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Spectrochimica Acta Part B 60 (2005) 1402 – 1411

SPECTROCHIMICA
ACTA
PART B

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High-resolution triple-resonance autoionization of uranium isotopes

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Received 13 June 2005; accepted 17 August 2005

Abstract

The near-threshold autoionization (AI) spectrum of uranium has been investigated by triple-resonance excitation with single-mode continuous lasers. Spectra were recorded over the first ~30 cm^{-1} above the first ionization limit at a resolution of 3×10^{-4} cm^{-1} using intermediate states with different J values (6, 7, 8) to assign AI level total angular momentum $J_{\mathrm{AI}}=5$ to 9. Resonances with widths ranging from 8 MHz to 30 GHz were observed; the strongest ones have $J_{\mathrm{AI}}=9$ and widths of ~60 MHz. Hyperfine structures for ^{235}U and isotope shifts for ^{234,235}U have been measured in the two intermediate levels and in the final AI level for the most favorable excitation path. These measurements were performed using aqueous samples containing sub-milligram quantities of uranium at natural isotopic abundances, indicating the potential of this approach for trace isotope ratio determinations.

PACS: 32.80.Dz; 31.30.Gs; 32.80.Fb; 32.80.Rm
Keywords: Uranium; Autoionization; Resonance ionization mass spectrometry; Laser spectroscopy

1. Introduction

Over the past five decades, the atomic spectroscopy of uranium has been investigated for many reasons. Uranium has one of the most complex atomic structures of the naturally occurring elements: six optically active electrons ($[\mathrm{Ra}]5f^3(^4I°)6d7s^2\ ^5L°$ ground term structure) result in extremely dense and complicated atomic spectra. Extensive data obtained from hollow cathode emission spectra have yielded total angular momentum (J), parity, and isotope shifts (IS) for many levels up to 42 000 cm^{-1}, as well as electronic configurations for many of the lower levels [1,2]. Transitions between these levels are also conveniently used as wavelength references throughout the uv to near-ir spectral range. Precision interferometric studies on selected lines using optogalvanic spectroscopy [3,4] have yielded wavelength standards with accuracy at the 0.0003 cm^{-1} level. Other interest derives from uranium's use as the primary feedstock in the nuclear power industry. In particular, Atomic Vapor Laser Isotope Separation (AVLIS) [5] motivated many laser-based studies of highly-excited states [6–11], and is conceptually similar to measurements reported in this paper. For AVLIS, efficient and selective multi-step resonant photoionization is required to separate ^{235}U from ^{238}U, while our interest lies in developing sensitive and selective detection methods for isotopic trace analysis. Recently, the world-wide distribution of undeclared enriched uranium and nuclear power plant accidents like Chernobyl have shown the importance of uranium ultratrace analysis for nuclear safeguards and environmental monitoring [12,13].

^{235}U/^{238}U ratios are commonly used to differentiate natural and processed uranium. However, for laser-based detection ^{234}U (5×10^{-5} natural abundance), which does not have complex hyperfine structure (hfs) like ^{235}U, may be a more sensitive indicator of enrichment/depletion processes. Another isotope of interest is ^{236}U ($t_{1/2}=2.3\times10^7$ y): formed from ^{235}U by neutron absorption (cosmogenic and self-activation), its isotopic abundance is expected to range from $\sim10^{-9}$ in uranium ores [14] down to $\sim10^{-14}$ in the general environment [15]. However, ^{236}U is produced prodigiously in nuclear reactors, with spent fuels from commercial power reactors containing 0.2–0.5% while that from high enrichment test reactors can contain up to 30% [16]. In the case of the Chernobyl reactor, which was ~1/3 of the way through a fuel

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doi:10.1016/j.sab.2005.08.010

cycle, the ^{236}U isotopic fraction was estimated at 0.2% [17]. As such, ^{236}U has been used to track migration of reactor irradiated uranium in the vicinity of the Chernobyl nuclear plant [12,18] and has been suggested for similar studies of environmental migration at the Mayak nuclear complex (site of the 1957 'Kyshtym accident') and Semipalatinsk-21 weapons test site in the Former Soviet Union [19]. More generally, ^{236}U may be considered a sensitive indicator of uranium irradiation and has indicated the presence of re-processed uranium in depleted uranium (DU) penetrator artillery rounds used in Kosovo [20–22]. Concern about similar occurrences in the private sector, such as the release of ~150 kg of DU in the 1992 El Al Boeing-747 crash in Amsterdam [23], also contribute to the need for rapid and sensitive methods capable of measuring the minor isotopes near (^{236}U) or below (^{234}U) their natural background levels. One promising method applicable to actinide analysis, due to good elemental and isotopic selectivity, is resonance ionization mass spectrometry (RIMS). This technique combines resonant multi-step photoionization with additional mass discrimination obtained from a mass spectrometer and has recently been used for quasi-routine analysis of Plutonium and Calcium isotopes [24].

Both AVLIS and RIMS require detailed spectroscopic examination of atomic levels to develop optimized resonant photoionization pathways. There have been many investigations on uranium using broad-band pulsed dye lasers, which is favorable for AVLIS where high efficiency and only moderate isotopic selectivity are needed. The importance of autoionizing (AI) levels for enhancing photoionization efficiency was recognized early [6], and recent studies found a large number of AI levels with high ionization cross-sections, including intense Rydberg series, within the first 300 cm^{-1} above the first ionization potential [25]. However, these experiments used pulsed lasers with linewidths $\geq$2 GHz, which yielded only limited information on natural lineshapes and no hfs or IS data. Our prior work on gadolinium autoionization with continuous-wave lasers revealed a number of narrow (<20 MHz) and strong autoionization resonances; one of the most efficient excitation paths demonstrated a photoionization cross-section of ~10^{-12} cm^2 [26]. Such high cross-sections yielded overall detection efficiencies on the order of 10^{-6}, enabling application of RIMS to isotope-selective ultratrace analysis of Gd [27]. In the current work, similar high resolution RIMS has been applied to uranium using a three-step, three-color photoionization scheme. The work concentrates on high angular momentum AI levels just above the ionization threshold and indicates that cw-RIMS can be used for the highly selective isotopic analysis of uranium in aqueous samples. The most favorable excitation path, into an AI level with a Lorentzian width of 65 MHz, has been characterized for the hfs of ^{235}U, IS for ^{234,235}U, and multi-dimensional excitation lineshapes.

2. Experimental

Fig. 1 diagrams the experimental setup used for studies reported in this paper. It consists of a graphite crucible atomizer used to dry, reduce, and vaporize aqueous samples, creating a weakly collimated (~10° FWHM) atomic beam, which is close-coupled into the source region of a linear quadrupole mass spectrometer. Within the interaction region a system of three continuous-wave single-mode lasers induces the uranium autoionization.

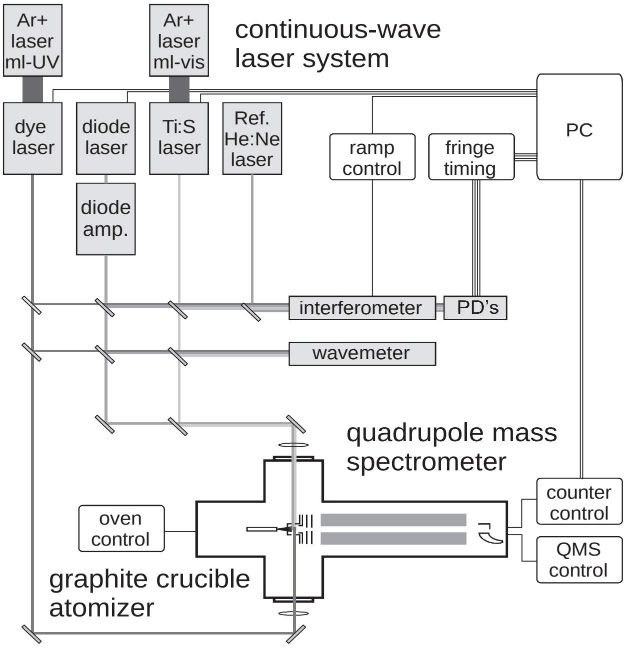

Fig. 1. Experimental setup used for triple resonance autoionization of uranium. PD=photodetector.

The excitation lasers are a ring dye laser (415 nm), an extended-cavity diode laser seeding a diode tapered amplifier chip (829 nm), and a ring titanium sapphire laser (707–724 nm). Both ring lasers are pumped by argon ion lasers, operating multiline-uv and multiline-visible, respectively. All three tunable lasers operate single mode with linewidths $\leq$1 MHz. Fringe-offset-locking [28] is used to stabilize and control the relative frequencies of all tunable lasers: sampled beams are spatially combined with a reference single-mode He:Ne laser and coupled into a scanning confocal Fabry–Perot interferometer (CFI). Transmitted light is spectrally separated with filters or small monochromators; intensities for all four lasers are detected with photodiodes or photomultipliers and peak sensing circuitry converts the CFI fringe transmission maxima into digital timing signals. Cavity spacing is ramped linearly with an offset stabilized to a transmission fringe of the reference He:Ne laser. Frequency drift correction and tuning are implemented using the time of the first fringe of a given tunable laser, after the reference He:Ne fringe, as the basis for a digital feedback loop. The time between successive fringes for a given laser corresponds to the precisely known 148.6296(2) MHz free spectral range (FSR) of the CFI and calibrates the offset from the reference He:Ne fringe. The tunable laser — He:Ne fringe offset is arbitrary and set by software: thus stabilization can be performed at any given frequency, while changing the desired offset yields programmable precision frequency scans. Precision is limited by CFI non-linearity over the one FSR used for locking (~100 kHz), and scale