

Radiative lifetimes, branching ratios and absolute transition probabilities of atomic uranium by delayed photoionization measurements

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Abstract Radiative lifetimes of ten even-parity energy levels of atomic uranium in the 15,500–19,000 cm^{-1} region and branching ratios of six transitions originating either from ground level ($^5L_6^0$) or from lowest metastable level ($^5K_3^0$) at 620.32 cm^{-1} are measured employing three-step delayed photoionization technique. The lifetimes of five energy levels and branching ratios of five transitions are measured for the first time. By combining the experimentally measured values of radiative lifetimes and branching ratios, we have determined the absolute transition probabilities of six transitions of uranium and compared with those previously reported in the literature.

1 Introduction

Radiative lifetime, branching ratio and transition probability are important parameters of an atomic system. The accurate knowledge of these parameters in general and transition probability in particular is of great interest in many areas of basic science such as atomic physics, laser physics, astrophysics and in laser-based applications such as isotope selective photoionization processes, elemental ultra-trace analysis, etc. The uranium atom, over the past three and half decades, has been a subject of intense spectroscopic investigations, which have resulted in large

information on these parameters [1–18 and references therein]. However, the precise information on these parameters is far from complete. Considering the ionization potential (IP) of uranium 49,958.4 cm^{-1} [11], a three-step resonant ionization is most appropriate for an isotope selective photoionization process based on visible lasers. In the three-step photoionization of uranium (Fig. 1), the atom in the ground level ($^5L_6^0$) or in the lowest metastable level ($^5K_3^0$) at 620.32 cm^{-1} is excited up in the ladder sequentially by first- and second-step lasers to one of the even-parity energy levels in the 15,000–19,000 cm^{-1} region and the odd-parity energy levels in the 30,000–36,000 cm^{-1} region, respectively, before it is finally photoionized in the third step by another laser. Therefore, the information on the spectroscopic parameters in these energy regions is prerequisite to identify an efficient three-step photoionization wavelength scheme for isotope selective photoionization process of uranium and its quantification.

Conventionally, the transition probabilities are obtained either from the measurement of relative line strengths in the emission spectra acquired from arcs, sparks or discharge lamps or from the measurement of absolute absorption [1–3, 13–16]. The accuracy of these measurements is limited by the uncertainties associated with the source temperature, relative emission intensities over wide wavelength range, atomic vapor density, density profile, path length, self-absorption, etc. In recent years, one of the most commonly used methods to obtain the transition probability is based on the measurements of branching ratio (β) and radiative lifetime (τ), where β is generally determined from the relative intensities of emission lines measured over a wide wavelength range using Fourier transform spectrometer and τ is measured independently [19, 20]. The absolute transition probability (A) is related to these two atomic parameters by a well-known relation,

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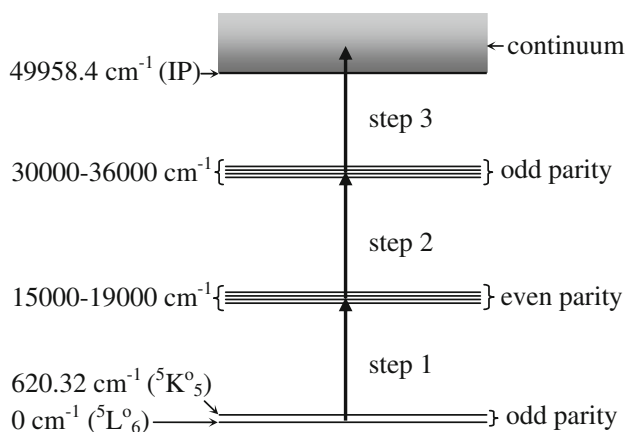


Fig. 1 Typical three-step photoionization pathway for atomic uranium using visible lasers

$A = \beta/\tau$, where β is the branching ratio of the transition and τ is the lifetime of the upper level. In this method, the complete understanding of the emission spectra is necessary for accurate measurement of the absolute transition probability. With the presence of six optically active electrons in the outer most shell, the electronic structure of uranium is quite complex and hence this method is not advantageous for such heavy elements. Avril et al. [17] have measured the β values of atomic uranium transitions originating from a highly excited odd-parity energy level at $34,659 \text{ cm}^{-1}$ using laser-induced fluorescence (LIF) and independently measured the τ -value of this level using delayed photoionization technique. However, one of the major disadvantages of this method is that a large number of undetected infrared transitions, particularly in case of uranium, may result in overestimation of transition probabilities. The other laser-based methods such as laser saturation of transition, Rabi frequency measurement and Autler–Townes splitting, etc. [21, 22] are not significantly

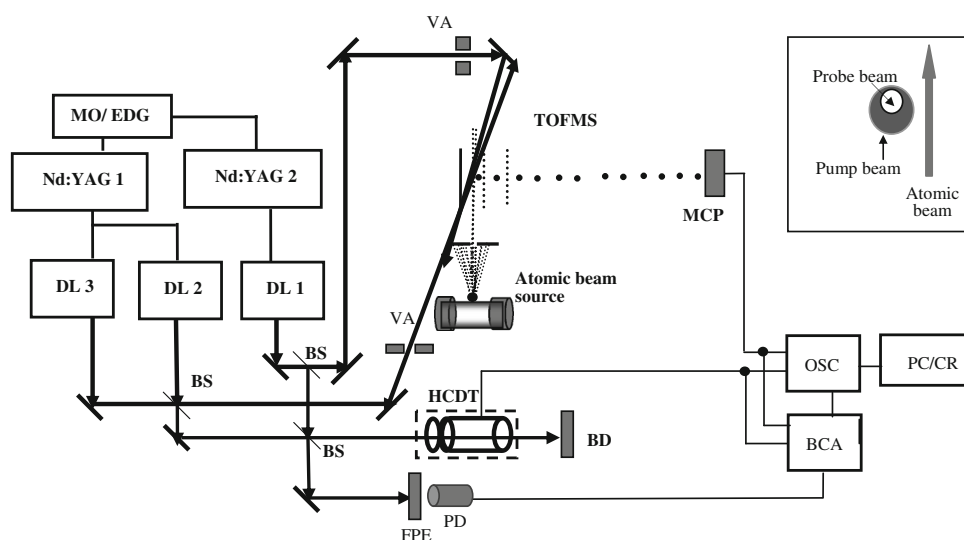
affected by these uncertainties, but put stringent requirements on the laser parameters such as spectral width and temporal profile of the laser pulse.

Carlson et al. [8] have developed an alternative method of measuring absolute transition probability based on the delayed photoionization technique which is not subjected to these difficulties. Using this method, they have measured branching ratios of uranium transitions at 4,362.1 and 4,393.6 Å wavelengths in the blue region of uranium spectra and radiative lifetimes of the upper levels of these transitions independently. Hackel et al. [9] have refined this to accurately measure the transition probability of a uranium transition at 6,395.42 Å in the red region of uranium spectrum. Miyabe et al. [23] have exploited the same to measure the absolute transition probabilities of gadolinium. Bisson et al. [24] have extended it further to measure the excited-state-to-excited-state transition probability of cerium. In this paper, we report the results of our measurements on radiative lifetimes and branching ratios of uranium performed in an atomic beam coupled to a time-of-flight mass spectrometer (TOFMS) in the $15,500\text{--}19,000 \text{ cm}^{-1}$ region employing the three-step delayed photoionization technique using Nd:YAG laser-pumped pulsed dye lasers. Further, by combining the measured values of the radiative lifetimes and the branching ratios, the absolute transition probabilities of six transitions of uranium are determined and compared with the values reported in the literature.

2 Experimental

Figure 2 shows the schematic diagram of the experimental setup used in these studies. It consists of three pulsed dye lasers pumped by second harmonic of two Nd:YAG lasers

Fig. 2 Schematic of experimental setup. MO master oscillator, EDG electronic delay generator, DL dye laser, BS beam splitter, HCDT hollow cathode discharge tube, BD beam dump, BCA box car averager, PC/CR personnel computer/ chart recorder, TOFMS time-of-flight mass spectrometer, DSO digital storage oscilloscope, MCP micro-channel plate detector, VA variable aperture, FPE Fabry–Perot etalon and PD photodiode. Inset cross-sectional view of the laser beams in the interaction zone



at 532 nm, a high temperature oven assembly coupled to a TOFMS built-in-house, a U–Ne hollow cathode discharge tube (HCDDT), Fabry–Perot (FP) etalon, photodiode, digital oscilloscope, etc. The spectral width, repetition rate and temporal pulse width of the lasers are $\sim 0.05 \text{ cm}^{-1}$, 20 Hz, $\sim 8 \text{ ns}$ (FWHM), respectively. One of the three dye lasers is used as a pump, and the other two are used as probe. Temporal sequencing of laser pulses from different lasers is achieved using an electronic delay generator. The pump and probe lasers are apertured individually and spatially overlapped in the interaction zone using beam steering optics. Uranium vapor is generated by resistively heating a few hundred mg of uranium metal in a high temperature oven at $\sim 1,600 \text{ }^\circ\text{C}$ in a vacuum chamber maintained at $2 \times 10^{-7} \text{ mbar}$ pressure. The uranium atoms effusing out of the oven through an orifice of 1.5 mm diameter are further apertured at a distance of $\sim 20 \text{ mm}$ downstream by placing another fixed aperture of diameter $\sim 2 \text{ mm}$ to form a well-collimated atomic beam. Typical atomic number density in the interaction region is $\sim 10^7 \text{ cm}^{-3}$. The atomic absorption line width in the interaction zone is about 50 MHz. Spatially overlapped laser beams interact with the atomic beam in a cross-configuration, and the resultant photo-ions produced are extracted, introduced into the TOFMS by a dc electric field of $\sim 120 \text{ V/cm}$ and finally detected by a micro-channel plate (MCP) detector. A part of the laser beam is made to pass through a U–Ne HCDDT and a FP etalon of 0.5 cm^{-1} free spectral range (FSR) for the purpose of laser wavelength calibration by simultaneously recording optogalvanic signal and FP etalon transmission fringes detected with a photodiode.

3 Results and discussions

3.1 Lifetime measurement

Schematic of photoionization sequence for lifetime measurements is shown as inset in Fig. 3. The radiative lifetime measurements are carried out using two pulsed dye laser systems whose pulse timing can be finely controlled to an accuracy of $\pm 1 \text{ ns}$. The first laser is used as a pump laser to excite the uranium atoms from the ground or the first metastable level to a level of interest in the energy region $15,500\text{--}19,000 \text{ cm}^{-1}$. The population in the excited level is monitored by ionizing the excited atoms by stepwise two-photon photoionization process, using the second dye laser (probe laser) at various time delays between the pump and probe lasers. For each lifetime measurement, about 12 data points are taken and each data point is obtained after taking an average of 64 laser pulses. To avoid the effect of the excited atoms drifting

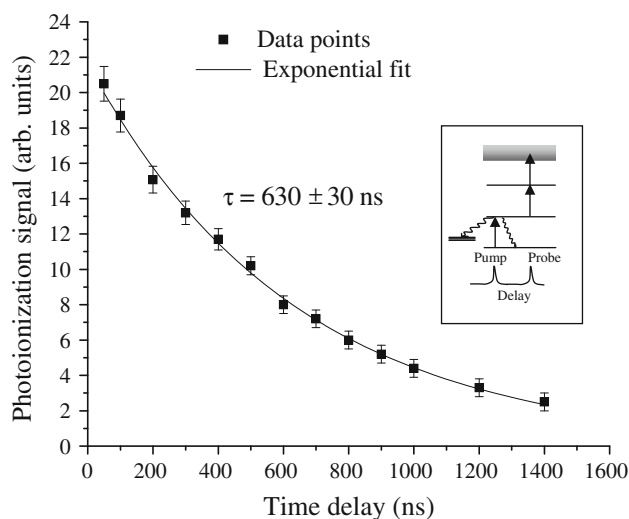
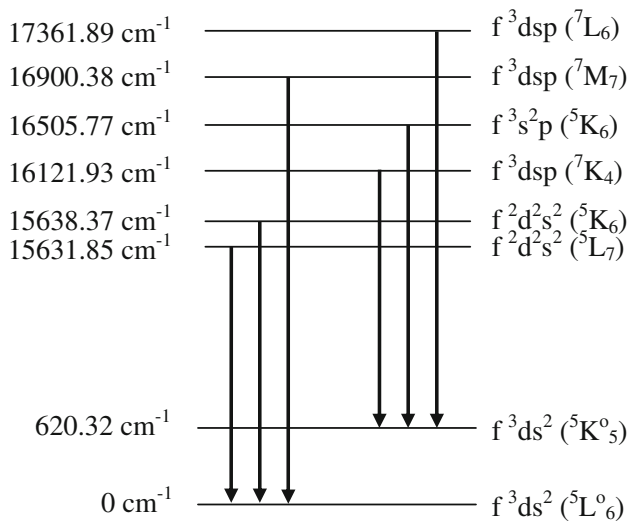


Fig. 3 Population decay curve of uranium atomic level at $15,631.85 \text{ cm}^{-1}$. The solid line is an exponential fit of the data. Inset schematic of photoionization sequence for lifetime measurements

out of the interaction volume due to atomic beam flow velocity, we have deliberately kept the pump laser beam diameter (4 mm) more compared to the probe laser diameter (2 mm). Further, the probe laser beam spot is kept downstream of the atomic beam as shown in Fig. 2 to minimize the effect of excited atoms drifting out of interaction volume at large time delays. A typical population decay curve of uranium level at $15,631.85 \text{ cm}^{-1}$ is shown in Fig. 3. These measurements have yielded the radiative lifetime of $630 \pm 30 \text{ ns}$ for this level which is close to the value of $607 \pm 20 \text{ ns}$ reported in the literature. The high resolution obtained in our TOFMS combined with that of delay generator has enabled us to make these measurements accurately. Employing the same technique, we have measured the radiative lifetimes of nine more even-parity levels of uranium in the energy region $15,500\text{--}19,000 \text{ cm}^{-1}$. The measured lifetime values of these energy levels along with reported ones are listed in Table 1. Most of the values are matching reasonably well with those reported in the literature with the exceptions of a few. Miron et al. [10] is one of the first groups who have done the most extensive work on lifetime measurements of uranium atomic levels. They have carried out the measurements in an argon buffer gas cell using LIF. Their values of lifetimes, particularly, of long-lived levels are relatively lower as compared to our values. The atomic collisions in buffer gas cell could be the reason for shortening the radiative lifetime even though the values have been corrected by extrapolating to zero pressure. In this work, the lifetimes of five even energy levels of atomic uranium have been measured for the first time.

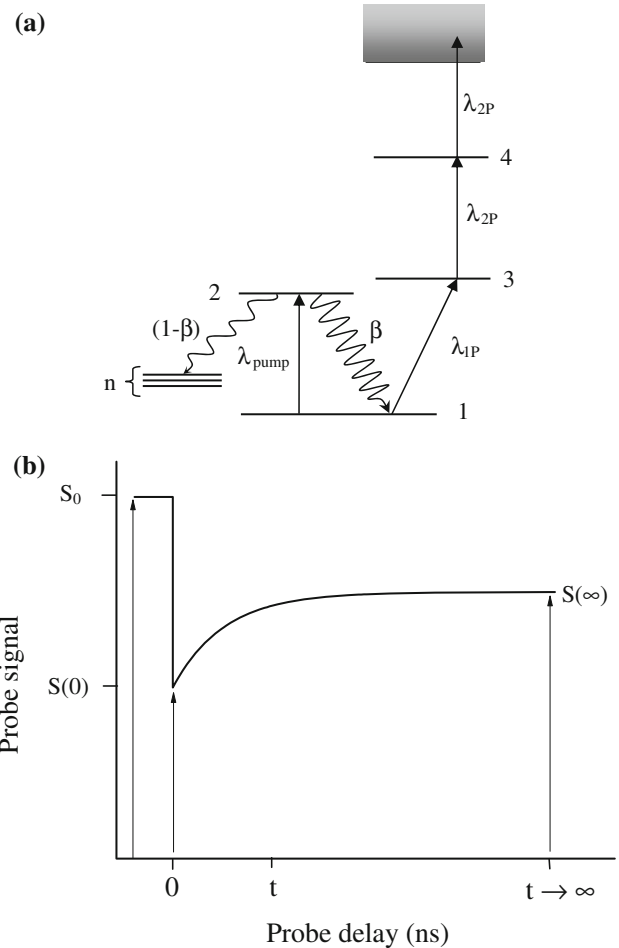
Table 1 Measured values of radiative lifetime of even-parity excited levels of uranium

Energy level (cm ⁻¹)	Angular momentum (<i>J</i>)	Measured lifetime τ (ns)	
		This work	From literature
15,631.85 ^a	7 ^a	630 ± 30	607 ± 20 ^b , 594 ^f
15,638.37 ^a	6 ^a	640 ± 40	452 ^f
16,121.93 ^a	4 ^a	275 ± 12	
16,505.77 ^a	6 ^a	585 ± 30	451 ^f , 400 ^c , 330 ± 10 ^e
16,900.38 ^a	7 ^a	200 ± 14	205 ^c , 200 ^d , 255 ± 25 ^e , 270 ^f
17,361.89 ^a	6 ^a	456 ± 30	410 ^e , 390 ± 50 ^e , 116 ^f
18,185.99 ^a	4 ^a	1,905 ± 130	
18,253.87 ^a	6 ^a	725 ± 50	
18,406.52 ^a	5 ^a	206 ± 10	
18,607.79 ^a	4 ^a	1,260 ± 80	

^a Blaise et al. [25]^b Hackel et al. [9]^c Miron et al. [10]^d Klose et al. [7]^e Carlson et al. [4]^f Arisawa et al. [12]**Fig. 4** Energy level diagram of the transitions whose branching ratios are measured

3.2 Branching ratio measurement

Six transitions of uranium whose branching ratios are measured in the present studies are as shown in Fig. 4. The measurement of branching ratio is performed using three pulsed dye lasers. One dye laser is used as a pump, and the

**Fig. 5** **a** Schematic of excitation pathways for the pump and probe lasers to measure the branching ratios. The pump laser λ_{pump} pulse excites the population from level 1 to level 2 of the transition whose branching ratio is to be determined and the laser pulses λ_{1P} plus $2 \lambda_{2P}$ generate probe signal. **b** Representative probe signal versus time delay between the pump and the probe laser pulses

other two are used as a probe. Level schematic of excitation pathways for the pump and probe lasers to measure branching ratios by delayed photoionization method is shown in Fig. 5a. The uranium atoms from level 1 (0 or 620.32 cm⁻¹) are excited to level 2 by the pump laser which is in resonance to the transition between levels 1 and 2. The population in level 1 is probed via two-color three-photon photoionization process using two synchronized probe lasers. The resultant photoionization signal is recorded as a function of delay between the pump and the probe lasers. Due to finite radiative lifetime (τ) of the excited level (2), the excited atoms decay back to various lower energy levels including level 1. The population dynamics of levels 1 and 2 just after the pump laser pulse can be written as

$$\frac{dN_1}{dt} = \beta \frac{N_2}{\tau} \quad (1)$$

$$\frac{dN_2}{dt} = -\frac{N_2}{\tau} \quad (2)$$

By solving these equations, we get

$$N_1(t) = N_1(0) + \beta N_2(0) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (3)$$

where $N_1(0)$ and $N_2(0)$ are the populations in levels 1 and 2, respectively, just after the pump laser pulse set at $t = 0$. In the case of complete saturation and equal level degeneracies, $N_1(0) = N_2(0) = N_{10}/2$, where N_{10} , is the initial population of level 1 just before the pump laser pulse. The photoionization signal produced by the probe lasers is directly proportional to the population of the level 1. Due to repopulation of the level 1 by spontaneous decay of the level 2, the probe signal increases with time delay between the pump and probe lasers. The delayed photoionization signal of the probe from the level 1 is depicted in Fig. 5b, where S_0 represents the photoionization signal of probe laser in the absence of pump laser, $S(0)$ is the signal of the probe laser when both the pump and probe lasers are synchronous, i.e., at $t = 0$ and $S(\infty)$ is the probe signal at infinite time delay between the pump and probe lasers, i.e., at $t \rightarrow \infty$. The branching ratio can then be written as $\beta = [S(\infty) - S(0)]/[S_0 - S(0)]$, where $[S_0 - S(0)]$ represents the depopulation of level 1 at time $t = 0$ and $[S(\infty) - S(0)]$ is the repopulation of the level 1 at time $t \rightarrow \infty$. Repopulation of level 1 due to the radiative decay from the level 2 is about 99.3 % at $t = 5\tau$, which is a good approximation for $t \rightarrow \infty$.

The experimental points on the repopulation curve for the branching ratio measurement of uranium transition at 6,395.42 Å are shown in Fig. 6. In these measurements, the pump laser wavelength (λ_{pump}) tuned to the uranium transition at 6,395.42 Å excites the atomic population to the upper level at 15,631.85 cm^{-1} from the lower level, i.e., the ground level. Due to finite lifetime of the upper level, its population decays back to various levels, including the ground level. The population of the lower level is monitored via two-color three-photon photoionization technique using the other two probe lasers. The first-step probe laser wavelength (λ_{1P}) tuned to the uranium transition 0–16,900.38 cm^{-1} at 5,915.4 Å excites the uranium atom from the ground level to the level at 16,900.38 cm^{-1} , and second-step probe laser tuned to the uranium transition 16,900.38–34,523.36 cm^{-1} at 5,672.8 Å excites the atoms further up in the ladder before the atoms are ionized by another photon from the same laser. Initially, when the pump and the probe lasers are simultaneous, maximum depopulation of the ground level

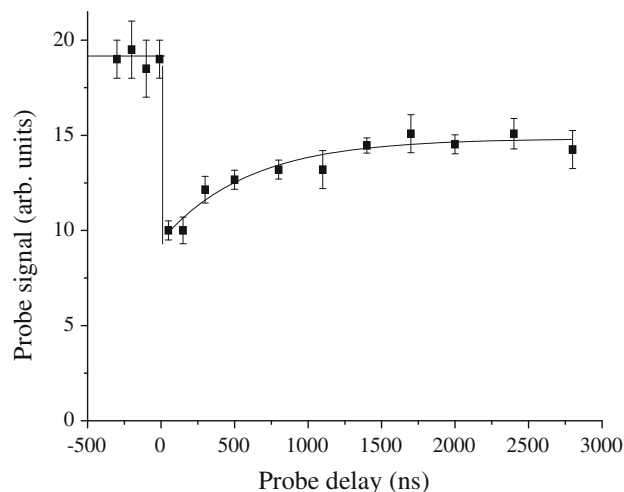


Fig. 6 Repopulation curve of the ground level of uranium from excited atomic level at 15,631.85 cm^{-1} . The solid line is a fit of the data using Eq. (3) for $\beta = 0.57 \pm 0.05$ and $\tau = 592 \pm 60$ ns

is observed. Thereafter repopulation of the lower level is monitored as a function of the delay between the pump and probe lasers. The value of the branching ratio for the uranium transition at 6,395.42 Å is obtained by fitting the repopulation data using Eq. (3), as shown in Fig. 6. The measured β value comes out equal to 0.57 ± 0.05 and match very well with the measurements made by Hackel et al. [9]. Table 2 lists the branching ratios of various transitions measured in the present work along with others reported in the literature. Branching ratios of five transitions in this work are measured for the first time to the best of our knowledge. Also listed in Table 2 are the gA values (g is the upper level degeneracy) of transitions obtained by combining the radiative lifetime and branching ratio. Our values of transition probabilities are on slightly higher side as compared to those of Corliss et al. [3]. They have made the measurements in an arc, in which high density of vapor could lead to lower values due to self-absorption. This is further corroborated by the fact that our values are matching exceedingly well with those of Kapoor et al. [16] who have taken care of self-absorption at the source in their measurements. In view of this, the gA values of the remaining three transitions as measured by Corliss et al. [3] need to be corrected.

In the present measurements following steps have been taken to minimize the error:

- Error due to transit time effect (drift out of excited atoms from interaction volume) is minimized by using a larger pump beam compared to probe beam of the lasers as shown in Fig. 2. In our experimental conditions, the estimated drift out time is $\sim 5 \mu\text{s}$ where as our measurements are limited to $3 \mu\text{s}$.

Table 2 Measured values of branching ratio and gA values of uranium

Energy levels (cm^{-1})		Present work		Reported	
Lower	Upper	β	gA value ($\times 10^6 \text{ s}^{-1}$)	β	gA value ($\times 10^6 \text{ s}^{-1}$)
0	15,631.85	0.57 ± 0.05	13.6 ± 1.35	0.586 ± 0.05^a	$14.5 \pm 1.25^a, 11^b$
0	15,638.37	0.19 ± 0.04	3.9 ± 0.86		3.5^b
620.32	16,121.93	0.88 ± 0.08	28.8 ± 2.90		$16^b, 32^c$
620.32	16,505.77	0.15 ± 0.04	3.3 ± 0.90		3^b
0	16,900.38	0.63 ± 0.06	47.3 ± 5.59		$53.8^c, 35^b, 68^d$
620.32	17,361.89	0.44 ± 0.04	12.5 ± 1.40		9.8^b

^a Hackel et al. [9]^b Corliss et al. [3]^c Kapoor et al. [16]^d Klose et al. [7]

- b. Error due to spatial variation in the laser intensity is minimized by selecting the central part of the laser beams with uniform intensity.
- c. Probe lasers wavelengths are chosen carefully so that these do not produce any two-color three-photon photoionization from the upper level of pump laser transition.
- d. Another potential source of error in the lifetime measurements could be the excitation of high-lying atomic levels via two-photon excitation for the laser intensities and line width used in these experiments. These can influence the lifetimes due to cascading effect. Since the lifetime values obtained through two independent measurements (radiative decay and repopulation of lower level) match well within our experimental errors, such a possibility is ruled out.
- e. Effect of pulse to pulse variation in the laser intensity is minimized by taking average of 64 laser pulses for each data point.
- f. Due to polarization of laser beams, pumping process and subsequent spontaneous decay will preferentially populate the specific magnetic sublevel (m_j). This could give rise to another source of error in the measurement of branching ratios, particularly in the case of elements with low J -values such as zirconium, samarium, etc. However, in the case of uranium, J -values are generally high; hence, this is also not expected to affect the measurements significantly [24]. Moreover, we have chosen the photoionization scheme for the probe such that J -values of the atomic levels involved in the scheme are either equal or increasing in order as we move up in the ladder, thus reducing any such error.

However, there is a statistical error of 4–7 % in the lifetime measurements, whereas in case of branching ratio measurements, this error is in the range of 5–10 % for high β values and could be up to 30 % for weak transitions. Poor

signal-to-noise ratio, particularly in the case of weak transitions, could be the reason for large error in the branching ratio and also the limiting factor in these measurements. In addition to the above, drift in oven temperature and subsequent change in atoms number density during measurements could be further source of additional error.

4 Conclusions

We have measured radiative lifetimes of ten even-parity energy levels of uranium in the 15,500–19,000 cm^{-1} region and branching ratios of six transitions originating either from ground level ($^5L_6^o$) or from lowest metastable level ($^5K_3^o$) at 620.32 cm^{-1} , employing three-step delayed photoionization technique. The lifetimes of five energy levels and the branching ratios of five transitions have been reported for the first time. Most of our measured values of lifetimes match well with those published in the literature, and the possible deviations have been explained. By combining these experimentally measured lifetimes and branching ratios, absolute transition probabilities of six transitions have been determined and compared with those reported in the literature.

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