ISSN 1068-3356, Bulletin of the Lebedev Physics Institute, 2023, Vol. 50, Suppl. 2, pp. S187–S193. © Allerton Press, Inc., 2023.
Russian Text © The Author(s), 2022, published in Kvantovaya Elektronika, 2022, Vol. 52, No. 10, pp. 912–916.

EFFECT OF LASER RADIATION ON MATTER. LASER PLASMA

Study of the Photoionization Spectrum in the Second Step of the Lutetium Photoionization Scheme

A. B. D'yachkov[a], A. A. Gorkunov[a], A. V. Labozin[a], S. M. Mironov[a], V. A. Firsov[a], G. O. Tsvetkov[a,*], and V. Ya. Panchenko[a]

[a] *National Research Center Kurchatov Institute, Moscow, 123182 Russia*

**e-mail: Tsvetkov_GO@nrcki.ru*

Received June 26, 2022; revised June 26, 2022; accepted June 26, 2022

Abstract—The photoionization spectrum in the second step of the three-step lutetium photoionization scheme $5d6s^2\,{}^2D_{3/2} - 5d6s6p^4F^o_{5/2} - 5d6s7s^4D_{3/2} - (53\ 375\ \text{cm}^{-1})^o_{1/2}$ has been measured. The effect of two-photon transitions has been studied experimentally compared to one-photon transitions.

Keywords: selective laser photoionization, ^{177}Lu isotope

DOI: 10.3103/S106833562314004X

1. INTRODUCTION

The selective photoionization of lutetium isotopes through the scheme $5d6s^2\,{}^2D_{3/2} - 5d6s6p^4F^o_{5/2} - 5d6s7s^4D_{3/2} - (53\ 375\ \text{cm}^{-1})^o_{1/2}$ using narrow-band tunable dye lasers (DLs) pumped by copper vapor lasers can be used to obtain the ^{177}Lu radionuclide applied in medicine. In [1, 2], we experimentally demonstrated the possibility of reaching high selectivity and efficiency of the photoionization separation of the ^{176}Lu and ^{177}Lu isotopes and the ^{177m}Lu isomer. Various effects beyond the incoherent description of photoionization using rate equations and effective transition cross sections were simultaneously detected. Two of these effects are the splitting of transition lines (Autler–Townes effect [3]) and the strong influence of two-photon processes on the selectivity of photoionization. These effects can be explained within the coherent description of laser photoexcitation processes using the density matrix formalism with steady-state oscillations of the populations of the intermediate levels of the photoionization scheme.

Selective multistep photoionization used to separate an isotope from a mixture was theoretically described in [4–6]. The most consistent study focused on the coherent description of the laser photoionization of lutetium through this scheme was reported in [4], where numerical calculations within the density matrix formalism to describe the interaction of atoms with laser radiation were presented. The dynamics of the populations was described taking into account the hyperfine structure of transitions and the effect of the spectral width, pulse shape, and intensity of laser radiation on the efficiency and selectivity of photoionization was examined. The influence of the Doppler effect was analyzed in application to the laser photoionization separation of the ^{176}Lu isotope from the natural mixture (the natural concentration of ^{176}Lu is 2.59%).

The main results obtained in [4] are important for the general development of the laser method and, in particular, for the separation of lutetium isotopes; some of them require direct experimental confirmation. This primarily concerns the calculations of two-dimensional (in frequencies of the laser radiation in the first and second steps) photoionization spectra of the natural ^{175}Lu and ^{176}Lu isotopes.

The photoionization schemes for ^{175}Lu and ^{176}Lu are presented in Fig. 1. The hyperfine splitting of the levels in these schemes are usually much larger than the spectral width of the laser radiation (100–150 MHz). Correspondingly, at a certain tuning of wavelengths, photoionization can be carried out only through a single channel, i.e., with a certain combination of the components of the hyperfine structure of the ground state, first and second excited states, and autoionization states ($F_0 \to F_1 \to F_2 \to F_3$). Taking into account the selection rules in the total angular momentum F ($\Delta F = 0, \pm 1$) for transitions, 44 photoionization channels are possible. The two-step photoionization in this scheme was considered in [4], whereas the interaction with the laser radiation in the third step was treated as nonresonant and this tran-

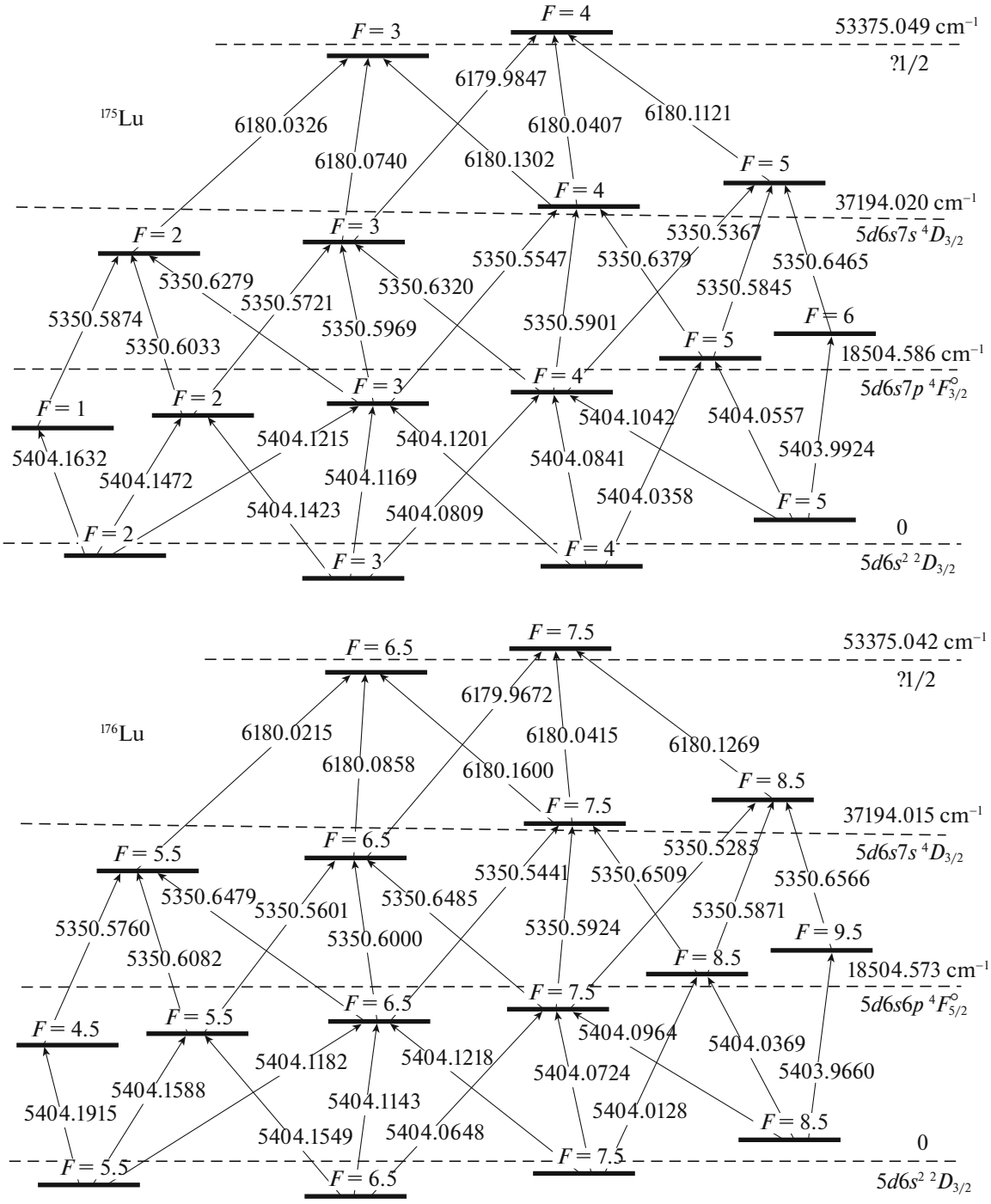

Fig. 1. Optical photoionization schemes for ^{175}Lu ($I = 7/2$) and ^{176}Lu ($I = 7$); numbers next to arrows are vacuum wavelengths of the corresponding transitions in angstrom [1].

sition was included in the description as the decay to an isolated state, which cannot be left by particles. This variant occurs in practice in the case of photoionization to continuum at a significant detuning of the laser radiation from the autoionization resonance in the third step. In this case, the number of the possible photoionization channels decreases to 28.

The efficiency of photoionization was calculated in [4] as a function of the wavelengths of the lasers in the first and second step (DL1 and DL2 lasers) with an intensity of 10 W/cm^2 and a spectral width of 100 MHz separately for the ^{175}Lu and ^{176}Lu isotopes. The calculations show that photoionization is possi-

ble not only through 28 channels allowed by the selection rules but also through channels where the initial state of the second transition differs from the final state of the first transition. In particular, when the laser radiation in the first step is tuned to the $F_0 = 8.5 \rightarrow F_1 = 9.5$ transition in the ^{176}Lu isotope, the photoionization peak is observed at the tuning of the wavelength of the DL2 laser to the $F_1 = 9.5 \rightarrow F_2 = 8.5$ transition ($8.5 \rightarrow 9.5 \rightarrow 8.5 \rightarrow$ continuum channel). However, photoionization peaks comparable in intensity are also observed then the DL2 laser is tuned to the $F_1 = 8.5 \rightarrow F_2 = 8.5$ transition and even to the $F_1 = 7.5 \rightarrow F_2 = 8.5$ transition. Calculations for the tuning of the DL1 laser to the other components of the first transition in ^{176}Lu and for the ^{175}Lu isotope give similar results.

We note that the $8.5 \rightarrow 9.5 \rightarrow 8.5 \rightarrow 7.5$ photoionization channel is the most important for the separation of the ^{176}Lu isotope from the natural mixture because it allows reaching high selectivity and efficiency. The author of [4] attributes the possibility of side channels to the population of the $F_1 = 8.5$ and $F_1 = 7.5$ components of the first excited state due to the laser radiation from the spectral wing of the laser line when the DL1 laser is tuned to the $F_0 = 8.5 \rightarrow F_1 = 9.5$ transition. In this case, the $F_0 = 7.5 \rightarrow F_1 = 8.5$, $F_0 = 8.5 \rightarrow F_1 = 8.5$ and $F_0 = 6.5 \rightarrow F_1 = 7.5$, $F_0 = 7.5 \rightarrow F_1 = 7.5$, $F_0 = 8.5 \rightarrow F_1 = 7.5$ transitions whose frequencies are separated from the frequency of the $F_0 = 8.5 \rightarrow F_1 = 9.5$ transition by 5 to 13 GHz are excited. The possibility of such a «long-range» influence of the spectral contour significantly affects the formation of the selectivity of photoionization and requires direct experimental proof.

2. EXPERIMENT

Photoionization spectra of transitions in the first and second steps of the $5d6s^2\,{}^2D_{3/2} - 5d6s6p^4F^o_{5/2} - 5d6s7s^4D_{3/2} - (53\,375\ \mathrm{cm}^{-1})^o_{1/2}$ photoionization scheme for ^{176}Lu were studied using laser resonance ionization mass spectroscopy (LRIMS). For the resonant excitation and ionization of atoms, we used the radiation from three single-mode pulsed dye lasers pumped by the radiation from copper vapor lasers. The spectral FWHM of dye lasers was 100–150 MHz, the FWHM duration of pulses was 20 ns, and the pulse repetition frequency was 10 kHz. The pulses of all three lasers were linearly polarized in the same direction and were time synchronized with zero delay, which ensured the simultaneous action of laser fields of all three photoionization steps on atoms. A commercial quadrupole mass spectrometer MS-7302 was used to detect photoions, and experiments were carried out with a collimated atomic beam (Doppler width of the atomic line was ~150 MHz). The technical parameters and features of the experimental setup were described in detail in [7, 8]. The DL1 laser was tuned to resonance with the first transition. The radiation from the DL3 laser, which was detuned from the wavelength of the autoionization transition 1 Å, induced the photoionization of atoms from the second excited state to continuum. The average radiation power densities in the first, second, and third steps were 5, 3, and 2500 mW/cm^2, respectively, which correspond to peak intensities of 25, 15, and 1.25×10^4 W/cm^2, respectively.

3. RESULTS AND DISCUSSION

The dependence of the photoion signal from ^{176}Lu on the wavelength of the DL2 laser when the DL1 laser is tuned to the resonance with the first $F_0 = 8.5 \rightarrow F_1 = 9.5$ (5403.9660 Å) transition is shown in Fig. 2. The intense peak corresponds to the second-step $F_1 = 9.5 \rightarrow F_2 = 8.5$ (5350.6566 Å) transition. The scanning of the wavelength of the DL2 laser demonstrated the absence of additional photoionization peaks predicted in [4] both in the region of the second $F_1 = 8.5 \rightarrow F_2 = 8.5$ (5350.5871 Å) transition and in the region of the $F_1 = 7.5 \rightarrow F_2 = 8.5$ (5350.5285 Å) transition. Two photoion signals separated by about ±2 GHz from the (5350.6566 Å) resonance are due to weak side longitudinal modes in the spectrum of the DL2 laser. A similar three-peak picture of photoionization was observed when the DL1 laser was tuned to resonance with the $F_0 = 5.5 \rightarrow F_1 = 4.5$ (5404.1915 Å) transition and the wavelength of the DL2 laser was scanned around the $F_1 = 4.5 \rightarrow F_2 = 5.5$ (5350.5760 Å) transition. Since the $F_1 = 9.5 \rightarrow F_2 = 8.5$ transition was saturated, the ratio of the signals from side modes to the resonance peak was significantly larger than the fraction of the intensity contained in side longitudinal modes (~10^{-3}). Thus, the sensitivity of the study to possible additional photoionization resonances was 10^{-3}.

Another significant difference of our experimental results from calculations in [4] is in the degree of influence of two-photon transitions on photoionization compared to the effect of one-photon transitions. Figure 3 presents results of the scanning of the wavelength of the DL2 laser around the $F_1 = 4.5 \rightarrow F_2 = 5.5$ (5350.5760 Å) resonance at different detunings of the DL1 laser from the $F_0 = 5.5 \rightarrow F_1 = 4.5$

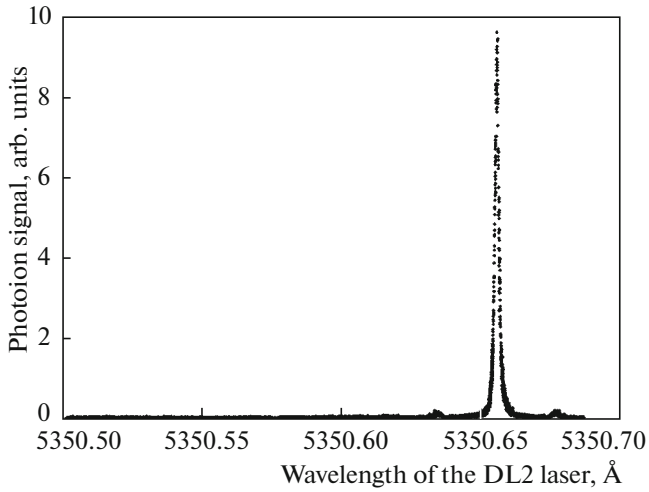

Fig. 2. Photoion signal of ^{176}Lu in the 8.5 → 9.5 → 8.5 → continuum channel at the scanning of the wavelength of the DL2 laser near the $F_1 = 9.5 \rightarrow F_2 = 8.5$ (5350.6566 Å) resonance.

(5404.1915 Å) resonance. It is seen that the spectra include not only the resonance peak but also an additional signal at the frequency spacing from the resonance that increases with the detuning of the wavelength of the DL1 laser from the $F_0 = 5.5 \rightarrow F_1 = 4.5$ resonance so that the sum of the energies of the photons from the DL1 and DL2 lasers does not change and is equal to the energy of the second excited state. Consequently, this peak corresponds to the two-photon transition from the ground state to the second excited state. According to the experimental results, the probability of two-photon transitions in the case of nonzero detuning is noticeably higher than the probability of several-step one-photon transitions. Similar results were obtained in [9], where the selective photoionization of calcium was studied. Two-photon transitions were presented in the form of diagonal ridges on two-dimensional maps calculated in [4], but their amplitudes were much lower than the amplitudes of one-photon transitions. It is noteworthy that calculations in [4] were performed for the laser radiation in the first and second steps with an intensity of 10 W/cm^2, whereas the intensity of the DL1 laser in our experiment was higher, 135 W/cm^2, which corresponds more to the working intensity of practical selective photoionization. A higher intensity of the laser radiation in the first step can change the relation between probabilities of resonance and two-photon transitions so that the probability of the latter transitions increases.

Figure 4 presents the dependences of the photoion signal on the detuning of the laser radiation in the first step at the frequency of the DL2 laser in resonance with the $F_1 = 4.5 \rightarrow F_2 = 5.5$ transition and on the simultaneous frequency detuning of the radiation from the DL1 and DL2 lasers so that the sum of the energies of two photons does not change. These dependences clearly characterize the relation between the effects of two-photon and step processes on photoionization and are of particular significance for the selective photoionization of lutetium. The hyperfine structures of the levels of the ^{176}Lu and ^{175}Lu isotopes are such that the frequencies of almost all lines of ^{176}Lu are higher in the first step and lower in the second step than the frequencies of the nearest lines of ^{175}Lu. In particular, if the difference between the frequencies of the first $F_0 = 8.5 \rightarrow F_1 = 9.5$ transition in the ^{176}Lu isotope and the nearest $F_0 = 5 \rightarrow F_1 = 6$ transition in the ^{175}Lu isotope is 2.8 GHz, the difference between the frequencies of the $F_1 = 9.5 \rightarrow F_2 = 8.5$ transition in the ^{176}Lu isotope in the second step and the nearest $F_1 = 6 \rightarrow F_2 = 5$ transition in the ^{175}Lu isotope is −1.1 GHz. Thus, the difference between the sums of frequencies of the first and second transitions decreases to 1.7 GHz, increasing the probability of the two-photon excitation of the isotope. This effect is particularly pronounced in the photoionization of the ^{177}Lu and ^{177m}Lu radionuclides, where the suppression of two-photon processes by means of the delay of the second- and third-step laser pulses with respect to the first-step pulses significantly increases the selectivity [1].

Figure 4 shows the dependence of the photoion signal at the detuning of the wavelength of the DL1 laser from the resonance. It is seen that the experimental data at a detuning larger than 500 MHz correspond well to the Lorentz contour with a FWHM of 30 MHz. Thus, the joint effect of the natural broadening of the atomic line, contour of the laser line, and oscillations of the populations with the Rabi frequency far from the resonance on the efficiency of photoionization is described by a homogeneous con-

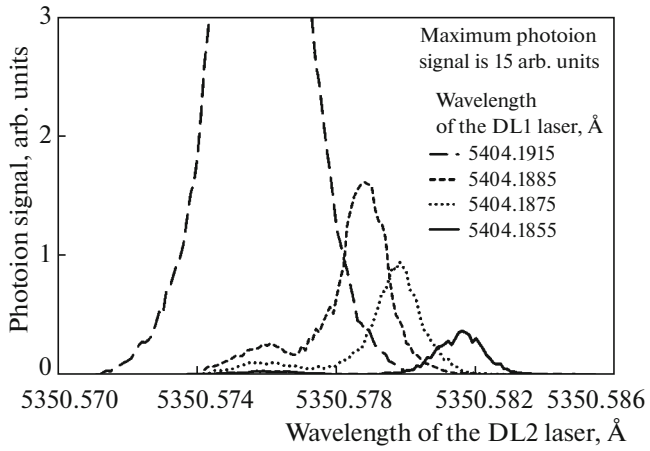

Fig. 3. Photoion signal of ^{176}Lu at the scanning of the wavelength of the DL2 laser near the $F_1 = 4.5 \rightarrow F_2 = 5.5$ (5350.5760 Å) resonance and at different detunings of the wavelength of the DL1 laser from the $F_0 = 5.5 \rightarrow F_1 = 4.5$ (5404.1915 Å) resonance. The radiation from the DL3 laser is in resonance with the $F_2 = 5.5 \rightarrow F_3 = 6.5$ (6180.0215 Å) transition. The intensities of the laser radiation in the first, second, and third steps are 135, 10, and 140 W/cm^2, respectively.

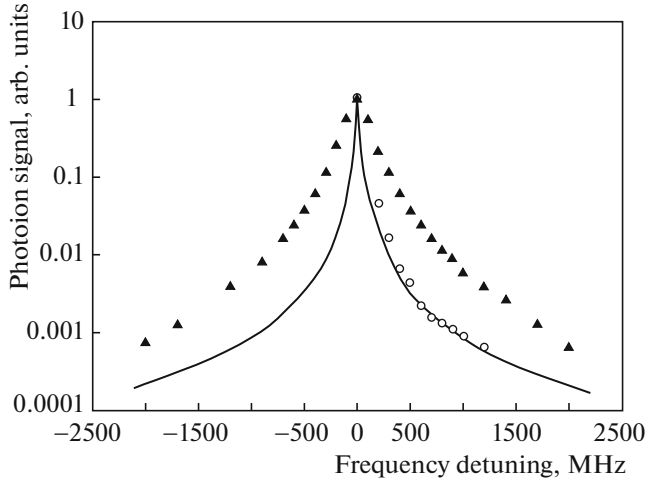

Fig. 4. Photoion signal of ^{176}Lu versus (circles) the frequency detuning of the DL1 laser from the $F_0 = 5.5 \rightarrow F_1 = 4.5$ (5404.1915 Å) resonance at the frequency of the DL2 laser in resonance with the $F_1 = 4.5 \rightarrow F_2 = 5.5$ (5350.5760 Å) transition and (triangles) the simultaneous detuning of the radiation from the DL1 laser and the DL2 laser from resonances with the conservation of the sum of the energies of two photons, as well as (solid line) the Lorentz contour with the FWHM $\Delta\nu_L = 30$ MHz. The intensities of the laser radiation in the first, second, and third steps are 135, 10, and 140 W/cm^2, respectively; the frequency of the DL3 laser is in resonance with the $F_2 = 5.5 \rightarrow F_3 = 6.5$ (6180.0215 Å) transition.

tour with a width of 30 MHz. In this case, the tuning of the DL1 laser to resonance with the $F_0 = 8.5 \rightarrow F_1 = 9.5$ transition in the ^{176}Lu isotope results in the excitation weaker by a factor of 10^4 of the undesired ^{175}Lu isotope on the $F_0 = 5 \rightarrow F_1 = 6$ transition, which is separated by 2.8 GHz from the $F_0 = 8.5 \rightarrow F_1 = 9.5$ transition in the ^{176}Lu isotope, which ensures the selectivity of photoexcitation in the first step of 10^4. Taking into account that the excited states with $F_1 = 7.5$ and 8.5 are separated from the $F_0 = 8.5 \rightarrow F_1 = 9.5$ resonance by 5 and 7 GHz, respectively, the photoionization of the ^{176}Lu isotope at the tuning of the DL2 laser to the second $F_1 = 7.5 \rightarrow F_2 = 8.5$ and $F_1 = 8.5 \rightarrow F_2 = 8.5$ transitions is 5.6×10^{-5} and 1.8×10^{-5}, respectively, of the photoionization through the $8.5 \rightarrow 9.5 \rightarrow 8.5$ continuum channel and is beyond an experiment sensitivity of 10^{-3}.

The contour of the spectrum of the dye lasers measured by the confocal scanning interferometer is the result of averaging over 10^4–10^5 pulses. It is obvious that a change in the length of the cavity of a dye laser

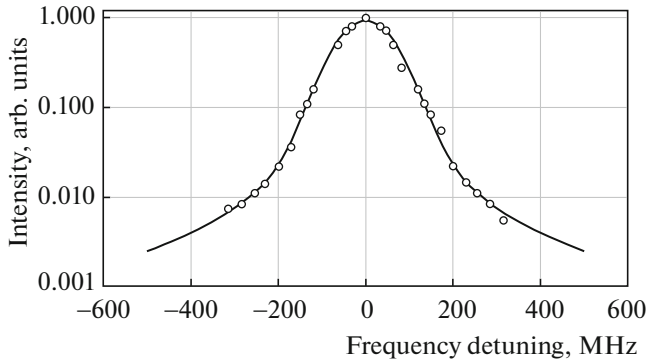

Fig. 5. (Circles) Experimental points of the contour of the spectrum of the dye laser and (solid line) the Voigt contour with a FWHM of 145 MHz, which is the sum of the homogeneous (25 MHz) and inhomogeneous (120 MHz) widths.

(mechanical vibrations, fluctuations of the flux density and the temperature of the dye solution, etc.) broadens the contour, and the spectral width in each single generation pulse is smaller. Figure 5 shows the spectral contour of the radiation from the dye laser, which is approximated by the Voigt function with an inhomogeneous width of 120 MHz and a homogeneous width of 25 MHz. The contour of the laser line far from the resonance is determined by the homogeneous width 25 MHz, which is in agreement with the photoionization spectrum in the first step (Fig. 4).

Significant differences between our experimental results and calculations in [4] can possibly be explained as follows. The Rabi frequency Ω characterizing oscillations of the populations of the levels involved in photoionization is given by the formula

$$\Omega = 2\sqrt{\frac{3g\gamma\lambda^3}{8\pi hc}}\sqrt{(2F+1)(2F'+1)}\begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}\sqrt{I}, \quad (1)$$

where g is the statistical weight of the upper level; γ is the transition strength; λ is the wavelength of the transition; h is the Planck constant; c is the speed of light; J and F (J' and F) are the quantum numbers of the lower (upper) state; I is the intensity of the laser radiation, and

$$\begin{Bmatrix} J & 1 & J' \\ F' & I & F \end{Bmatrix}$$

is the Wigner 6j symbol. The corresponding formula in [4] is proportional to the factor $3g\gamma\lambda^3/(8\pi hc)$ rather than to its square root as Eq. (1). This factor overestimates the Rabi frequency by several orders of magnitude and can be responsible for errors in calculations.

4. CONCLUSIONS

The photoionization spectra in the first and second steps of the three-step scheme of lutetium photoionization to continuum at the detuning of the wavelength of the dye laser in the third step from the autoionization resonance have been studied experimentally. The measurement of the second-step photoionization spectrum of natural lutetium isotopes at the tuning of the first-step laser to resonance with the first transition in the case of photoionization to continuum has shown the absence (within an accuracy of 10^{-3}) of additional photoionization peaks predicted in [4]. The second-step spectra recorded at different detunings of the first-step dye laser from the resonance have indicated that two-photon processes noticeably prevail over several-step resonant processes and can significantly affect the selectivity of photoionization.

The study of the photoionization spectrum in the first step has shown that the spectral wing in the case of the detuning of the dye laser from the resonance by more than 500 MHz corresponds to a homogeneous Lorentz contour with a width of 30 MHz, which is in good agreement with the contour of the line of the dye laser. The intensities of photoionization peaks predicted in [4] have been estimated at $(2–6) \times 10^{-5}$ of the amplitude of the main peak.

FUNDING

This work was supported by the Russian Science Foundation (project no. 17-13-01180).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Ageeva, I.V., Dyachkov, A.B., Gorkunov, A.A., Labozin, A.V., Mironov, S.M., Panchenko, V.Ya., Firsov, V.A., Tsvetkov G.O., and Tsvetkova, E.G., *Quantum Electron.,* 2019, vol. 49, no. 9, p. 832.
2. D'yachkov, A.B., Gorkunov, A.A., Labozin, A.V., Makoveeva, K.A., Mironov, S.M., Panchenko, V.Ya., Firsov, V.A., and Tsvetkov, G.O., *Opt. Spectrosc.,* 2020, vol. 128, p. 6.
3. Autler, S.H. and Townes, C.H., *Phys. Rev.,* 1955, vol. 100, p. 703.
4. Suryanarayana, M.V., *J. Opt. Soc. Am. B,* 2021, vol. 38, p. 353.
5. Choe, A.S., Rhee, Y., Lee, J., Kuzmina, M.A., and Mishin, V.A., *J. Phys. B At. Mol. Opt. Phys.,* 1995, vol. 28, p. 3805.
6. Choe, A.S., Rhee, Y., Lee, J., Borisov, S.K., Kuzmina, M.A., and Mishin, V.A., *Nonlinear Spectrosc. Ultrafast Phenom.,* 1996, vol. 2797, p. 290.
7. D'yachkov, A.B., Gorkunov, A.A., Labozin, A.V., Mironov, S.M., Panchenko, V.Ya., Firsov, V.A., and Tsvetkov, G.O., *Quantum Electron.,* 2018, vol. 48, no. 1, p. 75.
8. D'yachkov, A.B., Gorkunov, A.A., Labozin, A.V., Mironov, S.M., Panchenko, V.Ya., Firsov, V.A., and Tsvetkov, G.O., *Instruments Exp. Tech.,* 2018, vol. 61, p. 548.
9. Bushaw, B.A., Nörtershäuser, W., and Wendt, K., *Spectrochim. Acta, Part B At. Spectrosc.,* 1999, vol. 54, p. 321.

Translated by R. Tyapaev