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Determination of the first ionization potential of nine actinide elements by resonance ionization mass spectroscopy (RIMS)

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Abstract

The high sensitivity of RIMS enables the precise determination of the first ionization potential of actinide elements with a sample size of $\leq 10^{12}$ atoms. By multiple resonant laser excitation, the actinide atoms under investigation are ionized in the presence of an electric field, and the ions are mass-selectively detected in a time-of-flight spectrometer. The first ionization potential is obtained by scanning the wavelength of the laser used for the last excitation step across the ionization threshold W_{th}—indicated by a sudden increase of the ion count rate—at various electric field strengths. Extrapolation of W_{th} to electric field strength zero leads directly to the first ionization potential. The first ionization potentials (IP) of Am, Cm, Bk, Cf and Es were determined for the first time as $IP_{Am}=5.9736(3)$ eV, $IP_{Cm}=5.9914(2)$ eV, $IP_{Bk}=6.1979(2)$ eV, $IP_{Cf}=6.2817(2)$ eV, $IP_{Es}=6.3676(5)$ eV with samples of 10^{12} atoms. Furthermore, the ionization potentials of Th, U, Np and Pu were remeasured. © 1998 Elsevier Science S.A.

Keywords: First ionization potential; Actinides; RIMS

1. Introduction

The first ionization potential is a fundamental physical and chemical property of an element. Its accurate determination is important for identifying systematic trends in binding energies from element to element, and for drawing conclusions about the electronic structure of an atom as the first ionization potential is directly connected to the atomic spectra. Reliable information about the electronic structure of the heaviest elements is needed to predict deviations from the regularities of the periodic system of elements [1]. The ionization potentials can serve for a better understanding of relativistic effects in heavy elements, which are expected as a result of the relativistic mass increase of the inner electrons [2]. The precise determination of the ionization potential of the actinide elements allows to test the predictions of multi-configuration Dirac–Fock calculations [3], a very successful theoretical treatment for heavy multielectron atoms.

The first ionization potentials of the lanthanides, U, and the lighter transuranium elements, Np and Pu, were determined with high precision by the study of the convergence of long Rydberg series [4–7]. However, the Rydberg series can be perturbed by configuration interactions and, therefore, a large amount of data is required for a correct interpretation of the spectra. The determination of the ionization potential of Pu by Worden et al. [7] shows the limits of this method: as much as 2 g of the radioactive isotope ^{239}Pu were used throughout the measurements.

For the actinide elements up to Es, the first ionization potential was derived from extrapolated spectral properties [8,9]. Another approach, based on the semiempirical Slater–Condon method and ab initio Hartree–Fock calculations [10], used the analogy between lanthanides and actinides.

In this paper, we present a method which allows an accurate experimental determination of the ionization potential of the actinides, using samples of only 10^{12} atoms ($\approx$400 pg). With such quantities, we were able to measure the first ionization potential of Am, Cm, Bk, Cf

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and, very recently, of Es [11] for the first time. Furthermore, the first ionization potentials of Th, U, Np and Pu were remeasured.

2. Experimental

2.1. Experimental set-up

An atomic beam of an actinide element is obtained by resistive heating of a filament which consists of a thin metal backing foil, on which the element under investigation is electrolytically deposited in the form of its hydroxide and covered with a thin metal layer. By heating such a sandwich filament, the hydroxide is converted to the oxide which is reduced to the metallic state during diffusion through the covering layer. For the trans-protactinium elements, a combination of a tantalum backing with a titanium layer obtained by sputtering has proven to be most efficient for the production of an atomic beam [12].

For optical excitation and ionization of the atoms, a laser system consisting of three dye lasers, which are pumped by two copper vapor lasers of high pulse repetition rate (6.5 kHz, 30 and 50 W average output power, 30 ns pulse duration) is used [13]. The bandwidth of the dye lasers is typically several GHz and can be reduced to 1 GHz by means of an intracavity etalon. The wavelengths are determined by a pulsed wavemeter (Burleigh, model WA 4500, or—more recently—ATOS, Lambdameter) with a precision of $\Delta\lambda/\lambda=10^{-6}$. The dye laser beams are focused—either by quartz fibers or prisms—into the apparatus where they cross the atomic beam perpendicularly. The ions produced are accelerated by electric fields and detected with a multichannel plate detector after passing a field-free drift tube. This time-of-flight mass spectrometer is described in Ref. [14].

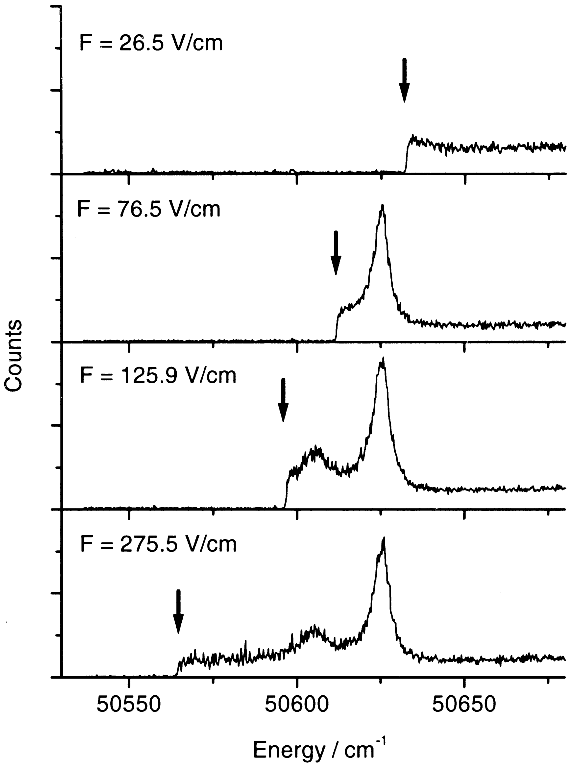

Fig. 1. Ionization thresholds of ^{249}Cf for four different electric field strengths *F*.

2.2. Photoionization threshold method

The method is based on the determination of photoionization thresholds in the presence of an external static electric field. According to the classical saddle point model [15], the excitation energy *W*(*r*) relative to the electronic ground state of an atom with one highly excited electron, located in an external electric field *F*, is—in a one-dimensional approximation—given by

$$W(r) = \mathrm{IP} - \frac{Z_{\mathrm{eff}} e^2}{4\pi\epsilon_0 r} - eFr, \qquad (1)$$

where e is the electric charge of the electron, Z_{eff} the effective charge number of the core, r the distance of the excited electron from the nucleus, ϵ_0 the permittivity of the vacuum, and IP the first ionization potential. The ionization threshold W_{th}, which is the maximum value of $W(r)$, depends on the electric field strength as follows:

Table 1
Excitation schemes for the determination of the first ionization potential of actinide elements by RIMS, starting from the ground state of the atom

Actinide element	λ_1 (nm)	1st step energy level (cm^{-1})	λ_2 (nm)	2nd step energy level (cm^{-1})	Ionizing laser (nm)
Th	580.58	17 224.3	623.07	33 273.8	≈568
U	639.72	15 631.9	591.64	32 534.1	≈577
			586.02	32 696.3	≈582
Np	311.90	32 061.3			≈541
Pu	649.07	15 406.6	629.75	31 285.9	≈579
Am	640.68	15 608.5	654.60	30 885.1	≈578
Cm	655.64	15 252.2	640.74	30 859.1	≈573
Bk	566.06	17 666.0	720.71	31 541.3	≈544
			664.70	32 710.3	≈581
Cf	572.76	17 459.2	625.21	33 453.7	≈583
Es	561.69	17 803.5	661.31	32 924.9	≈544

All wavelengths are vacuum wavelengths.

$$W_{\mathrm{th}}(F) = \mathrm{IP} - 2 \cdot \sqrt{\frac{Z_{\mathrm{eff}} e^3}{4\pi\epsilon_0}} \cdot \sqrt{F} = \mathrm{IP} - \mathrm{const} \cdot \sqrt{F}. \qquad (2)$$

For the determination of photoionization thresholds, a highly excited level of the atom is populated by a two-step or a one-step (Np) resonant excitation. The ionizing laser is scanned across the ionization threshold W_{th} in the presence of F. W_{th} is indicated by a sudden increase of the ion count rate. This procedure is repeated for various electric field strengths. Extrapolation of W_{th} to zero field strength leads directly to the first ionization potential.

3. Measurements and results

Table 1 summarizes the excitation schemes [16] used for the various actinides. The measurements of U and Bk were performed with two different second excitation levels differing in the J quantum number as an internal control of the method. As an example, Fig. 1 illustrates the shift of the photoionization threshold as a function of the electric field strength for ^{249}Cf ($T_{1/2} = 350.6$ a). The increase of the ion signal at the threshold can be determined with an accuracy between 0.5 and 2 cm^{-1}, depending on the counting statistics.

A plot of the obtained ionization thresholds versus the square root of the electric field strength F for five transplutonium elements is shown in Fig. 2. The ionization potentials are obtained by linear extrapolation to zero field strength by means of weighted least-squares fits. The ionization potentials of the actinide elements determined so far are summarized in Table 2, and compared with data given in the literature. The uncertainties for the experimental values derived in this work are the statistical errors (2σ) determined in the least-squares fit including the weighted errors for each datapoint. For Am, a second experimental value also listed in Table 2 was obtained by Rydberg convergence. More details are presented in Refs. [18–22].

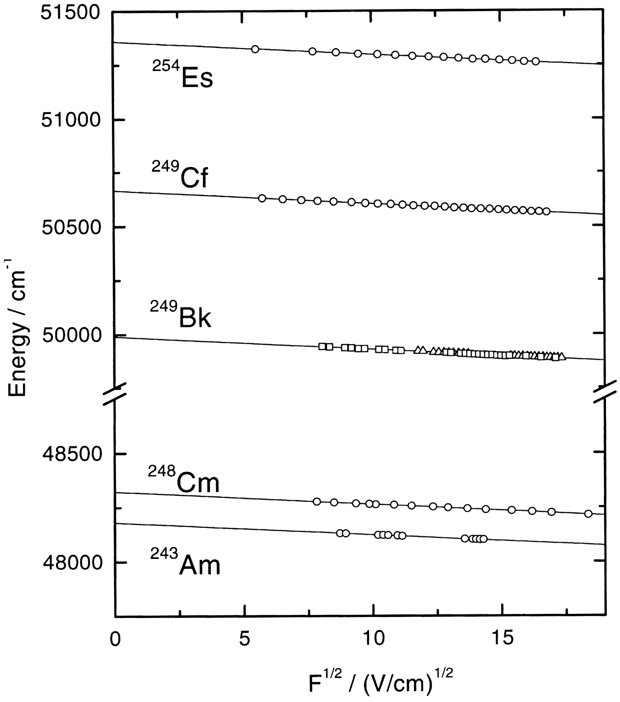

Fig. 2. Plot of ionization thresholds versus square root of the electric field strength F for five actinide elements. The first ionization potential is obtained by extrapolation to zero field strength.

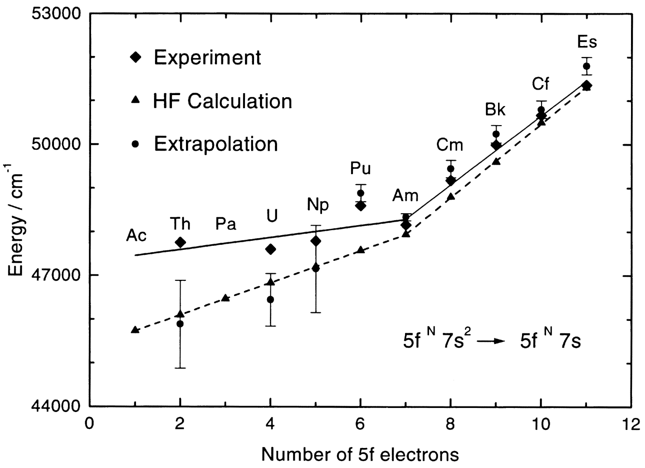

Fig. 3. Normalized first ionization potentials of actinide elements for the ionization process $5f^N7s^2 \rightarrow 5f^N7s$ as a function of N, the number of 5f electrons. Straight lines are drawn through our experimental (solid) and the calculated data (dashed). Plotted are the normalized experimental data by our group (◆), the values from extrapolated spectral properties [8,9], also normalized (●), and from Hartree–Fock calculations [10] (▲).

In Fig. 3, the first ionization potentials, normalized to $5f^N7s^2 \rightarrow 5f^N7s$ are plotted versus N. The experimental values of the heavier actinide elements are lower than the extrapolated data from Refs. [8,9], and always slightly above the Hartree–Fock calculations [10]. As pointed out in Ref. [10], the actinide ionization potentials follow the trend for binding energies of the s electrons by forming two straight lines, changing the slope at Am (half-filled 5f shell). While the experimental data from Am on agree very well with the assumption of a linear dependence, the ionization potentials of the lighter actinides show stronger deviations from a straight line.

4. Outlook

The experimental determination of the still unknown ionization potentials of Pa and Ac would be of interest. As a further test of theoretical calculations, we will try to measure the isotope dependence of the ionization potential. A difference in the ionization potential of 0.1 cm^{-1} for neighboring isotopes is expected (B. Fricke, private communication). For elements which differ greatly in their neutron number, such as ^{232}U ($T_{1/2} = 68.9$ a) and ^{238}U ($T_{1/2} = 4.47 \times 10^9$ a) or ^{236}Pu ($T_{1/2} = 2.858$ a) and ^{244}Pu ($T_{1/2} = 8.00 \times 10^7$ a), this effect might be observable.

Table 2
First ionization potentials of nine actinide elements

Actinide element	IP_{exp} (cm^{-1}) (this work)	IP_{exp} (eV) (this work)	IP^{b}_{exp} (cm^{-1})	IP_{th} (cm^{-1}) [8,9]
Th	50 867(2)	6.3067(2)	50 890(20) [17]	49 000(1000)
U	49 957(3)	6.1939(3)	49 958.4(5) [4]	48 800(600)
Np	50 353(2)	6.2655(2)	50 536(4) [6]	49 900(1000)
Pu	48 601(2)	6.0258(2)	48 604(1) [7]	48 890(200)
Am	48 180(3)	5.9736(3)		48 340(80)
	48 183(2)	5.9739(2)		
Cm	48 324(2)	5.9914(2)		48 560(200)
Bk	49 989(2)	6.1979(2)		50 240(200)
Cf	50 665(2)	6.2817(2)		50 800(200)
Es	51 358(5)	6.3676(5)		51 800(200)

Tabulated are the experimental data obtained in this work, IP_{exp}, experimental data previously known [4,6,7,17], IP^{b}_{exp}, and the predictions by extrapolated spectral properties [8,9], IP_{th}.

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