Observation of Autoionization Resonances in Uranium by Step-wise Laser Photoionization


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Abstract. A large number of autoionization resonances have been observed in uranium in the energy range 50,590–51,560 cm\(^{-1}\) by two-step three-photon ionization technique, using two copper vapor laser pumped dye lasers. A Rydberg series converging to the ionization limit of UII at 1749 cm\(^{-1}\) (\(6L_{13/2}\)) has been identified. Some of these resonances are very narrow with a fwhm of 0.1 cm\(^{-1}\). Possible origins of these are discussed.

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In recent years, autoionization studies in complex atoms have attracted considerable attention because of their important role in Laser Isotope Separation (LIS) research, Resonance Ionization Mass Spectrometry (RIMS), trace analysis etc. [1]. Autoionization by multistep laser excitation enhances the photoionization cross-section in the last step, and, therefore, the efficiency of the overall ionization process. Most of the known autoionization resonances for different elements are generally wide (> 10 cm\(^{-1}\)), and only in a few cases, narrow resonances (< 0.25 cm\(^{-1}\)) are known [1].

Using step-wise laser photoionization technique, autoionization resonances have been detected for some 4f and 5f elements – gadolinium [2, 3], ytterbium [4] and uranium [5–8]. Some autoionization resonances in ytterbium have been observed to be narrow (1 cm\(^{-1}\)), and one resonance in gadolinium very narrow (<0.1 cm\(^{-1}\)). Effect of low electric fields on these resonances has been studied, and theoretical models proposed to explain the small widths of these resonances and dependence of their widths on electric field [3]. The fwhm of autoionization resonance in gadolinium of 0.075 cm\(^{-1}\) corresponds to a cross-section of 10\(^{-15}\) cm\(^2\) for the ionizing step in the multi-step laser ionization process. This cross-section is comparable with cross-sections for transitions to bound states.

Identification of the Rydberg levels of uranium from about 200 cm\(^{-1}\) below its first ionization limit and of autoionization levels to 2000 cm\(^{-1}\) or so above it, evaluating cross sections for transitions to these levels for radiation above 500 nm, and understanding the effect of electric and magnetic fields on them is of paramount interest not only for a theoretical understanding of the energy level structure of uranium atom, but also for practical considerations.

Extensive studies of this nature have been carried out on uranium in the last few years by several groups [5–10], but very little is published. The only detailed papers in this area are those of Solarz et al. [5–6] and Coste et al. [8]. Using a four-step laser ionization scheme, three lasers in the visible region and CO\(_2\) laser, Solarz et al. identified a few Rydberg series within 1000 cm\(^{-1}\) of the first ionization limit of uranium, and proposed that the series belong to highly excited configurations, \(5f^37s^2np\) and \(5f^37s^2nf\), \(n\) exceeding 40. Using a three-step ionization scheme, all steps provided by dye lasers in the visible region, Coste et al. [8] studied the ionization spectrum of uranium from below its first ionization limit to over 400 cm\(^{-1}\) above it. They identified two Rydberg series of \(5f^37s^2np\) and \(5f^37s^2nf\) configurations converging to the lowest ionization limit \(5f^37s^2(4^1\Sigma_g^+)\) of UI and three series, \(f^3dnp\), \(f^3dsn\), and \(f^3dsnd\), lying between the lowest and the next ionization limit of uranium. They, in
particular, reported that amongst all the resonances they observed above the second ionization limit of uranium, viz., above 50,250 cm\(^{-1}\), no narrow resonances were found.

As a part of an extensive program undertaken in our laboratory to study the high lying energy levels of uranium [11–16], we have carried out two-step three-photon ionization of uranium using two CVL pumped dye lasers. We report here the observation of a rich autoionization spectrum from the 33,801.05 cm\(^{-1}\) level of uranium, which was reached by single-colour two-photon excitation from the ground level.

Experimental

The experimental set-up used has been described earlier [12]. Briefly, it consists of two pulsed tunable dye lasers, DL\(_1\) and DL\(_2\), pumped by a single copper vapour laser. The two dye laser beams were focussed to spatially overlap onto the uranium atomic beam in a quadrupole mass analyser. The first dye laser, DL\(_1\), excites uranium atoms from the ground state to the level at 33801.05 cm\(^{-1}\) by two-photon absorption; the corresponding wavelength was fixed by an interferometric wavelength control set-up [17]. The second dye laser was scanned in the range 560–600 nm, and autoionization resonances were recorded. The relevant excitation scheme is shown in Fig. 1. The time delay of 25 ns between the first and the second dye laser pulses (fwhm: 15 ns) avoided any significant temporal overlap between them and ensured that the ionization sequence is, as shown in Fig. 1. The linewidth of the first dye laser, DL\(_1\), was narrow (0.08 cm\(^{-1}\)) so that a simultaneous excitation of the \(^{3}M_{J}\) resonance level of uranium at 16900.38 cm\(^{-1}\) did not take place. This was verified by the absence of optogalvanic signal in an uranium hollow cathode discharge at this DL\(_1\) wavelength and its strong appearance when DL\(_1\) was tuned to a slightly longer wavelength. Single-colour ionization spectrum, with DL\(_1\) blocked and DL\(_2\) scanning, was taken to identify single-colour resonances in our ionization spectrum.

Recording of the spectrum was done, as described in [12]. The absolute wavelength scale was generated by optogalvanic spectrum in an uranium hollow cathode discharge and the relative scale by F.P. interferometer fringes. The accuracy of measurement of autoionization resonances was ±0.10 cm\(^{-1}\).

Results and Discussion

Operating from the 33801.05 cm\(^{-1}\) odd level of UI, we have been able to explore its autoionization levels in the energy region 50,590–51,560 cm\(^{-1}\), i.e. 630–1600 cm\(^{-1}\) above the ionization limit. We could observe over 200 resonances having fwhm mostly ranging from ~0.1 to about 1.0 cm\(^{-1}\). There are about ten resonances with widths >1.0 cm\(^{-1}\). Figure 2 shows a portion of the autoionization spectrum of uranium. Positions of the autoionization resonances and their widths and intensities are given in Table 1. The peak intensities of the resonances are given in an arbitrary scale taking the intensity of the strongest peak as 100. The actual widths of the very narrow resonances (~0.1 cm\(^{-1}\)) observed must be lower than that shown in Table 1 since the linewidth of the scanning laser itself was 0.08 cm\(^{-1}\). To the best of our knowledge, observation of such narrow resonances in uranium is being reported for the first time. Very narrow ionization resonances imply large decay life times (~1 ns) and relatively large peak photoionization cross sections.

To be able to understand, even qualitatively, the observed autoionization resonances in a complex atom like uranium, one should have a reasonable idea of the energy level structure of the neutral uranium atom above its ionization limit. In the region from below 500 cm\(^{-1}\) to the ionization limit of uranium, we have short lived valence states with low \(n\) values and