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Accurate determination of the first ionization potential of actinides by laser spectroscopy

N. Trautmann
Institut für Kernchemie, Universität Mainz, D-55099 Mainz (Germany)

Abstract

A new method is described for the precise determination of the first ionization potential of elements which are available only in small amounts such as the heavier actinides. It is based on resonance ionization mass spectroscopy (RIMS) in the presence of an external electric field. Extrapolation of the ionization thresholds obtained with different electric field strengths to field strength zero leads directly to the first ionization potential. With samples of 10^{12} atoms of ^{237}Np and ^{243}Am experimental values for the first ionization potential of neptunium of $IP_{Np} = 6.2655(2)$ eV and of americium of $IP_{Am} = 5.9738(2)$ eV were obtained. This technique was also applied to thorium yielding a value of $IP_{Th} = 6.3067(2)$ eV. In addition the precision of the method was confirmed by the convergences of Rydberg series of americium measured by means of RIMS.

1. Introduction

The investigation of the physical and chemical properties of the elements of the actinide and the beginning of the transactinide series is of general interest because relativistic effects may cause deviations from the regularities of the periodic system of the elements especially near the end of the periodic table. Ionization potentials are fundamental properties of atoms. Their precise determination can help in the interpretation of atomic spectra and is useful in identifying systematic trends in binding energies from element to element. Furthermore, the ionization potentials of the heaviest elements can serve for a crucial test of multiconfiguration Dirac–Fock calculations, at present the most successful theoretical treatment for heavy multielectron atoms [1, 2], and for computing relativistic effects including the predictions of chemical properties of the actinide and transactinide elements [3, 4].

The first ionization potentials of the lighter actinides have been determined by various techniques such as surface ionization, electron impact and laser spectroscopy [5–9]. Values for the ionization energies of the actinides have also been derived from thermochemical data and appropriate Born–Haber cycles [10], from first principles calculations [11] and by utilizing interpolated spectral properties of these atoms [12, 13]. The most accurate ionization potentials were obtained from the measurement of long Rydberg series. However, in many cases the Rydberg series are disturbed by configuration interaction requiring a large number of data for a correct interpretation of the spectra.

For the actinides beyond plutonium, so far no experimental data for the first ionization potential are known. This might be due to the fact that it is rather difficult to handle these strongly radioactive elements and that only small quantities of the heavier actinides are available.

We present a fast and sensitive method for the accurate determination of the first ionization potential by resonance ionization mass spectroscopy (RIMS) through variation of the electric field strength in the ionization region. This method requiring only ultratrace amounts has been applied thus far for the measurement of the first ionization potentials of neptunium, americium and also for thorium. Its precision was confirmed by the analysis of Rydberg series of americium.

2. Experimental details

The experimental set-up consists of three tunable dye lasers (Lambda Physik, Model F 2001) pumped simultaneously by two pulsed copper vapour lasers (Oxford Lasers, Model Cu-40) which emit laser light at 510.6 nm and 578.2 nm with an intensity ratio of 2:1 at a pulse repetition rate of 6.5 kHz and a pulse length of about 30 ns. With an unstable resonator configuration an average output power of 30 W for each copper vapour laser is achieved. The bandwidth of the dye laser radiation is normally several Gigahertz and can be reduced to 1 GHz by means of an intracavity

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etalon. The dye laser beams are injected into a time-of-flight mass spectrometer either with prisms or by coupling into quartz fibres. Depending on the dyes a wavelength range from 520 nm to 850 nm is covered and by frequency doubling with a barium β-borate (BBO) crystal it is extended to 260–425 nm. The wavelengths of the laser beams are determined by a Burleigh pulsed wavemeter (WA-4500). In addition, the absorption of molecular iodine can be recorded for calibration of the wavelengths if the lasers are operated in the narrow band mode.

Atomic beams of neptunium and americium are produced in an evaporation process from a rhenium foil of 25 μm thickness, on which they are deposited by electrolysis as hydroxides in a 2–3 mm spot and covered electrolytically with a thin rhenium or a lead-doped platinum layer [14]. Efficient release from these filaments occurs at 1500–2000 °C. A metallic foil of thorium is used for the generation of an atomic beam of this element. The ions produced by interaction of the laser light with the atomic beam are accelerated to an energy of 2.9 keV by the potentials of two grids and detected by a channel plate detector after a drift length of 2 m. The resonance ionization mass spectrometer is described in detail by Ruster *et al.* [15].

3. Measurements and results

For the determination of the first ionization potential the wavelength of the laser for the ionization step is scanned in the presence of an external electric field E. A sudden increase in the ion count rate marks the ionization threshold. By variation of the field strength the dependence of this threshold on the electric field can be measured and extrapolation to $E=0$ gives directly the first ionization potential.

According to the saddle point model the excitation energy relative to the electronic ground state of an atom with one highly excited electron located in a constant electric field consists of the Coulomb energy of the electron interacting with the core, its potential energy in the external field and a constant equal to the ionization potential IP. In one dimension ($r=z$) the excitation energy $W(r)$ is given by

$$W(r) = -eEr - \frac{Z_{\text{eff}}\, e^2}{4\pi\epsilon_0 r} + \text{IP} \tag{1}$$

where e is the charge of the electron, Z_{eff} the effective charge number of the core, r the distance of the excited electron from the nucleus and ϵ_0 the permittivity of the vacuum. For the ionization threshold W_{th} which is the maximum value of $W(r)$ the expression

$$W_{\text{th}} = \text{IP} - 2\left(\frac{Z_{\text{eff}} e^3}{4\pi\epsilon_0}\right)^{1/2} E^{1/2} = \text{IP} - \text{constant} \times E^{1/2} \tag{2}$$

results. As can be seen from eqn. (2) there is a proportionality between the ionization threshold and the square root of the electric field strength and extrapolation to $E=0$ yields the first ionization potential.

The precision of this simple method has been tested by remeasuring the first ionization potential of neptunium with samples of 10^{12} atoms of ^{237}Np using a two-step, two-colour excitation scheme [16]. A value for the first ionization potential IP_{Np} of neptunium of 6.2655(2) eV was obtained which is in excellent agreement with the Rydberg series convergence measurement of Worden and Conway [8], who obtained $\text{IP}_{\text{Np}} = 6.2657(5)$ eV.

The excitation schemes used for resonance ionization measurements of thorium and americium are shown in Fig. 1. In both cases a three-step, three-colour excitation–ionization has been applied for the determination of the ionization potential. As an example Fig. 2 shows two scans of the wavelengths of the third laser over the region of the ionization threshold of thorium for electric field strengths of 120 V cm^{-1} and 96 V cm^{-1} together with a plot of the thresholds as a function of $E^{1/2}$. The data are well described by a straight line as predicted by the saddle point model. Linear extrapolation to zero field strength by a least-squares fit gives an ionization potential IP_{Th} for thorium of 50 867(2) cm^{-1}$\triangleq$6.3067(2) eV which is in good agreement with the ionization limit very recently published by Johnson *et al.* [9] who have measured a value of $\text{IP}_{\text{Th}} = 50\,890(20)$ cm^{-1}$\triangleq$6.310(2) eV applying resonance ionization mass spectrometry.

For americium no experimental value for the first ionization potential is known. By interpolating series properties of the members 5f^{7}7s^2 and 5f^{7}7s8s of the actinides an ionization energy of 48 340(80) cm^{-1}$\triangleq$5.993(10) eV has been derived for americium [13]. Our measurements were performed with the longest-lived isotope of americium, ^{243}Am, which has a half-life $T_{1/2} = 7370$ a. A sample containing 10^{12} atoms of ^{243}Am was inserted and the wavelength λ_3 of the ionizing laser was scanned in the range of the ionization threshold applying various field strengths in the interaction region. The ionization threshold is marked by a sudden increase in the photo-ion signal as illustrated in Fig. 3 for field strengths of 120 V cm^{-1} and 108 V cm^{-1}. The peaks at the right of the onset of the ion signal result from Stark splitting of Rydberg states in the electric field. A plot of the ionization thresholds *vs.* the square root of the electric field E is also shown in Fig. 3(c). As can be seen the data points lie on a straight line. Linear extrapolation to zero field strength by a least-squares

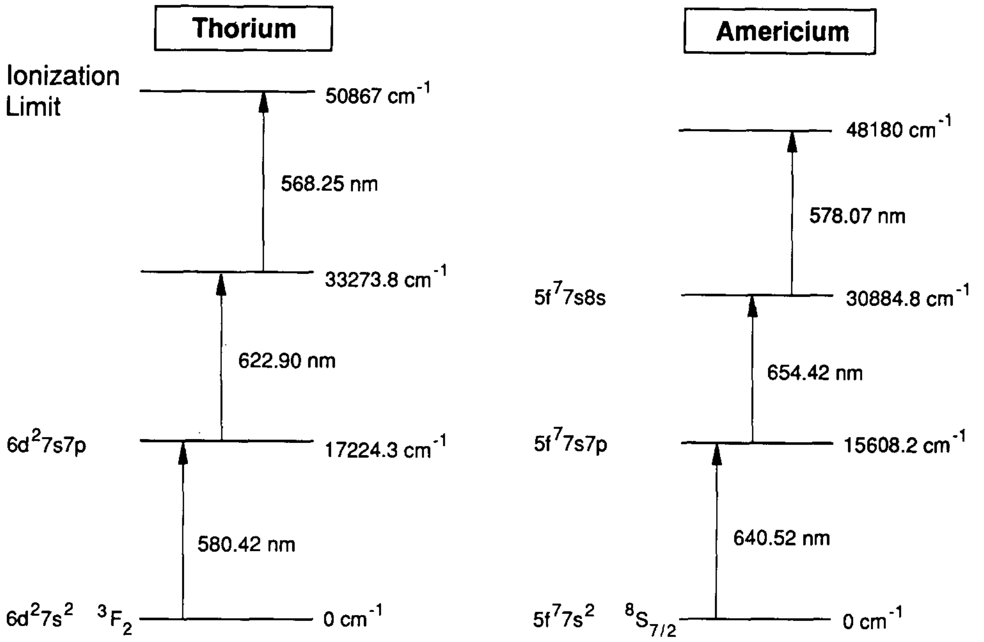

Fig. 1. Excitation schemes of thorium and americium for RIMS to determine the first ionization potential of these elements.

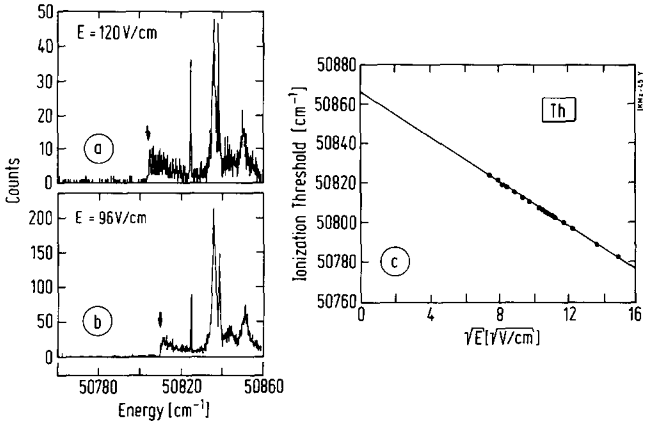

Fig. 2. Ionization threshold of thorium in electric fields of (a) 120 V cm^{-1} and (b) 96 V cm^{-1}. The ion count rate is recorded as a function of the total photon energy $h(\nu_1+\nu_2+\nu_3)$ by scanning the wavelength of the third laser beam. The ionization thresholds are indicated by the arrows. (c) Plot of the ionization thresholds as a function of the square root of the electric field strength E in the interaction region. A least-squares fit to the experimental data and extrapolation to zero field strength yield the first ionization potential IP_{Th} of thorium of 50 867(2) cm$^{-1}\triangleq$6.3067(2) eV.

fit yields an ionization potential $IP_{Am}=48\,180(3)$ cm$^{-1}\triangleq$5.9736(3) eV. The error of this value comprises the uncertainty in the determination of the onset of the photo-ion signal at a given electric field and the uncertainty in the extrapolation to $E=0$. In this experiment the dye laser for the ionization step was equipped with an intracavity etalon and the calibration of the wavelength occurred with an iodine cell.

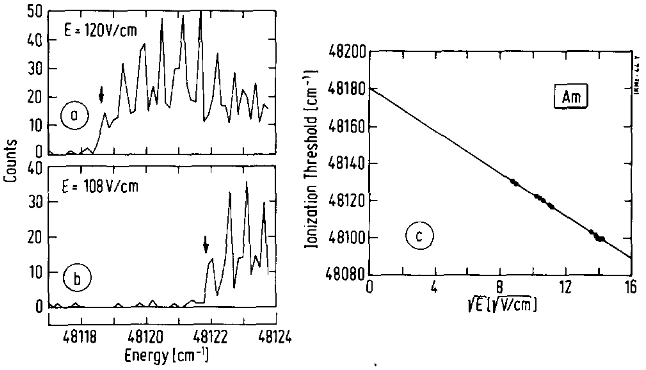

Fig. 3. Ionization thresholds (arrows) of americium obtained with electric field strengths of (a) 120 V cm^{-1} and (b) 108 V cm^{-1} in the interaction zone. The ion count rate is recorded as a function of the laser wavelength λ_3. On the x axis the total photon energy is given. From (c) the plot of the ionization thresholds *vs.* the square root of the electric field strength E a first ionization potential IP_{Am} of americium of 48 180(3) cm$^{-1}\triangleq$5.9736(3) eV results by extrapolation to $E=0$. The data points are fitted by a straight line.

In order to confirm the precision of the resonance ionization method in an electric field the ionization potential of americium was also measured by determination of the convergence limit of Rydberg series. For that, high-lying Rydberg states were populated by scanning the wavelength of the third dye laser. A pulsed electric field of 100 V cm^{-1} delayed by 10 μs with respect to the laser pulse was used for field ionization of the Rydberg states. With this time delay the shorter lived, high-lying levels with low principal quantum number are suppressed and do not complicate the spectra.

TABLE 1. First ionization potentials IP of the actinide elements thorium, neptunium and americium determined by ionization in an electric field and Rydberg convergences

Element	IP (this work)	Method[a]	IP (literature)	Method[a]
Thorium	6.3067(2) eV	EF	6.310(2) eV [9]	EF
Neptunium	6.2655(2) eV	EF	6.2657(5) eV [8]	RC
Americium	5.9736(3) eV 5.9739(2) eV	EF RC		
Average	5.9738(2) eV		5.993(10) eV [13]	Calculated

[a] EF, ionization in an electric field; RC, Rydberg convergences.

Three different series of states were found. A spectrum is shown in Fig. 4 with peaks that can be attributed to the three Rydberg series.

The level energy E_n of the Rydberg states of principal quantum number n can be calculated from the total photon energy $h(\nu_1+\nu_2+\nu_3)$. It is correlated with the effective principal quantum number n^* and the Rydberg constant R_{Am} of americium in the following way:

$$E_n = \mathrm{IP} - \frac{R_{\mathrm{Am}}}{(n^*)^2} \tag{3}$$

For large principal quantum numbers ($n > 20$) and in absence of perturbations the quantum defect $\delta = n - n^*$ is a slowly varying function of the level energy and therefore to a good approximation a linear function of the term energy $\mathrm{IP} - E_n$ and

$$\delta = a + b(\mathrm{IP} - E_n) \tag{4}$$

results [17]. Equation (3) can be written as

$$E_n = \mathrm{IP} - \frac{R_{\mathrm{Am}}}{\{n - [a + b(\mathrm{IP} - E_n)]\}^2} \tag{5}$$

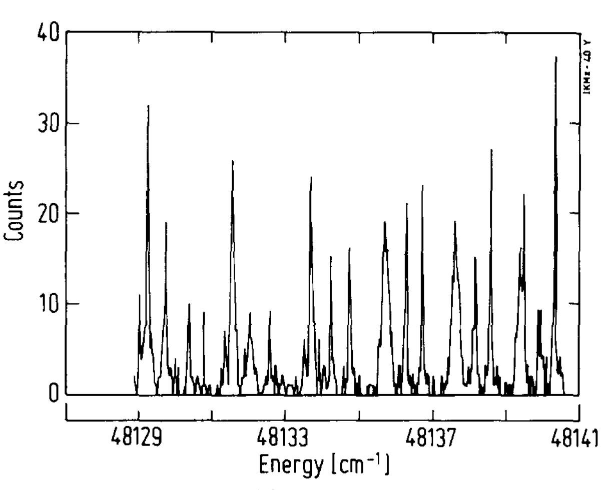

Fig. 4. Rydberg series in ^{243}Am obtained by field ionization with a pulsed electric field (100 V cm^{-1}) delayed by 10 μs with respect to the laser pulse.

By a least-squares fit of the experimental E_n values of a Rydberg series the constants a, b and IP can be determined. The obtained experimental data of americium are described very well by eqn. (5) and deviations due to perturbation by near-lying levels were not observed within the accuracy of our measurement, which is a few Gigahertz. The fits of the three Rydberg series investigated lead to convergence limits of 48 182.1 cm^{-1}, 48 182.7 cm^{-1} and 48 183.1 cm^{-1}. For these values an overall error of 2 cm^{-1} is estimated considering the uncertainty in the extrapolation and the wavelengths. As a weighted mean a first ionization potential $\mathrm{IP}_{\mathrm{Am}} = 48\,182.6$ cm^{-1} results. This result is in excellent agreement with that obtained from resonance ionization in an electric field and extrapolation to field strength zero. The weighted mean of our two experiments gives for the first ionization potential of americium $\mathrm{IP}_{\mathrm{Am}} = 48\,182(2)$ cm$^{-1} \triangleq 5.9738(2)$ eV. The calculated value $\mathrm{IP}_{\mathrm{Am}} = 5.993(10)$ eV [13] is in fair agreement with the experimental value. In Table 1 our measurements of the first ionization potentials of thorium, neptunium and americium together with the literature data are summarized.

We have just started to determine the ionization potential of curium using samples of 10^{12} atoms of ^{248}Cm. From the very preliminary first experiments one can conclude that the experimental value is at least 0.3 eV lower than the value calculated by Sugar [13]. At the moment we cannot say whether this discrepancy may result from procedural errors in our measurement or from the method applied by Sugar to calculate the ionization potentials for the actinide series. Therefore further experiments are required to determine precisely the first ionization potential of curium.

4. Conclusions

Our experiments have shown that RIMS is a well-suited method for the accurate determination of the first ionization potential of actinides. The onset of ionization as a function of the electric field strength within the interaction region and extrapolation to field strength zero leads to a precise value of the first ionization potential. Because of the sensitivity of this technique it can be applied to elements such as the heavier actinides which are accessible only in small amounts. The first ionization potential IP_{Am} of americium of 5.9738(2) eV was determined experimentally for the first time with RIMS by use of only 10^{12} atoms of ^{243}Am. The extension of this method to even heavier actinide elements, for which only calculated ionization potentials are published, is intended.

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References

1 J.-P. Desclaux and B. Fricke, *J. Phys. (Paris), 41* (1980) 943.

2 E. Johnson, B. Fricke, O.L. Keller, C.W. Nestor and T.C. Tucker, *J. Chem. Phys., 93* (1990) 8041.

3 V.A. Glebov, L. Kasztura, V.S. Nefedov and B.L. Zhuikov, *Radiochim. Acta, 46* (1989) 117.

4 P. Pyykkö, *Chem. Rev., 88* (1988) 563.

5 D.H. Smith and G.R. Hertel, *J. Chem. Phys., 51* (1969) 3105.

6 D.L. Hildenbrand and E. Murad, *J. Chem. Phys., 61* (1974) 5466.

7 R.W. Solarz, C.A. May, L.R. Carlson, E.F. Worden, S.A. Johnson, J.A. Paisner and L.J. Radziemski, *Phys. Rev. A, 14* (1976) 1129.

8 E.F. Worden and J.C. Conway, *J. Opt. Soc. Am., 69* (1979) 733.

9 S.G. Johnson, B.L. Fearey, C.M. Miller and N.S. Nogar, *Spectrochim. Acta B, 47* (1992) 633.

10 L.R. Morss, *J. Phys. Chem., 75* (1971) 392.

11 T.A. Carlson, C.W. Nestor, N. Wasserman and J.D. McDowell, *Oak Ridge National Laboratory Rep. ORNL-4562*, 1970.

12 J. Sugar, *J. Chem. Phys., 59* (1973) 788.

13 J. Sugar, *J. Chem. Phys., 60* (1974) 4103.

14 H. Wendeler, R. Deissenberger, F.-J. Urban, N. Trautmann and G. Herrmann, *Nucl. Instrum. Methods Phys. Res. A, 334* (1993) 93.

15 W. Ruster, F. Ames, H.-J. Kluge, E.-W. Otten, D. Rehklau, F. Scheerer, G. Herrmann, C. Mühleck, J. Riegel, H. Rimke, P. Sattelberger and N. Trautmann, *Nucl. Instrum. Methods Phys. Res. A, 281* (1989) 547.

16 J. Riegel, R. Deissenberger, G. Herrmann, S. Köhler, P. Sattelberger, N. Trautmann, H. Wendeler, F. Ames, H.-J. Kluge, F. Scheerer and F.-J. Urban, *Appl. Phys. B, 56* (1993) 275.

17 A.N. Zherikin, V.I. Mishin and V.N. Fedoseev, *Opt. Spectrosc., 57* (1984) 476.