



# Electronic excitation of uranium atoms sputtered from uranium metal and oxides



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## ABSTRACT

Atoms sputtered from solids by energetic ion irradiation often partition across electronically excited states. We developed a resonance ionization method to measure the population of the uranium  $^5K_5$  state ( $620\text{ cm}^{-1}$ ) relative to the  $^6L_6$  ground state for atoms sputtered from metallic and oxide surfaces. A considerable fraction of sputtered atoms reside in the  $^5K_5$  state, and the fraction increases as the surface oxidizes. The effect is consistent across uranium metal,  $UO_2$ , and  $U_3O_8$ , and is invariant with the departing velocity of the sputtered atom. The data are not sufficient to determine the excitation mechanism, however they are qualitatively consistent with resonant electron transfer from the surface to the departing atom.

## 1. Introduction

Resonance Ionization Mass Spectrometry (RIMS) has been applied to uranium for a number of years. RIMS uses lasers tuned to electronic transitions to ionize elements selectively and efficiently, and is useful for elemental and isotopic analysis of solids. Because of the generally high efficiency of resonance ionization, RIMS can achieve very high useful yield (defined as the number of atoms detected normalized by the number removed from the sample) [1]. For basic science applications, RIMS (or the complementary technique laser photoionization opticalgalvanic spectroscopy) has long been used to supplement conventional atomic spectroscopy by discovering high lying electronic states [2–13] and autoionizing states [14–18]. These studies generally use atomic beams generated by heating uranium compounds in an oven or on a filament, and it is not unusual to encounter population in bound electronic states above the ground state. For example, Mago et al. [7,19] generated U atomic vapor by heating a  $URe_2$  filament, and observed ten different populated electronic states with energies as high as  $7005\text{ cm}^{-1}$  above the ground state. Donohue et al. [20] vaporized U from a heated Re filament and observed 18 states up to  $11,969\text{ cm}^{-1}$ . These energies are much too high to be described by a Boltzmann energy distribution at the temperatures used to vaporize U. None of these studies quantified the relative populations of excited states, however the distribution of U atom population across many different states could have a significant effect on uranium useful yield in RIMS, since practical RIMS excitation schemes generally originate on a single initial state.

Less is known about the population of excited states when solid uranium or uranium oxide is atomized by ion beam sputtering rather than thermal vaporization. The ground electronic state of U is  $^5L_6$  (electron configuration:  $[Rn] 5f^36d7s^2$ ), however RIMS techniques that rely on sputtering sometimes make use of laser ionization schemes that originate on a low-lying  $^5K_5$  electronic state at  $620\text{ cm}^{-1}$  [10,21]. Indeed, Erdmann et al. [22] observed resonances in RIMS spectra of U atoms sputtered from uranium metal that could be assigned to transitions originating from the  $^5K_5$  state as well as the  $^5L_7$  state in the ground-state multiplet at  $3800\text{ cm}^{-1}$ , but did not quantify the relative populations. Wright et al. [23] used laser-induced fluorescence of U atoms sputtered from uranium metal to measure the relative populations of four states –  $^5L_6$ ,  $^5K_5$ ,  $^5L_7$ , and  $^3H_3$  ( $^3H_3$  energy =  $3868\text{ cm}^{-1}$ ) – and found nearly all of the population in the first two states. The  $^5K_5/^6L_6$  ratio was  $0.21 \pm 0.06$ , with only  $\sim 0.3\%$  of the population in the other two states. Thus, a significant effect on uranium useful yield in RIMS is the fraction of U atoms that sputter into the  $^5K_5$  excited electronic state rather than the ground state, and resonance ionization schemes that do not access both states are necessarily limited in their achievable useful yield. We recently developed a 2-color resonance ionization scheme to address this issue, and increased the attainable useful yield for uranium by RIMS from 24% to 38% [24].

The population of excited electronic states in atoms by ion sputtering is a well-known phenomenon (see e.g. the review by Gnasr [25]). While more than one process is responsible, the dominant mechanism is likely resonant electron transfer (RET) from the surface to the departing atom. In this view, the departing species is ionic, with the

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ion and solid strongly coupled in the vicinity of the surface. Electron transfer from the surface to the ion creates states that evolve from surface valence states to discrete atomic states as the separation increases. Electrons are transferred at rates depending on the density of surface states that match atomic states in the energy window between the work function of the surface and the ionization potential of the atom (e.g. see Fig. 5 of ref. [26]). In the case of uranium, the relevant energy region for populating the  $^5K_5$  state is  $\sim 3$  eV below the Fermi level.

In this work we present a new four-color resonance ionization scheme for U that accesses both the ground and  $^5K_5$  states. We show its effectiveness in saturating the ionization of atoms from both the ground and excited states and use it to investigate the relative populations of the two states in sputtered atoms as a function the oxygen content of the surface and the velocity of departing atoms.

## 2. Experimental

### 2.1. Samples

Three different materials were analyzed in this study. Uranium dioxide and triuranium octoxide samples were standard reference materials from the US Department of Energy New Brunswick Laboratory, CRM 125A, and CRM U500. The uranium dioxide disc ( $\sim 1$  cm in diameter) was glued to a sample stub using a conductive acrylic adhesive, while a powdered sample of triuranium octoxide was pressed into indium metal. Natural uranium metal was potted in epoxy and coated with a thin gold layer to provide electrical conductivity and protect it from oxidation when outside vacuum.

### 2.2. Instruments and methods

All RIMS measurements were made on the LION (Laser Ionization Of Neutrals) mass spectrometer at Lawrence Livermore National Laboratory. In brief, material is sputtered from a solid by means of a pulsed ion beam and ionized above the surface by one or more pulsed lasers tuned to electronic resonances in the element of interest. The ions are then detected by time-of-flight mass spectrometry. Details are given elsewhere [1,27].

A Hiden IG20 ion gun was used to bombard samples with 3 keV  $Ar^+$  at an incident angle of  $60^\circ$  from the surface normal prior to analysis. An IonOptika IOG 25 AU liquid metal ion gun was then used to sputter material for RIMS analysis. The gun delivered  $^{69}Ga^+$  ions at 15 keV with a spot size of  $\sim 1 \mu m$  at an incident angle of  $60^\circ$  from the surface normal. Both the  $Ar^+$  and  $Ga^+$  beams were rastered over the surface. The  $Ar^+$  beam was rastered over an area of  $\sim 350 \times 350 \mu m^2$ , while the  $Ga^+$  beam was rastered over a  $25 \times 25 \mu m^2$  area centered in the  $Ar^+$ -bombarded area.

The Ti:Sapphire lasers were essentially identical to those described previously [1,27]. The pulse repetition rate was 1 kHz. Pulse energies ranged up to 2 mJ per pulse for fundamental beams (700–1000 nm) and 0.72 mJ per pulse for second harmonic beams (350–500 nm). The bandwidths of the fundamental beams were 0.1 to  $0.2 \text{ cm}^{-1}$  FWHM, while those of the second harmonic beams were 0.2– $0.3 \text{ cm}^{-1}$ . The beams were aligned in a nearly co-linear fashion such that they intersected in the ionization region of the mass spectrometer  $\sim 1$  mm above the surface. The angle between the beams was  $< 1^\circ$ . The quasi-collimated beams were passed through the ionization region of the instrument and reflected back on themselves to both raise the total irradiance and to mitigate the Doppler shift arising from the fact that the primary ion beam is off-normal. Off-normal sputtering results in an anisotropic sputtered flux distribution which, in our instrument, has a velocity component along the laser beam. The individual beams were approximately collimated such that their diameters at the ionization region were 1.0 to 1.5 mm FWHM and did not change  $> 10\%$  over a distance of  $\sim 1$  m, which is the round trip distance to and from the mirror used to

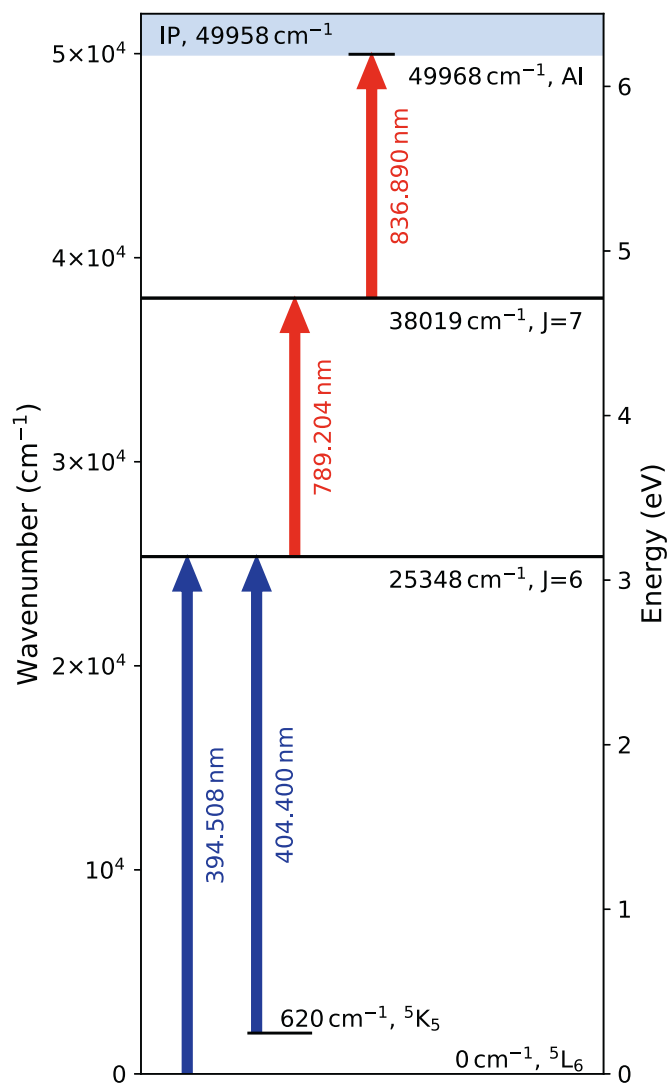


Fig. 1. Resonance ionization schemes used in this work. Exact state energies for each isotope are given in Table 1.

reflect them back on themselves. The laser pulsewidths were 9–20 ns (FWHM) depending on the laser wavelength and setup; the reflected beams increased the effective pulsewidths in the ionization region by 3 ns (1 m round trip). Measured pulse energies, pulsewidths, and beam sizes were used for the irradiance calculations for individual beams.

The resonance ionization scheme used in this work is shown in Fig. 1. Exact state energies for each of the schemes are given in Table 1. The scheme is based on one developed by Hakimi et al. [21,28]. That scheme started with a transition from the  $^5K_5$  state; we added a fourth laser to access the ground state as shown in Fig. 1. We also used a different autoionizing (AI) state. The total 3-photon energy in our scheme is  $49,968.591 \text{ cm}^{-1}$ , which is  $10 \text{ cm}^{-1}$  above the IP and is close

Table 1  
State assignments and level energies for the RIS schemes in Fig. 1.

State	$^{235}U$ Energy ( $\text{cm}^{-1}$ )	$^{238}U$ Energy ( $\text{cm}^{-1}$ )
$^5K_5$	620.318	620.323
$J = 6$	24,349.253	25,348.972
$J = 7$	38,019.583	38,019.153
AI $J = 6$	–	49,968.591

Bound state energies and assignments from ref. [28]; AI state from ref. [16] (see text for details).

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