ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 876–878

Journal of ALLOYS AND COMPOUNDS

Determination of the first ionization potential of einsteinium by resonance ionization mass spectroscopy (RIMS)

J.R. Peterson[a], N. Erdmann[b], M. Nunnemann[c], K. Eberhardt[b], G. Huber[c], J.V. Kratz[b], G. Passler[c], O. Stetzer[b], P. Thörle[b], N. Trautmann[b,]*, A. Waldek[b]

[a]*Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA*
[b]*Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany*
[c]*Institut für Physik, Universität Mainz, D-55099 Mainz, Germany*

Abstract

The first ionization potential of einsteinium (IP_{Es}) was determined by resonance ionization mass spectroscopy (RIMS) using samples with $\leq 10^{12}$ atoms of ^{254}Es ($T_{1/2}$=276 days). This method is based on the measurement of photoionization thresholds as a function of applied electric field strength, followed by extrapolation to zero field strength to yield IP_{Es}. An atomic beam of Es was created by heating a filament on which einsteinium was electrodeposited from an aqueous solution onto a tantalum backing and covered with titanium metal. Es atoms were ionized via a three-step excitation scheme, and the ions mass-selectively detected in a time-of-flight (TOF) mass spectrometer. The excitation scheme used included a previously unknown EsI level at 32 924.9 cm^{-1}. Furthermore, an autoionizing state at 51 447.3 cm^{-1} was also found. The first ionization potential of Es was determined to be 6.3676(5) eV (≡51 358(5) cm^{-1}). © 1998 Elsevier Science S.A.

Keywords: First ionization potential; Einsteinium; RIMS

1. Introduction

The first ionization potential is a fundamental physical and chemical property of an element. Knowledge of the ionization potentials of the heavier actinides can help in understanding relativistic effects in these heavy elements, which are expected as a result of the relativistic mass increase of the inner electrons [1], and enables a test of multiconfiguration Dirac–Fock calculations [2], a successful theoretical treatment for heavy multielectron atoms.

The most accurate experimental values for ionization potentials are obtained by laser spectroscopic methods [3,4]. We have developed a technique which allows such measurements with samples of $\leq 10^{12}$ atoms. More details are given elsewhere [5,6].

2. Production of ^{254}Es and preparation of Es filaments

2.1. Production and purification of ^{254}Es

The ^{254}Es ($T_{1/2}$=276 days, α-emitter) was synthesized in the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory, as part of the US Department of Energy's transuranium elements production and research program. Four fractions of mixed Es isotopes generated during the Radiochemical Engineering Development Center (REDC) processing campaign 69 (March '96) were combined for recovery and purification of the remaining ^{254}Es. Gross α-counting and α-pulse height analysis showed that this composite feed material contained 279.1 ng ^{254}Es, 133.9 μg ^{249}Cf and 1.6 μg ^{250}Cf. Suspected plutonium contamination was confirmed by α-particle analysis to consist of 5.1 μg ^{238}Pu and 24.7 μg ^{240}Pu. No ^{253}Es was detected by γ-spectroscopy, and all other γ-emitting impurities were below minimum detectable limits.

Purification of this composite feed material was accom-

---

*Corresponding author. Tel.: +49 6131 395847; fax: +49 6131 394488.

0925-8388/98/$19.00
PII: S0925-8388(98)00238-2

plished by a cationic exchange column run with selective elution using α-hydroxyisobutyric acid, followed by a final cationic cleanup column and concentration run, to isolate the ^{254}Es from the other transuranium elements and the mono- and divalent metal impurities [7]. Analysis of the final Es product showed the presence of 173.9 ng ^{254}Es with <0.002 ng ^{249}Cf and <0.003 ng ^{249}Bk per ng of ^{254}Es. No other transplutonium elements were detected. The only γ-emitter detected was ^{144}Ce at a concentration of 0.009 ng per ng ^{254}Es.

An aliquot containing 57 ng ^{254}Es was drawn from this final product solution in 6 M HCl and evaporated in the tip of a leached quartz cone for shipment to the Institut für Kernchemie at the Universität Mainz, Germany.

2.2. Chemical preparation of filaments in Mainz

The ^{254}Es residue was dissolved in 1 ml of 1 M HCl. An aliquot containing $\approx 10^{12}$ atoms of ^{254}Es was transferred into an electrolytic cell filled with 4 ml of NH_4Cl solution (0.1 g NH_4Cl ml^{-1}; pH=1.8). The einsteinium was electrodeposited onto a 50 μm thick tantalum backing foil over a 3 mm spot by applying a current density of 4.5 A cm^{-2} for 90 min. After deposition the filament was covered with a ~1 μm layer of titanium metal by sputtering. The thickness of the titanium layer was determined by measuring the energy loss of the α-particles in the covering layer and applying the Bethe–Bloch equation [8]. The evaporation temperature of einsteinium as neutral atoms from such filaments is as low as ≈630°C.

3. Experimental setup

The experimental setup for RIMS consists of three tunable dye lasers pumped by two copper vapor lasers (6.5 kHz pulse repetition rate, 30 and 50 W average output power, 30 ns pulse duration). The dye laser beams are coupled into a quartz fiber and focused into the interaction zone of a time-of-flight (TOF) mass spectrometer where they cross the atomic beam of Es produced by resistive heating of the filament. The ions produced are accelerated by an electric field and mass-selectively detected by a channel plate detector [9,10]. The wavelengths of the dye lasers were determined with a pulsed wavemeter (ATOS, Lambdameter) with a precision of $\Delta\lambda/\lambda = 10^{-6}$. All wavelengths given here are in vacuum.

4. Measurements and results

The experimental technique is based on the determination of photoionization thresholds as a function of an external electric field, followed by extrapolation to zero electric field strength. According to the classical saddle point model [11], the ionization threshold of an atom with one highly excited electron located in an external electric field shows a linear dependence on the square root of the applied electric field. In this experiment a highly excited EsI level was populated by a two-step resonant excitation scheme. The ionizing laser was scanned across the ionization threshold in the presence of an applied electric field, which also served to accelerate the ions in the TOF spectrometer. Electric field strengths varying from 25 to 270 V cm^{-1} were applied. The ionization threshold is indicated by a sudden onset of the ion signal at mass 254.

Using the first and second excitation level from data published by Blaise and Wyart [12] for ^{253}Es, and taking into account the isotope shift between ^{253}Es and ^{254}Es, an initial excitation scheme was chosen with $E_1 = 17\,803.5$ cm^{-1} ($\lambda_1 = 561.69$ nm) and $E_2 = 33\,829.9$ cm^{-1} ($\lambda_2 = 623.97$ nm). The third step was performed with $\lambda_3 \approx 540$ nm, leading nonresonantly to the continuum above the theoretical ionization potential predicted previously [13]. Keeping the first and third excitation steps constant, the second dye laser wavelength was scanned from 665.5 to 657.4 nm in order to find a second excitation level low enough in energy that an additional photon of λ_1 would not be energetically sufficient to produce ionization. Thus, a second excitation level at 32 924.9 cm^{-1}, obtained with $\lambda_2 = 661.31$ nm, was found suitable for the determination of the ionization thresholds under different electric field strengths. This excitation scheme is shown in Fig. 1. The third excitation step was scanned between 545.5 and 543.1 nm under different electric field strengths. The shift of the onset of the ion signal, which denotes the ionization threshold, toward higher energy with decreasing electric

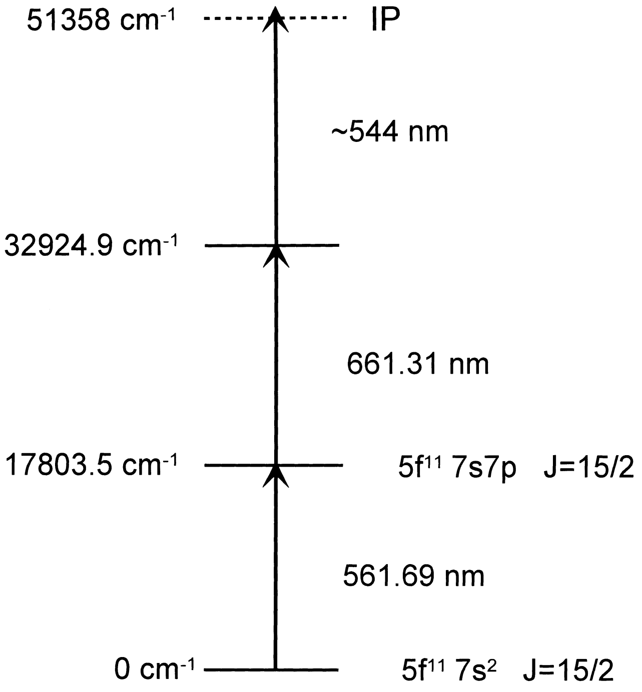

Fig. 1. Excitation scheme used for the determination of the first ionization potential of ^{254}Es.

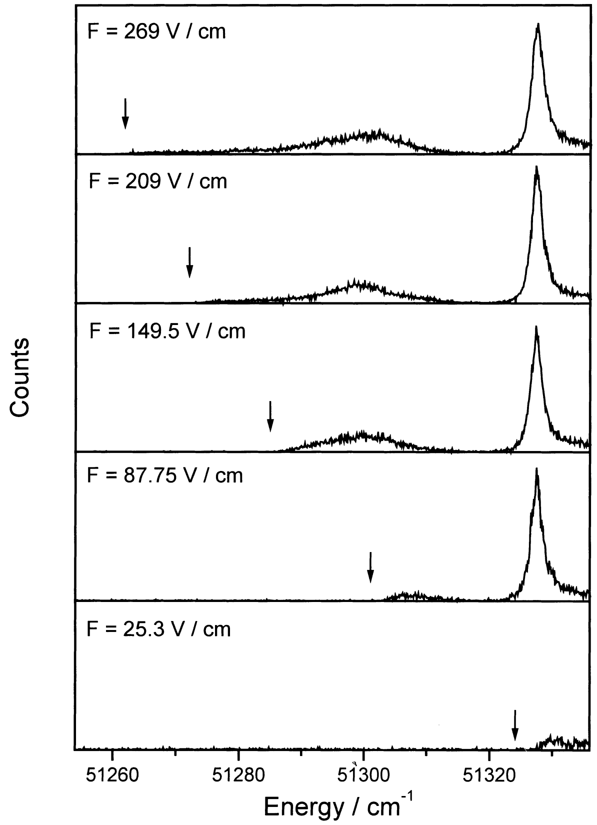

Fig. 2. Photoionization thresholds (indicated by arrows) of ^{254}Es under five different electric field strengths.

field strength is illustrated in Fig. 2. The very low background present below the ionization threshold is attributed to nonresonant multiphoton ionization. The ionization thresholds have been determined with a precision of ≈2 cm^{-1}, including the uncertainties in wavelength determination. The first ionization potential was obtained by a linear least squares fit of the ionization thresholds determined for various electric field strengths versus the square root of the electric field strength and extrapolation to zero field strength. This fit and the extrapolation are shown in Fig. 3. The value for the ionization potential of Es is $IP_{Es}=51\,358(5)$ cm^{-1} (≡6.3676(5) eV). The error considers the uncertainty from the least squares fit including the weighted errors for the single data points plus the uncertainty in the hyperfine splitting of the ground state of the ^{254}Es atom due to its nuclear spin $I=7$ and electronic ground state $J=15/2$. Further investigations of the hyperfine splitting of the first excitation step will reduce the error. By scanning the third excitation step above the ionization potential, an autoionizing state at 51 447.3 cm^{-1} was also found.

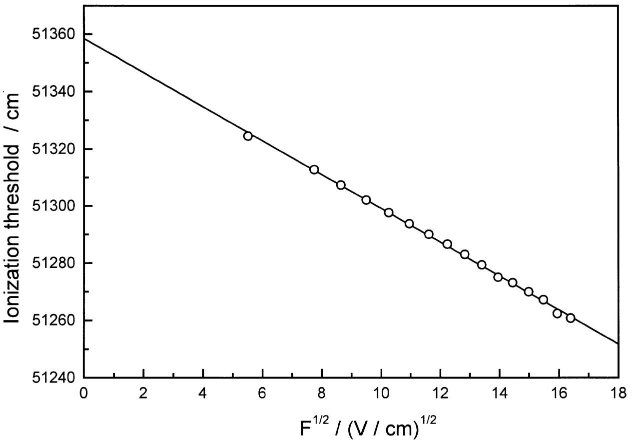

Fig. 3. Plot of the ionization thresholds of ^{254}Es versus the square root of the applied electric field strength F. The ionization potential was obtained by a linear extrapolation to zero field strength applying a least squares weighted fit.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft. The authors are indebted for the use of the ^{254}Es to the Office of Basic Energy Sciences, US Department of Energy, through the transplutonium element production facilities at the Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. under contract No. DE-AC05-96OR22464.

References

[1] P. Pyykkö, J.P. Desclaux, Acc. Chem. Res. 12 (1979) 276.
[2] B. Fricke, E. Johnson, G.M. Rivera, Radiochim. Acta 62 (1993) 17.
[3] E.F. Worden, J.G. Conway, J. Opt. Soc. Am. 69 (1979) 733.
[4] E.F. Worden, L.R. Carlson, S.A. Johnson, J.A. Paisner, R.W. Solarz, J. Opt. Soc. Am. Part B 10 (1993) 1998.
[5] N. Erdmann, M. Nunnemann, K. Eberhardt, G. Herrmann, G. Huber, S. Köhler, J.V. Kratz, G. Passler, J.R. Peterson, N. Trautmann, A. Waldek, J. Alloys Comp., this volume.
[6] S. Köhler, R. Deißenberger, K. Eberhardt, N. Erdmann, G. Herrmann, G. Huber, J.V. Kratz, M. Nunnemann, G. Passler, P.M. Rao, J. Riegel, N. Trautmann, K. Wendt, Spectrochim. Acta Part B 52 (1997) 717.
[7] R.D. Baybarz, J.B. Knauer, P.B. Orr, Final Isolation and Purification of the Transplutonium Elements from Twelve Campaigns Conducted at TRU during the Period August 1967 to December 1971, US Atomic Energy Commission Document No. ORNL-4672, 1973.
[8] P. Marmier, E. Sheldon, Physics of Nuclei and Particles, Academic Press, New York, 1969, p. 156.
[9] W. Ruster, F. Ames, H.-J. Kluge, E.-W. Otten, D. Rehklau, F. Scheerer, G. Herrmann, C. Mühleck, J. Riegel, H. Rimke, P. Sattelberger, N. Trautmann, Nucl. Instr. Meth. Phys. Res. Part A 281 (1989) 547.
[10] F.J. Urban, R. Deißenberger, G. Herrmann, S. Köhler, J. Riegel, N. Trautmann, H. Wendeler, F. Albus, F. Ames, H.-J. Kluge, S. Kraß, F. Scheerer, Resonance ionization spectroscopy, Inst. Phys. Conf. Ser. 128 (1992) 233.
[11] B.H. Bransden, C.J. Joachain, Physics of Atoms and Molecules, Longman, London, 1983.
[12] J. Blaise, J.-F. Wyart, Energy levels and atomic spectra of actinides, Tables Internationales de Constantes Sélectionnées, Université P. et Marie Curie, Vol. 20, Paris, 1992.
[13] J. Sŭgar, J. Chem. Phys. 60 (1974) 4103.