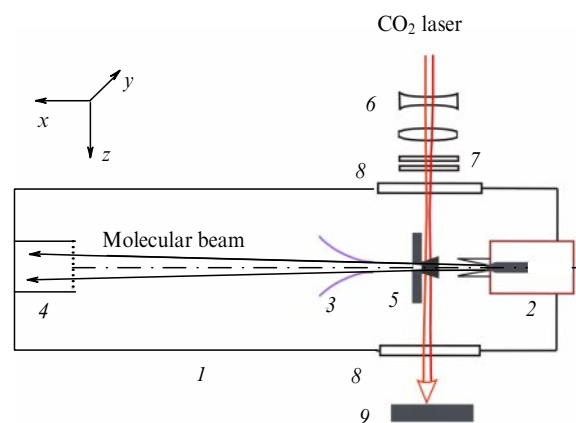
Figure 22. Schematic of the experimental setup. *1* — high-vacuum chamber; *2* — pulsed nozzle; *3* — skimmer; *4* — quadrupole mass spectrometer; *5* — substrate with a truncated tetrahedral pyramid for producing a shock wave; *6* — cylindrical lenses; *7* — attenuators; *8* — NaCl windows; *9* — absorber [280].

intersection region was $\approx 8 \times 6$ mm; the distance from the nozzle to the middle of the irradiated region of the molecular beam was 3.5 cm. In order to detect and study the dissociation selectivity of CF_3Br and CF_2HCl molecules, the laser was tuned to the 1084.635-cm^{-1} 9R(30) emission line. This line falls between the Q-branches of the v_1 absorption spectra of $CF_3{}^{79}Br$ (1084.769 cm^{-1}) and $CF_3{}^{81}Br$ (1084.521 cm^{-1}) molecules [264]. The laser line detunings from Q-branches are 0.134 and 0.114 cm^{-1}, respectively. This laser line falls into the v_3 P-branch of CF_2HCl molecules and is strongly absorbed by them. The detuning of this line from the v_3 Q-branch of CF_2HCl is about 24.4 cm^{-1} [284].

In experiments with a molecular beam incident on a surface, a duralumin substrate 6 mm in thickness and 50 mm in diameter was located at a distance of $x = 50$ mm from a nozzle perpendicular to the beam [280–283]. The substrate had a polished cone hole in its center with an entrance diameter (from the nozzle side) of 1.2 mm and exit diameter of 5.0 mm. When an intense pulse molecular beam was incident of this plate, a pressure shock (shock wave) was formed in front of it [285–287] with inhomogeneous, nonstationary, and nonequilibrium conditions [275, 276]. The characteristic size of the pressure shock front, which is of the order of the free path of molecules [286, 287], was 5–7 mm in these experiments [275, 276, 278]. To obtain a more intense pressure shock, a converging truncated hollow tetrahedral pyramid 12 mm in height was attached to the plate on the nozzle side. The two faces of the pyramid were made of thin NaCl plates transparent to laser radiation.

10.3.2 Research technique. The laser IR dissociation of CF_3Br molecules produces CF_3 radicals and Br atoms, while the final products of dissociation and ensuing chemical reactions are C_2F_6 and Br_2 molecules [291]. Products of the laser IR dissociations of CF_2HCl molecules are CF_2 radicals and HCl molecules. The subsequent recombination of CF_2 radicals results in the formation of C_2F_4 molecules [292]. The dissociation energies of CF_3Br and CF_2HCl molecules are 66.9 ± 3.0 and 47.9 ± 4.0 kcal mol^{-1} [44].

The dissociation selectivity of CF_3Br molecules with respect to bromine isotopes was determined by measuring the enrichment coefficient in the Br_2 product [280–283].

In experiments, the $^{79}Br^{79}Br^+$, $^{79}Br^{81}Br^+$, and $^{81}Br^{81}Br^+$ ($m/z = 158$, 160, and 162) ion signals appearing in a mass spectrometer due to laser irradiation of a molecular beam were measured. The concentration ratio ($R_L = {}^{79}Br/{}^{81}Br$) in the Br_2 product formed was compared with this ratio in a nonirradiated CF_3Br molecular gas. According to the natural percentage of CF_3Br (50.56% $CF_3{}^{79}Br$ and 49.44% $CF_3{}^{81}Br$), the concentration ratio of bromine isotopes in a nonirradiated CF_3Br gas is $R_0 = {}^{79}Br/{}^{81}Br \approx 1.023$. The enrichment coefficient in the Br_2 product is defined as

$$K_{enr}\left(\frac{^{79}Br}{^{81}Br}\right) = \frac{R_L}{R_0} = \frac{\left(^{79}Br/^{81}Br\right)_{in\ Br_2}}{\left(^{79}Br/^{81}Br\right)_{in\ CF_3Br}}. \qquad (13)$$

The dissociation yields β_{35} and β_{79} of CF_2HCl and CF_3Br molecules were determined by measuring the intensities of time-of-flight spectra of the $CF_2H^{35}Cl^+$ molecular ion ($m/z = 86$) and the $CF_2{}^{79}Br^+$ ($m/z = 129$) ion fragment. The time-of-flight spectra of these ions were measured both in the absence of excited molecules in a pressure shock produced in front of the surface and upon their laser excitation. Thus, in the case of CF_2HCl,

$$S_L = S_0(1 - \beta_{35}\Gamma), \qquad (14)$$

where S_0 and S_L are the time-of-flight $CF_2H^{35}Cl^+$ ion signals in the absence of excitation of molecules and upon their laser excitation, and Γ is the ratio of the irradiated volume to the total volume of the molecular flow. In experiments, the composition of only the irradiated part of the molecular flow was analyzed with a mass spectrometer. Therefore, in our case, the condition $\Gamma = 1$ was valid.

The ^{35}Cl enrichment coefficient $K_{enr}({}^{35}Cl/{}^{37}Cl)$ with respect to the ^{37}Cl isotope was defined as the concentration ratio of ^{35}Cl and ^{37}Cl isotopes in the residual CF_2HCl gas after irradiation to this ratio for chlorine isotopes in the initial (natural) CF_2HCl gas using the relation

$$K_{enr}\left(\frac{^{35}Cl}{^{37}Cl}\right) = \frac{1 - \beta_{35}}{1 - \beta_{37}}. \qquad (15)$$

Based on relations analogous to (14) and (15), the dissociation yield β_{79} and the enrichment coefficient $K_{enr}({}^{79}Br/{}^{81}Br)$ in the residual CF_3Br gas after irradiation were measured.

Experiments were performed online, which provided information on the dissociation of molecules and products in each individual excitation pulse. The main goal of papers [280–283] was to study the possibility of achieving a selectivity with respect to bromine and chlorine isotopes upon dissociation of CF_3Br and CF_2HCl molecules using a new approach.

10.4 Results of studies and analysis
10.4.1 Selective dissociation of CF_3Br molecules. The dissociation of CF_3Br molecules was performed under three different conditions: in an unperturbed molecular flow, in a flow incident on a surface, and in a pressure shock [280–282]. Figure 23a shows the dependences of the dissociation yield β_{79} of $CF_3{}^{79}Br$ molecules on the laser radiation energy density Φ measured by a $CF_3{}^{79}Br^+$ ion cluster signal upon excitation of molecules in an unperturbed molecular flow (1), in a flow incident on a surface (2), and in a pressure shock (3). Molecules were excited by the 9R(30) laser line. One can see that in a broad range of $\Phi = 0.75 - 4.9$ J cm^{-2} the dissociation yield of $CF_3{}^{79}Br$ molecules excited in a pressure shock or in a flow incident on a surface greatly exceeds this
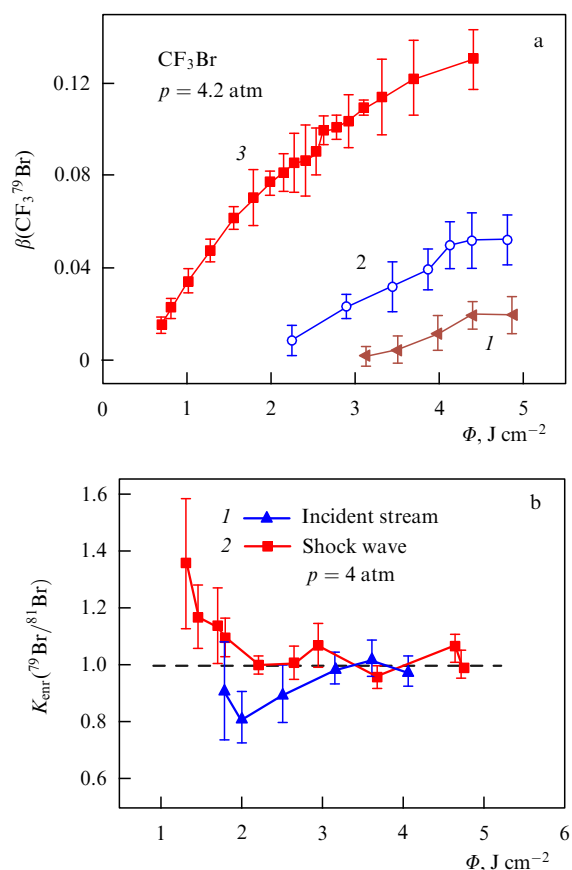
Figure 23. (a) Dependences of the dissociation yield of CF_3Br molecules on laser radiation energy density upon excitation of molecules in (1) an unperturbed molecular flow, (2) a flow incident on a surface, and (3) a pressure shock (shock wave). Molecules were excited by the 1084.635 cm^{-1} 9R(30) laser line. The gas pressure over the nozzle was 4.2 atm. The nozzle pulse duration was 310 μs [280]. (b) Dependences of enrichment coefficient $K_{enr}({}^{79}Br/{}^{81}Br)$ in the Br_2 product on the excitation energy density in the CF_3Br flow incident on a surface (1) and in a pressure shock (shock wave) (2). Molecules were excited by the 9R(30) laser line. Gas pressure over the nozzle was 4 atm. Nozzle pulse duration was 350 μs [280].

yield upon excitation in an unperturbed flow. This difference increases for excitation energy densities smaller than 2 J cm^{-2}. Figure 23a also shows that the dissociation threshold in cases (2) and (3) considerably decreases (3–5 times). These results suggest that, upon excitation of molecules in a pressure shock and in a flow incident on a surface, the total dissociation yield is considerably determined by the excitation and dissociation of colliding molecules in a pressure shock formed in front of the surface [181, 275, 276].

The increase in the dissociation yield of $CF_3{}^{79}Br$ molecules in cases (2) and (3) of their excitation compared to excitation in an unperturbed flow in case (1) is explained as follows. When molecules are irradiated in an unperturbed flow, they dissociate only due to radiative excitation (their collisions are absent in the flow), whereas upon excitation of molecules in a flow incident on a surface and in a pressure shock, they dissociate due to radiative and collision excitation mechanisms [274–278]. In addition, when molecules are irradiated directly in a pressure shock, their excitation efficiency considerably increases because of the higher gas density and temperature in the shock compared to those in the unperturbed flow. Estimates made in [280] show that the

concentration of CF_3Br molecules in a pressure shock was $\approx 7.9 \times 10^{16}$ cm^{-3}, which corresponds to a pressure of ≈ 2.2 Torr. The high pressure and translational temperature of the gas in the pressure shock also facilitate the more efficient formation of dissociation products — C_2F_6 and Br_2 molecules.

The results presented in Fig. 23a also show that a very weak dissociation of CF_3Br molecules in the case of their excitation in an unperturbed flow occurs at the given excitation frequency only at very high energy densities ($\Phi \geqslant 4.5-5$ J cm^{-2}), whereas, for $\Phi \leqslant 3.5-4$ J cm^{-2}, the dissociation of molecules is absent in fact. At the same time, at high excitation energy densities, the selective dissociation of molecules does not occur because of the large dynamic field broadening of excited molecular transitions (the Rabi frequency) and a small isotopic shift in the IR absorption spectra of CF_3Br isotopomers.

Therefore, the isotope-selective dissociation of CF_3Br molecules can be performed only at low excitation energy densities $\Phi \leqslant 1.5-2$ J cm^{-2}, i.e., when molecules are excited in a flow incident on a surface or in a pressure shock. In the first case, the conditions of laser excitation of molecules are the same as in an unperturbed flow, whereas, upon excitation in a pressure shock, these conditions are absolutely different (see relation (12)). The concentration and rotational temperature of molecules in a pressure shock are much higher than in an unperturbed flow [275, 276].

It was found in [280] that the dissociation of CF_3Br molecules in a flow incident on a surface occurred nonselectively for $\Phi \geqslant 3-3.5$ J cm^{-2}, whereas, for $\Phi \leqslant 2.0$ J cm^{-2}, isotope-selective dissociation was observed. The absence of selectivity at high excitation energy densities is mainly explained by large dynamic field broadening of molecular transitions determined by the Rabi frequency: $\Delta \nu_R = \mu E / \hbar c$, where μ is the transition dipole moment, E is the laser pulse electric field strength, $\hbar$ is Planck's constant, and c is the speed of light. Thus, for $\Phi \approx 2.5$ J cm^{-2} and $\mu \approx 0.23D$ [293], the Rabi frequency reaches $\Delta \nu_R \approx 0.53$ cm^{-1}. It exceeds laser detunings from the Q-band frequencies of excited transitions and an isotopic shift of ≈ 0.245 cm^{-1} in the IR absorption spectra of $CF_3{}^{79}Br$ and $CF_3{}^{81}Br$ molecules. For this reason, such high-power laser pulses probably efficiently excite both CF_3Br isotopomers.

Figure 23b shows the dependences of enrichment coefficients in the Br_2 product on the energy density in the range $\Phi = 1.25-4.75$ J cm^{-2} in the case of excitation of molecules in a flow incident on a surface (*1*) and directly in a pressure shock (*2*). In both cases, excitation was performed by the 1084.635-cm^{-1} 9R(30) laser line. One can see from this figure that, for comparatively high $\Phi \approx 2.5-4.75$ J cm^{-2}, the enrichment coefficients are in fact unity. The dissociation of CF_3Br molecules occurs nonselectively. The dissociation selectivity is observed only at low energy densities ($\Phi \leqslant 2.0$ J cm^{-2}) and increases with decreasing excitation energy density. Thus, for $\Phi \approx 1.75$ J cm^{-2}, the enrichment coefficient in the Br_2 product in the presence of exciting molecules in a pressure shock is $K_{enr}({}^{79}Br/{}^{81}Br) \approx 1.20 \pm 0.09$, while, in a flow incident on a surface, $K_{enr}({}^{79}Br/{}^{81}Br) \approx 0.85 \pm 0.07$. The dissociation selectivity of CF_3Br molecules tends to increase further with decreasing excitation energy density. This suggests that, using the two-frequency excitation and dissociation of molecules, much higher enrichment coefficients can be obtained. The different values of enrichment coefficients

with respect to unity in the two cases considered are probably explained by absolutely different thermodynamic conditions existing in a flow incident on a surface and in a pressure shock (see relations (10)–(12)).

10.4.2 Mutual increase in the dissociation efficiency of CF_2HCl and CF_3Br molecules in a pressure shock upon irradiation in a bimolecular mixture. The study of the dissociation of CF_2HCl and CF_3Br molecules in a pressure shock revealed a mutual strong increase in dissociation efficiency upon irradiation in a bimolecular mixture, unlike the irradiation of these molecules separately. Figure 24a shows the dependences of the dissociation yield of β_{35} of $CF_2H^{35}Cl$ molecules on the excitation energy density Φ measured by the $CF_2H^{35}Cl^+$ ion signal by irradiating molecules in a pressure shock in a CF_2HCl molecular flow (*1*) and in a $CF_2HCl/CF_3Br = 1:1$ mixture flow (*2*). In both cases, the total gas pressure over the nozzle was 4.0 atm. Molecules were excited by the 9R(30) laser line. It can be seen that, in a broad range of $\Phi \approx 0.2-3.0$ J cm^{-2}, the dissociation yield of CF_2HCl molecules excited in a mixture with CF_3Br molecules is much higher (4–7 times) than upon excitation without CF_3Br.

Figure 24b shows the dependences of the dissociation yield β_{79} of $CF_3{}^{79}Br$ molecules on the excitation energy density measured by the $CF_2{}^{79}Br^+$ ion signal in a CF_3Br molecular flow (*1*) and a $CF_2HCl/CF_3Br = 1:1$ gas mixture flow (*2*). The total gas pressure over the nozzle was 5.2 atm. One can see that, for $\Phi \approx 0.75-3.0$ J cm^{-2}, the dissociation yield of CF_3Br molecules excited in a mixture with CF_2HCl molecules considerable exceeds (1.5–2 times) this yield in the case of excitation without CF_2HCl.

Note that results presented in Fig. 24 for a mixture of molecules are not normalized to the partial content of CF_2HCl and CF_3Br molecules in the flow. The content of molecules of both types upon irradiation in their mixture is approximately half of their content in the case of their separate irradiation. Therefore, their dissociation yields in the mixture calculated per molecule differ from dissociation yields in individual gases even more greatly than in Fig. 24.

Figure 24 shows that the IR dissociation thresholds of CF_2HCl and CF_3Br molecules in the CF_2HCl/CF_3Br mixture are considerably lower than in the case of their irradiation separately. This is especially strongly manifested for the dissociation of CF_2HCl molecules with a dissociation energy considerable lower than for CF_3Br molecules. Thus, in the case of irradiation of a pure CF_2HCl gas, the dissociation threshold of molecules (the energy density at which the dissociation yield is $\approx 1\%$) is about ≈ 1.0 J cm^{-2}, whereas, upon irradiation of CF_2HCl in a mixture with CF_3Br, this yield is $\approx 0.15-0.2$ J cm^{-2}.

When molecules are irradiated in a pressure shock, the total dissociation yield is considerably determined by molecular collisions and energy exchange due to the $V-V$ relaxation which occurs at comparatively high gas densities (pressure $\approx 1.5-2.5$ Torr) [275, 276]. In our opinion, rapid collisions of excited molecules with each other, including mutual collisions of two types of molecules in a mixture, result, along with resonance radiative excitation of both types of molecules, in a great increase in their dissociation yield in a mixture compared to the case of their irradiation separately. The role of the $V-V$ energy exchange between molecules, in particular, of different types, is especially important in the presence of almost resonant vibrational levels of molecules of both types [244], which was realized in our experiments.
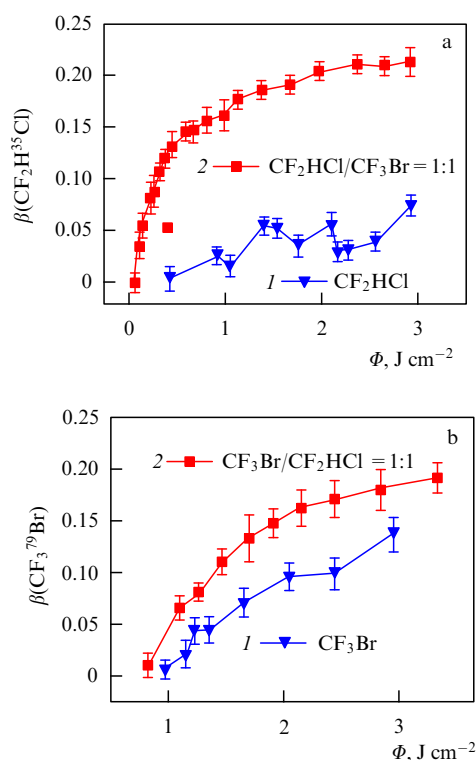
Figure 24. (a) Dependences of the dissociation yield of $CF_2H^{35}Cl$ molecules on the exciting radiation energy density upon irradiation of molecules in a pressure shock in the case of a CF_2HCl molecular flow (*1*) and a $CF_2HCl/CF_3Br = 1:1$ gas mixture flow (*2*). Total gas pressure over the nozzle was 4.0 atm [281, 282]. (b) Dependences of the dissociation yield of $CF_3^{79}Br$ molecules on the laser radiation energy density for a pure CF_3Br gas irradiated in a shock wave (*1*) and for a $CF_2HCl/CF_3Br = 1:1$ molecular mixture (*2*). (a, b) Molecules were excited by the 9R(30) laser line. Gas pressure over the nozzle was 4 atm (a) and 5.2 atm (b). Nozzle pulse duration was 400 μs (a) and 390 μs (b) [282].

Figure 25. (a) Mass spectra of CF_2HCl molecules ($m/z = 86, 87, 88$) before (*1*) and after (*2*) irradiation of a $CF_2HCl/CF_3Br = 1:1$ mixture in a shock wave. Molecules were excited by the 2.2-J cm^{-2}, 1084.635-cm^{-1} 9R(30) laser line [282, 283]. (b) Dependence of the enrichment coefficient $K_{enr}(^{35}Cl/^{37}Cl)$ in the CF_2HCl residual gas upon irradiation of the $CF_2HCl/CF_3Br = 1:1$ molecular mixture by the 9R(30) laser line. (a, b) Gas pressure over the nozzle was 8 atm, nozzle pulse duration was 475 μs [282, 283].

10.4.3 Isotope-selective dissociation of CF_2HCl molecules.

The use of nonequilibrium thermodynamic conditions of a pressure shock and the effect of a mutual increase in the dissociation efficiency of molecules in a mixture ensured the isotope-selective IR dissociation of CF_2HCl and CF_3Br molecules for moderate excitation energy densities [281–283]. Figure 25a shows the mass spectrum of CF_2HCl molecules in the region of $m/z = 86, 87, 88$ ($CF_2H^{35}Cl^+$, $CF_2^{37}Cl^+$, and $CF_2H^{37}Cl^+$, respectively) without irradiation of the $CF_2HCl/CF_3Br = 1:1$ mixture (*1*) and upon laser irradiation (*2*). Molecules were excited in a pressure shock at the 1084.635-cm^{-1} 9R(30) laser line at $\Phi = 2.2$ J cm^{-2}. One can see from Fig. 25a that the dissociation of $CF_2H^{35}Cl$ molecules predominantly takes place over the dissociation of $CF_2H^{37}Cl$ molecules.

Figure 25b shows the enrichment coefficient $K_{enr}(^{35}Cl/^{37}Cl)$ in a residual CF_2HCl gas in an irradiated $CF_2HCl/CF_3Br = 1:1$ mixture as a function of the excitation energy density. Molecules were excited by the 9R(30) laser line. Figure 25b shows that, for comparatively high excitation energy densities $\Phi \geqslant 2.5$ J cm^{-2}, the dissociation of CF_2HCl molecules occurs nonselectively. Selective dissociation is observed only for low $\Phi \leqslant 1.5-2.0$ J cm^{-2}. For $\Phi \approx 1.3$ J cm^{-2}, the enrichment coefficient $K_{enr}(^{35}Cl/^{37}Cl) = 0.90 \pm 0.05$ was obtained. In addition, the selective dissociation of CF_2HCl molecules in the pressure shock is possible only in a mixture with CF_3Br molecules, because, at low excitation energy densities, the dissociation of CF_2HCl molecules in a pure gas does not in fact occur (Fig. 24a).

10.5 Conclusions

Studies [280–283] showed using the example of CF_3Br molecules that, upon excitation of molecules in a pressure shock and in a flow incident on a surface, the dissociation yield of molecules significantly increases (5–10 times) compared to the dissociation yield in an unperturbed flow, and the dissociation threshold considerably decreases (3–5 times). This makes possible the efficient isotope-selective IR dissociation of molecules at comparatively low laser pulse energies ($\Phi \leqslant 1.5-2.0$ J cm^{-2}), thereby increasing the dissociation selectivity.

It is shown that the combined action of the radiative and collision excitation mechanisms taking place in a molecular flow incident on a surface and in a pressure shock provides a significant increase in the dissociation yield and the formation of products upon IR laser excitation of molecules and a considerable decrease in the dissociation threshold. This is

especially important in the isotope separation in molecules with a small isotopic shift in IR absorption spectra, because, in this case, due to the dynamic field broadening of vibrational transitions of molecules, the dissociation selectivity can be observed only for low laser pulse energy densities.

The results obtained for CF_3Br and CF_2HCl molecules suggest that the effect observed also concerns other molecules. First of all, this is related to molecules containing heavy-element isotopes, which are characterized by a small isotopic shift in IR absorption spectra. The dissociation of such molecules should be preferably performed at low excitation energy densities. Thus, for example, upon the isotope-selective IR dissociation of UF_6 molecules by laser excitation of a ≈ 627-cm^{-1} v_3 vibration [107], SF_6 molecules can be used as a sensitizer absorbing radiation in the 16-μm region (the 615-cm^{-1} v_4 vibration [106, 175]).

11. Conclusions

For the last half century, beginning in the 1970s, great progress has been achieved in the study of the selective interaction of IR laser radiation with molecules. This is confirmed by many reviews and monographs on this problem, some of them mentioned in the present review. Undoubtedly, based on the knowledge obtained in these studies, the laboratory research on selective IR laser photophysics and photochemistry can be rapidly developed in the future. However, the possibility of large-scale technological applications of these results obtained remains doubtful. Definitely, there was a period of deep frustration and disappointment in the field of laser isotope separation, because initially great hope existed in the possibility of building industrial facilities. It seems that one of the reasons why this did not occur is the great lag of theoretical studies from experimental results, as was observed for the IR MPD of molecules.

Extensive studies within the framework of projects on laser uranium isotope separation resulted in significant achievements in the spectroscopy of uranium atoms, the spectroscopy and intramolecular dynamics of polyatomic molecules and clusters, including UF_6 molecules and clusters, and the development of lasers for multiphoton excitation of uranium atoms and vibrational excitation of UF_6 molecules. Continuous and pulsed nozzles of different configurations and lengths were developed in order to obtain cooled molecular and cluster flows and to study their spectra at low temperatures, in particular, under conditions close to those planned for obtainment in large technological processes. Laser methods were developed for studying the spectra and intramolecular dynamics of molecules and molecular clusters. Low-energy MLIS methods are being proposed and developed, in particular, for uranium isotopes. Alternative methods of the selective dissociation of molecules under new thermodynamic nonequilibrium conditions are being developed and studied.

At present, the most studied and probably the most promising method for uranium isotope separation is selective IR laser control of molecular clustering in gas-dynamic jets and flows, although any data on the efficiency of this method are absent. Taking into account that a very strongly diluted UF_6 molecular gas in a carrier gas is used in this method and that the size of the laser irradiated region of molecules should be small (within a few nozzle calibers) [85–88], we can assume that the method efficiency is not very high. By separating

isotopes using UF_6 molecules, this method can be combined with the IR predissociation of clusters. These methods are probably used in the SILEX technology.

Methods based on the heterogeneous processes of interaction of vibrationally excited and unexcited molecules with a cold surface covered with molecules (clusters) described in Section 9.4 (see also review [33]) are more efficient than methods mentioned above, because they do not require the strong dilution of an initial molecular gas in a carrier. They are also simpler in operation in practice. However, the selectivity of the processes underlying them has been poorly studied so far. Therefore, further studies of the selectivity of these methods are required.

The isotope-selective IR dissociation of molecules under nonequilibrium conditions of a pressure shock can be considered, in our opinion, to be a promising alternative to low-energy MLIS methods for uranium. Although this method is based on the dissociation of molecules, because of the low energy density required for dissociation, it can be assigned to low-energy methods. This method is well studied, has a high efficiency compared to low-energy MLIS methods (because it does not require the strong dilution of the initial molecular gas in a carrier either), and can be readily used in practice.

Thus, among all of the low-energy MLIS methods considered here, the most promising today from the point of view of their efficiency and simplicity of realization in practice are those based on the isotope-selective condensation of molecules on a surface (see also review [33]) and the control of molecular clustering and cluster dissociation. An alternative to these approaches is the selective IR MPD of molecules under nonequilibrium thermodynamic conditions of a pressure shock.

Projects on laser uranium isotope separation were shut down, in particular, because this idea was ahead of its time. Many projects were started in the 1970s–early 1980s, when the development level of laser technology was very far from the parameters required. For this reason, aside from purely scientific problems, which should be solved to realize physical ideas, huge efforts and funds, as well as a long time, were spent on the development of the laser equipment itself. This is especially true of the AVLIS technology. To a somewhat lesser degree, this also concerns the MLIS technology. Thus, only within about 10 years after the start of the project, the parameters of a para-H_2 laser at AEC (South Africa) approached values required by the process economics.

As for the choice between the AVLIS and MLIS technologies for uranium isotope separation, different points of view exist in this respect. Both technologies are based on rather sophisticated physical processes requiring careful study and optimization of the elementary separation event. The choice of the AVLIS in the USA was probably considerably motivated by the higher selectivity of the process and the potential to use this technology for plutonium isotope separation. Concerning the production of low-enrichment uranium, it seems that the MLIS technology is preferable. Its use does not involve problems of obtaining an atomic vapor and its subsequent manipulations, as in the AVLIS method. A working material is the UF_6 gas produced in required amounts. In the case of the MLIS technology, the laser equipment is also simpler. The results of studies show that the molecular variant has more advantages and potential than the atomic method for development and technological applications. In addition, within the framework of the molecular variant, several low-energy methods were pro-

posed and developed. The selective dissociation of molecules, which is an alternative to low-energy methods, is being studied quite extensively.

In conclusion, note that researchers' great interest in the development of laser technologies for uranium isotope separation, their huge contribution to this field, and the demand for the development of more economical technologies (compared to centrifuging technology) for uranium enrichment suggest that the technology of molecular laser separation of uranium isotopes will be realized with time. Undoubtedly, such an interesting, exciting, and much-needed research field will remain in the scope of activity of new-generation researchers.

References

1. Ambartsumyan R V, Kalinin V P, Letokhov V S *JETP Lett.* **13** 217 (1971); *Pis'ma Zh. Eksp. Teor. Fiz.* **13** 305 (1971)
2. Ambartsumyan R V et al. *JETP Lett.* **17** 63 (1973); *Pis'ma Zh. Eksp. Teor. Fiz.* **17** 91 (1973)
3. Ambartsumyan R V et al. *JETP Lett.* **20** 273 (1974); *Pis'ma Zh. Eksp. Teor. Fiz.* **20** 597 (1974)
4. Ambartsumyan R V et al. *JETP Lett.* **21** 171 (1975); *Pis'ma Zh. Eksp. Teor. Fiz.* **21** 375 (1975)
5. Ambartsumyan R V et al. *JETP Lett.* **22** 43 (1975); *Pis'ma Zh. Eksp. Teor. Fiz.* **22** 96 (1975)
6. Metz W D *Science* **185** 602 (1974)
7. Glass A J (Sci. Ed.), Cummings K L (Gen. Ed.) "Laser Program Annual Report — 1975", UCRL-50021-75 (Livermore, CA: Lawrence Livermore Laboratory, Univ. of California, 1975)
8. Jensen R J et al. *Laser Focus* **12** (5) 51 (1976)
9. Jensen R J, Sullivan J Al, Finch F T *Separat. Sci. Technol.* **15** 509 (1980)
10. Jensen R J, Judd O P, Sullivan J A *Los Alamos Sci.* (4) 2 (1982)
11. Greenland P T *Contemp. Phys.* **31** 405 (1990)
12. Guyot J et al. "Uranium enrichment activities: the SILVA program", Demande d'autorisation NIG No. 316, DCC, SACLAY, DPE, 28 Jun 94, https://inis.iaea.org/collection/NCLCollectionStore/_Public/27/010/27010992.pdf?r=1&r=1
13. Camarcat N et al. *Proc. SPIE* **1859** 14 (1993)
14. "Soviet Research on Laser Isotope Separation for Uranium Enrichment". Central Intelligence Agency. Freedom of Information Act Electronic Reading Room, https://www.cia.gov/readingroom/document/0000680142
15. Ramakoteswara Rao P *Current Sci.* **85** 615 (2003)
16. Mathi P et al. *Proc. Natl. Acad. Sci. India A* (2015) https://doi.org/10.1007/s40010-015-0249-6
17. Schneider K R, in *Proc. of the 6th Intern. Symp. on Advanced Nuclear Energy Research. Innovative Laser Technologies in Nuclear Energy, March 23–25, 1994 at Mito Plaza Hotel, Mito, Ibaraki, Japan, 1995* (Mito: Japan Atomic Energy Research Institute, 1995) p. 280; https://inis.iaea.org/collection/NCLCollectionStore/_Public/27/014/27014297.pdf
18. Becker F S, Kompa K L *Nucl. Technol.* **58** 329 (1982)
19. Meyer-Kretschmer G, Jetter H *Naturwissenschaften* **70** 7 (1983)
20. Kato S et al., in *Intern. Symp. Advanced Nuclear Energy Research. Near-Future Chemistry in Nuclear Fuel* (Tokyo, 1989) p. 53
21. Paisner J A (Ed.) *Laser Isotope Separation, 19–20 January 1993, Los Angeles, California* (Proc. SPIE, Vol. 1859) (Bellingham, WA: SPIE, 1993)
22. Eerkens J W (Ed.) *Selected Papers on Laser Isotope Separation — Science and Technology* (SPIE Milestone Series, Vol. MS 113) (Bellingham, WA: SPIE Optical Engineering Press, 1995) pp. 108–147, 257–687
23. Baranov V Yu et al., in *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Production, Application) Vol. 1 (Ed. V Yu Baranov) (Moscow: Fizmatlit, 2005) p. 474
24. Bokhan P A et al. *Laser Isotope Separation in Atomic Vapor* (Berlin: Wiley-VCH, 2006)
25. Radziemski L J, Solarz R W, Paisner J A (Eds) *Laser Spectroscopy and its Applications* (Optical Engineering, Vol. 11) (New York: M. Dekker, 1987) Ch. 3
26. Grigor'ev I S, Labozin V P, Pesnya A V, in *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Production, Application) Vol. 1 (Ed. V Yu Baranov) (Moscow: Fizmatlit, 2005) p. 374
27. Fuß W "Laser isotope separation and proliferation risks", Report MPQ 346, February 2015 (Garching: Max-Planck-Institute für Quantenopti, 2015); https://www.mpq.mpg.de/5178012/MPQ346.pdf
28. Atomic energy 2.0, https://www.atomic-energy.ru/Megatons-to-Megawatts?
29. "Megatons to Megawatts program concludes", World Nuclear News, 11 December 2013, https://www.world-nuclear-news.org/ENF-Megatons-to-Megawatts-program-concludes-1112134.html
30. Eerkens J W *Nucl. Sci. Eng.* **150** 1 (2005)
31. Kim J W et al. "Current status of the MLIS uranium enrichment process", *Proc. of the Korean Nuclear Society Spring Meeting, Korea, May 22, 2009*
32. Eerkens J W, Kim J *AIChE J.* **56** 2331 (2010)
33. Makarov G N *Phys. Usp.* **58** 670 (2015); *Usp. Fiz. Nauk* **185** 717 (2015)
34. Makarov G N *Phys. Usp.* **63** 245 (2020); *Usp. Fiz. Nauk* **190** 264 (2020)
35. Silex Systems Ltd, http://www.silex.com.au
36. Silex: History, https://www.silex.com.au/silex-technology/silex-uranium-enrichment-technology/
37. SILEX Process, http://www.chemeurope.com/en/encyclopedia/Silex_Process.html
38. SILEX Uranium Enrichment, SILEX Annual Report 2019, https://clients3.weblink.com.au/pdf/SLX/02140214.pdf
39. SILEX Uranium Enrichment, SILEX Annual Report 2020, http://www.silex.com.au
40. "Skol'ko atomnykh stantsii rabotaet v mire i v Rossii?" ("How many atomic stations are working in the world and Russia?"). Website of JSC Atomenergomash, http://www.aem-group.ru/mediacenter/informatoriy/skolko-atomnyix-stanczij-rabotaet-v-mire-i-v-rossii.html
41. Bekman I N, Yadernaya Industriya (Nuclear Industry). Special Course. Lecture 35. Ekonomicheskie aspekty yadernoi industrii (Economical Aspects of Nuclear Industry), p. 20, http://profbeckman.narod.ru/NIL35.pdf
42. Letokhov V S *Lazernaya Foto-ionizatsionnaya Spektroskopiya* (Laser Photoionization Spectroscopy) (Moscow: Nauka, 1987)
43. Letokhov V S *Nelineinye Selektivnye Fotoprotsessy v Atomakh i Molekulakh* (Nonlinear Selective Processes in Atoms and Molecules) (Moscow: Nauka, 1983)
44. Gurvich L V et al. *Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu* (Dissociation Energy of Chemical Bonds. Ionization Potentials and the Electron Affinity) (Exec. Ed. V N Kondrat'ev) (Moscow: Nauka, 1974)
45. Lide D R (Ed.) *Handbook of Chemistry and Physics* 74th ed. (Boca Raton, FL: CRC Press, 1993–1994)
46. Hildenbrand D *J. Chem. Phys.* **66** 4788 (1977)
47. Letokhov V S *Nature* **277** 605 (1979)
48. Yeung E S, Moore C B *Appl. Phys. Lett.* **21** 109 (1972)
49. Letokhov V S *Chem. Phys. Lett.* **15** 221 (1972)
50. Letokhov V S, Moore C B *Sov. J. Quantum Electron.* **6** 129 (1976); *Kvantovaya Elektron.* **3** 248 (1976); *Sov. J. Quantum Electron.* **6** 259 (1976); *Kvantovaya Elektron.* **3** 485 (1976)

51. Ambartsumyan R V et al. *JETP Lett.* **15** 501 (1972); *Pis'ma Zh. Eksp. Teor. Fiz.* **15** 709 (1972)
52. Ambartzumian R V et al. *Chem. Phys. Lett.* **16** 252 (1972)
53. Ambartzumian R V et al. *Dokl. Akad. Nauk SSSR* **211** 365 (1973)
54. Knyazev I N et al. *Appl. Phys.* **17** 427 (1978)
55. Ambartzumian R V et al. *Sov. J. Quantum Electron.* **8** 910 (1978); *Kvantovaya Elektron.* **5** 1593 (1978)
56. Kim K C et al. *J. Chem. Phys.* **78** 32 (1983)
57. Alexandre M et al. *J. Chim. Phys.* **80** 331 (1983)
58. Isenor N R et al. *Canad. J. Phys.* **51** 1281 (1973)
59. Ambartzumian R V et al. *Chem. Phys. Lett.* **25** 515 (1974)
60. Lyman J L et al. *Appl. Phys. Lett.* **27** 87 (1975)
61. Bagratashvili V N et al. *Multiple Photon Infrared Laser Photophysics and Photochemistry* (Chur: Harwood Acad. Publ., 1985)
62. Cantrell C D (Ed.) *Multiple-Photon Excitation and Dissociation of Polyatomic Molecules* (Topics in Current Physics, Vol. 35) (Berlin: Springer-Verlag, 1986)
63. Lyman J L, in *Laser Spectroscopy and Its Applications* (Optical Engineering, Vol. 11, Eds L J Radziemski, R W Solarz, J A Raisner) (New York: M. Dekker, 1987) p. 417
64. Makarov G N *Phys. Usp.* **48** 37 (2005); *Usp. Fiz. Nauk* **175** 41 (2005)
65. Baranov V Yu et al., in *Fiziko-khimicheskie Protsessy pri Selektsii Atomov i Molekul: Sbornik Dokladov 2-i Vserossiiskoi Nauchnoi Konf., 29 Sentyabrya–3 Oktyabrya 1997, Zvenigorod* (Physico-chemical Processes in the Selection of Atoms and Molecules: Collection of Reports of the 2nd Scientific Conf., 29 September–3 October, 1997, Zvenigorod) (Eds V Yu Baranov, Yu A Kolesnikov) (Moscow: TsNIIatominform, 1997) p. 21
66. Baranov V Yu (Ed.) *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Production, Application) (Moscow: Fizmatlit, 2005)
67. Letokhov V S, Ryabov E A, in *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Production, Application) Vol. 1 (Ed. V Yu Baranov) (Moscow: Fizmatlit, 2005) p. 445
68. Baranov V Yu, in *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Production, Application) Vol. 1 (Ed. V Yu Baranov) (Moscow: Fizmatlit, 2005) p. 460
69. Ambartsumyan R V et al. *JETP Lett.* **23** 194 (1976); *Pis'ma Zh. Eksp. Teor. Fiz.* **23** 217 (1976)
70. Ambartzumian R V et al. *Opt. Commun.* **18** 517 (1976)
71. Ambartsumyan R V et al. *Sov. J. Quantum Electron.* **7** 904 (1977); *Kvantovaya Elektron.* **4** 1590 (1977)
72. Ambartzumian R V et al. *Opt. Lett.* **1** 22 (1977)
73. Bagratashvili V N et al. *Opt. Commun.* **18** 525 (1976)
74. Akulin V M et al. *JETP Lett.* **25** 400 (1977); *Pis'ma Zh. Eksp. Teor. Fiz.* **25** 428 (1977)
75. Ambartzumian R V et al. *Chem. Phys. Lett.* **45** 231 (1977)
76. Ambartzumian R V et al. *Opt. Commun.* **25** 69 (1978)
77. Ambartzumian R V, Makarov G N, Puretzky A A *Opt. Commun.* **27** 79 (1978)
78. Zellweger J-M et al. *Phys. Rev. Lett.* **52** 522 (1984)
79. Philippoz J M et al. *J. Phys. Chem.* **88** 3936 (1984)
80. Philippoz J-M et al. *Surf. Sci.* **156** 701 (1985)
81. Philippoz J-M et al. *Berichte Bunsengesellschaft phys. Chem.* **89** (3) 291 (1985)
82. Van den Bergh H *Laser Optoelektron.* (3) 263 (1985)
83. Apatin V M et al. *J. Exp. Theor. Phys.* **125** 531 (2017); *Zh. Eksp. Teor. Fiz.* **152** 627 (2017)
84. Apatin V M et al. *Quantum Electron.* **48** 157 (2018); *Kvantovaya Elektron.* **48** 157 (2018)
85. Apatin V M et al. *J. Exp. Theor. Phys.* **127** 244 (2018); *Zh. Eksp. Teor. Fiz.* **154** 287 (2018)
86. Makarov G N, Ogurok N-D D, Petin A N *Quantum Electron.* **48** 667 (2018); *Kvantovaya Elektron.* **48** 667 (2018)
87. Lokhman V N et al. *Laser Phys.* **28** 105703 (2018)
88. Lokhman V N et al. *J. Exp. Theor. Phys.* **128** 188 (2019); *Zh. Eksp. Teor. Fiz.* **155** 216 (2019)
89. Petin A N, Makarov G N *Quantum Electron.* **49** 593 (2019); *Kvantovaya Elektron.* **49** 593 (2019)
90. Apatin V M et al. *Opt. Spectrosc.* **127** 61 (2019); *Opt. Spektrosk.* **127** 66 (2019)
91. Makarov G N *Phys. Usp.* **60** 227 (2017); *Usp. Fiz. Nauk* **187** 241 (2017)
92. Kappes M, Leutwyler S, in *Atomic and Molecular Beam Methods* Vol. 1 (Ed. G Scoles) (New York: Oxford Univ. Press, 1988) p. 380
93. Janda K C *Adv. Chem. Phys.* **60** 201 (1985)
94. Celii F G, Janda K C *Chem. Rev.* **86** 507 (1986)
95. Miller R E *J. Phys. Chem.* **90** 3301 (1986)
96. Buck U *Adv. Atom. Mol. Opt. Phys.* **35** 121 (1995)
97. Makarov G N *Phys. Usp.* **61** 617 (2018); *Usp. Fiz. Nauk* **188** 689 (2018)
98. Lee Y T "Isotope separation by photodissociation of Van der Waals molecules", US Patent 4,032,306 (1977)
99. Casassa M P, Bomse D S, Janda K C *J. Phys. Chem.* **85** 2623 (1981)
100. Schwab C et al. *Prog. Nucl. Energy* **33** 217 (1998)
101. Snavely B B, in *Proc. of the VIII Intern. Conf. on Quantum Electronics, San Francisco, California, June 10–13, 1974*; Preprint UCRL-75725, CONF-740617 (Livermore, CA: Lawrence Livermore National Laboratory, 1974)
102. Janes G et al. *IEEE J. Quantum. Electron.* **12** (2) 111 (1976)
103. Forsen H K, in *Intern. Conf. Nuclear Fuel Cycle, Amsterdam, The Netherlands, September 1980*
104. Letokhov V S, Mishin V I, Puretzky A A *Prog. Quantum Electron.* **5** 139 (1977)
105. Bar-Ziv E, Freiberg M, Weiss S *Spectrochim. Acta A* **28** 2025 (1972)
106. Chapados C, Birnbaum G *J. Mol. Spectrosc.* **132** 323 (1988)
107. Aldridge J P et al. *J. Chem. Phys.* **83** 34 (1985)
108. Ambartsumyan R V et al. *Sov. Phys. JETP* **42** 993 (1975); *Zh. Eksp. Teor. Fiz.* **69** 1956 (1975)
109. Ambartsumyan R V et al. *JETP Lett.* **23** 22 (1976); *Pis'ma Zh. Eksp. Teor. Fiz.* **23** 26 (1976)
110. Ambartsumyan R V et al. *Sov. Phys. JETP* **44** 231 (1976); *Zh. Eksp. Teor. Fiz.* **71** 440 (1976)
111. Ambartsumyan R V, Makarov G N, Puretskii A A *JETP Lett.* **28** 647 (1978); *Pis'ma Zh. Eksp. Teor. Fiz.* **28** 696 (1978)
112. Anderson J B, in *Molecular Beams and Low Density Gasdynamics* (Gasdynamics, Vol. 4, Ed. P P Wegener) (New York: M. Dekker, 1974)
113. Tanimura S, Okada Y, Takeuchi K *J. Phys. Chem.* **100** 2842 (1996)
114. Okada Y et al. *Appl. Phys. B* **63** 57 (1996)
115. Okada Y et al. *J. Mol. Struct.* **410–411** 299 (1997)
116. Beu T A, Onoe J, Takeuchi K *J. Chem. Phys.* **106** 5910 (1997)
117. Beu T A, Onoe J, Takeuchi K *J. Chem. Phys.* **109** 8295 (1998)
118. Depoorter G L, Rofer-depoorter C K *Spectrosc. Lett.* **8** 521 (1975)
119. Rianda R, Frueholz R P, Kuppermann A *J. Chem. Phys.* **70** 1056 (1979)
120. Alexandre M et al. *J. Chim. Phys.* **80** 331 (1983)
121. Kroger P M, Riley S J, Kwei G H *J. Chem. Phys.* **68** 4195 (1978)
122. Fuss W et al. *Isotopenpraxis Isotopes Environmental Health Studies* **30** (2–3) 199 (1994)
123. Subbiah J et al. *Indian J. Phys.* **54B** 121 (1986)
124. Wenzel R G, Arnold G P *Appl. Opt.* **15** 1322 (1976)
125. Tiee J J, Wittig C *Appl. Phys. Lett.* **30** 420 (1977)
126. McDowell R S et al. *Opt. Lett.* **4** 274 (1979)
127. Tiee J J, Fischer T A, Wittig C *Rev. Sci. Instrum.* **50** 958 (1979)
128. Alimpiev S S et al. *Sov. J. Quantum Electron.* **9** 329 (1979); *Kvantovaya Elektron.* **6** 553 (1979)
129. Grasyuk A Z, Letokhov V S, Lobko V V *Sov. J. Quantum Electron.* **10** 1317 (1980); *Kvantovaya Elektron.* **7** 2261 (1980)
130. Grasiuk A Z, Letokhov V S, Lobko V V *Prog. Quantum Electron.* **6** 245 (1980)
131. Alimpiev S S et al. *Sov. J. Quantum Electron.* **10** 1087 (1980); *Kvantovaya Elektron.* **7** 1885 (1980)
132. Eckhardt R, Telle J, Haynes L *J. Opt. Soc. Am.* **72** 40 (1982)
133. Jones C R, Telle J M, Buchwald M I, in *Proc. of the Tenth Intern. Quantum Electronics Conf., Atlanta, Georgia, 1978* (Washington, DC: Optical Society of America, 1978) paper K7
134. Baranov V Yu et al. *Sov. J. Quantum Electron.* **10** 47 (1980); *Kvantovaya Elektron.* **7** 87 (1980)
135. Sinha S *J. Appl. Phys.* **71** 4145 (1992)
136. Gupta P K, Mehendale S C *Hyperfine Interactions* **37** 243 (1987)
137. Telle J *IEEE J. Quantum. Electron.* **19** 1469 (1983)
138. Gorokhov Yu A et al. *Sov. J. Quantum Electron.* **9** 1402 (1979); *Kvantovaya Elektron.* **6** 2382 (1979)
139. Knyazev I N, Letokhov V S, Lobko V V *Opt. Commun.* **29** 73 (1979)

140. Babichev A P et al. *Sov. J. Quantum Electron.* **11** 141 (1981); *Kvantovaya Elektron.* **8** 231 (1981)
141. Stein A, Rabinowitz P, Kaldor A *Opt. Lett.* **3** 97 (1978)
142. Hawkins K C, Peacock R, Rutt H N *J. Phys. D* **18** 191 (1985)
143. Gundersen M, Yocom T *IEEE J. Quantum Electron.* **18** 1237 (1982)
144. Byer R *IEEE J. Quantum Electron.* **12** 732 (1976)
145. Trutna W R, Byer R L *Appl. Opt.* **19** 301 (1980)
146. Rabinowitz P et al. *Opt. Lett.* **3** 147 (1978)
147. UK Patent GB 2256 082 A
148. Byer R L, Trutna W R *Opt. Lett.* **3** 144 (1978)
149. Midorikawa K et al. *Appl. Phys. Lett.* **47** 1033 (1985)
150. AIP interviews: Interview of George Janes by Joan Bromberg on 1984 September 19, Niels Bohr Library and Archives, American Institute of Physics, College Park, MD USA, http://www.aip.org/history-programs/niels-bohr-library/oral-histories/5069
151. Cox D M et al. *Science* **205** 390 (1979)
152. Horsley J A et al. *J. Chem. Phys.* **73** 3660 (1980)
153. Lewis G K, Cremers D A *J. Laser Appl.* **7** 224 (1995)
154. McDowell R S, Aldridge J P, Holland R F *J. Phys. Chem.* **80** 1203 (1976)
155. Brock E G et al. *J. Mol. Spectrosc.* **76** 301 (1979)
156. Krohn B J et al. *J. Mol. Spectrosc.* **132** 285 (1988)
157. McDowell R S, Patterson C W, Harter W G *Los Alamos Sci.* (4) 38 (1982); https://permalink.lanl.gov/object/tr?what = info:lanl-repo/lareport/LA-UR-82-5178
158. Krohn B J, Kim K C *J. Chem. Phys.* **77** 1645 (1982)
159. Lyman J L, Galbraith H W, Ackerhalt J R *Los Alamos Sci.* (4) 66 (1982)
160. Alimpiev S S et al. *Sov. J. Quantum Electron.* **13** 331 (1983); *Kvantovaya Elektron.* **10** 562 (1983)
161. Ambartsumyan R V, Gorokhov Yu A, Furzikov N P *Sov. J. Quantum Electron.* **6** 1251 (1976); *Kvantovaya Elektron.* **3** 2293 (1976)
162. Ambartsumyan R V et al. *Sov. J. Quantum Electron.* **9** 1546 (1979); *Kvantovaya Elektron.* **6** 2612 (1979)
163. Ambartsumyan R V et al. *Sov. J. Quantum Electron.* **10** 1152 (1980); *Kvantovaya Elektron.* **7** 1998 (1980)
164. Averin V G et al. *Sov. J. Quantum Electron.* **9** 1565 (1979); *Kvantovaya Elektron.* **6** 2637 (1979)
165. Alimpiev S S et al. *Sov. J. Quantum Electron.* **9** 1263 (1979); *Kvantovaya Elektron.* **6** 2155 (1979)
166. Baronov G S et al. *Sov. J. Quantum Electron.* **11** 947 (1981); *Kvantovaya Elektron.* **8** 1573 (1981)
167. Baranov V Yu et al. *Quantum Electron.* **26** 762 (1996); *Kvantovaya Elektron.* **23** 782 (1996)
168. Alimpiev S S et al. *Sov. J. Quantum Electron.* **11** 375 (1981); *Kvantovaya Elektron.* **8** 623 (1981)
169. Ambartzumian R V, Letokhov V S, in *Chemical and Biochemical Applications of Lasers* Vol. 3 (Ed. C B Moore) (New York: Academic Press, 1977) Ch. 2
170. Letokhov V S, Makarov A A *Sov. Phys. Usp.* **24** 366 (1981); *Usp. Fiz. Nauk* **134** 45 (1981)
171. Letokhov V S *Phys. Today* **33** (11) 34 (1980)
172. Karlov N V, Prokhorov A M *Sov. Phys. Usp.* **19** 285 (1976); *Usp. Fiz. Nauk* **118** 583 (1976)
173. Bagratashvili V N et al. *Sov. Phys. JETP* **50** 1075 (1979); *Zh. Eksp. Teor. Fiz.* **77** 2238 (1979)
174. Evseev A V, Puretskii A A, Tyakht V V *Sov. Phys. JETP* **61** 34 (1985); *Zh. Eksp. Teor. Fiz.* **88** 60 (1985)
175. McDowell R S et al. *Spectrochim. Acta A* **42** 351 (1986)
176. Baldacchini G, Marchetti S, Montelatici V *J. Mol. Spectrosc.* **91** 80 (1982)
177. Apatin V M, Makarov G N *Appl. Phys. B* **28** 367 (1982)
178. Apatin V M, Makarov G N *Sov. Phys. JETP* **57** 8 (1983); *Zh. Eksp. Teor. Fiz.* **84** 15 (1983)
179. Apatin V M et al. *JETP Lett.* **37** 431 (1983); *Pis'ma Zh. Eksp. Teor. Fiz.* **37** 365 (1983)
180. Apatin V M et al. *Opt. Commun.* **47** 251 (1983)
181. Makarov G N *Phys. Usp.* **46** 889 (2003); *Usp. Fiz. Nauk* **173** 913 (2003)
182. McDowell R S, Goldblatt M *Inorg. Chem.* **10** 625 (1971)
183. McDowell R S et al. *J. Chem. Phys.* **69** 1513 (1978)
184. Velikhov E P et al. *Impul'snye CO_2 Lazery i Ikh Primenenie dlya Razdeleniya Izotopov* (Pulsed CO_2 Lasers and Their Application for Isotope Separation) (Exec. Ed. B M Smirnov) (Moscow: Nauka, 1983)
185. Velikhov E P et al. *Sov. J. Quantum Electron.* **9** 179 (1979); *Kvantovaya Elektron.* **6** 317 (1979)
186. Baranov V Yu et al. *Sov. J. Quantum Electron.* **9** 486 (1979); *Kvantovaya Elektron.* **6** 823 (1979)
187. Baranov V Yu et al. *Sov. J. Quantum Electron.* **9** 621 (1979); *Kvantovaya Elektron.* **6** 1062 (1979)
188. Abdushelishvili G I et al. *Sov. J. Quantum Electron.* **12** 459 (1982); *Kvantovaya Elektron.* **9** 743 (1982)
189. Letokhov V S (Ed.) *Laser Spectroscopy of Highly Vibrationally Excited Molecules* (Bristol: A. Hilger, 1989)
190. Makarov G N, Doctoral Thesis (Physical and Mathematical Sciences) (Troitsk: Institute of Spectroscopy, USSR Academy of Sciences, 1989)
191. Makarov A A, Malinovsky A L, Ryabov E A *Phys. Usp.* **55** 977 (2012); *Usp. Fiz. Nauk* **182** 1047 (2012)
192. Grigor'ev G Yu et al. *Atom. Energy* **104** 398 (2008); *Atom. Energ.* **104** 302 (2008)
193. Budilova O V et al. *Opt. Commun.* **363** 26 (2016)
194. Budilova O V et al. *Opt. Commun.* **345** 163 (2015)
195. Bohn W et al. *Quantum Electron.* **35** 1126 (2005); *Kvantovaya Elektron.* **35** 1126 (2005)
196. Baranov I Y, Koptev A V *Proc. SPIE* **7915** 7915F (2011)
197. Camarcat N et al. *Ann. Nucl. Energy* **129** 399 (2019)
198. Sarkar S K, Parthasarathy V "Molecular laser isotope separation programme at BARC", Report BARC/2007/E/014 (Mumbai: Bhabha Atomic Research Centre, 2007)
199. Sarkar S K et al. *Chem. Phys.* **113** 159 (1987)
200. Sarkar S K *Natl. Acad. Sci. Lett.* **25** 258 (2002)
201. Karve R S et al. *Chem. Phys. Lett.* **78** 273 (1981)
202. Karve R S et al. *Appl. Phys. B* **53** 108 (1991)
203. Sarkar S K *Indian J. Chem. A* **44** 49 (2005)
204. Mathi P et al. *J. Photochem. Photobiol. A* **194** (2–3) 344 (2007)
205. Sarkar S K *J. Indian Chem. Soc.* **87** 195 (2010)
206. Dickinson G J *Nucl. Eng.* **33** (6) 162 (1992)
207. Meyer-Kretschmer G, Schweizer G, in *Proc. of the Intern. Symp. on Isotope Separation and Chemical Exchange Uranium Enrichment, Tokyo, 21 Oct.–1 Nov., 1990* (Eds Y Fujii, T Ishida, K Takeuchi) (Tokyo: Tokyo Institute of Technology, 1992) p. 123
208. Becker F S "Beitrag zur Klärung der Zukunftsaussichten der Laserisotopentrennung beim Uran", Report MPQ-44 (Garching, München: Max-Planck-Institut fur Quantenoptik, 1981)
209. Destro M G et al. "Separating uranium by laser: the atomic process", in *General Congress on Nuclear Energy, Rio de Janeiro, RJ, Brazil, 27 Oct.–1 Nov. 1996*; https://inis.iaea.org/collection/NCLCollectionStore/_Public/31/031/31031705.pdf?r = 1
210. Schwab C et al. *Prog. Nucl. Energy* **33** 217 (1998)
211. Neri J W et al., in *Proc. of the 10th Intern. Workshop on Separation Phenomena in Liquids and Gases, Angra dos Reis, Brazil, Aug. 11–14, 2008* (Ed. N A S Rodrigues) p. 113
212. Rodrigues N A S et al. *J. Phys. B* **33** 3685 (2000)
213. Botha R L et al. *South African J. Sci.* **88** 529 (1992)
214. Ronander E, Rohwer E G *Proc. SPIE* **1810** 49 (1993)
215. Makarov G N et al. *Appl. Phys. B* **65** 583 (1997)
216. Makarov G N, Lokhman V N, Ronander E *Opt. Spectrosc.* **83** 215 (1997); *Opt. Spektrosk.* **83** 232 (1997)
217. "New South African enrichment process", World Nuclear News, 04 September 2008, https://www.world-nuclear-news.org/ENF_New_South_African_enrichment_process_announced_0409081.html
218. Klydon (Pty) Ltd, http://www.klydon.co.za
219. Ronander E, Strydom H J, Botha R L *Prama J. Phys.* **82** 49 (2014)
220. Albright D, Kelleher-Vergantini S "Lashkar Ab'ad: Iran's unexplained laser enrichment capabilities", Institute for Science and International Security, ISIS Imagery Brief, July 29, 2013, https://isis-online.org/uploads/isis-reports/documents/Lashkar_Abad_29July2013.pdf
221. Ferguson C D, Boureston J "Focusing on Iran's Laser Enrichment Program", https://www.iranwatch.org/sites/default/files/perspex-fwi-Laser.pdf
222. Khlopkov A *J. Nonproliferation Rev.* **20** (1) 39 (2013)

223. Ding H-B, Shen Z Y, Zhang C H *Proc. SPIE* **1859** 234 (1993)
224. Xu B et al. "CO laser-induced chemical reaction of UF_6 with HCl and its application to uranium isotope separation", Paper NUCL 68, National Meeting of the American Chem. Soc., Boston, MA, USA, 22–27 Apr. 1990, CONF-900402 (Washington, DC: American Chemical Soc., Division of Nucl. Chem. and Technol., 1990) p. 21; https://inis.iaea.org/search/search.aspx?orig_q = RN:21077879
225. Li Y et al. *Opt. Commun.* **283** 2575 (2010)
226. Eerkens J W et al., in *Conf. on Lasers and Electro-Optics, San Francisco, California, United States, 9–13 June 1986* (OSA Technical Digest) (Washington, DC: Optica Publ. Group, 1986) paper TUI4, https://doi.org/10.1364/CLEO.1986.TUI4
227. Gorwitz M "The South Korean laser isotope separation experience" (2004), https://www.semanticscholar.org/paper/The-South-Korean-Laser-Isotope-Separation-Gorwitz/731585d3bd54cbb5ad9ad70837a0ef50b1c577dc
228. Kim J, Eerkens J W, Miller W H *Nucl. Sci. Eng.* **156** 219 (2007)
229. Takeuchi K et al. *J. Nucl. Sci. Technol.* **23** 282 (1986)
230. Kato S et al. *J. Nucl. Sci. Technol.* **26** 256 (1989)
231. Kato S et al., in *Intern. Symp. Advanced Nuclear Energy Research. Near-Future Chemistry in Nuclear Fuel, Tokyo, 1989*, p. 53
232. Takeuchi K et al. *J. Nucl. Sci. Technol.* **26** 301 (1989)
233. Takami M et al. *Jpn. J. Appl. Phys.* **23** L88 (1984)
234. Kramer G M et al. *Inorg. Chem.* **19** 1340 (1980)
235. Kaldor A et al. *J. Am. Chem. Soc.* **101** 4465 (1979)
236. Cox D M, Horsley J A *J. Chem. Phys.* **72** 864 (1980)
237. Cox D M, Maas E T (Jr.) *Chem. Phys. Lett.* **71** 330 (1980)
238. Ekstrom A et al. *J. Phys. Chem.* **84** 2626 (1980)
239. Miller S S et al. *J. Am. Chem. Soc.* **101** 1036 (1979)
240. Angelie C, Cauchetier M, Paris J *Chem. Phys.* **66** 129 (1982)
241. Chin C et al. *Chem. Phys. Lett.* **101** 69 (1983)
242. Kim K C et al. *J. Chem. Phys.* **78** 32 (1983)
243. Cox D M, Gnauck A *J. Mol. Spectrosc.* **81** 207 (1980)
244. Mahan B H *J. Chem. Phys.* **46** 98 (1967)
245. Tiee J J, Wittig C *Opt. Commun.* **27** 377 (1978)
246. Koren G, Dahan M, Oppenheim U P *Opt. Commun.* **38** 265 (1981)
247. Okada Y, Tashiro H, Takeuchi K *J. Nucl. Sci. Technol.* **30** 762 (1993)
248. Okada Y et al. *Appl. Phys. B* **59** 475 (1994)
249. Rabinowitz P, Stein A, Kaldor A *Opt. Commun.* **27** 381 (1978)
250. Koren G *J. Appl. Phys.* **54** 2827 (1983)
251. Harzer R, Schweizer G, Selter K *J. Mol. Spectrosc.* **132** 310 (1988)
252. Cox D M, Elliott J *Spectrosc. Lett.* **12** 275 (1979)
253. Rabinowitz P et al. *Opt. Lett.* **7** 212 (1982)
254. Rabinowitz P, Kaldar A, Gnauk A *Appl. Phys. B* **28** 187 (1982) in de Martino A et al. "Laser chemical physics II: Infrared multiple photon dissociation" *Appl. Phys. B* **28** 180–189 (1982) https://doi.org/10.1007/BF00697844, 12th Intern. Quantum Electronics Conf.
255. Koren G, Gertner Y, Shreter U *Appl. Phys. Lett.* **41** 397 (1982)
256. Okada Y et al. *Appl. Phys. B* **62** 77 (1996)
257. Makarov G N, Petin A N *Chem. Phys. Lett.* **426** 464 (2006)
258. Makarov G N, Petin A N *Quantum Electron.* **36** 889 (2006); *Kvantovaya Elektron.* **36** 889 (2006)
259. Makarov G N, Petin A N *J. Exp. Theor. Phys.* **103** 697 (2006); *Zh. Eksp. Teor. Fiz.* **130** 804 (2006)
260. Becker E W, Bier K, Burghoff H *Z. Naturforschung A* **10** 565 (1955)
261. Rousseau D, Lepingwell J "Isotope separation by laser based technologies: safeguards related aspects", Paper Number IAEA-CN-184/262
262. Grossman E M "New enrichment technology offers detectable 'signatures' advocate says", Global Security Newswire, 2 August 2010, https://www.nti.org/
263. Lyman J L "Enrichment separative capacity for SILEX", Report LA-UR-05-3786 (Los Alamos, NM: Los Alamos National Laboratory, 2005)
264. Pietropolli Charmet A et al. *Phys. Chem. Chem. Phys.* **8** 2491 (2006)
265. Geraedts J et al. *Chem. Phys. Lett.* **78** 277 (1981)
266. Geraedts J, Stolte S, Reuss J *Z. Phys. A* **304** 167 (1982)
267. Geraedts J et al. *Faraday Discuss. Chem. Soc.* **73** 375 (1982)
268. Rettner C T et al. *J. Phys. Chem.* **100** 13021 (1996)
269. Weaver J F, Carlsson A F, Madix R J *Surf. Sci. Rep.* **50** 107 (2003)
270. Eerkens J W, Isotope Technologies Report IT-88-004 (1988) pp. 3, 8, 24
271. Kim J, Eerkens J W, Miller W H *Nucl. Sci. Eng.* **156** 219 (2007)
272. Makarov G N, Petin A N *Quantum Electron.* **46** 248 (2016); *Kvantovaya Elektron.* **46** 248 (2016)
273. Makarov G N, Petin A N *JETP Lett.* **71** 399 (2000); *Pis'ma Zh. Eksp. Teor. Fiz.* **71** 583 (2000)
274. Makarov G N, Petin A N *Chem. Phys. Lett.* **323** 345 (2000)
275. Makarov G N, Petin A N *J. Exp. Theor. Phys.* **92** 1 (2001); *Zh. Eksp. Teor. Fiz.* **119** 5 (2001)
276. Makarov G N, Petin A N *Chem. Phys.* **266** 125 (2001)
277. Apatin V M et al. *Opt. Spectrosc.* **91** 852 (2001); *Opt. Spektrosk.* **91** 910 (2001)
278. Makarov G N, Mochalov S A, Petin A N *Quantum Electron.* **31** 263 (2001); *Kvantovaya Elektron.* **31** 263 (2001)
279. Fuss W *Spectrochim. Acta A* **38** 829 (1982)
280. Makarov G N, Petin A N *JETP Lett.* **111** 325 (2020); *Pis'ma Zh. Eksp. Teor. Fiz.* **111** 361 (2020)
281. Makarov G N, Petin A N *JETP Lett.* **112** 213 (2020); *Pis'ma Zh. Eksp. Teor. Fiz.* **112** 226 (2020)
282. Makarov G N, Petin A N *Quantum Electron.* **50** 1036 (2020); *Kvantovaya Elektron.* **50** 1036 (2020)
283. Makarov G N, Petin A N *J. Exp. Theor. Phys.* **132** 233 (2021); *Zh. Eksp. Teor. Fiz.* **159** 281 (2021)
284. Snels M, D'Amico G *J. Mol. Spectrosc.* **209** 1 (2001)
285. Landau L D, Lifshitz E M *Fluid Mechanics* (Oxford: Pergamon Press, 1987); Translated from Russian: *Gidrodinamika* (Moscow: Nauka, 1986)
286. Zel'dovich Ya B, Raizer Yu P *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (New York: Academic Press, 1966, 1967); Translated from Russian: *Fizika Udarnykh Voln i Vysokotemperaturnykh Gidrodinamicheskikh Yavlenii* (Moscow: Nauka, 1966)
287. Abramovich G N *Prikladnaya Gazovaya Dinamika* (Applied Gas Dynamics) Pt. 1 (Moscow: Nauka, 1991)
288. Stupochenko Ye V, Losev S A, Osipov A I *Relaxation in Shock Waves* (New York: Springer-Verlag, 1967); Translated from Russian: *Relaksatsionnye Protsessy v Udarnykh Volnakh* (Moscow: Nauka, 1965)
289. Kadibelban R, Ahrens-Botzong R, Hess P *Z. Naturforschung A* **37** 271 (1982)
290. Tosa V et al. *Laser Chem.* **15** 47 (1994)
291. Drouin M et al. *Chem. Phys. Lett.* **60** 16 (1978)
292. King D S, Stephenson J C *Chem. Phys. Lett.* **66** 33 (1979)
293. Narahari Rao K, in *Molecular Spectroscopy: Modern Research* Vol. 3 (Eds K Narahari Rao) (New York: Academic Press, 1985) Ch. 3