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Two-Step Single-Colour Photoionization Spectroscopy of Atomic Uranium

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Abstract. The single-colour photoionization spectrum of atomic uranium is recorded in the spectral region from 366 to 371 nm. Most of the 43 observed resonances are found to be associated with the two-step photoionization process. Based on known energy levels seven new transitions have been proposed. Three of these transitions originate either from the ground state or the lowest metastable state at 620 cm^{-1}.

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The use of laser-ionization as a spectroscopic tool to study the energy levels of complex atoms, like uranium, was first reported by Janes et al. [1]. Since then considerable work on the spectrum of uranium atoms using variations of the laser-ionization technique has been reported from different laboratories. Generally, one requires more than one tunable laser for a systematic and detailed spectroscopic investigation of atoms by photoionization. On the other hand, single-colour ionization using a single dye laser is a simple technique and is useful for some studies, even though information obtainable from such studies is limited.

Single-colour ionization of uranium has been reported in the visible spectral region by several groups: Donohue et al. [2] from 580 to 607 nm, Mago et al. [3] from 550 to 580 nm, Chang-Tai et al. [4] from 587 to 600 nm, and Ray et al. [5] from 615 to 670 nm. Most of these studies suggest a three-photon ionization process for the observed resonances except for the last work in which some four-photon resonances have also been suggested. Here, we report the results of photoionization studies carried out on uranium atoms in the ultraviolet region, viz. 366 to 371 nm. Since the ionization potential of uranium is 49,958.4 cm^{-1}, only two-photons are required to ionize a uranium atom from its ground and low-lying metastable states. The interpretation of single-colour three/four-photon resonance ionization spectra is in general complicated as there are many available ionization pathways [3, 5]. On the other hand, single-colour two-photon ionization spectra are simple to understand as they involve only one pathway, namely the two-step ionization. Furthermore, the photoionization yield of a single-colour two-step process is, in general, higher than that of a single-colour resonant three-photon process. Therefore, a two-step ionization process has higher sensitivity for trace analysis by the resonance ionization mass spectrometric (RIMS) technique.

In the present study 43 ionization resonances have been observed. 33 of these have been identified as two-step photoionization resonances, using known transition assignments [6] for the first-step. Plausible identification of the first resonant step for eight out of the remaining ten resonances have also been suggested. As a result seven new transitions are proposed. Three of these transitions originate either from the ground state or the lowest metastable state at 620 cm^{-1}. The rest start from other low-lying odd-parity states of uranium.

Experimental Details

The experimental arrangement is an extension of the one described earlier [3]. Figure 1 shows a schematic diagram of the experimental setup. A beam of neutral uranium atoms, generated in a vacuum chamber by heating a uranium-rhenium alloy, is allowed to interact with UV photons from a tunable laser. The second-harmonic of a Nd:YAG laser pumps a dye laser (rhodamine 6G). The tunable output of the dye laser (559 nm–569 nm) is frequency mixed with the Nd:YAG fundamental at 1064 nm, using a KD^*P crystal in the wavelength extension (WEX) unit of the system. This frequency-mixed output is tunable in the ultraviolet range from 366 to 371 nm and is used for the photoionization experiments. The tunable UV radiation has a linewidth of about 1 cm^{-1}, pulse duration of 7 ns and pulse energy density varying from 50–100 $\mu J/cm^2$ over its tuning range.

A two-stage time-of-flight mass spectrometer has been incorporated for mass analysis of the ions produced in the interaction region [5]. The interaction of the laser beam with the atomic beam takes place between the ion-repeller anode and the first grid. In the first stage of acceleration a small electric field (74 V/cm) extracts ions from the interaction region through the first grid into another region of higher electric field (740 V/cm). This field accelerates the ions to full energy and allows them to pass into a

field-free drift tube, where they travel about one meter before reaching the electron multiplier detector. The mass-resolution (≅ 200) was sufficient to resolve the signal due to uranium ions from those due to UO^+ and UO_2^+ ions present as impurities in the atomic beam. For the initial identification of resonances, an optogalvanic signal from a uranium-argon hollow-cathode lamp and interference fringes from a Fabry-Perot etalon (FSR ≅ 0.98 cm^{-1}), obtained by utilizing a part of the visible dye laser beam as it is scanned, are recorded simultaneously on a three-pen chart-recorder. Strong resonances are identified in the ionization spectrum. These resonances are then used for measuring the wavenumbers of all the other resonances.

Results and Discussions

A typical part of the photoionization spectrum obtained with the tunable UV laser beam, together with the Fabry-Perot etalon fringes, recorded with the visible output of the dye laser is presented in Fig. 2. Table 1 lists the vacuum wavenumber of all the resonances observed in the photoionization spectrum along with their relative intensities and widths (FWHM). The wavenumbers listed are averages of measurements on three different spectra recorded under identical conditions, and were reproducible to within ±0.3 cm $^{-1}$. The FWHM of the majority of resonances is around 1 cm^{-1}, which is same as the linewidth of the radiation used.

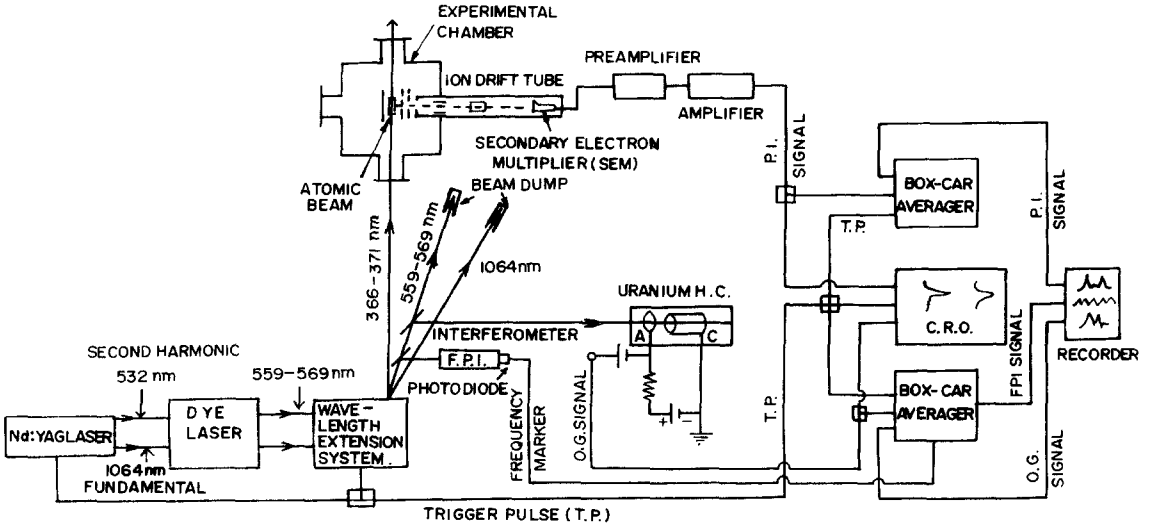

Fig. 1. Schematics of the single-colour photoionization setup

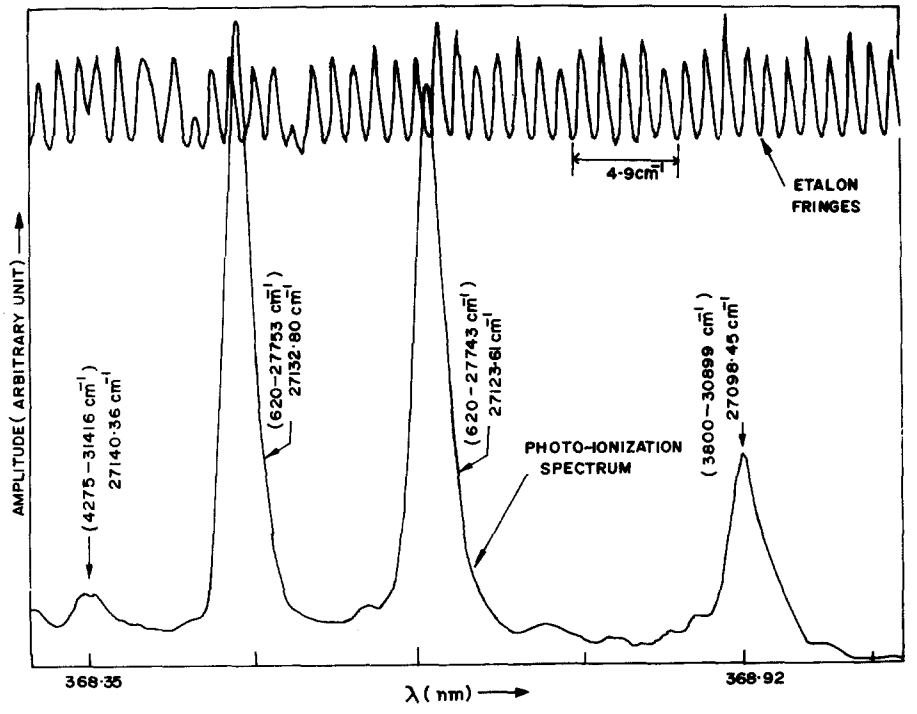

Fig. 2. A part of the photoionization spectrum of uranium in the UV region

Table 1. Resonances observed in the single-colour two-step photoionization spectrum of atomic uranium in the spectral region 366.47–370.48 nm

Observed resonance	Relative intensity	FWHM	First-step transition[a]					Diff.
			Initial level (odd)		Excited level (even)		Transition energy	
[cm^{-1}]		[cm^{-1}]	[cm^{-1}]	J	[cm^{-1}]	J	[cm^{-1}]	[cm^{-1}]
26984.1[b]	60	1.0	0	6	26984	5	26983.95	0.15
26985.5	25	1.0	620	5	27605	6	26985.44	0.06
26989.1	10	1.1	4453	4	31442	5	26988.85	0.25
26995.3	270	1.1	620	5	27615	6	26995.46	−0.16
27000.2	30	1.4	4275	6	31275	7	27000.26	−0.06
27009.2[b]	160	1.0	620	5	27630	4	27009.19	0 01
27013.1[b]	75	1.0	620	5	27633	5	27013.11	−0.01
27020.4	20	1.1	4275	6	31296	6	27020.48	−0.08
27025.2	25	1.7	4275	6	31301	7	27025.36	−0.16
27030.4	370	1.2	620	5	27650	6	27030.32	0 08
27035.4	170	1.2	0	6	27035	7	27035.44	−0.04
27040.5	45	1.4	3800	7	30841	8	27040.32	0.18
27050.3	30	1.5	3868	3	30918	4	27050.00	0.3
			5991	4	33041	8	27050.58	−0.28
27062.0	50	1.2	620	5	27682	5	27061.90	0.10
27072.4	380	1.0	0	6	27072	6	27072.38	0.12
27077.4	10	1.2	3800	7	30878	7	27077.47	−0.07
27085.8	10	1.2	3800	7	30886	7	27085.67	0.13
			4275	6	31361	6	27085.67	0.13
27098.2	30	1.1	3800	7	30899	6	27098.45	−0.25
27108.8	70	1.4	620	5	27729	5	27108.91	−0.11
27123.6	180	1.2	620	5	27743	6	27123.61	−0.01
27132.8	200	1.1	620	5	27753	4	27132.80	0.00
27140.5[b]	10	1.1	4275	6	31416	6	27140.36	0.14
27148.2	660	1.2	0	6	27148	6	27148.04	0.16
27159.7	50	1.5	4275	6	31435	7	27159.70	0.00
27164.6	40	1.5	3800	7	30965	6	27164.55	0.05
27170.8	110	1.5	620	5	27791	5	27170.82	−0.02
27175.4	15	1.1						
27177.8[b]	15	1.1	3868	3	31406	3	27177.58[c]	0.22
27185.2	200	1.1	3800	7	30986	8	27185.45	−0.25
27191.9	60	2.4	4275	6	31467	6	27191.89	0.01
27200.2[b]	20	1.4	4453	4	31653	3	27200.05	0.15
27209.5	200	1.7	620	5	27829	4	27209.59	−0.09
27212.5	15	1.0	4275	6	31488	5	27212.51	−0.01
27217.7[b]	10	1.2	6249	6	33466	5	27217.61	0.09
27224.2[b]	80	1.4	3800	7	31024	7	27223.96	0.24
27229.1	40	1.9	4275	6	31504	7	27228.82	0.28
27238.4	80	1.1						
27252.2	130	1.0	0	6	27252	5	27252.36	−0.16
27261.6	140	1.2	0	6	27261	6	27261.54	0.06
27267.3	100	1.0	0	6	27267	5	27267.27	0.03
27270 4	270	1.1	620	5	27890	4	27270.40	0.00
27275.3	35	1.6	4453	4	31728	4	27275.09	0.21
27279.6	10	1.4	5762	5	33041	5	27279.71	−0.11

[a] See Uranium atlas [6]

[b] Suggested new first-step transitions based on known energy levels. Transition energies (column 6) for these resonances are based on the corresponding energy level differences

[c] Listed transition in uranium atlas without assignment

With single-colour photons of energy $h\nu$, uranium atoms are ionized by the following two-step process:

$$U_i \xrightarrow{h\nu} U^* \xrightarrow{h\nu} U^+ + e,$$

where U_i represents uranium atoms in the initial state, either ground state or a low-lying odd-parity state of energy E_i, and U^* corresponds to an excited even-parity state of uranium with energy $E_i + h\nu$. Thus, the uranium atom in one of its low-lying odd-parity states is resonantly excited by absorption of a photon and the excited atom is then photoionized by further absorption of a second photon of the same energy.

Based on available information of known transition assignments in the uranium atlas [6], a majority of the ionization resonances have been identified. Identification of

Table 2. Comparison of the number of transitions observed in the present investigation and those reported in the literature in the spectral region 366.47 nm–370.48 nm originating from low-lying odd-parity states in uranium

Initial state (odd-parity)		Number of known transitions reported in literature[a]	Number of transitions observed in the present work
[cm^{-1}]	J		
0	6	6	6
620	5	10	10
3800	7	8	7
3868	3	8	1
4275	6	10	7
4453	4	8	2
5762	5	6	1
5991	4	5	1
6249	6	3	0
7005	6	1	0

[a] See uranium atlas [6]

these resonances is summarized in columns 4–6 of Table 1. Columns 4 and 5 indicate the initial state (U_i) and the excited intermediate state (U^*) respectively along with their J values. Column 6 lists the corresponding transition energy as reported in the uranium atlas. Column 7 gives the difference between transition energies obtained from our data and those reported in the uranium atlas. The resonances observed at 27050.3 and 27085.8 cm^{-1} have been associated with two first-step transitions each. Thus 33 out of the 43 observed resonances could be identified in a straight-forward manner.

In the spectral region covered 16 single-photon transitions originating either from the ground state or the first metastable state at 620 cm^{-1} have been reported in the uranium atlas [6]. All these have been observed in our ionization spectrum as two-step photoionization resonances. However, in the same spectral region many of the transitions reported in the uranium atlas, from other low-lying odd-parity states, have not been observed as two-step ionization resonances (see Table 2).

Like all the identified resonances, it is expected that the unidentified resonances also originate from low-lying odd-parity states. The lowest known even-parity state is at 7020 cm^{-1}. Starting from different known initial odd-parity energy states, E_i upto the one at 7005 cm^{-1}, we looked for excited energy states at $E_i + h\nu$ of appropriate J and parity within the experimental error in the literature. Thus, identification of eight of the remaining ten observed resonances have been suggested using known energy levels. These resonances are marked (\$) in Table 1 and correspond to new identified transitions. Three of these resonances with medium intensity have been associated with the ground or 620 cm^{-1} states which are the most populated states in the atomic beam. Furthermore, the resonance at 27177.8 cm^{-1} is listed in the uranium atlas [6] without any assignment. Based on our data we have suggested this as a transition starting from the 3868 cm^{-1} state.

The observed strength of any ionization resonance depends upon the thermal population in the initial state, the cross-sections for the first and second steps (i.e. the effective cross-section of the two-step process), the bandwidth and the intensity of the laser radiation.

The problem of two-colour two-step photoionization has been treated analytically by Letokhov et al. [7] for monochromatic radiation. The results can be easily extended to single-colour two-step photoionization. The photoionization yield in a single-colour two-step photoionization process depends in a complicated manner on the excitation cross section (σ_1), ionization cross section (σ_2), the laser intensity (I), and the laser pulse duration (τ). In certain limiting cases the yield depends on the product $n_0\sigma_1\sigma_2 I^2\tau^2$ (low intensity limit, no saturation), $0.5 n_0\sigma_2 I\tau$ (intermediate intensity limit, saturation in first-step excitation) and n_0 (high-intensity limit, saturation in both steps). Here n_0 is the number of atoms in the initial state in the interaction volume and is assumed that the life time of the intermediate state is much larger than the pulse duration of the laser radiation. The observation that different ionization resonances starting from the same initial state have different relative intensities as well as the fact that many resonances starting from reasonably populated low-lying odd parity states have not been observed at all, suggests that values of σ_1 and σ_2 have a large variation for different transitions.

Conclusions

The single-colour two-step photoionization spectrum of uranium contains several sharp and strong resonances. All the observed resonances in the 366–371 nm region, except two, have been identified. The strong and medium intensity resonances can be used for analytical studies of uranium. For example, three strong resonances at 27148, 27072 and 27030 cm^{-1}, observed in the present study, can be used in trace analysis of uranium by resonance-ionization mass-spectrometry.

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References

1. G.S. Janes, I. Itzkan, C.T. Pike, R.H. Levy, L. Levin: IEEE J. QE-**12**, 111 (1976)
2. D.L. Donohue, J.P. Young, D.H. Smith: Appl. Spectrosc. **39**, 93 (1985)
3. V.K. Mago, B. Lal, A.K. Ray, P.R.K. Rao, S.D. Sharma: J. Phys. B **20**, 6531 (1987)
4. Jin Chang-Tai, Liang Xiu-Quing, Wang Cheng-Fei, Li Yu-Fu, Zhou Da-Fan: Chinese Science Bulletin **37**, 30 (1992)
5. A.K. Ray, B. Lal, V.K. Mago, P.R.K. Rao: J. Opt. Soc. Am. B (in Press 1992)
6. D.W. Steinhaus, L.J. Radziemski Jr., R.D. Cowan, J. Blaise, G. Guelachvili, Z.B. Osman, J. Verges: *Present status of the analysis of the first and second spectra of uranium (UI and UII) as derived from measurements of optical spectra* (Los Alamos Scientific Laboratory Report, No. LA-4501 1971)
7. V.S. Letokhov, V.I. Mishin, A.A. Puretzky: Prog. Quant. Electron. **5**, 139 (1979)