Possibility of resonant three-photon isotope-selective excitation of vibrational states with $v = 3$ of the UF_6 molecule mode ν_3 by radiation from two pulsed IR lasers in a gas-dynamically cooled molecular flow

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Abstract. **We consider the possibility of resonant isotope-selective population of states with $v = 3$ of the vibrational mode ν_3 of UF_6 molecules as a result of three-photon bichromatic excitation of the molecules by IR radiation from two pulsed CF_4 lasers and two pulsed para-H_2 lasers. We propose specific schemes and analyse the possibility of exciting the $^{238}UF_6$ and $^{235}UF_6$ molecules into states with $v = 3$ of the vibrational mode ν_3 using two CF_4 lasers (or para-H_2 lasers) generating in the region of 16 μm at frequencies that are significantly (by $\sim 3.5 – 17$ cm^{-1}) detuned from the linear absorption bands at the frequencies of ν_3 vibration of these molecules in a gas-dynamically cooled molecular flow. However, the sum of the doubled lasing frequency $2\nu_{L1}$ of the first laser and the frequency ν_{L2} of the second laser is equal to a frequency of the transition $v = 0 \rightarrow v = 3$ of the vibrational mode ν_3 of the UF_6 molecules. When both laser pulses coincide in time, the possibility of selective excitation of UF_6 molecules from the ground vibrational state with $v = 0$ to the state with $v = 3$ of the vibrational mode ν_3 is realised. The proposed schemes for the excitation of UF_6 molecules to states with $v = 3$ are compared with the previously implemented schemes for the effective excitation of states with $v = 3$ of the vibrational mode $\nu_3(F_1)$ and states with $v = 2$ of the vibrational mode $\nu_3 (A_1)$ of SF_6 molecules by three- and two-frequency radiation of pulsed CO_2 lasers, respectively.**

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1. Introduction

Many projects for laser separation of uranium isotopes that existed at the end of the last century were cancelled for a number of reasons, but research in this direction has been continued in many countries to this day [1–12] (see also reviews [1, 8, 9] and references therein). Today, research is

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mainly focused on the development of low-energy methods for molecular laser isotope separation (MLIS) of uranium. Two of them are considered the most promising [1, 8, 9]: the method of isotope-selective suppression of the clustering of molecules and the method of isotope-selective dissociation of small weakly bound van der Waals clusters (in particular, dimers) [1, 8–17]. Probably, these processes underlie the SILEX (separation of isotopes by laser excitation) laser enrichment technology of uranium, which is being currently developed in the USA and Australia [10–12] (see also reviews [1, 9]).

To conduct experimental studies and implement projects on MLIS of uranium by isotope-selective IR-multiphoton dissociation (MPD) of UF_6 molecules, lasers have been developed that generate in the 16 μm region: a molecular CF_4 laser optically pumped by radiation from a high-power CO_2 laser [18, 19], and a para-H_2 laser based on the frequency shift of the CO_2 laser into the 16-μm region due to stimulated Raman scattering at rotational transitions of hydrogen molecules [20]. These lasers are capable of generating radiation pulses with a duration of $\sim 10^{-7}$ s at a pulse energy of up to $0.5 – 1.0$ J. In many respects, they meet the requirements for working on large-scale installations [9].

Lasing of the CF_4 laser occurs at the transition $v = 1(\nu_2) + v = 1(\nu_4) \rightarrow v = 1(\nu_2)$ of the molecule [18, 21–23]. The frequency $\nu_2 + \nu_4$ (~ 1067 cm^{-1}) of the Raman band of the CF_4 molecule overlaps with the lasing frequencies of the CO_2 laser. The excitation of this Raman band by the radiation of a high-power CO_2 laser results in stimulated emission in the region of 16 μm at the given transition. The radiation from the CF_4 laser can be discretely retuned in the region of $\sim 612 – 650$ cm^{-1} [21, 22]. The pulse energy can reach $0.4 – 0.5$ J [19, 23–25], with a pulse repetition rate being 10 Hz [23–25]. The laser generation spectrum contains more than one hundred lines [21, 22].

Due to the rich spectral substructure of transitions in the CF_4 molecule, the laser can potentially be used to fine-tune the radiation frequency with a step of no more than 0.1 cm^{-1} [24, 26]. To more precisely adjust the lasing frequency of the CF_4 laser at the absorption line of UF_6 molecules, CF_4 molecules were also pumped using high-pressure CO_2 lasers with smooth frequency tuning [26, 27].

The significant disadvantages of CF_4 laser with respect to the separation of uranium isotopes are the discrete tuning of

the radiation frequency along individual lines and the absence of strong and tunable lasing lines in the Q-branch region of the vibration v_3 of the $^{235}UF_6$ molecules (near the frequency of 628.3 cm^{-1} [28]). This is probably why the isotope-selective dissociation of UF_6 molecules could not be implemented with this laser. However, in a number of studies, it was used in experiments on two-frequency excitation and dissociation of UF_6 molecules, including in combination with a CO_2 laser, to study various aspects of IR MPD [9] that are not related to the isotopic selectivity of the process.

So far, the only effective source of IR radiation that has sufficient energy and provides the possibility of selective excitation of $^{235}UF_6$ molecules is the para-H_2 laser, and this applies to both the MLIS method and the SILEX technology. The scheme of an effective radiation source in the region of 16 μm with a relatively high energy was first proposed by Bayer [20]. This scheme makes it possible to convert the energy of the CO_2 laser into the energy of the Stokes wave with an efficiency of at least 20 % (see [9] references therein).

The operation of the para-H_2 laser is based on the process of stimulated Raman scattering of high-power CO_2 laser radiation at rotational transitions in molecular hydrogen. As a rule, the H_2 paracomponent is used (the nuclear spins of two atoms are parallel). In the process of such inelastic scattering, the CO_2 laser radiation frequency decreases by the value of the rotational quantum of the H_2 molecule (~354.33 cm^{-1}) [20]. Tuning the CO_2 laser radiation frequency automatically sets the radiation frequency of the para-H_2 laser. To obtain the necessary gain and a relatively large conversion coefficient, a special multi-pass cell is used [29].

It should be noted that in the case of the para-H_2 laser, there is no exact coincidence of its lasing lines with the Q-branch centre of the absorption band of the vibration v_3 of the $^{235}UF_6$ molecule (~628.32 cm^{-1} [28]). To ensure such a coincidence, a high-pressure CO_2 laser can be used with the replacement of the isotopic composition of the laser's active medium in relation to carbon and oxygen and a smooth tuning of the frequency towards the desired value. However, this significantly complicates the experimental and engineering implementation of isotope-selective excitation of molecules. At the same time, the use of para-H_2 lasers made it possible to realise the isotope-selective dissociation of UF_6 molecules and the separation of uranium isotopes with a relatively high selectivity of the process ($\alpha \geqslant 4$) [30, 31]. The experiments were conducted by Japanese researchers at the Institute of Chemical and Physical Research (RIKEN) using two [30] and three [31] para-H_2 lasers.

At the initial stage of work on the IR laser dissociation of UF_6 molecules, there were still no high-power lasers emitting in the 16-μm region. This stimulated active research in this direction. Among the first methods proposed for obtaining radiation tunable along the lasing lines in the region of 16 μm were the following [32, 33]: generation of the difference frequencies of CO and CO_2 laser radiation, mixing of the bending vibration frequencies of CO_2 molecules (~667 cm^{-1}) in a nonlinear optical CdTe crystal, stimulated Raman scattering at electronic transitions, and the use of an optical parametric oscillator pumped by HF-laser radiation [34]. Other lasers have recently been developed to excite UF_6 molecules. In work [35], the effective generation of the difference frequencies of the radiation of CO and CO_2 lasers in

the region of 16 μm in the nonlinear optical crystal $AgGaSe_2$ is demonstrated.

As another approach to the MLIS of uranium, the method of isotope-selective excitation by CO-laser radiation of the state with $v = 3$ of the vibrational mode v_3 of $^{235}UF_6$ molecules, for which the isotopic shift is ~1.81 cm^{-1} [28, 36], is actively discussed [7, 37–40]. Thus, in work [7], the kinetics of the separation of uranium isotopes was considered using the chemical reaction of vibrationally excited UF_6 molecules with HCl molecules, proposed by Eerkens [37]. The excitation of UF_6 molecules in the vibrational band $3v_3$ (~1876 cm^{-1} [36]) by CO-laser radiation at a wavelength of 5.33 μm was studied. Due to the weak absorption of the vibration $3v_3$ of UF_6 molecules, their excitation was considered in a cooled intracavity cell. The separation of uranium isotopes was conducted due to the difference in the reaction rates of vibrationally excited and non-excited UF_6 molecules with HCl molecules. This method was used in work [38] to separate uranium isotopes with selectivity $\alpha = 1.2$.

To implement this method, high-power (~2–3 kW) CO lasers are being developed [39, 40], emitting in the region of 5.3 μm, which can be used to separate uranium isotopes when UF_6 molecules are excited in the $3v_3$ vibration band. Projects are being developed for intracavity laser separation of uranium isotopes by suppressing the condensation of UF_6 molecules using an actively mode-locked CO laser [40]. At the same time, it should be noted that the effective population of the overtone state with $v = 3$ of the vibrational mode v_3 of UF_6 molecules by radiation with a wavelength of ~5.33 μm is problematic due to the weak absorption of UF_6 molecules at the vibrational transition $v = 0 \rightarrow v = 3$. The ratio $\Gamma_{0-3}/\Gamma_{0-1}$ of the integral absorption $\Gamma_{0-3} = 3.8 \times 10^{-2}$ km mol^{-1} in the band $v = 0 \rightarrow v = 3$ of the vibrational mode v_3 of the UF_6 molecule to the integral absorption Γ_{0-1} in the band $v = 0 \rightarrow v = 1$ is equal to 5.6×10^{-5} [41].

In this regard, the search for alternative schemes for resonant isotope-selective excitation of high vibrational states and dissociation of $^{235}UF_6$ molecules is, in our opinion, very important and relevant. The aim of this work is to discuss and analyse alternative schemes for the IR laser excitation of UF_6 molecules into high vibrational states. We consider the possibility of effective resonant isotope-selective population of overtone states with $v = 3$ of the vibrational mode v_3 of UF_6 molecules due to multiphoton bichromatic excitation of the molecules by IR radiation from two CF_4 lasers and two para-H_2 lasers. A similar approach was successfully implemented experimentally on the example of resonant excitation of the high states with $v = 2$ and $v = 3$ of the vibrational mode v_3 of SF_6 molecules by radiation from two [42] and three [43] pulsed CO_2 lasers.

2. Examples of implementation of two- and three-frequency excitation of high vibrational states of SF_6 molecules

It is known [44] that multiphoton excitation of high vibrational states of molecules by intense laser radiation is possible under the coherent action of several fields, the sum of the frequencies of which satisfies the condition of multi-

photon resonance. In works [42, 43], using SF_6 as an example, it was shown that the effective population of high vibrational states of molecules can be realised as a result of multiphoton excitation of molecules by two [42] or three [43] laser radiation pulses having different frequencies, the sum of which is equal to the frequency of the transition of molecules from the ground vibrational state to the excited high-lying state.

In work [42], the resonant population of the state with $v = 2$ of the vibrational mode v_3 (A_1) ($\sim$1889.0 cm^{-1} [45]) of SF_6 molecules was conducted under the simultaneous action of two laser fields symmetrically detuned from the resonance with the transition $v = 0 \rightarrow v = 1$. SF_6 molecules cooled in a pulsed gas-dynamic jet (in a mixture of $[SF_6]:[H_2] = 1:20$) were excited by the radiation of a continuously tunable high-pressure CO_2 laser and a TEA CO_2 laser continuously tunable along the lasing lines with frequencies v_{L1} and v_{L2}, respectively. The Q-branch frequency of the absorption band of the vibrational mode v_3 of the SF_6 molecule is $\sim$948.1 cm^{-1} [46]. The radiation frequency v_{L1} of the continuously tunable CO_2 laser was varied in the range of 936–952 cm^{-1}. A discretely frequency-tunable laser was tuned in the low-frequency region of the linear absorption band of the vibrational mode v_3 of the SF_6 molecule to the 10P(26) radiation line (frequency $v_{L2} = 938.69$ cm^{-1}) or the 10P(28) radiation line ($v_{L2} = 936.80$ cm^{-1}).

The resonant excitation of the state with $v = 2$ of the vibrational mode v_3 (A_1) ($\sim$1889.0 cm^{-1}) of SF_6 molecules occurred when the condition $v_{L1} + v_{L2} = 1889.0$ cm^{-1} was met. The dissociation of the molecules was performed at a frequency of $v_{L3} = 929.02$ cm^{-1} [10P(36) laser line]. The SF_6 dissociation yield was measured by the IR luminescence intensity of vibrationally excited HF^* molecules formed as a result of the reaction of fluorine atoms (the product of SF_6 dissociation) with hydrogen molecules. It is shown [42] that the used scheme allows excitation of about 30% of SF_6 molecules from the ground state through the state with $v = 2$ of the vibrational mode v_3 (A_1). The resonant excitation of the high vibrational states of the mode v_3 ($\sim$960 cm^{-1} [47]) of the OsO_4 molecules was performed in a similar way in work [42]. It was found [42] that this technique can be used for isotope-selective dissociation of molecules.

In work [43], an effective resonant excitation of the state with $v = 3$ of the vibrational mode v_3 (F_1) ($\sim$2827.55 cm^{-1} [45]) of SF_6 molecules cooled in a pulsed gas-dynamic jet by radiation pulses from three discrete frequency-tunable CO_2 lasers was implemented. The vibrational, rotational and translational temperatures of molecules in the jet were as follows: $T_{vib} \leqslant 150$ K, $T_{rot} \approx T_{tr} \leqslant 20$ K [48]. The IR absorption band width at the transition $v = 0 \rightarrow v = 1$ of the vibrational mode v_3 of SF_6 molecules under such cooling is less than 3.5 cm^{-1} at half maximum [48]. The lasers used to excite 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} [10P(44) line]. The detuning of these lasing frequencies from the Q-branch frequency of the $v = 0 \rightarrow v = 1$ transition in SF_6 molecules was $\sim$3.1–27.2 cm^{-1}.

Note that none of the lasing frequencies of the lasers used to excite SF_6 molecules, either individually or in pairs, were in resonance with the low-lying vibrational transitions of the molecule. However, the total laser radiation frequency with a fairly good accuracy (detuning less than 0.35 cm^{-1}) was equal to the transition frequency $v = 0 \rightarrow v = 3$ of the vibrational mode v_3 (F_1) ($\sim$2827.55 cm^{-1} [45]) ($v_{L1} + v_{L2} + v_{L3} = 2827.20$ cm^{-1} [43]). The effect of resonant population of the state with $v = 3$ of the vibrational mode v_3 (F_1) of SF_6 molecules was recorded by measuring the energy absorbed by the molecules under conditions of separate and simultaneous exposure to all three pulses. In work [43], it has been found that when all three pulses coincide in time, the effective excitation of SF_6 molecules occurs through the $v = 3$ (v_3, F_1) vibrational state. In this case, the molecules are also excited to higher vibrational states.

3. Proposed schemes for resonant three-photon bichromatic excitation of states with $v = 3$ of the vibrational mode v_3 of UF_6 molecules

Based on the analysis of data on the energy levels of the excited vibrational states of the $^{238}UF_6$ molecules [28, 36] and the radiation frequencies of the CF_4 laser [21, 22] and the para-H_2 laser, we propose specific schemes of isotopic selective three-photon population of overtone states with $v = 3$ of the vibrational modes v_3 (F_1), v_3 (F_2), and v_3 (A_2) of the $^{238}UF_6$ and $^{235}UF_6$ molecules with radiation from two CF_4 lasers, as well as from two para-H_2 lasers. These schemes are applicable to UF_6 molecules cooled in a gas-dynamic flow (see below). When selecting and analysing the schemes and excitation frequencies of $^{235}UF_6$ molecules, the value of the isotopic shift in the IR absorption spectra in the vibrational mode v_3 of $^{235}UF_6$ and $^{238}UF_6$ molecules was taken into account, which for the third vibration overtones of the vibrations of these molecules is $\sim$1.8 cm^{-1} [28]. When selecting the optimal frequencies for the excitation of UF_6 molecules, only the most intense lasing lines of CF_4 [21, 22] and CO_2 lasers, which are used for pumping para-H_2 lasers, were taken into consideration. When using the proposed schemes for the excitation of states with $v = 3$ of the vibrational mode v_3 of UF_6 molecules, there is no need for additional tuning of the lasing frequencies for resonant excitation of molecules, since the detuning of the total laser radiation frequencies from the frequencies of the excited states is insignificant (see Fig. 1a, as well as Tables 1 and 2).

The most intense lasing line of the CF_4 laser is the line with a frequency of $\sim$615.1 cm^{-1} [21, 22], which is generated when the CF_4 molecules are pumped by the CO_2 laser on the 9R(12) line (frequency 1073.28 cm^{-1}). The CF_4 emission lines at frequencies of $\sim$612.2, $\sim$618.2, $\sim$631.4, $\sim$642.4, $\sim$643.1, and $\sim$645.1 cm^{-1} are also quite intense [21, 22]. When selecting the frequencies for the multiphoton excitation of the states with $v = 3$ of the vibrational mode v_3 of UF_6 molecules, we took into account, first of all, these emission lines of the CF_4 laser. It should be noted that the frequencies of many of these lines were determined with an error of at least 0.1 cm^{-1} [21, 22]. With a much smaller error ($\sim$0.01 cm^{-1}), the energies (frequencies) of the excited vibrational states were determined up to the states with $v = 6$ of the vibrational mode v_3 of the $^{238}UF_6$ molecules [36]. The energies of the excited vibrational states of the $^{235}UF_6$ molecules were determined taking into account the isotopic shifts of $\Delta_{is} \approx 0.604$ cm^{-1} [28] in the states with $v = 1$ of the vibrational modes v_3 for the $^{238}UF_6$ and $^{235}UF_6$ molecules, and the isotopic shifts of $\Delta_{is} \approx$

Energy levels of the mode v_3
$^{238}UF_6$ molecule/cm^{-1}

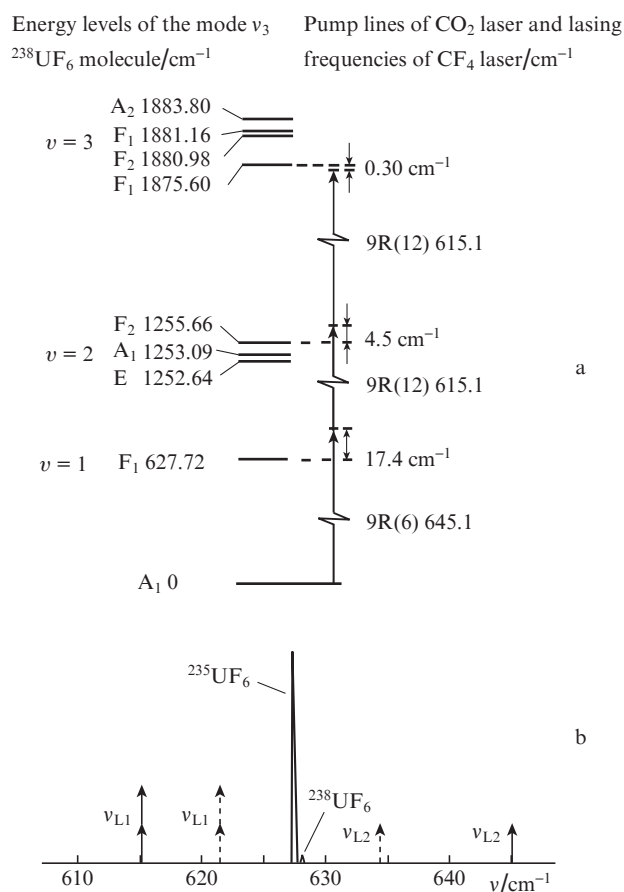Pump lines of CO_2 laser and lasing
frequencies of CF_4 laser/cm^{-1}

Figure 1. (a) Diagram of resonant three-photon bichromatic excitation of $^{238}UF_6$ molecules to the state with $v = 3$ of the vibrational mode v_3 (F$_1$) (~1875.6 cm^{-1}) by the radiation from two CF_4 lasers (the energy levels of the v_3 mode of $^{238}UF_6$ molecules are taken from [36]), and (b) the 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 $^{238}UF_6$ and $^{235}UF_6$ molecules to the states with $v = 3$ of the vibrational mode v_3 (F$_1$) (~1875.6 cm^{-1} for $^{238}UF_6$ and ~1877.4 cm^{-1} for $^{235}UF_6$), as well as the Q-branch of linear absorption bands at the fundamental vibration frequencies v_3 of $^{238}UF_6$ and $^{235}UF_6$ molecules in a gas-dynamically cooled molecular flow at $T \leqslant 50$ K (Q-branches are shown qualitatively [32]).

1.81 cm^{-1} in the states with $v = 3$ of the vibrational modes v_3 for the same molecules.

Figure 1a shows the population diagram of the state with $v = 3$ of the vibrational mode v_3 (F$_1$) of $^{238}UF_6$ mole-

cules (~1875.6 cm^{-1} [36]) by radiation from two CF_4 lasers operating at frequencies $v_{L1} \approx 615.1$ cm^{-1} and $v_{L2} \approx 645.1$ cm^{-1}. Three-photon bichromatic excitation of this state is realised with detuning in the final state $\Delta v_{fin} \approx +0.3$ cm^{-1} ($2v_{L1} + v_{L2} = 1875.3$ cm^{-1}). Figure 1b for this example shows the frequencies of the CF_4 lasing lines and the Q-branches of the linear absorption bands at the fundamental vibration frequencies v_3 of the $^{238}UF_6$ and $^{235}UF_6$ molecules [32]. The lasing line frequencies of the para-H$_2$ lasers for one of the excitation schemes (see below) are marked with dashed arrows. The widths of the P and R branches (not shown in Fig. 1) of gas-dynamically cooled UF_6 molecules at $T \leqslant 50$ K do not exceed 2 cm^{-1} [28].

Note that the specified lasing frequencies, either individually or in pairs, are not in resonance with the low-lying transitions of UF_6 molecules [36]. Under conditions of low vibrational and low rotational temperatures of the molecules in a gas-dynamically cooled flow, this means that the molecules can be excited to high vibrational states mainly through the resonance channel, i.e., through the state with $v = 3$ of the vibrational mode v_3 (F$_1$). Further excitation and dissociation of the excited molecules are possible due to the high density of vibrational states of the $^{238}UF_6$ molecules, mainly at the expense of the absorption of laser radiation having a lower frequency $v_{L1} \approx 615.1$ cm^{-1}, since it is in 'better' resonance with the high-lying vibrational transitions of the molecule. Note that in this example, the combination of laser radiation frequencies used to excite the state with $v = 3$ of the vibrational mode v_3 (F$_1$) of the $^{238}UF_6$ molecule is also suitable for further resonant excitation of molecules from the vibrational state with $v = 3$ (v_3, F$_1$) to the states with $v = 6$ (v_3, A$_1$) (~3750.92 cm^{-1} [36]) with a frequency detuning of only about +0.3 cm^{-1}.

Table 1 lists the parameters of the proposed possible schemes for resonant three-photon bichromatic population of the states with $v = 3$ of the vibrational modes v_3 of the $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two CF_4 lasers; in particular, the first line contains the parameters of the above-mentioned scheme for the excitation of the state with $v = 3$ (v_3, F$_1$). The energies of the states with $v = 3$ (v_3) of the $^{235}UF_6$ molecule were determined by shifting the levels with $v = 3$ (v_3) of the $^{238}UF_6$ molecule into the high-frequency region by the value of the isotopic shift for these molecules in the state with $v = 3$ (v_3), equal to ~1.81 cm^{-1} (with allowance for the isotopic shift $\Delta v_{is} \approx 0.604$ cm^{-1} for the state with $v = 1$ of the vibrational mode v_3 [28]).

Table 2 shows the parameters of the proposed possible schemes for resonant three-photon bichromatic population of

Table 1. Parameters of possible schemes of resonant three-photon bichromatic excitation of states with $v = 3$ of vibrational modes v_3 of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation of two CF_4 lasers.

Scheme	Molecule	Excited state and its energy /cm^{-1}	Lasing frequency v_{L1} of the CF_4 laser 1 /cm^{-1}	Line and lasing frequency of the CO_2 pump laser 1 /cm^{-1}	Lasing frequency v_{L2} of the CF_4 laser 2 /cm^{-1}	Line and lasing frequency of the CO_2 pump laser 2 /cm^{-1}	Frequency detuning in the final state $\Delta v_{fin} = 3v_3 - (2v_{L1} + v_{L2})$ /cm^{-1}
1	$^{238}UF_6$	$3v_3$ F$_1$ (1875.60)	615.1×2	9R(12),1073.28	645.1	9R(6), 1058.95	+0.30
2	$^{238}UF_6$	$3v_3$ F$_2$ (1880.98)	631.4×2	9R(22), 1079.85	618.2	9R(10), 1071.90	−0.02
3	$^{238}UF_6$	$3v_3$ F$_1$ (1881.16)	618.2×2	9R(10), 1071.90	645.1	9P(6), 1058.96	−0.34
4	$^{235}UF_6$	$3v_3$ F$_1$ (1877.41)	618.2×2	9R(10), 1071.90	640.9	9R(16), 1075.99	+0.11
5	$^{235}UF_6$	$3v_3$ F$_1$ (1877.41)	631.4×2	9R(22), 1079.85	615.1	9R(12), 1073.28	−0.49
6	$^{235}UF_6$	$3v_3$ F$_2$ (1882.78)	615.1×2	9R(12), 1073.28	652.2	9P(10), 1055.63	+0.38

Table 2. Parameters of possible schemes for resonant three-photon bichromatic excitation of states with $v = 3$ of the vibrational modes v_3 of $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation of two para-H_2 lasers. In the case of stimulated Raman scattering at the rotational levels of parahydrogen, the lasing frequency of the CO_2 laser decreases by 354.33 cm^{-1} [20].

Scheme	Molecule	Excited state and its energy /cm^{-1}	Lasing frequency v_{L1} of the para-H_2 laser 1 /cm^{-1}	Line and lasing frequency of the CO_2 pump laser 1 /cm^{-1}	Lasing frequency v_{L2} of the para-H_2 laser 2 /cm^{-1}	Line and lasing frequency of the CO_2 pump laser 2 /cm^{-1}	Frequency detuning in the final state $\Delta v_{fin} = 3v_3 - (2v_{L1} + v_{L2})$ /cm^{-1}
1	$^{238}UF_6$	$3v_3$ F_1 (1875.60)	621.60×2	10R(20), 975.93	632.24	10R(38), 986.57	+0.16
2	$^{238}UF_6$	$3v_3$ F_2 (1880.98)	622.88×2	10R(22), 977.21	635.32	10R(44), 989.65	−0.10
3	$^{238}UF_6$	$3v_3$ F_1 (1881.16)	622.88×2	10R(22), 977.21	635.32	10R(44), 989.65	+0.08
4	$^{235}UF_6$	$3v_3$ F_1 (1877.41)	621.60×2	10R(20), 975.93	634.32	10R(42), 988.65	−0.11
5	$^{235}UF_6$	$3v_3$ F_2 (1882.79)	631.16×2	10R(36), 985.49	620.29	10R(18), 974.62	+0.18
6	$^{235}UF_6$	$3v_3$ A_2 (1885.61)	626.58×2	10R(28), 980.91	632.24	10R(38), 986.57	+0.21

the states with $v = 3$ of vibrational modes v_3 of the $^{238}UF_6$ and $^{235}UF_6$ molecules by IR radiation from two para-H_2 lasers. In Fig. 1b, dashed lines indicate the frequencies of the lasing lines of the para-H_2 lasers for scheme 4 (Table 2) of the excitation of the state with $v = 3$ of the vibrational mode v_3 (F_1) of the $^{235}UF_6$ molecule. Note that in schemes 2–4, the 10R(42) and 10R(44) emission lines of the CO_2 lasers, which are used to pump the para-H_2 lasers, are located relatively far from the maximum of the 10R-branch lasing band. The radiation energies of the CO_2 lasers on these lines are probably not too large. Schemes 1, 5, and 6 use sufficiently intense CO_2 lasing lines, which also make it possible to obtain intense generation of para-H_2 lasers.

It should be noted that for optimal isotope-selective excitation of states with $v = 3$ of vibrational modes v_3 of $^{238}UF_6$ molecules, it is necessary to provide either the most accurate resonance during excitation, or excitation with a small positive detuning of the total lasing frequency of the lasers from the frequency of the state being excited ($\Delta v_{fin} = 3v_3 - (2v_{L1} + v_{L2}) > 0$), while for optimal isotope-selective excitation of states with $v = 3$ of vibrational modes v_3 of $^{235}UF_6$ molecules, it is necessary to provide either the most accurate resonance during excitation, or excitation with a small negative detuning of the total lasing frequency of the lasers from the frequency of the state being excited ($\Delta v_{fin} < 0$). 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 [9, 32] are located at low-lying vibrational levels with $v = 1$ ($v_6 \approx 143$ cm^{-1}), with $v = 1$ ($v_4 \approx 187.5$ cm^{-1}), with $v = 1$ ($v_5 \approx 201$ cm^{-1}), and with $v = 2$ ($2v_6 \approx 286$ cm^{-1}) [28]. For example, at a sufficiently low temperature ($T \approx 70$ K), the population of the ground vibrational state of UF_6 molecules does not exceed 75%, while the remaining molecules are distributed between low-lying vibrational levels. And only at a temperature of $T \leqslant 50$ K, the population of this state is no less than 92% [1, 32]. The frequencies of transitions of molecules from low-lying vibrational levels are slightly shifted due to intermode anharmonicity to the red region relative to the absorption band of molecules from the ground vibrational state [49]. Therefore, at relatively high UF_6 temperatures, along with 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 upper-level excitation process.

Note that the effective bichromatic isotope-selective excitation of states with $v = 2$ of vibrational modes v_3 of UF_6

molecules (~ 1253 cm^{-1} [36]) can be performed using two IR lasers. This is of great interest for the implementation of more efficient excitation of molecules due to two-photon processes. However, from the point of view of practical implementation of the considered method of separation of uranium isotopes, resonant three-photon excitation of states with $v = 3$ of vibrational modes v_3 of UF_6 molecules by the radiation of two lasers seems to be more preferable. With this excitation, as already mentioned above, for the same lasers, in some cases, resonant transitions to sufficiently high vibrational states with $v = 6$ (v_3) are realised. Further dissociation of molecules from these states, located in the region of very high density of vibrational levels, will effectively occur under the action of the same laser pulses. In addition, as shown by the example of SF_6 molecules in works [42, 43], in the case of three-photon excitation of molecules, when all three laser pulses coincide in time, a more contrasting population of the excited state with $v = 3$ (v_3) is achieved than in the case of two-photon excitation of the state with $v = 2$ (v_3). This means that in the first case, a rather narrow distribution of vibrationally excited molecules is formed, which leads to a higher selectivity of their dissociation process [49].

4. Conclusions

Based on spectroscopic data on the overtone states of the vibrational mode v_3 of UF_6 molecules and the isotopic shift for $^{238}UF_6$ and $^{235}UF_6$ molecules in this mode, we have analysed the possibility of resonant multiphoton isotope-selective excitation of states with $v = 3$ of vibrational modes v_3 of UF_6 molecules by radiation from two pulsed IR lasers.

We have considered specific schemes for using the radiation of two CF_4 lasers and two para-H_2 lasers for the resonant three-photon bichromatic population of the states with $v = 3$ (v_3) of $^{238}UF_6$ and $^{235}UF_6$ molecules cooled in a gas-dynamic flow to a temperature of $T \leqslant 50 – 70$ K.

In our opinion, the schemes of resonant isotope-selective three-photon bichromatic excitation of vibrational states with $v = 3$ (v_3) of UF_6 molecules proposed in this work should be taken into consideration in the development of MLIS technologies for uranium, along with other schemes and methods of isotope-selective laser IR excitation and dissociation of UF_6 molecules.

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