On the Possibility of the Effective Isotope-Selective Infrared Dissociation of $^{235}\text{UF}_6$ Molecules Vibrationally Excited by Bichromatic Laser Radiation

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Using the spectroscopic data on the $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules and on the lasing frequencies of CF$_4$ and para-H$_2$ lasers and recent results, a method has been proposed to increase the efficiency of the isotope-selective infrared laser dissociation of $^{235}\text{UF}_6$ molecules under nonequilibrium thermodynamic shock conditions. The method involves two processes: (i) the resonant multiphoton excitation of $^{235}\text{UF}_6$ molecules to the $3\nu_3$ or $2\nu_3$ vibrational states by the bichromatic infrared radiation of two CF$_4$ or para-H$_2$ lasers and (ii) the irradiation of $^{235}\text{UF}_6$ molecules with SF$_6$ molecules serving as sensitizers resonantly absorbing the radiation of these lasers. The essence of the method has been described. Schemes and parameters for isotope-selective dissociation of $^{235}\text{UF}_6$ molecules using this method has been presented.

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1. INTRODUCTION

Numerous recent studies have been devoted to molecular laser isotope separation (MLIS) [1–23]. The main aim of many studies is to develop uranium isotope separation methods involving UF$_6$ molecules [1–7, 10–22]. Most of the laser uranium isotope separation projects carried out in the United States, Germany, United Kingdom, France, Japan, and Australia at the end of the past century were closed. At the same time, studies on uranium MLIS are currently performed in many countries [1–7, 20–22]. It is expected that the application of lasers will allow the development of a laser uranium enrichment technology more economical and efficient than centrifuging. Current research is focused on the development of low-energy MLIS methods [1–3, 10–22] and alternative methods [2, 3, 13, 24, 25].

Two important problems of laser separation of uranium isotopes involving UF$_6$ molecules are (i) a small isotopic shift in infrared absorption spectra of laser-excited $\nu_3$ vibrations of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules and (ii) the absence of intense and efficient laser sources for isotope-selective vibrational excitation and dissociation of UF$_6$ molecules. The isotopic shift in the $\nu_3$ vibrational mode ($\approx 627.7$ cm$^{-1}$) for $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules is $\Delta\nu_{\text{is}} = 0.604$ cm$^{-1}$ [26]. Because of a small isotopic shift and a comparatively large width (about 20 cm$^{-1}$) of the infrared absorption band of molecules at room temperature [2, 27], isotope-selective infrared dissociation of UF$_6$ molecules is possible only at a low temperature of the gas when the infrared absorption band of UF$_6$ molecules with different U isotopes is much narrower [1, 2, 27].

Two tunable radiation sources in the 16 $\mu$m range were developed for projects on uranium MLIS using isotope-selective infrared multiphoton dissociation of UF$_6$ molecules. These are a molecular CF$_4$ laser optically pumped by the intense radiation of a CO$_2$ laser [28, 29] and the so-called para-H$_2$ laser source based on the shift of the radiation frequency of the CO$_2$ laser to the 16 $\mu$m range caused by the stimulated Raman scattering on rotational transitions of para-hydrogen molecules [30, 31]. These lasers in many parameters satisfy the requirements for operation at megafacilities [2]. However, significant disadvantages of both CF$_4$ and para-H$_2$ lasers in application to uranium isotope separation are discreteness of the frequency tuning and the absence of strong tunable lasing lines in the region of the Q branch of the $\nu_3$ vibrational mode of $^{235}\text{UF}_6$ molecules (in the 628.32 cm$^{-1}$ range [26]).

As a possible approach to uranium MLIS, we consider isotope-selective excitation of $3\nu_3$ states of $^{235}\text{UF}_6$ molecules ($\approx 1877.5$ cm$^{-1}$) [32], where the isotopic shift is about 1.81 cm$^{-1}$ [26], by the radiation of a CO laser [33–36]. This approach involves the chemical reaction of vibrationally excited UF$_6$ molecules with HCl molecules [33, 34]. Uranium isotopes are separated because the reaction rates of vibrationally
excited and unexcited UF₆ molecules with HCl molecules are different. For this approach, high-power CO lasers [35, 36] generating in the 5.3 μm range are being produced; they are planned to be used to excite ²³⁵UF₆ molecules. However, the efficient excitation of 3ν₃ states of UF₆ molecules by infrared radiation with a wavelength of ≈5.3 μm is problematic because absorption of UF₆ molecules at the 0ν₃ → 3ν₃ vibrational transition is weak. The integral absorption of the overtone 0ν₃ → 3ν₃ band of UF₆ molecules is about a factor of 1.8 × 10⁴ lower than the integral absorption of the main 0ν₃ → 1ν₃ band of UF₆ molecules [32]. Consequently, the search for alternative schemes for isotope-selective excitation and dissociation of ²³⁵UF₆ molecules is a very important relevant task. In this work, we propose a new method for the efficient isotope-selective laser infrared dissociation of ²³⁵UF₆ molecules.

2. FOUNDATIONS OF THE METHOD

The proposed method is based on the process of resonant three- or two-photon excitation of ²³⁵UF₆ molecules to the 3ν₃ or 2ν₃ vibrational states by the bichromatic infrared radiation of two pulsed CF₄ or para-H₂ lasers [18, 19] and on the irradiation of excited ²³⁵UF₆ molecules with SF₆ molecules serving as sensitizers resonantly absorbing the radiation of these lasers [16, 17, 23]. In addition, it is proposed to perform the excitation of molecules under nonequilibrium thermodynamic shock conditions formed in front of a solid surface on which a gas-dynamically cooled intense supersonic molecular flow is incident [1, 2, 24, 25].

As shown in [37, 38], radiation pulses of the CO₂ laser can efficiently excite SF₆ molecules to the high 2ν₃ and 3ν₃ vibrational states by means of the resonant two- [37] and three-frequency [38] excitation of SF₆ molecules cooled in a gas-dynamic jet. Recent studies [16, 23] demonstrate the possibility of a strong increase in the dissociation yield of CF₂HCl molecules irradiated under shock conditions together with CF₃Br sensitizers molecules resonantly absorbing the laser radiation. It was established that the processes mentioned above are also applicable to other molecules [16, 23, 37], in particular, UF₆ molecules. These processes are involved in the proposed method implemented under nonequilibrium thermodynamic shock conditions.

To form the molecular flow, it is proposed to use the UF₆/SF₆/CH₄ molecular mixture with a pressure ratio of about 1/3/10 [39], where SF₆ molecules serve as sensitizers and CH₄ molecules are used as acceptors of F atoms produced in the dissociation of UF₆ and SF₆ molecules. At the indicated pressure ratio of used gases, the vibrational temperature of UF₆ molecules (and SF₆ molecules) in the flow incident on the surface and in the compression shock will be $T_{\text{vib}} \leq 100$ K [27, 39]. The population of the ground vibrational state of UF₆ molecules at this vibrational temperature is about 50% [2, 27], and UF₆ molecules have comparatively narrow (a FWHM of about 7–8 cm⁻¹) infrared absorption bands [39].

The same laser pulses exciting ²³⁵UF₆ molecules also resonantly excite SF₆ molecules used as sensitizers. The frequency of the ν₄ vibrational mode of SF₆ molecules ($≈615$ cm⁻¹ [40, 41]) is in very good resonance with high-lying transitions of vibrationally excited ²³⁵UF₆ molecules. For this reason, the energy is efficiently transferred from SF₆ molecules excited by the CF₄ or para-H₂ lasers to vibrationally excited ²³⁵UF₆ molecules. As a result, the efficient isotope-selective dissociation of ²³⁵UF₆ molecules is ensured by radiative and collisional excitation processes [16, 17, 23].

It is noteworthy that SF₆ molecules were used as sensitizers for the excitation and dissociation of UF₆ molecules in many works (see, e.g., [2, 42] and references therein). However, SF₆ molecules were used in those works for the preliminary accumulation of the vibrational energy through their excitation by the pulsed radiation of the CO₂ laser. SF₆ molecules have an intense absorption band in the 10.6 μm range ($ν_3$ vibrational mode at a frequency of $≈948$ cm⁻¹ [43]). Subsequently, the energy accumulated by SF₆ molecules was transferred to the $ν_3$ mode of UF₆ molecules through the $ν_4$ mode resonant to the former, which led to their excitation and dissociation [2, 42].

Unlike the cited works, sensitizers and ²³⁵UF₆ molecules in the proposed method should be excited simultaneously by the resonant radiation of CF₄ or para-H₂ lasers, which significantly increases the efficiency of the dissociation of ²³⁵UF₆ molecules [16, 17, 23]. Since the dissociation energy of UF₆ molecules ($≈68$ kcal/mol [44]) is much lower than that of SF₆ molecules ($≈92$ kcal/mol [45]), the dissociation of UF₆ molecules in the process of irradiation of the mixture will occur at a much lower vibrational temperature than the dissociation of SF₆ molecules. As a result, under certain conditions possible at a low fluence of excited laser radiation ($Φ \leq 1.5–2$ J/cm²), UF₆ molecules will be dissociated, whereas the dissociation of SF₆ molecules will not occur [16, 17, 23].

The translational, rotational, and vibrational temperatures of polyatomic molecules in the gas-dynamically cooled molecular flow are related as [46] $T_{\text{1,tr}} \leq T_{\text{1,rot}} \leq T_{\text{1,vib}}$. In the compression shock [47], because of the different translational, rotational, and
vibrational relaxation rates [48], inverse nonequilibrium relation \( T_{2,\text{tr}} \geq T_{2,\text{rot}} \geq T_{2,\text{vib}} \) occurs [1, 2, 24]. The subscripts 1 and 2 indicate the temperatures of molecules in the incident flow and compression shock, respectively. In this case, because of a long vibrational–translational relaxation time of molecules (e.g., \( \tau_{\text{v}-\text{t}} \approx 150 \) µs Torr for SF6 [49], \( \tau_{\text{v}-\text{t}} \approx 32 \) µs Torr for UF6 [50]), the vibrational temperature of molecules in the compression shock in the case of the pulsed rarefied gas flow can be approximately equal to the vibrational temperature of molecules in the incident flow (\( T_{2,\text{vib}} \approx T_{1,\text{vib}} \)), whereas the translational and rotational temperatures of molecules in the compression shock are much higher than the respective temperatures in the unperturbed flow: \( T_{2,\text{tr}} > T_{1,\text{tr}} \) and \( T_{2,\text{rot}} > T_{1,\text{rot}} \). Thus, new nonequilibrium conditions are formed in the compression shock, where the vibrational temperature of molecules is much lower than their translational and rotational temperatures.

For the resonant excitation of the \( 2\nu_3 \) and \( 3\nu_3 \) vibrational states of \( ^{235}\text{UF}_6 \) molecules by the radiation of two pulsed infrared lasers, it is necessary [51] to satisfy the following relations between the frequencies \( \nu_{1L} \) and \( \nu_{2L} \) of these lasers and the frequency \( \nu_3 \) of the excited vibrational mode of \( ^{235}\text{UF}_6 \) molecules:

\[
\nu_{1L} + \nu_{2L} = 2\nu_3, \tag{1}
\]
\[
2\nu_{1L} + \nu_{2L} = 3\nu_3. \tag{2}
\]

One can quite easily ensure resonance conditions for the excitation of high vibrational levels of molecules using two or three lasers with different frequencies, particularly, high-pressure lasers with smooth radiation frequency tuning. To carry out such experiments, it is necessary to exactly know the frequencies (energies) of high vibrational levels of the studied molecules. These data for the SF6 [52] and UF6 [53] molecules were obtained at the Los Alamos National Laboratory in the course of projects on the molecular laser separation of uranium isotopes.

Advantages of the irradiation of \( ^{235}\text{UF}_6 \) molecules with an SF6 sensitizer resonantly absorbing laser radiation to increase the efficiency of their dissociation are illustrated in Fig. 1. This figure shows the infrared absorption band of the \( \nu_4 \) vibrational mode (frequency of 615 cm\(^{-1} \) [41, 54]) of molecules of SF6 resonantly absorbing the radiation of the CF4 laser at a temperature of \( T = 213 \) K [54] and the infrared absorption band of the \( \nu_3 \) vibrational mode (\( \approx 627.72 \) cm\(^{-1} \) [26]) of UF6 molecules cooled in a supersonic gas-dynamic jet in a mixture with argon at a temperature of \( T \leq 130 \) K [39]. The vertical arrows in Fig. 1 mark the frequencies of 618.2 and 640.9 cm\(^{-1} \) of the lasing lines of the CF4 laser at which it is proposed to excite \( ^{235}\text{UF}_6 \) molecules to the \( 3\nu_3 \) \( F_1 \) (1877.41 cm\(^{-1} \)) state (see below).

The horizontal arrows indicate the direction of the redshift of the absorption bands of the UF6 and SF6 molecules under their vibrational excitation.

Because of the anharmonicity of vibrations, the resonant excitation of \( ^{235}\text{UF}_6 \) molecules to the \( 2\nu_3 \) and \( 3\nu_3 \) vibrational states by bichromatic infrared laser radiation leads to the shift of their infrared absorption band to the low-frequency range coinciding with the infrared absorption band of the \( \nu_4 \) vibrational mode of SF6 molecules. As a result, the effective resonant radiation–collisional excitation of vibrationally excited \( ^{235}\text{UF}_6 \) molecules and SF6 molecules occurs [16, 17, 23, 42]. Laser-excited SF6 molecules transfer the absorbed energy to \( ^{235}\text{UF}_6 \) molecules through the vibrational–vibrational (\( V-V \)) energy exchange, increasing their dissociation yield. The process of \( V-V \) energy exchange between molecules is highly efficient because it occurs at small frequency detuning between vibrational transitions in SF6 and UF6 molecules [42, 55]. This high efficiency is also due to a comparatively high density of particles in the compression shock \((\approx(5-7) \times 10^{16} \) [23, 24]) and high vibrational and rotational temperatures of molecules (\( \approx 550 \) K [23, 24]).

3. SCHEMES AND PARAMETERS FOR RESONANT EXCITATION OF THE \( 2\nu_3 \) AND \( 3\nu_3 \) STATES OF \( ^{235}\text{UF}_6 \) MOLECULES

We calculated the \( 2\nu_3 \) and \( 3\nu_3 \) states of \( ^{235}\text{UF}_6 \) molecules taking into account the isotopic shift
In the absorption band of the $\nu_3$ vibrational mode for $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$, the isotope shift in the $2\nu_3$ and $3\nu_3$ states is taken as 1.21 and 1.81 cm$^{-1}$, respectively. The $2\nu_3$ and $3\nu_3$ energy levels of $^{235}\text{UF}_6$ molecules are shifted by these values toward higher energies. Two infrared lasers allow the efficient isotope-selective excitation of both $2\nu_3$ and $3\nu_3$ vibrational states of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules [18, 19]. We consider the excitation of only those $2\nu_3$ and $3\nu_3$ states of $^{235}\text{UF}_6$ molecules through which $^{235}\text{UF}_6$ molecules can be resonantly excited to higher $4\nu_3$ and $6\nu_3$ vibrational states.

Figure 2a shows the scheme of excitation of the $3\nu_3 F_1$ vibrational state of $^{235}\text{UF}_6$ molecules (1877.41 cm$^{-1}$ [53]) by radiation of two CF$_4$ lasers at frequencies of $\nu_{L_1} = 618.2$ cm$^{-1}$ and $\nu_{L_2} = 640.9$ cm$^{-1}$. The three-photon bichromatic excitation of the $3\nu_3 F_1$ level is performed with the detuning in the final state $\Delta \nu_{fin} = 0.11$ cm$^{-1}$ ($2\nu_{L_1} + \nu_{L_2} = 1877.3$ cm$^{-1}$). For this case, the solid arrows in Fig. 2b mark the frequencies of the lasing lines of the CF$_4$ lasers with respect to Q branches of the $\nu_3$ mode of $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ molecules in the gas-dynamically cooled molecular flow at a temperature of $T \leq 50–70$ K [27]. The solid arrows in Fig. 2b mark the frequencies of the lasing lines of the para-H$_2$ lasers for the excitation of the $3\nu_3 F_1$ state of $^{235}\text{UF}_6$ molecules. When choosing the schemes for resonant excitation of molecules, we took into account only the most intense radiation lines of the CF$_4$ [56] and para-H$_2$ lasers. The lasing frequencies of the lasers are neither individually nor pairwise in resonance with low-lying transitions in UF$_6$ molecules.

Possible schemes proposed for the resonant two-photon bichromatic excitation of $2\nu_3$ vibrational states of $^{235}\text{UF}_6$ molecules by the infrared radiation of two CF$_4$ lasers and two para-H$_2$ lasers are summarized in Table 1. Table 2 presents the schemes proposed for the resonant three-photon bichromatic excitation of $3\nu_3$ vibrational states of $^{235}\text{UF}_6$ molecules by the infrared radiation of two CF$_4$ lasers and two para-H$_2$ lasers. According to Tables 1 and 2, both types of lasers can provide the resonant excitation of the $2\nu_3$ and $3\nu_3$ states of $^{235}\text{UF}_6$ molecules with a small frequency detuning in the final state, which promotes a high selectivity of the excitation of $^{235}\text{UF}_6$ molecules. In all schemes presented in Tables 1 and 2 for the excitation of the $2\nu_3$ and $3\nu_3$ states of $^{235}\text{UF}_6$ molecules, the $4\nu_3$ and $6\nu_3$ states of $^{235}\text{UF}_6$ molecules can also be resonantly populated by the same laser pulses. This possibility is valuable because this ensures [57] a more efficient excitation of molecules to high vibrational states and their subsequent dissociation. The conditions for the optimal isotope-selective population of the $2\nu_3$ and $3\nu_3$ states of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules were discussed in [19].
4. CONCLUSIONS

A method has been proposed to increase the efficiency of the isotope-selective infrared laser dissociation of $^{235}$UF$_6$ molecules under nonequilibrium thermodynamic shock conditions. The method is based on the selective excitation of the $2\nu_3$ and $3\nu_3$ vibrational states in $^{235}$UF$_6$ molecules by the bichromatic radiation of two CF$_4$ or para-H$_2$ lasers using SF$_6$ molecules that serve as a sensitizer resonantly absorbing the radiation of these lasers. Schemes and parameters for resonant two- and three-photon bichromatic excitation of the $2\nu_3$ and $3\nu_3$ states in $^{235}$UF$_6$ molecules, which are cooled in a gas-dynamic flow to a temperature of $T \leq 100$ K, by the radiation of the mentioned lasers are given. The results can be applied when using laser infrared dissociation of molecules to separate isotopes.

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.
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