New approaches to molecular laser separation of uranium isotopes

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Abstract. Significant interest in the laser separation of uranium isotopes at the turn of the century stimulated the search for and development of a number of methods and approaches that use both atomic and molecular mechanisms of isotope separation. Effective laser methods for the separation of uranium isotopes are currently under active development in many countries. New approaches to the molecular laser isotope separation (MLIS) of uranium are reviewed. They are based on resonant isotope-selective multiphoton excitation of high vibrational states ($2v_3$ and $3v_3$) of $^{235}UF_6$ and $^{238}UF_6$ molecules in gas-dynamically cooled molecular flows by bichromatic IR laser radiation and the subsequent dissociation of the excited molecules by the same laser pulses. The foundations of these approaches are analyzed. The results of experiments on two- and three-photon excitation of SF_6 molecules, whose spectroscopic properties are similar to those of UF_6 molecules, into the $2v_3$ and $3v_3$ vibrational states by, respectively, two- and three-frequency radiation of pulsed CO_2 lasers are presented and discussed. Specific setups and parameters of resonant two- and three-photon isotope-selective excitation of $^{235}UF_6$ and $^{238}UF_6$ molecules into the $2v_3$ and $3v_3$ vibrational states by bichromatic IR radiation from two pulsed CF_4 lasers and two para-H_2 lasers with emissions in the 16-μm region are proposed and analyzed. A method is considered for the isotope-selective excitation and dissociation of UF_6 molecules in a mixture with a sensitizer (SF_6 molecules) under nonequilibrium thermodynamic conditions of a shock wave. Low-energy MLIS methods for uranium based on the proposed approaches are shown to be feasible.

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

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1. Introduction

Almost immediately after lasers were created, one of the most important areas of their application became selective photophysics and photochemistry, including research on laser separation of isotopes of various elements, including uranium isotopes [1–7]. Laser separation of uranium isotopes was studied in two approaches in which the atomic vapor of metallic uranium (Atomic Vapor Laser Isotope Separation; AVLIS method) [7–17] and UF_6 molecular gas (Molecular Laser Isotope Separation; MLIS) [7, 10, 13, 17–25] were used as the starting material.

In the AVLIS method, wavelength-tunable dye lasers pumped by copper vapor lasers were used to excite uranium atoms in experimental studies and in technology for isotope-selective excitation of uranium atoms [2, 8–17]. In the overwhelming majority of experiments, three- or four-frequency atom ionization schemes were used [2, 23].

In exploring the molecular version of the separation of uranium isotopes, quite a few methods based on the selective dissociation of UF_6 molecules were used [2]. The list of the techniques includes the method of isotope-selective dissociation of UF_6 by ultraviolet (UV) laser radiation, the method of two-stage $IR + UV$ dissociation of UF_6, the method of multistage $IR + UV$ dissociation of UF_6, and the methods of two- and three-frequency IR multiphoton dissociation (MPD) of

UF$_6$ molecules. Studies have also been carried out using low-energy methods of isotope-selective suppression of clustering of UF$_6$ molecules and selective dissociation of small UF$_6$ clusters by laser IR radiation (see review [2] and the references therein). The best results were obtained using the method of isotope-selective IR multiphoton dissociation of UF$_6$ molecules [1–7].

Studies on MLIS of uranium by the selective IR multiphoton dissociation of UF$_6$ molecules used a molecular CF$_4$ laser, generating in the 16-μm region, which is optically pumped by the radiation of a powerful CO$_2$ laser [26, 27], and a para-H$_2$ laser [28] operating based on a shift of the CO$_2$ laser frequency to the 16-μm region due to stimulated Raman scattering in para-hydrogen.

In the 1970s and 1980s, some technologically developed countries (USA, Germany, UK, France, Japan, Australia) carried out classified studies on the laser separation of uranium isotopes [8–13, 17–24], exploring both atomic and molecular versions. It was expected that the use of lasers enabling development of a laser-based technology of uranium enrichment would be more economical and efficient than the use of centrifuges.

However, most of the projects on laser separation of uranium isotopes were closed in the late 20th century for a number of reasons [1, 2]. In many cases, this was due to economic factors and the lack of powerful and efficient lasers. It was believed that, at the then stage of development of laser technology, the creation of industrial-scale facilities for laser separation of uranium isotopes was unprofitable [25]. However, some projects [2, 8, 9, 11, 12, 24] have shown that the economic efficiency of laser-based uranium enrichment methods is comparable to that of the most advanced centrifuge techniques. Projects on the laser separation of uranium isotopes were closed primarily due to political and financial reasons as a result of the Megatons to Megawatts Program, the HEU–LEU (highly enriched uranium–low enriched uranium) intergovernmental agreement [29, 30] concluded in 1993 between Russia and the United States, which had been in effect for 20 years (until 2013). According to the agreement, the United States purchased for its nuclear power plants low-enriched uranium produced from weapons-grade uranium in Russia. This resulted in a slowdown in the development of technologies for separating uranium isotopes in the USA. However, in many countries (USA, Australia, Japan, South Korea, India, Iran, China, and South Africa), research on the laser separation of uranium isotopes is ongoing [1, 2, 31–41].

Currently, such research is primarily focused on the development of low-energy MLIS methods for uranium [1, 2, 7, 33, 42–51]. Alternative techniques are also being explored [52–55]. Among the low-energy MLIS methods, the most promising [1, 2, 47, 51] are the isotope-selective suppression of molecular clustering and isotope-selective dissociation of small weakly-bound van der Waals clusters (in particular, dimers). It is probably these processes that underlay SILEX (Separation of Isotopes by Laser EXcitation), a laser uranium enrichment technology currently being developed in the USA and Australia [56–60] (see also reviews [1, 2, 51]).

During the implementation of projects on the laser separation of uranium isotopes, the initial characteristics of the lasers employed were optimized and enhanced. Today, optically pumped molecular CF$_4$ and para-H$_2$ lasers used to excite UF$_6$ molecules can generate radiation pulses with a duration of about 100 ns with a pulse energy of up to 0.5–1.0 J and a spectral lasing linewidth of $\leqslant 0.05$ cm^{-1} [2, 13, 61–64]. In many respects, these lasers meet the requirements for operation in large-scale installations [2, 13, 61–64].

The CF$_4$ laser, which emits radiation in the frequency range of 612–650 cm^{-1} [61, 62, 65–67], has more than a hundred lasing lines [65, 66]. The para-H$_2$ laser operates based on stimulated Raman scattering of radiation from a powerful CO$_2$ laser on rotational transitions of molecular hydrogen. Under such inelastic scattering, the CO$_2$ laser radiation frequency decreases by the amount of the rotational quantum of the H$_2$ molecule (≈ 354.33 cm^{-1}) and falls into the 16-μm range [28]. Tuning the CO$_2$ laser radiation frequency automatically leads to tuning the para-H$_2$ laser radiation frequency.

Significant disadvantages of both the CF$_4$ laser and the para-H$_2$ laser in what regards the separation of uranium isotopes are the discrete tuning of the emission frequency of these lasers and the absence of strong and tunable lasing lines in the region of the Q-branch of v_3 vibrations of ^{235}UF$_6$ molecules (in the 628.32-cm^{-1} region [68, 69]). Therefore, the CF$_4$ laser is not suitable for implementing isotope-selective dissociation of UF$_6$ molecules, although in some studies it was used in experiments on two-frequency excitation and dissociation of UF$_6$ [2, 70]. Uranium isotopes have been separated with a relatively high selectivity of the process ($\alpha \geqslant 4$) in [71, 72] by IR MPD of UF$_6$ molecules using two [71] and three [72] para-H$_2$ lasers. At the first stage, isotope-selective excitation of ^{235}UF$_6$ molecules was carried out by a laser with a continuously tunable radiation frequency, while their further excitation and dissociation was implemented using lasers with a fixed generation frequency. It should be noted that the use of para-H$_2$ lasers with a continuously variable radiation frequency significantly complicates the technical implementation of this method in practice.

Considered as an alternative to MLIS of uranium is isotope-selective excitation of the $3v_3$ state of ^{235}UF$_6$ molecules (≈ 1877.5 cm^{-1} [73, 74]), in which the isotopic shift is about 1.81 cm^{-1} [68, 69], by CO laser radiation [37–40, 75, 76]. This approach uses a chemical reaction of vibrationally excited UF$_6$ molecules with HCl molecules [37–40]. Uranium isotopes are separated due to the difference between the rates of reaction of vibrationally excited and unexcited UF$_6$ molecules and HCl molecules. In [38], this method was applied to separate uranium isotopes with selectivity $\alpha = 1.2$. For this approach, high-power CO lasers are being developed [75, 76], generating in the 5.3-μm region, which will be used to excite ^{235}UF$_6$ molecules. However, effective excitation of the $3v_3$ states of UF$_6$ molecules by IR radiation with a wavelength of ≈ 5.33 μm is problematic due to the weak absorption of UF$_6$ molecules at the vibrational transition $0v_3 \rightarrow 3v_3$. The integral absorption of the overtone band $0v_3 \rightarrow 3v_3$ of UF$_6$ molecules ($\Gamma_{0\rightarrow3} = 3.8 \times 10^{-2}$ km mol^{-1}) is more than four orders of magnitude (about 1.8×10^4 times) less than the integral absorption of the main band $0v_3 \rightarrow 1v_3$ of UF$_6$ ($\Gamma_{0\rightarrow1} \approx 6.7 \times 10^2$ km mol^{-1}) [73].

Therefore, the search for alternative schemes for isotope-selective excitation of high vibrational states of ^{235}UF$_6$ molecules is very urgent. An alternative may be provided by methods based on resonant multiphoton excitation of high vibrational states of ^{235}UF$_6$ and ^{238}UF$_6$ molecules by multi-frequency IR laser radiation [77]. It should be noted that resonant multiphoton excitation of high vibrational states of molecules by two- or three-frequency IR radiation is also of

great interest in research on the development and creation of optically pumped molecular lasers [61, 64, 78].

The excitation of UF_6 molecules into high vibrational states $2v_3$ and $3v_3$ can be used to separate uranium isotopes using low-energy methods, which are based on processes with an activation energy not exceeding 0.1–0.2 eV [1, 2, 50, 51]. Such activation energies are typical of adsorption and desorption of molecules on the surface, including processes on the surface of clusters and for dissociation and fragmentation of weakly-bound van der Waals molecules (for example, the dissociation energy of $UF_6 - Ar \leqslant 0.1$ eV [1, 2, 79, 80]).

The review is organized as follows. Section 2 provides a brief description of the method of resonant multiphoton excitation of high vibrational states of molecules by multi-frequency IR laser radiation. Section 3 presents and discusses in detail the results of early studies on the resonant multi-photon excitation of SF_6 molecules into vibrational states $2v_3$ and $3v_3$ by, respectively, two- and three-frequency radiation from pulsed CO_2 lasers. Section 4 presents and analyzes specific techniques and parameters of resonant two- and three-photon isotope-selective excitation of $^{235}UF_6$ and $^{238}UF_6$ molecules into vibrational states $2v_3$ and $3v_3$ by bichromatic IR radiation from two pulsed CF_4 lasers and two para-H_2 lasers generating in the 16-μm region. Section 5 contains a brief discussion of the proposed approaches in terms of realizing the optimal selectivity of dissociation of UF_6 molecules. Section 6 is devoted to selective excitation of $^{235}UF_6$ and $^{238}UF_6$ molecules into vibrational states $2v_3$ and $3v_3$ and their dissociation from these states under none-quilibrium thermodynamic conditions of a shock wave using a sensitizer, SF_6 molecules, to enhance the efficiency of the processes. Concluding Section 7 presents the main results of the work and the conclusions drawn from them.

2. Basics of the method of resonant multifrequency excitation of high vibrational states of molecules

Multiphoton excitation of high vibrational states of molecules can be realized by the coherent action on the molecules of more than one laser field, whose summed frequency satisfies the condition of multiphoton resonance [77]. For example, resonant excitation of the vibrational states $2v_3$ and $3v_3$ of UF_6 molecules by radiation from two pulsed IR lasers requires the following relationships to be satisfied between the frequencies v_{L1} and v_{L2} of the radiation of the lasers used and the frequency v_3 of the excited vibration of UF_6 molecules:

$$v_{L1} + v_{L2} = 2v_3 \,, \tag{1}$$

$$2v_{L1} + v_{L2} = 3v_3 \,, \tag{2a}$$

$$v_{L1} + 2v_{L2} = 3v_3 \,. \tag{2b}$$

In relation (2a), it is assumed that the $3v_3$ UF_6 state is excited upon absorption of two photons from the field of one laser pulse (for example, with a frequency lower than the frequency of v_3 vibration of the UF_6 molecule) and one photon from the field of another laser pulse (whose frequency is higher than that of v_3 vibration of the molecule). In relation (2b), it is assumed that the $3v_3$ UF_6 state is excited upon absorption of one photon from the field of a low-frequency laser pulse and two photons from the field of a laser pulse whose frequency is higher than that of v_3 vibration of the UF_6 molecule.

Using two or three lasers with different radiation frequencies, it is relatively easy to provide resonant conditions for the excitation of high vibrational levels of molecules. This is especially easy to implement if high-pressure lasers with continuous tuning of the radiation frequency are used. A necessary condition for conducting such experiments is accurate knowledge of the frequencies (energies) of high vibrational levels of the molecules under study. For SF_6 [81] and UF_6 [74] molecules, such data were obtained at the Los Alamos National Laboratory in projects on molecular laser separation of uranium isotopes.

3. Resonant multiphoton excitation of $2v_3$ and $3v_3$ vibrational states of SF_6 molecules by multifrequency radiation from pulsed CO_2 lasers

In [82, 83], SF_6 was used as an example to show that the high vibrational states of molecules can be effectively populated as a result of their multiphoton excitation using two [82] or three [83] laser pulses with different frequencies, the total frequency of which is equal to that of the transition of molecules from the ground vibrational state to the excited high-lying state. In [82], the resonant population of the $2v_3$ A_1 state (≈ 1889.0 cm^{-1} [81]) of SF_6 was attained when the molecules were simulta-neously exposed to two laser fields symmetrically detuned from resonance (Fig. 1a). The SF_6 molecules cooled in a pulsed gas-dynamic jet (in an SF_6/H_2 mixture at a pressure ratio of 1/20) were excited by radiation from a continuously tunable high-pressure CO_2 laser and a TEA CO_2 laser tunable over the generation lines with frequencies, respectively, v_{L1} and v_{L2}. The frequency of the Q-branch of the absorption band of the v_3 vibration of $^{32}SF_6$ is ≈ 948.1 cm^{-1} [81]. The emission frequency v_{L1} of the continuously tunable CO_2 laser varied in the range of 936–952 cm^{-1}. The laser, discretely tunable in frequency, was tuned in the low-frequency region of the linear absorption band of the v_3 vibration of SF_6 molecules to either the 10P(26) (frequency $v_{L2} = 939.69$ cm^{-1}) or 10P(28) ($v_{L2} = 936.80$ cm^{-1}) emission line.

Resonant excitation of the $2v_3$ A_1 state (≈ 1889.0 cm^{-1}) of SF_6 molecules occurred when the condition $v_{L1} + v_{L2} = 1889.0$ cm^{-1} was fulfilled. The molecules disso-ciated at frequency $v_{L3} = 929.02$ cm^{-1} (10P(36) laser line). The SF_6 dissociation yield was measured by the intensity of IR luminescence (Fig. 1b) of vibrationally excited HF* molecules formed in the reaction of fluorine atoms (the SF_6 dissociation product) with hydrogen molecules. It was shown in [82] that this scheme can be used to excite, via the $2v_3$ A_1 state at relatively moderate laser radiation energy densities ($\approx 0.2-0.3$ J cm^{-2}), about 30% of SF_6 molecules from the ground state. It was found in [82] (see also Fig. 1b) that the spectral widths of the observed bands of resonant two-photon excitation of SF_6 molecules by bichromatic radiation from two pulsed CO_2 lasers are relatively small ($\leqslant 0.1$ cm^{-1}). They are significantly smaller than the isotopic shift in the IR absorption spectra of the v_3 vibrations of SF_6 molecules ($\Delta_{is} \approx 17$ cm^{-1} $^{32}SF_6$ and $^{34}SF_6$ [1, 2] for molecules) and are approximately comparable to the widths of Q-branches in the absorption spectra of SF_6 and UF_6 molecules vibrationally cooled in a gas-dynamic jet ($\leqslant 0.2-0.3$ cm^{-1} [22]). Conse-quently, this technique can be used for isotope-selective dissociation of molecules.
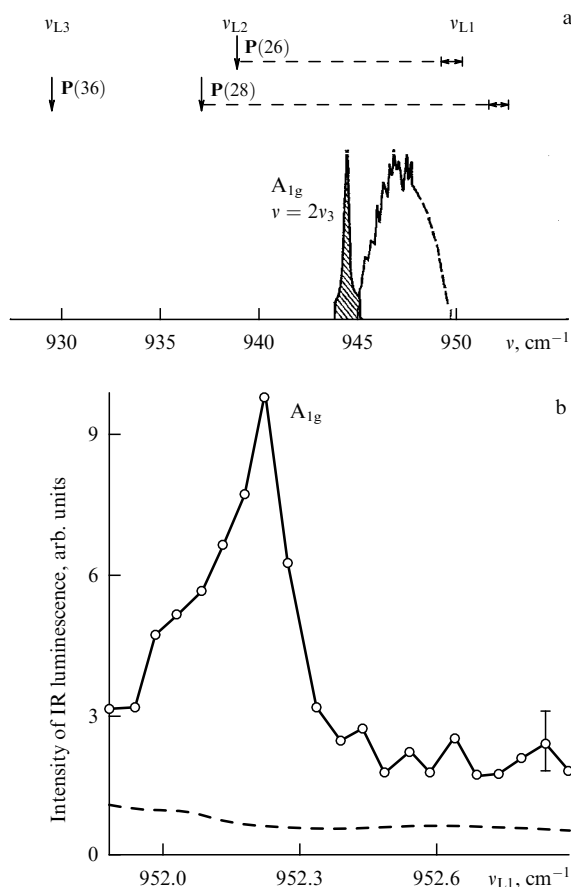
Figure 1. (a) Radiation frequencies of CO_2 lasers for bichromatic excitation of SF_6 molecules into the $2v_3$ A_1 state (≈ 1889.0 cm^{-1}) and their subsequent dissociation by a third laser pulse [82]. Displayed below is the spectrum of multiphoton excitation of SF_6 molecules in a gas-dynamically cooled molecular flow obtained in [84] using a high-pressure CO_2 laser with continuous frequency tuning. Peak of two-photon excitation of molecules by monochromatic radiation into the $2v_3$ A_1 state is shaded. (b) Spectral dependence of the IR luminescence intensity upon bichromatic excitation of SF_6 for $v_{L1} = 951.7 - 952.8$ cm^{-1}, $v_{L2} = 936.8$ cm^{-1} (line 10P(28)); dotted line is the 'background' signal in the absence of a field at frequency v_{L2} [82].
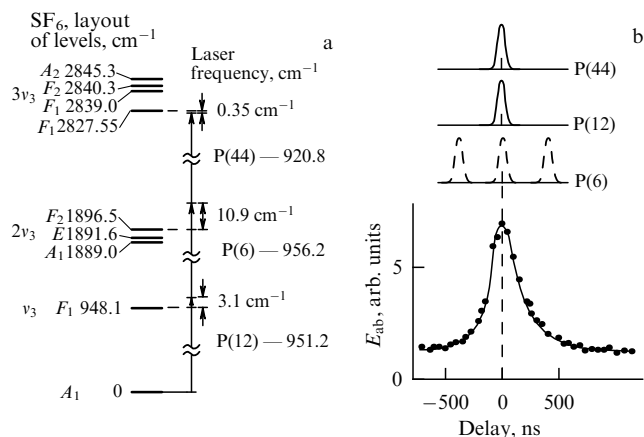

Figure 2. (a) Three-frequency excitation of the $3v_3$ F_1 state (2827.55 cm^{-1}) of SF_6 molecules in a gas-dynamically cooled molecular flow [83]. (b) Dependence of the energy absorbed by SF_6 molecules on the time of delay between two pre-synchronized CO_2 laser pulses (P(12) + P(44)) and a third pulse (P(6)) at an energy density on the P(6), P(12), and P(44) lines equal to 0.6, 0.2, and 0.5 J cm^{-2}, respectively [83].

By the same token, in [82], resonant excitation of high vibrational states of the v_3 mode of OsO_4 molecules was carried out. Studying the multiphoton excitation spectrum of OsO_4 using this technique made it possible to identify resonances located near the Q-branch of the main transition of the molecule (≈ 961 cm^{-1} [85, 86]). This range is inaccessible for monochromatic excitation, since it falls into the gap between the P and R branches of CO_2 laser generation.

In [83], effective resonant excitation of the $3v_3$ F_1 state (≈ 2827.55 cm^{-1} [81]) of SF_6 molecules cooled in a pulsed gas-dynamic jet was realized using radiation pulses from three discretely frequency-tunable CO_2 lasers (Fig. 2a). The vibrational, rotational, and translational temperatures of the molecules in the jet were $T_{vib} \leqslant 150$ K and $T_{rot} \approx T_{tr} \leqslant 20$ K, respectively [87]. The IR absorption band width of the v_3 vibration of SF_6 under such cooling is less than 3.5 cm^{-1} at half maximum [68]. The lasers used to excite the molecules operated at frequencies $v_{L1} = 951.19$ cm^{-1} (10P(12) line), $v_{L2} = 956.18$ cm^{-1} (10P(6) line), and $v_{L3} = 920.83$ cm^{-1} (10R(44) line). The detuning of these laser

generation frequencies from the frequency of the Q-branch of the $0v_3 \rightarrow 1v_3$ transition of SF_6 molecules ranged from 3.1 to 27.2 cm^{-1}.

It is noteworthy that none of the laser emission frequencies used to excite SF_6 molecules, either individually or in pairs, was in resonance with low-lying vibrational transitions of the molecule. However, the total frequency of laser radiation with fairly good accuracy (deviation of less than 0.35 cm^{-1}) was equal to the frequency of the $0v_3 \rightarrow 3v_3$ F_1 transition (≈ 2827.55 cm^{-1} [81]) ($v_{L1} + v_{L2} + v_{L3} = 2827.20$ cm^{-1} [83]). The effect of resonant population of the $3v_3$ F_1 state of SF_6 molecules was detected by measuring the energy absorbed by the molecules under conditions of separate and simultaneous exposure of the molecules to all three pulses (Fig. 2b). It was found in [83] that, when all three laser pulses coincide in time, effective excitation of SF_6 molecules occurs via the vibrational $3v_3$ F_1 state. The molecules were also excited to higher vibrational states. It has been shown that, in the case of three-photon excitation of SF_6, a more contrasting population of the excited $3v_3$ state is achieved than in the case of two-photon excitation of the $2v_3$ state. This conclusion can be made from a comparison of the ratios (contrasts) of the magnitudes of resonant signals to the magnitudes of background signals (see Figs 2b and 1b), which are associated with the excitation of molecules into nonresonant states. This results in a higher selectivity of the process of dissociation of molecules in the former case [4, 88, 89]. It was also found in [83, 89] that the method described makes it possible to populate high vibrational states of SF_6 molecules much more efficiently than methods of single-frequency and sequential two- or three-frequency excitation.

4. Techniques and parameters of resonant isotope-selective two- and three-photon excitation of $2v_3$ and $3v_3$ states of $^{235}UF_6$ and $^{238}UF_6$ molecules by laser IR radiation

4.1 Background information
In implementing projects on molecular laser separation of uranium isotopes, vast and valuable spectroscopic infor-

mation was obtained about both the UF_6 molecule itself and the lasers used to excite and dissociate UF_6 molecules [20–28, 61–68] (see also review [2] and references therein). The results obtained make it possible to predict patterns of resonant multiphoton excitation of high vibrational states of UF_6 molecules by radiation from more than one IR laser. Proposed in [90–92] were specific techniques and parameters of isotope-selective two-photon [90, 92] and three-photon [91, 92] bichromatic excitation of the $2v_3$ and $3v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ molecules by radiation from two CF_4 lasers and two para-H_2 lasers.

In choosing schemes for the excitation of UF_6 molecules and analyzing data on laser generation frequencies, the magnitude of the isotopic shift in the IR absorption spectra of v_3 vibration of UF_6 molecules was taken into account, which is $\Delta_{is} \approx 0.604$ cm^{-1} [68, 69] in the $1v_3$ state for $^{238}UF_6$ and $^{235}UF_6$ molecules. In selecting the optimal frequencies for the excitation of molecules, only the most intense generation lines of both CF_4 lasers [65, 66] and CO_2 lasers used to pump para-H_2 lasers were considered. The most intense generation line of a CF_4 laser is that at the frequency of ≈ 615.1 cm^{-1} [65, 66], which is emitted when CF_4 molecules are pumped at the 9R(12) line of a CO_2 laser (frequency 1073.28 cm^{-1}). The emission lines of the CF_4 laser at frequencies of ≈ 612.2 cm^{-1}, ≈ 618.2 cm^{-1}, ≈ 631.4 cm^{-1}, ≈ 642.4 cm^{-1}, ≈ 643.1 cm^{-1}, and ≈ 645.1 cm^{-1} are also fairly intense [65, 66]. In choosing the frequencies for multiphoton excitation of UF_6 molecules, it is these CF_4 laser emission lines that were primarily taken into account.

It should be noted that the frequencies of many CF_4 laser emission lines were determined with an error of no less than 0.1 cm^{-1} [65, 66]. The energies (frequencies) of excited vibrational states up to the states of $8v_3$ molecules of $^{238}UF_6$ were determined with a much smaller error (≈ 0.01 cm^{-1}) [74]. The energies of the excited vibrational states of $^{235}UF_6$ molecules were established taking into account the isotopic shift $\Delta_{is} \approx 0.604$ cm^{-1} [68, 69] in the v_3 vibration for molecules $^{238}UF_6$ and $^{235}UF_6$, $\Delta_{is} \approx 1.21$ cm^{-1} in the $2v_3$ state, and $\Delta_{is} \approx 1.81$ cm^{-1} in the $3v_3$ state of UF_6. The schemes proposed for the excitation of the $2v_3$ and $3v_3$ states of UF_6 molecules do not need additional adjustment of the laser frequency for resonant excitation of molecules, since the detuning of the total laser radiation frequencies from the frequencies of the excited states is insignificant (see Figs 3a and 4a and Tables 1–4 below).
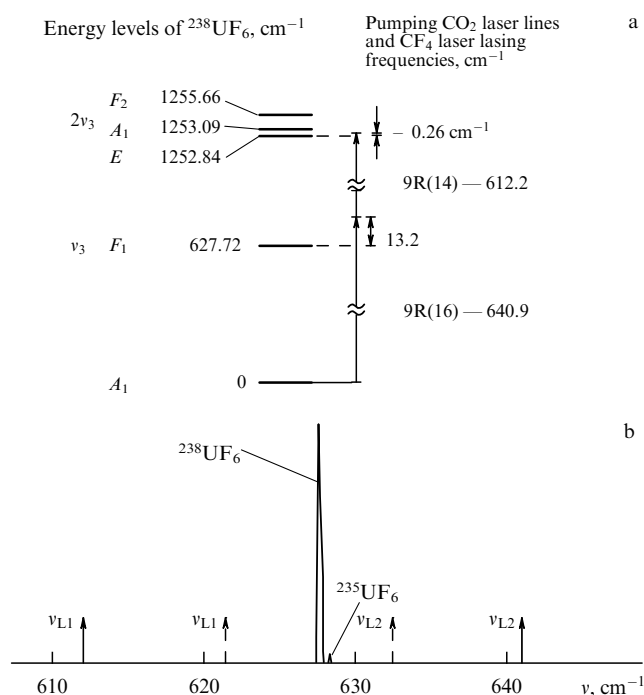
Figure 3. (a) Resonant two-photon bichromatic excitation of $^{238}UF_6$ molecules into the $2v_3$ E state (≈ 1252.84 cm^{-1}) by radiation from two CF_4 lasers. Shown on the right are lines of the CO_2 laser and lasing frequencies of the CF_4 laser [90]. Energy levels of the v_3 mode of $^{238}UF_6$ molecules were taken from [74]. (b) Emission line frequencies of two CF_4 lasers (solid arrows) and two para-H_2 lasers (dashed arrows) used for resonant two-photon bichromatic excitation of $^{238}UF_6$ molecules into the $2v_3$ E state (≈ 1252.84 cm^{-1}) (Table 1, line 1) and $^{235}UF_6$ molecules into the $2v_3$ E state (≈ 1254.05 cm^{-1}) (Table 2, line 4), and Q-branches of linear absorption bands of the v_3 vibration of $^{238}UF_6$ and $^{235}UF_6$ molecules in a gas-dynamically cooled molecular flow at $T \leqslant 50$ K [90]. (Q-branches are shown qualitatively [22].)

4.2 Resonant two-photon excitation of $2v_3$ states of $^{238}UF_6$ and $^{235}UF_6$ molecules

Using two IR lasers, it is possible [90, 92] to perform isotope-selective excitation of the $2v_3$ vibrational states of UF_6 molecules (≈ 1253 cm^{-1} [74]). Figure 3a shows a diagram of the excitation of the vibrational state $2v_3$ E of $^{238}UF_6$ molecules (≈ 1252.84 cm^{-1} [74]) by radiation from two CF_4 lasers operating at frequencies $v_{L1} \approx 612.2$ cm^{-1} and $v_{L2} \approx 640.9$ cm^{-1}, respectively. Two-photon bichromatic excitation of the $2v_3$ E level is realized with a detuning in the

Table 1. Resonant two-photon bichromatic excitation of $2v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two CF_4 lasers [90].

Molecule	Excited state and its frequency, cm^{-1}	Frequency of CF_4 laser 1 v_{L1}, cm^{-1}	Line and frequency of CO_2 pumping laser 1, cm^{-1}	Frequency of CF_4 laser 2 v_{L2}, cm^{-1}	Line and frequency of CO_2 pumping laser 2, cm^{-1}	Final state frequency detuning, $\Delta v_{fin} = 2v_3 - (v_{L1} + v_{L2})$, cm^{-1}
$^{238}UF_6$	$2v_3$ E (1252.84)	612.2	9R(14), 1074.65	640.9	9R(16), 1075.99	-0.26
$^{238}UF_6$	$2v_3$ A_1 (1253.09)	612.2	9R(14), 1074.65	640.9	9R(16), 1075.99	-0.01
$^{238}UF_6$	$2v_3$ F_2 (1255.66)	612.2	9R(14), 1074.65	643.1	9R(20), 1078.59	$+0.36$
$^{235}UF_6$	$2v_3$ E (1254.05)	612.2	9R(14), 1074.65	641.9	9R(18), 1077.30	-0.05
$^{235}UF_6$	$2v_3$ A_1 (1254.30)	612.2	9R(14), 1074.65	642.4	9P(4), 1060.57	-0.30
$^{235}UF_6$	$2v_3$ F_2 (1256.87)	615.1	9R(12), 1073.28	641.9	9R(18), 1077.30	-0.13

Figure 4. (a) Resonant three-photon bichromatic excitation of $^{238}UF_6$ molecules into the $3v_3$ F_1 state (≈ 1875.6 cm^{-1}) by radiation from two CF$_4$ lasers [91]. Energy levels of the v_3 mode of $^{238}UF_6$ molecules were taken from [74]. (b) Emission line frequencies of two CF$_4$ lasers (solid arrows) and two para-H$_2$ lasers (dashed arrows) used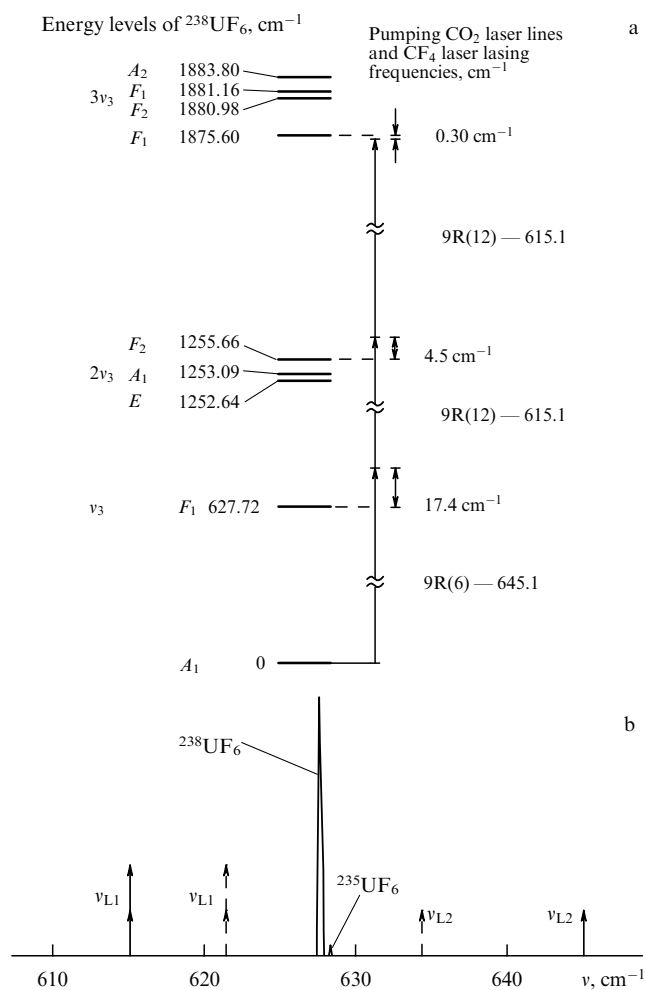 for resonant three-photon bichromatic excitation of $^{238}UF_6$ molecules into the $3v_3$ F_1 state (≈ 1875.6 cm^{-1}) (Table 3, line 1) and $^{235}UF_6$ molecules into the $3v_3$ F_1 state (≈ 1877.4 cm^{-1}) (Table 4, line 4), and Q-branches of linear absorption bands of the v_3 vibration of $^{238}UF_6$ molecules and $^{235}UF_6$ in a gas-dynamically cooled molecular flow at $T \leqslant 50$ K [91]. (Q-branches are shown qualitatively [22].)

final state $\Delta v_{\text{fin}} \approx -0.26$ cm^{-1} ($v_{\text{L1}} + v_{\text{L2}} = 1253.1$ cm^{-1}). For this example, shown in Fig. 3b (solid arrows) are the frequencies of the generation lines of CF$_4$ lasers and the Q-branch of absorption bands at the fundamental frequencies of the v_3 vibration of $^{238}UF_6$ and $^{235}UF_6$ molecules in a gas-dynamic cooled molecular flow. The widths of the P- and R-branches (not shown in Fig. 3b) of the IR absorption spectrum of v_3 vibrations of UF$_6$ molecules at $T \leqslant 50$ K do not exceed 2 cm^{-1} [68].

Table 1 shows parameters of the proposed schemes for resonant two-photon bichromatic excitation of the $2v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ by IR radiation from two CF$_4$ lasers. The energy levels of the $2v_3$ states of $^{235}UF_6$ were determined by shifting the $2v_3$ levels of $^{238}UF_6$ to higher frequencies by the value of the isotopic shift in the $2v_3$ state for these molecules, which is ≈ 1.21 cm^{-1}.

Table 2 shows the parameters of techniques for resonant two-photon bichromatic excitation of the $2v_3$ vibrational

states of $^{238}UF_6$ and $^{235}UF_6$ by IR radiation from two para-H$_2$ lasers. The frequencies of the generation lines of para-H$_2$ lasers for the excitation of the $2v_3$ E $^{235}UF_6$ state (≈ 1254.05 cm^{-1}) (see Table 2, line 4) are marked in Fig. 3b with dashed arrows. Tables 1 and 2 show that, if both types of lasers are used, resonant excitation of the $2v_3$ states of $^{238}UF_6$ and $^{235}UF_6$ can be realized with a small frequency detuning in the final state, which facilitates achieving high selectivity of the excitation process of UF$_6$ molecules.

It should be noted that, for some schemes for the excitation of $2v_3$ states of UF$_6$, a resonant population of $4v_3$ states of UF$_6$ by the same laser pulses can also occur. For example, in the scheme shown in Table 1, line 1, the resonant excitation of $^{238}UF_6$ molecules into the $4v_3$ E state (≈ 2506.60 cm^{-1}) is realized with a frequency detuning in the final state of $+0.4$ cm^{-1}. For the scheme shown in Table 1, line 5, $^{235}UF_6$ molecules can be excited into the $4v_3$ A_1 state (≈ 2509.29 cm^{-1}) and into the $4v_3$ E state (≈ 2509.02 cm^{-1}) with a frequency detuning in the final state of $+0.09$ cm^{-1} and -0.18 cm^{-1}, respectively. The feasibility of this option is a positive factor, since in this case a much more efficient excitation of molecules into high vibrational states occurs [88, 89].

4.3 Resonant three-photon excitation of $3v_3$ states of $^{238}UF_6$ and $^{235}UF_6$ molecules

Bichromatic radiation from two IR lasers can also effectively excite the $3v_3$ vibrational states of UF$_6$ molecules. In [91, 92], an analysis was carried out and specific approaches were proposed for the isotope-selective three-photon population of the overtone vibrational states $3v_3$ F_1, $3v_3$ F_2, and $3v_3$ A_2 of $^{238}UF_6$ and $^{235}UF_6$ molecules by radiation from two CF$_4$ lasers and two para-H$_2$ lasers. We now consider the main results of these studies. Figure 4a shows a method of population of the vibrational $3v_3$ F_1 state of $^{238}UF_6$ molecules (≈ 1875.6 cm^{-1} [74]) by radiation from two CF$_4$ lasers operating at frequencies $v_{\text{L1}} \approx 615.1$ cm^{-1} and $v_{\text{L2}} \approx 645.1$ cm^{-1}, respectively. Three-photon bichromatic excitation of this $3v_3$ F_1 level is realized with detuning in the final state $\Delta v_{\text{fin}} \approx +0.3$ cm^{-1} ($2v_{\text{L1}} + v_{\text{L2}} = 1875.3$ cm^{-1}). For this example, Figure 4b shows the frequencies of the emission lines of CF$_4$ lasers and the Q-branch of the linear absorption bands at the fundamental frequencies of the v_3 vibration of $^{238}UF_6$ and $^{235}UF_6$ molecules [91]. The generation frequencies of para-H$_2$ lasers for one of the excitation schemes (see below) are marked with dashed arrows.

It should be noted that the indicated laser frequencies, whether individually or in pairs, are not in resonance with low-lying transitions of UF$_6$ molecules [74]. Under conditions of low vibrational and low rotational temperatures of molecules in a gas-dynamically cooled flow, this implies that molecules can be primarily excited into high vibrational states only through a resonant channel, i.e., via the $3v_3$ F_1 state. Further excitation and dissociation of excited molecules is possible due to the high density of vibrational states of $^{238}UF_6$ molecules, primarily due to the absorption of photons from the laser, which has a lower frequency $v_{\text{L1}} \approx 615.1$ cm^{-1}, since it is in better resonance with high-lying vibrational transitions of the molecule. It is noteworthy that, in this particular example, the combination of laser frequencies used to excite the $3v_3$ F_1 state of $^{238}UF_6$ is also suitable for further resonant excitation of molecules from the $3v_3$ F_1 vibrational state to the $6v_3$ A_1 state

Table 2. Resonant two-photon bichromatic excitation of $2v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two para-H_2 lasers [90]. Under stimulated Raman scattering at the rotational levels of para-hydrogen molecules, the CO_2 lasing frequency decreases by 354.33 cm^{-1} [28].

Molecule	Excited state and its frequency, cm^{-1}	Frequency of para-H_2 laser 1 v_{L1}, cm^{-1}	Line and frequency of CO_2 pumping laser 1, cm^{-1}	Frequency of para-H_2 laser 2 v_{L2}, cm^{-1}	Line and frequency of CO_2 pumping laser 2, cm^{-1}	Final state frequency detuning, $\Delta v_{fin} = 2v_3 - (v_{L1} + v_{L2})$, cm^{-1}
$^{238}UF_6$	$2v_3\ E$ (1252.84)	621.63	10R(20), 975.93	631.19	10R(36), 985.49	+0.02
$^{238}UF_6$	$2v_3\ A_1$ (1253.09)	622.91	10R(22), 977.21	630.08	10R(34), 984.38	+0.10
$^{238}UF_6$	$2v_3\ F_2$ (1255.66)	620.32	10R(18), 974.62	635.35	10R(44), 989.65	−0.01
$^{235}UF_6$	$2v_3\ E$ (1254.05)	621.63	10R(20), 975.93	632.27	10R(38), 986.57	+0.15
$^{235}UF_6$	$2v_3\ E$ (1254.05)	622.91	10R(22), 977.21	631.19	10R(36), 985.49	−0.05
$^{235}UF_6$	$2v_3\ A_1$ (1254.30)	618.96	10R(16), 973.29	635.35	10R(44), 989.65	−0.01
$^{235}UF_6$	$2v_3\ A_1$ (1254.30)	624.17	10R(24), 978.47	630.08	10R(34), 984.38	+0.05
$^{235}UF_6$	$2v_3\ F_2$ (1256.87)	621.63	10R(20), 975.93	635.35	10R(44), 989.65	−0.11

Table 3. Resonant three-photon bichromatic excitation of $3v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two CF$_4$ lasers [91].

Molecule	Excited state and its frequency, cm^{-1}	Frequency of CF$_4$ laser 1 v_{L1}, cm^{-1}	Line and frequency of CO_2 pumping laser 1, cm^{-1}	Frequency of CF$_4$ laser 2 v_{L2}, cm^{-1}	Line and frequency of CO_2 pumping laser 2, cm^{-1}	Final state frequency detuning, $\Delta v_{fin} = 3v_3 - (2v_{L1} + v_{L2})$, cm^{-1}
$^{238}UF_6$	$3v_3\ F_1$ (1875.60)	615.1	9R(12), 1073.28	645.1	9R(6), 1058.95	+0.30
$^{238}UF_6$	$3v_3\ F_2$ (1880.98)	631.4	9R(22), 1079.85	618.2	9R(10), 1071.90	−0.02
$^{238}UF_6$	$3v_3\ F_1$ (1881.16)	618.2	9R(10), 1071.90	645.1	9P(6), 1058.96	−0.34
$^{235}UF_6$	$3v_3\ F_1$ (1877.41)	618.2	9R(10), 1071.90	640.9	9R(16), 1075.99	+0.11
$^{235}UF_6$	$3v_3\ F_1$ (1877.41)	631.4	9R(22), 1079.85	615.1	9R(12), 1073.28	−0.49
$^{235}UF_6$	$3v_3\ F_2$ (1882.78)	615.1	9R(12), 1073.28	652.2	9P(10), 1055.63	+0.38

Table 4. Resonant three-photon bichromatic excitation of $3v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two para-H_2 lasers [91].

Molecule	Excited state and its frequency, cm^{-1}	Frequency of para-H_2 laser 1 v_{L1}, cm^{-1}	Line and frequency of CO_2 pumping laser 1, cm^{-1}	Frequency of para-H_2 laser 2 v_{L2}, cm^{-1}	Line and frequency of CO_2 pumping laser 2, cm^{-1}	Final state frequency detuning, $\Delta v_{fin} = 3v_3 - (2v_{L1} + v_{L2})$, cm^{-1}
$^{238}UF_6$	$3v_3\ F_1$ (1875.60)	621.60	10R(20), 975.93	632.24	10R(38), 986.57	+0.16
$^{238}UF_6$	$3v_3\ F_2$ (1880.98)	622.88	10R(22), 977.21	635.32	10R(44), 989.65	−0.10
$^{238}UF_6$	$3v_3\ F_1$ (1881.16)	622.88	10R(22), 977.21	635.32	10R(44), 989.65	+0.08
$^{235}UF_6$	$3v_3\ F_1$ (1877.41)	621.60	10R(20), 975.93	634.32	10R(42), 988.65	−0.11
$^{235}UF_6$	$3v_3\ F_2$ (1882.79)	631.16	10R(36), 985.49	620.29	10R(18), 974.62	+0.18
$^{235}UF_6$	$3v_3\ A_2$ (1885.61)	626.58	10R(28), 980.91	632.24	10R(38), 986.57	+0.21

(≈ 3750.92 cm^{-1} [74]), also with a frequency detuning of only about +0.3 cm^{-1}.

Table 3 shows parameters of the proposed schemes for a resonant three-photon bichromatic population of the $3v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ by IR radiation from two CF$_4$ lasers. The first row of the table shows the excitation scheme for the $3v_3$ F_1 state considered above. The energy levels of the $3v_3$ states of $^{235}UF_6$ were determined by the shift of the $3v_3$ levels of $^{238}UF_6$ to the higher frequencies side by the isotopic shift for these molecules in the $3v_3$ state, ≈ 1.81 cm^{-1}.

Table 4 shows parameters of techniques for the resonant three-photon bichromatic population of the $3v_3$ vibrational states of $^{238}UF_6$ and $^{235}UF_6$ by IR radiation from two para-H_2 lasers. The frequencies of the lasing lines of para-H_2 lasers for the excitation scheme of the $3v_3$ F_1 state of $^{235}UF_6$ displayed in Table 4, line 4 are shown in Fig. 4b with dashed arrows. It should be noted that the techniques to pump para-H_2 lasers presented in Table 4, lines 2–4 use the 10R(42) and 10R(44) radiation lines of CO_2 lasers, which are located relatively far from the maximum of the 10R-branch lasing band. The energies of radiation of CO_2 lasers on these lines are low. In the techniques presented in Table 4, lines 1, 5, and 6, fairly intense lasing lines of CO_2 lasers are used, which also makes it possible to obtain intense generation of para-H_2 lasers.

5. Discussion of techniques for isotope-selective population of $2v_3$ and $3v_3$ states of $^{235}UF_6$ and $^{238}UF_6$ molecules

We now analyze the proposed techniques for bichromatic excitation of UF_6 molecules in the context of enhancing selectivity and dissociation yield. It should be noted that, for optimal isotope-selective excitation of the $2v_3$ and $3v_3$ states of $^{238}UF_6$, it is necessary to ensure either the most accurate resonance during excitation or excitation with a small positive detuning of the total lasing frequency from the frequency of the excited state. For example, with three-photon excitation, it is necessary to have fulfilled the condition $\Delta v_{fin} = 3v_3 - (2v_{L1} + v_{L2}) \geqslant 0$, while for optimal isotope-selective excitation of the $2v_3$ and $3v_3$ states of $^{235}UF_6$, it is necessary to ensure either the most accurate resonance possible during excitation or excitation with a small negative detuning of the total laser generation frequency from the frequency of the excited state ($\Delta v_{fin} \leqslant 0$). This is due to the fact that, even in the case of deep cooling of UF_6 in gas-dynamic flows, a relatively large proportion of molecules [2, 22] are at low-lying vibrational levels: v_6 (≈ 143 cm^{-1}), v_4 (≈ 187.5 cm^{-1}), v_5 (≈ 201 cm^{-1}), $2v_6$ (≈ 286 cm^{-1}). For example, at a fairly low temperature $T \approx 70$ K, the population of the ground vibrational state does not exceed 75%, while the remaining molecules are distributed between low-lying vibrational levels. It is only at a temperature of $T \approx 50$ K that the population of the ground vibrational state of UF_6 is $\geqslant 92\%$ [2, 22]. The frequencies of transitions of molecules from low-lying vibrational levels are slightly shifted due to intermodal anharmonicity to the red region relative to the absorption band of molecules from the ground vibrational state [2, 4]. Therefore, at relatively high temperatures of UF_6, along with the resonant excitation of molecules from the ground state, it is possible, at the same laser frequencies, to excite molecules from populated low-lying vibrational states, which can lead to a noticeable decrease in the isotopic selectivity of the process of the excitation of upper levels.

In terms of the practical implementation of the considered MLIS method, to separate uranium isotopes by the molecular dissociation technique, the resonant excitation of $3v_3$ vibrational states of UF_6 by radiation from two lasers seems to be preferable and expedient compared to the excitation of $2v_3$ states. As mentioned above, in the case of three-photon bichromatic excitation of $3v_3$ UF_6 states, for the same laser pulses, resonant transitions to rather high vibrational $6v_3$ states of UF_6 occur. Further dissociation of molecules from these states, which are located in the region of a very high density of vibrational levels (in the vibrational quasi-continuum region [4, 5]), effectively occurs under the influence of the same laser pulses. In addition, as shown for the example of SF_6 molecules in [83, 88, 89], in the case of three-photon excitation of molecules, when all three laser pulses coincide in time, a more contrasting population of the excited $3v_3$ state is attained than that of the $2v_3$ state with two-photon excitation. This implies that, in the former case, a fairly narrow distribution of vibrationally excited SF_6 molecules is created, resulting in a higher selectivity of their dissociation [4, 89].

In applying MLIS methods to uranium, isotope-selective dissociation or excitation (in the case of low-energy methods) of $^{235}UF_6$ molecules is usually carried out. Studies [90–92] examine the techniques and parameters of isotope-selective two- and three-photon excitation of the $2v_3$ and $3v_3$ states for both $^{235}UF_6$ and $^{238}UF_6$ molecules. Data for $^{238}UF_6$ molecules are useful at the stage of studying the efficiency and selectivity of the proposed techniques for excitation and dissociation of UF_6.

The option to implement in the proposed techniques the resonant multiphoton population of the $4v_3$ and $6v_3$ states of UF_6 molecules with the same laser pulses that are used for isotope-selective excitation of the $2v_3$ and $3v_3$ states facilitates enhancement of efficiency and selectivity of molecular excitation. This was experimentally shown in [83, 88, 89] using the example of resonant transitions during multiphoton excitation of SF_6 molecules.

6. Method of isotope-selective excitation and dissociation of UF_6 molecules with a sensitizer by dichromatic laser IR radiation in a shock wave

The efficiency of isotope-selective excitation of $^{235}UF_6$ and $^{238}UF_6$ molecules into vibrational $2v_3$ and $3v_3$ states and their dissociation from these states can be significantly enhanced if they are irradiated in a mixture with a sensitizer [92]. Recently, studies [54, 93, 94] used the example of isotope-selective dissociation of CF_3Br and CF_2HCl molecules, characterized by small ($\leqslant 0.25$ cm^{-1}) isotopic shifts (relative to bromine and chlorine isotopes), in the IR absorption spectra to show that the selectivity and yield of dissociation of molecules can be significantly enhanced if they are irradiated in a mixture with a resonantly absorbing gas. This is due to the excitation energy of the molecules of the resonantly absorbing gas being effectively transferred to the molecules under study. In [92], this method was used as the basis for isotope-selective laser IR dissociation of $^{235}UF_6$ molecules. We now examine it in more detail.

The proposed method is based on the use of two processes: resonant three- or two-photon excitation of UF_6 molecules into $3v_3$ or $2v_3$ states by bichromatic IR radiation from two pulsed CF_4 or para-H_2 lasers [90, 91] and dissociation of vibrationally excited UF_6 molecules in a medium with a sensitizer that resonantly absorbs the radiation of these lasers [55, 93, 94]. The excitation and dissociation of UF_6 molecules is proposed to be carried out under nonequilibrium thermodynamic conditions of a shock wave, which is formed in front of a solid surface hit by an intense supersonic gas-dynamically cooled molecular flow [1, 2, 55, 95].

To form a molecular flow, it is proposed to use a mixture of $UF_6/SF_6/CH_4$ molecules at a pressure ratio of approximately 1/3/10 [96]. SF_6 molecules are used as sensitizers, while CH_4 molecules are used as acceptors of fluorine atoms formed in the dissociation of UF_6 and SF_6 molecules. At the indicated pressure ratio of the gases used, the vibrational temperature of UF_6 molecules (as well as SF_6 molecules) in the flow incident on the surface and in the shock wave is $T_{vib} \leqslant 100$ K [20, 96]. At such a vibrational temperature, the population of the ground vibrational state of UF_6 molecules is about 50% [2, 20], and UF_6 molecules feature relatively narrow ($\approx 7-8$ cm^{-1} at half maximum) IR absorption bands [2, 20, 68].

The SF_6 molecules used as a sensitizer are resonantly excited by the same laser pulses as the UF_6 molecules. The vibrational frequency of the v_4 mode of SF_6 molecules (≈ 615 cm^{-1} [97, 98]) is in very good resonance with high-lying transitions of vibrationally excited $^{235}UF_6$ molecules.

This ensures efficient energy transfer from SF_6 molecules excited by CF_4 or para-H_2 lasers to vibrationally excited $^{235}UF_6$ molecules. As a result, effective isotope-selective dissociation of $^{235}UF_6$ molecules is realized due to radiative-collisional excitation processes [93, 94, 99, 100].

SF_6 molecules are relatively neutral in chemical terms and feature a fairly high dissociation energy. They were used in many studies as sensitizers for vibrational excitation and dissociation of UF_6 molecules (see, for example, [2, 101] and references therein). However, SF_6 molecules were used in these studies for preliminary accumulation of vibrational energy as a result of their excitation by pulsed radiation from a CO_2 laser. SF_6 molecules have an intense absorption band in the 10.6-μm region (vibration mode v_3, frequency ≈ 948 cm^{-1} [102]). Subsequently, the energy stored by the SF_6 molecules was transferred through the v_4 mode resonant with the v_3 mode of the UF_6 molecules to these molecules, which led to their excitation and dissociation [2, 101].

In contrast, in the method proposed in [92], the sensitizer molecules and $^{235}UF_6$ molecules are concurrently excited by the resonant radiation of CF_4 or para-H_2 lasers, which leads to a significant increase in the efficiency of dissociation of $^{235}UF_6$ molecules [93, 94, 99, 100]. Since the dissociation energy of UF_6 molecules (≈ 68 kcal mol^{-1} [103]) is much less than that of SF_6 molecules (≈ 92 kcal mol^{-1} [104]), during the irradiation of the mixture, the UF_6 molecules dissociated at a vibrational temperature much lower than that of the dissociation of SF_6 molecules. As a result, at a low energy density of the exciting laser radiation ($\Phi \leqslant 1.5-2$ J cm^{-2}), conditions can be fulfilled when UF_6 molecules dissociate, while SF_6 molecules do not undergo dissociation [93, 94, 99].

In a gas-dynamically cooled molecular flow, the translational, rotational, and vibrational temperatures of polyatomic molecules fulfill the conditions $T_{1,\text{tr}} \leqslant T_{1,\text{rot}} \leqslant T_{1,\text{vib}}$ [105]. In a shock wave [106], due to the difference among the rates of translational, rotational, and vibrational relaxations [107], inverse nonequilibrium conditions are realized; namely, $T_{2,\text{tr}} \geqslant T_{2,\text{rot}} \geqslant T_{2,\text{vib}}$ [1, 2, 95]. Moreover, due to the large time of vibrational-translational relaxation of molecules (for example, for SF_6 $p\tau_{\text{V–T}} \approx 150$ μs Torr [108] and for UF_6, $p\tau_{\text{V–T}} \approx 32$ μs Torr [109]), the vibrational temperature of molecules in the shock wave where a pulsed rarefied flow gas is used may virtually coincide with the vibrational temperature of the molecules in the incident flow ($T_{2,\text{vib}} \approx T_{1,\text{vib}}$), while the translational and rotational temperatures of the molecules in the shock wave are significantly higher than in the undisturbed flow: $T_{2,\text{tr}} > T_{1,\text{tr}}$ and $T_{2,\text{rot}} > T_{1,\text{rot}}$. Thus, new nonequilibrium conditions are set in the compression shock, which are characterized by the vibrational temperature of the molecules being significantly lower than the translational and rotational temperatures.

In [110] (see also review [95]), the example of SF_6 molecules was used to show that the dominant factor in the formation of dissociation selectivity is the vibrational rather than the rotational temperature of the molecules. This is due to the fact that vibrationally cooled molecules (at $T_{\text{vib}} \leqslant 150$ K), even at a fairly high rotational temperature ($T_{\text{rot}} \approx 570$ K), feature (due to the absence of 'hot bands') narrower linear and multiphoton absorption spectra than at room temperature. Therefore, in a vibrationally 'cold' shock wave, even under conditions of high translational and rotational gas temperatures and the occurrence of collisions,
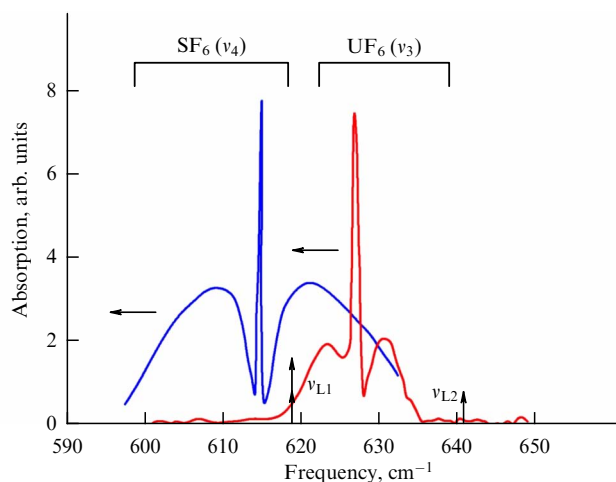

Figure 5. IR absorption band of the v_4 vibration of SF_6 molecules at temperature $T = 213$ K [111] and IR absorption band of the v_3 vibration of UF_6 molecules cooled in a supersonic gas-dynamic jet mixed with argon at temperature $T \leqslant 130$ K [96]. Vertical arrows indicate the frequency positions of CF_4 lasing lines, at which excitation of $^{235}UF_6$ molecules into the $3v_3$ F_1 state (1877.41cm^{-1}) is assumed. Horizontal arrows indicate the direction of the shift of absorption bands of UF_6 and SF_6 molecules to the low-frequency region during their vibrational excitation.

which reduce the selectivity of the process due to vibrational $V–V$ energy exchange between molecules, molecular dissociation selectivity is fairly high [110].

The advantages of irradiation of $^{235}UF_6$ molecules with an SF_6 sensitizer that resonantly absorbs laser radiation to enhance the efficiency of their dissociation are explained in Fig. 5. It shows the IR absorption band of the v_4 vibration (frequency of 615 cm^{-1} [98, 111]) of SF_6 molecules resonantly absorbing radiation from a CF_4 laser at temperature $T = 213$ K [111] and the IR absorption band of the v_3 vibration (≈ 627.72 cm^{-1} [20, 68]) of UF_6 molecules cooled in a supersonic gas-dynamic jet mixed with argon at temperature $T \leqslant 130$ K [96]. In Fig. 5, vertical arrows also show the frequency positions of the CF_4 lasing lines (frequencies of 618.2 and 640.9 cm^{-1}), at which it is supposed to excite $^{235}UF_6$ molecules into the $3v_3$ F_1 state (1877.41 cm^{-1}). Horizontal arrows indicate the direction of the shift of the absorption bands of UF_6 and SF_6 molecules to the low-frequency region in the process of their vibrational excitation.

Resonant excitation of $^{235}UF_6$ molecules into vibrational $2v_3$ and $3v_3$ states by bichromatic laser IR radiation leads, due to the anharmonicity of vibrations, to a shift of their IR absorption bands to the low-frequency region, coinciding with the IR absorption band of v_4 vibration of SF_6 molecules. As a result, for vibrationally excited $^{235}UF_6$ molecules and SF_6 molecules, the effective resonant radiation-collisional excitation of molecules is realized [93, 94, 99], leading to a significant enhancement of the dissociation yield of $^{235}UF_6$ molecules. Due to vibrational $V–V$ energy exchange, SF_6 molecules excited by a laser transfer the absorbed energy to $^{235}UF_6$ molecules, leading to an increase in their dissociation yield. Since the $V–V$ energy exchange between molecules occurs under conditions of small frequency detuning between vibrational transitions of SF_6 and UF_6 molecules, energy transfer between molecules is very efficient [101, 112]. This leads to an increase in the efficiency of dissociation of resonantly excited $^{235}UF_6$ molecules.

7. Conclusion

Experimental studies of resonant multiphoton excitation of the $2v_3$ and $3v_3$ states of SF_6 molecules by multifrequency laser radiation from pulsed CO_2 lasers show that the method under consideration is a relatively simple and effective way to excite molecules into high vibrational states and dissociate them from such states. It has been established that this method makes it possible to populate high vibrational levels of molecules more effectively than the methods of single-frequency or sequential two- or three-frequency excitation of molecules.

Based on spectroscopic data on the overtone states of the v_3 vibration of UF_6 molecules and on the lasing frequencies of CF_4 and para-H_2 lasers, an analysis was performed and techniques were proposed for isotope-selective resonant bichromatic excitation of the $2v_3$ and $3v_3$ states of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two CF_4 lasers and two para-H_2 lasers. Selective excitation of the overtone vibrational $2v_3$ and $3v_3$ states of $^{238}UF_6$ and $^{235}UF_6$ molecules by bichromatic radiation can be used for laser separation of uranium isotopes employing low-energy methods.

A method has been proposed to enhance the efficiency of isotope-selective laser dissociation of $^{235}UF_6$ molecules under nonequilibrium thermodynamic shock conditions, based on selective excitation of the vibrational $2v_3$ and $3v_3$ states of $^{235}UF_6$ by bichromatic radiation from two CF_4 or para-H_2 lasers and using a sensitizer, SF_6 molecules, that resonantly absorbs the radiation of these lasers.

If the IR multiphoton dissociation of molecules is used for the separation of uranium isotopes, resonant excitation of vibrational $3v_3$ states of UF_6 by radiation from two lasers followed by their dissociation by the same laser pulses is preferable to resonant excitation of $2v_3$ states of UF_6. In the former case, it is possible to attain a higher selectivity of the excitation and dissociation of molecules. If low-energy MLIS methods of uranium in molecular flows are used in practice, schemes for resonant isotope-selective excitation of the $2v_3$ states of UF_6 molecules by bichromatic radiation from two CF_4 or para-H_2 lasers may be more effective.

The methods and systems for resonant isotope-selective bichromatic excitation of the vibrational $2v_3$ and $3v_3$ states of the $^{235}UF_6$ and $^{238}UF_6$ molecules proposed in the studies reviewed above can form the basis for the MLIS of uranium and be of great interest for the development of technology for laser separation of uranium isotopes.

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