Investigation of the atomic structure of curium and determination of its first ionization potential

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Abstract. We report on the investigation of the atomic structure of curium (Z = 96) by resonance ionization spectroscopy. Three different excited energy levels were populated from the 5f76d7s29D2 ground state as first excitation steps. Wide-range scans were performed for the search of second excitation steps around the literature value of the ionization potential. These spectra were analyzed to identify Rydberg levels through the evaluation of Rydberg convergences and the complementary approach of DC electric field ionization by evaluating the ionization threshold according to the saddle point model. The new result deviates by 6.7 cm⁻¹ from the literature value of 48324(2) cm⁻¹ by Köhler et al. [15] and is about one order of magnitude more precise.

1 Introduction

The element curium (Z = 96) is exclusively man-made and was discovered in 1946 by the group around Glenn T. Seaborg [1]. At that time, the isotope 242Cm was produced by bombarding 239Pu with α-particles [2]. Curium is present in spent nuclear fuel with about 20 g/ton, produced by successive neutron capture and β⁻-decays from 238U [3]. To date, curium isotopes from 233Cm to 253Cm are known, of which the isotopes 242, 243, 244Cm and 245Cm exhibit long half-lives in the order of 1 up to 10⁷ years [4]. These allow for a variety of spectroscopic studies in this element. Curium isotopes are relevant in the field of radioanalytics and radio protection, e.g., after the Chernobyl reactor accident in 1986. In this context, 242Cm (T1/2 = 162.6 d) is one of the strongest α-particle emitters and is 14 times more active than, e.g., 239, 240Pu [5]. Thus, curium appears as a major component of the radiotoxic nuclear fallout.

The accurate determination of the total curium content and isotope ratios is in addition relevant for nuclear proliferation; but also for other fields, e.g., transmutation attempts as well as for the safe disposal of this particularly long-lived radioactive waste constituent. In this field, Gorietti et al. studied metal waste samples with different radiochemical and analytical methods, e.g., ICP-MS¹ and α-spectrometry to determine the relevant plutonium and americium/curium isotope ratios [6]. Resonant Laser-Secondary Neutral Mass Spectrometry (rL-SNMS) is a new and well-suited method to quantitatively determine curium contents including precise isotope ratios with spatial resolution in small particles and on surfaces. This technique has been successfully applied for ultra-sensitive and highly element-selective analyses of radiotoxic isotopes including the actinide isotopes 236, 238–242U, 241, 243Am, and 99Tc [7,8]. Highly efficient and element-selective ionization schemes are crucial for a high sensitivity and to suppress isobaric interferences, e.g., observed in the cases of 238U versus 235U, 234Pu, 241Am versus 244Pu, or 242Am versus 242Cm. Such schemes must be identified in all elements of interest by laser spectroscopy [9]. For this, detailed information about the atomic structure of the respective element must be collected.

On the other hand, laser spectroscopy is a highly suitable method for the study of atomic spectra, specifically in combination with a resonant laser ionization step for efficient ion production. The high efficiency and element selectivity of two- or three-step resonance ionization spectroscopy (RIS) makes it particularly suitable for such studies on minuscule sample amounts down to the picogram level [10]. Across the periodic table, the highest spectral line density is found in the lan-
thanides and actinides, having an open f-shell in the atomic ground state (GS). In particular, actinide spectra are strongly influenced by relativistic effects as well as intense electron correlations and corresponding configuration interactions [11]. In the curium atom (Cm I), Worden et al. spectroscopically identified more than 13,000 lines, which they assigned to 335 odd and 348 even parity levels pointing out its enormous atomic level density and the resulting complexity of the curium atomic structure [12,13]. They used 2mg of $^{244}$Cm ($T_{1/2} = 18.10$y) and performed the measurement at the large 9.15m Paschen Runge spectrograph of Argonne National Laboratory.

The ionization potential (IP) of curium was first estimated by interpolating the IPs of other actinides to $E_{IP,\text{Interp.}} = 49100(200)\text{cm}^{-1}$ [14]. It was measured in 1996 with the electric field ionization (FI) technique in three-step RIS to $E_{IP,\text{FI}} = 48324(2)\text{cm}^{-1}$ [15]. This method applying the classical saddle point model is ideally suited to extract the IP from the complex atomic spectra of actinides, where convergences of Rydberg series may not be easily identified due to high spectral density and disturbances from configuration interactions.

In this work, ionization schemes were developed performing laser spectroscopy of high lying states and AI resonances around the first IP of curium. The identiﬁcation of Rydberg states leads to a re-determination of the IP of the curium atom via two-step RIS. The IP value was determined by analyzing the Rydberg series and additionally conﬁrmed by using the electric ﬁeld ionization method.

2 Experimental setup

The experiment to determine the IP of curium through Rydberg convergences was carried out at the off-line radioactive ion beam facility RISIKO at Mainz University. Experimental details on the RISIKO mass separator can be found in [16]. The development of three RIS schemes as well as the final FI studies was performed at the MABU apparatus, as described in [9], while more details relevant for the individual measurements will be given in the following sections. A simpliﬁed sketch of the experimental setup of both devices showing the individual components is given in Fig. 1. The MABU is less sensitive compared to the 30keV RISIKO mass separator due to the lower acceleration potential of just $\sim 200\text{V}$ and the limited transmission of the $90^\circ$ deflector and the quadrupole mass filter.

The Mainz Ti:sapphire laser system was used to excite and ionize the sample atoms. As a pump laser, a commercial Nd:YAG laser at 532nm with a pulse repetition rate of 10kHz and a power of about 14W per Ti:sapphire laser was used. The wavelength was selected by a birefringent filter in combination with a thin etalon in case of the standard Ti:sapphire laser and by a reflective grating on a fully automated rotational stage for the tunable Ti:sapphire laser [18]. The second harmonics was generated in both laser types by an intra-cavity BBO crystal. The scan speed and the power of the tunable Ti:sapphire laser were computer-controlled over the whole scan range. The frequency-doubled laser average output power reaches up to 1.2W in case of the standard Ti:sapphire laser and up to 400mW for the tunable Ti:sapphire laser. The tunable laser had a spectral linewidth of 2GHz and the standard laser of typically 7GHz. The fundamental wavelengths of the lasers were measured by using a High Finesse WSU-30 wavemeter, which has an absolute uncertainty of 30MHz. The actual accuracy corresponds to 20% of the laser beam width, i.e., $\approx 0.12\text{cm}^{-1}$. For the measurements with higher spectral resolution, an additional etalon was inserted into the laser resonator, reducing the linewidth to slightly below 1GHz [19].

At RISIKO, samples with $2 \times 10^9$ atoms of $^{218}$Cm were used. The material was dissolved in nitric acid and pipetted onto a 5 $\times$ 5 mm$^2$ zirconium foil of 25$\mu$m thickness. After evaporation of the liquid, the sample was folded and placed into the ion source, which is a tantalum tube of 350mm length and 2.5mm inner diameter. It also serves as a confinement of the ionization region. The tube was heated stepwise up to 2300K. The first curium signal was detected at a temperature of about 1700K. In addition to resonant laser ionization, atoms were also ionized by contacts with the hot cavity surfaces, producing surface ions. Due to the very efficient and selective resonant laser ionization process,

2 Resonance Ionization Spectroscopy In Kollinear Geometry
3 Mainz Atomic Beam Unit.

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\caption{Schematic sketch of the experimental setups used for the experiments. Top: The Mainz atomic beam unit (MABU), involving 90° ion beam deflection and a quadrupole mass filter. It was used for ionization scheme development as well as for IP determination by field ionization (FI). Bottom: The RISIKO mass separator with a 60° sector field magnet used for spectroscopic studies of the Rydberg series.}
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the surface ion contribution to the total signal was only of the order of 1%.

The ionization scheme development was carried out at MABU [9,20], which is equipped with an atomizer geometry similar to the RISIKO mass separator. However, due to the significantly lower transmission of the MABU, larger samples with $2 \times 10^{12}$ atoms of $^{248}$Cm atoms were used. Ions were extracted from the ion source by three extraction electrodes, providing a potential of 200V for acceleration. The electrodes for ion source by three extraction electrodes, providing a specific mass-over-charge ratio. The subsequent detection of single ions was done by a channel electron multiplier. For ionization scheme development, as discussed in the next section, the laser beams were introduced longitudinally into the ion source through the deflector.

3 Excitation schemes

Starting from the odd-parity ground state $5f^76d7s^2\,^9D_2$, the three even-parity excited states $5f^76d7s7p^6\,^9D_3$ (A), $5f^76d7s^9D_1$ (B) and $5f^76d7s7p^7\,^7D_2$ (C), located at $23083.19\,\text{cm}^{-1}$, $24747.71\,\text{cm}^{-1}$ and $25287.08\,\text{cm}^{-1}$, were explored. These experimentally determined energies measured in $^{248}$Cm are in good agreement with the values from Blaise et al. [22] given for $^{244}$Cm, considering IS, which was extrapolated by Worden et al. [21]. Figure 2 shows the investigated ionization schemes at the top and the measured line profiles of the three first excitation steps (FES) at the bottom. FES$_C$ exhibits strong saturation broadening due to high laser power used.

In curium, the odd-parity ground state configuration $5f^76d7s^2\,^9D^o$ splits into five low-lying fine-structure components with $J = 2$ to $J = 6$ located at 0cm$^{-1}$, 302.153cm$^{-1}$, 815.655cm$^{-1}$, 1764.268cm$^{-1}$ and 3089.355cm$^{-1}$. In addition, the level scheme exhibits an atomic level with an even-parity configuration $5f^87s^2\,^{7}F_4$ at 1214.203cm$^{-1}$, which also features a significant thermal population in the hot atomizer source. All energy levels are taken from [22]. Across the relevant temperature range of 1700K to 2300K the GS has the highest relative population of 37%, closely followed by the level at 302.153cm$^{-1}$ with populations of 27%. While scanning the laser for the second excitation step (SES), resonant excitations from the other low-lying populated levels could occur and generate additional peaks in the spectra. In such a case, a two-step, one-color non-resonant ionization could occur or the other fixed laser frequency could similarly ionize the atom non-resonantly over the IP, if the total energy is high enough. Both processes occur in the spectrum taken for scheme A as shown in Fig. 3. These artifacts in the ionization spectrum are rather easily distinguished by their narrow and Gaussian line shape compared to the broad and Fano-shaped profiles of the AIs, and can be specifically selected by scanning the examined range with the SES laser only. This confirmed that the investigated excitation steps indeed start from the GS.

Figure 3 shows the ionization spectrum of scheme A just above the IP using both lasers. Three energy levels were identified as FES, which started from different low-lying levels. Peaks 1 and 2 represent the total excitation energies at 48382.96cm$^{-1}$ and 48414.29cm$^{-1}$. Starting from the low-lying energy level at 302.153cm$^{-1}$ with its electron configuration $5f^76d7s^2\,^9D_3$, they were identified as FES into energy levels at 24997.81cm$^{-1}$ and 25029.14cm$^{-1}$. Both levels are known and listed with their electron configurations $5f^76d7s\,7p\,^1D_4$ and $5f^86d7s\,^9D_2$ in [22]. Peak 3 was assigned to a FES at 55580.02cm$^{-1}$ with the electron configuration $5f^76d7s\,7p\,^3D_2$, $J = 5$, starting from the low-lying level of $5f^76d7s^2\,^9D_3^o$ at 815.655cm$^{-1}$ [22]. The few remaining very narrow peaks could be further FES, but were not listed in the tables [13, 22] and thus were not investigated further. The AI used for scheme A is highlighted with a yellow box and is the strongest AI level in the entire scan range. It enhances the ion signal by two orders of magnitude compared to non-resonant ionization for this particular ionization scheme.

In direct comparison, scheme B proved to be the most efficient of the three schemes studied for similar laser powers. As determined by non-resonant RIS, the GS transition FES$_B$ to 24747.71cm$^{-1}$ is somewhat stronger than those to FES$_A$ and FES$_C$ to 23083.19cm$^{-1}$ and 25287.08cm$^{-1}$. Scheme A has already been successfully used for RIMS at Mainz University as well as for ultra-trace analysis at Hannover University using rL-SNMS [23]. In these studies, scheme A was superior in elemental selectivity, as, e.g., americium was completely suppressed when the lasers were configured for the ioniza-
Fig. 3 Measured ionization spectrum of scheme A. The identified AI is highlighted by a yellow box and was used as SES in case of scheme A. The literature value of the IP with \(48324(2)\text{cm}^{-1}\) [15] is marked by a purple solid line. The dashed lines indicate FES starting not from the GS but from different initial states [13].

Fig. 4 Measured spectra of schemes A, B and C (cf. Fig. 2). The literature value of the IP of \(48324(2)\text{cm}^{-1}\) [15] is indicated by a purple line, with the magenta band depicting the \(2\sigma\) uncertainty. Expected values for Rydberg resonances with a quantum defect of \(\delta_0 \approx 0.9\) are marked by a solid line, those with a \(\delta_0 \approx 0.5\) by a dashed line.
The quantum defect $\delta_0 \mod 1$ versus the effective quantum number $n^*$, shown for six different ionization limits $E_\infty$. Resonances observed in scheme B are given by gray marked points. Two Rydberg series are identified in plot c) and are marked in green ($s$-series) and red ($d$-series) in all plots. Both have a particularly constant $\delta(n)$ slope for the IP of $48330.7 \text{cm}^{-1}$. The error bars indicate the uncertainty, which is dominated by systematics. The six plots illustrate the influence of different ionization limits on the $\delta(n)$ slope; plot f) visualizes the situation for the literature value of the ionization potential (IP).

Due to the complex spectra with its high line densities, the $\delta_0 \mod 1$ versus $n^*$ plot alone did not provide suitable information for a direct assignment of Rydberg states to a specific series. Hence, the resonance lines were compared in regard to their widths and intensities to identify regularities. Rydberg levels obviously affected by perturbations as visible by strong fluctuations in intensity, width and shape compared to their neighbors were not assigned to one Rydberg series and thus not considered in the Rydberg analysis.

Figure 5 shows the influence of the series limit $E_\infty$, indicated in the upper right corner, on the quantum defect plot for spectrum B. For the correct series limit, an arrangement of the data points with horizontal lines of constant quantum defect is expected, which is observed best in Fig. 5 c) for $E_\infty = 48330.7 \text{cm}^{-1}$. For this value, the error bars are also given, which have been omitted in the other five plots for the sake of clarity.

In all excitation schemes, two series at $\delta_0 \mod 1 \approx 0.9$ and $\approx 0.5$ were identified, shown in Fig. 6 for all three schemes A, B and C under study and for the optimum $E_\infty$ of Fig. 5.

Already a deviation of $1 \text{cm}^{-1}$ changes the rather constant $\delta(n)$ progression of c) into a significantly increasing or decreasing slope. A similar situation of constant $\delta$-values could be identified in all the three $\delta$ versus $n^*$-plots (based on spectra A, B and C) for series limit of $48330.7 \text{cm}^{-1}$. In all three spectra, the two Rydberg series were clearly visible with $\delta_0 \mod 1 \approx 0.5$ and $\approx 0.9$. Energetic positions of the identified Rydberg levels including their principal quantum numbers $n$ are listed in Table 4 of the $d$-series and in Table 5 of the $s$-series. The further Rydberg analysis was done for these six Rydberg series independently.

The extracted quantum defects were compared with the theoretical values from [25]. Considering the electron configurations and parity of the respective intermediate states, the series with $\delta_0 \mod 1 \approx 0.5$ (cf.
Table 1 Summary of the series limits $E_{\infty,R}$ determined from Rydberg-Ritz fits of Rydberg series. In each ionization spectrum, two series were identified. The series indicated are given with the number of assigned resonances and the quantum defect $\delta_0$ mod 1

| Scheme | Series | $n$ interval | # peaks | $\delta_0$ mod 1 | $E_{\infty,R}$ [cm$^{-1}$] |
|--------|--------|--------------|---------|----------------|--------------------------|
| A      | $d$    | 27–54        | 19      | 0.90(3)        | 48331.09(38)             |
| A      | $s$    | 36–47        | 9       | 0.40(6)        | 48330.54(34)             |
| B      | $d$    | 27–57        | 27      | 0.87(8)        | 48330.62(8)              |
| B      | $s$    | 37–46        | 10      | 0.50(3)        | 48330.72(22)             |
| C      | $d$    | 25–56        | 25      | 0.884(6)       | 48330.56(9)              |
| C      | $s$    | 29–63        | 14      | 0.470(8)       | 48330.76(7)              |

Fig. 5 green series) was identified as $s$-series. The second Rydberg series with the quantum defect of $\delta_0$ mod 1 $\approx 0.9$ (cf. Fig. 5 red series) is assigned to a $d$-series due to parity considerations. In particular, this $d$-series was strongly influenced by perturbations at quantum numbers $n = 37, 43, 47$, corresponding to 48245 cm$^{-1}$, 48265 cm$^{-1}$ and 48280 cm$^{-1}$, respectively, which are well visible in Fig. 5. In all Rydberg series, the occurrence of mixed states cannot be excluded. Exemplarily, a fit of the Rydberg-Ritz formula to the series with $\delta_0$ mod 1 $\approx 0.9$ of excitation scheme B is given in Fig. 7 together with the residual, showing the accuracy of the description using Eqs. 1 and 2 and few outliers caused by the perturbations.

An overview of the results for all investigated Rydberg series is given in Table 1. All Rydberg resonances were fitted by Gaussian profiles. All six individually determined $E_{\infty}$ values are in good agreement within their uncertainties. The weighted average was calculated from the six $E_{\infty}$ values and their uncertainties, to give the IP, denoted $E_{\text{IP,R}}$, with a value of 48330.66(4) stat (12) sys cm$^{-1}$. Due to somewhat vague procedure for the assignment of the Rydberg states in the complex spectra and the significant deviation from the previously reported result of 48324(2) cm$^{-1}$ Köhler [15], the IP was afterward independently determined by field ionization.

5 Electric field ionization

The saddle point model for electric field ionization (FI) was used as a further method for IP extrapolation since no assignment of individual series and no distinction between Rydberg and other valence states are required. The method is discussed in detail by Littman et al. [26]. In order to perform well-controlled electric FI, the first excitation step laser beam was irradiated transversely between the two aperture electrodes $U_1$ and $U_2$ of the MABU spectrometer with diameters of 3 mm (cf. Fig. 1). Here, a well-defined electric field strength could be set by applying a positive voltage to $U_1$ and a negative voltage to $U_2$, with both electrodes being precisely installed 1 cm apart. The ions produced by surface ionization inside the atomizer were suppressed by $U_1$. Only neutral species diffused into the ionization region between $U_1$ and $U_2$. The interaction volume of the ionization process was spatially defined by the overlap of the laser beam for excitation of the SES and the laser beam for excitation of the SES, which were arranged in transversal and longitudinal direction, respectively. In this way, ionization no longer takes place inside the atomizer, but exclusively in the intersection region of the two laser beams inside the homogeneous electric field with an electric field strength of $F = (U_1 - U_2)/d$. For each field strength setting, the voltages of electrode $U_3$, the downstream einzel lens, and the 90° quadrupole deflector were optimized to ensure the highest ion beam transmission. This experimental setup for FI has already been successfully used by Studer et al. [20] to determine the IP value of promethium.

The electric field reduces the ionization threshold $W_s \sim IP - \sqrt{F_T}$, with the subscript $T$ denoting the field threshold, at which a highly excited atom is ionized [26,27]. The saddle point $W_s$ of the potential is given by

$$W_s = E_{\text{IP}} - 2 \sqrt{\frac{Z_{\text{eff}}^3}{4\pi\epsilon_0}} F_T,$$

where $Z_{\text{eff}}$ is the effective charge of the atomic core. For highly excited states, the ionization threshold can be simplified to $W_s = E_{\text{IP}} - 6.12 (\text{V/cm})^{-1/2} \cdot \sqrt{F_T}$ under the assumption of $Z_{\text{eff}} = 1$. Thus, the ionization threshold $W_s$ can be measured for several field strengths for subsequent extrapolation to $F_T = 0$ to determine the IP.

The energy levels of excitation scheme B were used as a starting point for the FI studies due to the higher spectral line density below the ionization potential compared to spectra A and C (cf. Fig. 4), as well as the significantly higher count rates. Köhler et al. performed field ionization inspecting the range of 48210 cm$^{-1}$ – 48290 cm$^{-1}$, while in this work, FI data were taken between 48245 cm$^{-1}$ and 48305 cm$^{-1}$ and thus closer to the expected $E_{\text{IP,R}}$ value. In this way a more reliable and precise extrapolation to zero field is expected.

In an initial experimental approach for FI, the extended range of 48228 cm$^{-1}$ up to 48348 cm$^{-1}$ was scanned for several applied electric field strengths in the range of 55 V/cm to 220 V/cm. Four spectra for the cases of $F = 55, 70, 140$ and 220 V/cm are given in

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Fig. 8 Spectroscopic studies of FI using scheme B. Scans at different fixed electric fields at MABU in comparison to a spectrum from RISIKO with ionization in the atomizer are given. The dashed line marks the last measured and the next expected energy level. The \( F_T \) is located between both resonances and its expected position is marked by a solid line. The \( F_T \) was measured independently for fixed wavelengths marked with a green solid line and numbered by variation of the field strength with fixed laser excitation at this position. The reference AI is shown with an orange solid line.

Fig. 9 Step function of the \( F_T \) for the energy levels 48294.37 cm\(^{-1}\) in a) and 48275.21 cm\(^{-1}\) in b). The indicated reversal points of the sigmoid fit (red line, error band orange) correspond to the \( F_T \). The round braces indicate the statistical errors and curly braces the systematic errors.

Table 2: Eight energy levels \( W_s \) situated just below the ionization potential for which the electric field ionization thresholds \( F_T^{1/2} \) were determined. For the latter, round braces indicate the statistical errors and curly braces the systematic errors.

| #  | \( W_s \) (cm\(^{-1}\)) | \( F_T^{1/2} \) (V/cm\(^{1/2}\)) |
|----|---------------------|----------------------|
| 1  | 48246.64(28)        | 14.454(4)\(\{1\}\) |
| 2  | 48251.86(28)        | 13.173(5)\(\{1\}\) |
| 3  | 48265.83(27)        | 10.909(3)\(\{1\}\) |
| 4  | 48275.21(29)        | 9.382(4)\(\{1\}\)  |
| 5  | 48282.81(21)        | 8.546(10)\(\{1\}\)  |
| 6  | 48294.37(28)        | 6.390(5)\(\{2\}\)  |
| 7  | 48304.30(21)        | 5.482(20)\(\{3\}\)  |
| 8  | 48303.21(21)        | 4.118(9)\(\{2\}\)  |

Fig. 8. The plot is complemented by a spectrum from RISIKO, taken in collinear geometry, where also all Rydberg levels below the IP are ionized due to the conditions in the hot cavity. In contrast, only energy levels above the ionization threshold were ionized using the FI setup at MABU. The ionization threshold lies between the last measured and the next expected energy level, marked by dashed lines and the shaded area in the spectra. These data did not deliver a conclusive database for an IP fit with reasonable precision. Thus, in a second approach, the ionization threshold was measured by successively fixing the laser excitation to a fixed wavelength and in each case varying the electric field strength \( F \). In this way, the ionization threshold was measured for eight different energy levels between 48245.9 cm\(^{-1}\) and 48304.30 cm\(^{-1}\), which are marked by the green solid lines in Fig. 8. After each scan, a reference scan was performed using the AI state at 48338.11 cm\(^{-1}\) for correction of the threshold data. The ion signal of an AI state is not sensitive to the weak electric fields and therefore this reference scan maps the ion optics transmission for the respective field scan. Two examples for measurements of such electric field ionization threshold measurements are given in Fig. 9 a) and b). The data are described by a sigmoid function

\[
S(F) = A_0 + \frac{A_1}{1 + e^{-k(F-F_T)}}
\]

with the offset \( A_0 \), the amplitude \( A_1 \) as well as the turning point \( F_T \), which can be understood as the ionization threshold for the expected resonance, assuming the laser excitation is centered on the respective transition [20]. \( F_T \) was thus obtained for eight energy levels and is given in Table 2.

For these studies, systematic errors were similar as in the case of the Rydberg measurements and were described specifically for the electric field ionization in detail in [20]. Further errors results in 0.2 cm\(^{-1}\), including the wavemeter uncertainty of 0.12 cm\(^{-1}\) and the laser fluctuations of 0.08 cm\(^{-1}\) during the measurements. The estimation of \( \Delta F_T \) turned out to be more complicated. The systematic error includes the distance uncertainty between \( U_1 \) and \( U_2 \) of 1% and influences by the field leakage through the transmission holes. The statistical error was set as the standard deviation of the voltage values during the measurements. Including the fit error this amounts to about \( 10^{-1} \) to \( 10^{-2} \) V for a measured threshold. The uncertainties given in Table 2 include the statistical and systematic errors.

For IP determination, \( W_s \) was plotted against \( F_T^{1/2} \) (cf. Fig. 10). The data points 1-6 can be described very accurately by a linear function with the values 7 and 8 at lowest electric fields showing slight deviations.
Fig. 10 Extracted ionization thresholds plotted against the square root of the field strength $F_1^{1/2}$. The ionization limit can be determined from the y-axis intersection. The bright red area indicates the confidence interval for the linear fit, including the x and y errors equally. The inset shows a more detailed view on the $W_s$-intersection. The values $E_{IP,F}$ and $E_{IP,R}$ agree within the limits of their errors from the straight line. Shifting and splitting of spectral lines could be caused by the Stark effect. Nevertheless, this influence should be smallest for the weakest field strengths. Additionally, the influence of the Stark effect was checked by measuring specific energy levels at different electric fields and comparing their spectral position. No measurable shift, line broadening or splitting could be observed. This indicates that the Stark effect has no significant influence on the measured turning points for individual resonances. A reason for the deviations of the values of data points 7 and 8 is seen in the fact, that in comparison to Studer et al. [20], larger apertures were used for both electrodes $U_1$ and $U_2$. Thus, the measurements of the ionization thresholds of data points 7 and 8 could have been influenced by variations in the ion optical settings and according to changes in the stray fields, which most strongly affect small $F$ settings. Overlapping signals from neighboring broad resonances could additionally contribute; point 8, e.g., was measured on a signal maximum consisting of several resonances.

The data were described by a linear function, fitted according to Deming regression [28]. This linear regression method is based on a maximum likelihood estimation of the regression parameters. The residuals of the x and y values are both assumed to be independent and normally distributed. Finally, the y-axis intercept corresponds to the IP yielding a value of 48333(2) cm$^{-1}$. The slope of the linear function is $-6.04(23)$ (V/cm)$^{-1/2}$ perfectly confirming the expectation of $-6.12$ (V/cm)$^{-1/2}$ [20].

### Table 3
Overview of the ionization potentials (IPs) determined in this work ($E_{IP,R}$, $E_{IP,FI}$ and $E_{IP,av}$) in comparison to $E_{IP,Lit}$.  

| $E_{IP}$ (cm$^{-1}$) | $E_{IP,R}$ | $E_{IP,FI}$ | $E_{IP,av}$ | $E_{IP,Lit}$ |
|---------------------|------------|-------------|-------------|--------------|
| This work           | 48330.66(16) | 48333(2)    | 48330.68(16) | 48324(2)     |

### Table 4
Measured Rydberg resonances of spectra A, B and C. The principal quantum number is given for each energy level. The series were assigned based on Fano et al. [25], in this case as a $d$-series. The uncertainties include the fit errors as well as the systematic and statistical errors (cf. Ch. 4).

| n | $E_A$ (cm$^{-1}$) | $E_B$ (cm$^{-1}$) | $E_C$ (cm$^{-1}$) |
|---|-----------------|-----------------|-----------------|
| 25 | – | 48125.08(14) | 48124.97(16) |
| 26 | – | 48142.10(9) | 48142.25(12) |
| 27 | 48156.93(14) | – | 48157.23(14) |
| 28 | – | 48170.43(14) | 48169.89(21) |
| 29 | – | 48182.07(11) | – |
| 30 | 48191.76(17) | 48191.76(14) | 48191.76(14) |
| 31 | 48201.15(16) | 48201.17(15) | 48201.34(17) |
| 32 | 48209.56(15) | 48209.60(12) | 48209.54(15) |
| 33 | – | 48217.36(16) | 48217.33(17) |
| 34 | – | 48223.81(15) | 48224.44(15) |
| 35 | – | 48230.60(15) | 48230.60(11) |
| 36 | 48236.49(17) | 48236.28(14) | 48236.42(19) |
| 37 | – | 48241.37(15) | 48241.36(17) |
| 38 | 48251.10(14) | – | – |
| 39 | – | 48251.17(17) | – |
| 40 | – | 48255.16(15) | – |
| 41 | – | 48255.16(15) | – |
| 42 | – | 48255.16(15) | – |
| 43 | 48259.03(15) | 48259.95(15) | – |
| 44 | 48262.75(15) | 48262.36(14) | 48262.43(16) |
| 45 | 48265.92(16) | 48265.73(17) | 48265.75(16) |
| 46 | 48269.12(9) | – | 48269.15(15) |
| 47 | 48271.78(15) | 48271.67(18) | 48271.78(16) |
| 48 | 48274.32(17) | 48274.21(15) | 48274.32(17) |
| 49 | 48276.62(15) | 48276.64(17) | 48276.70(11) |
| 50 | 48279.03(15) | – | 48278.95(15) |
| 51 | – | 48281.43(17) | 48281.47(16) |
| 52 | – | 48283.32(9) | 48283.40(17) |
| 53 | 48285.24(10) | 48285.26(17) | 48285.18(17) |
| 54 | 48287.03(10) | 48286.96(16) | 48286.91(17) |
| 55 | – | 48288.66(17) | 48288.31(18) |
| 56 | – | 48290.16(18) | 48289.93(16) |
| 57 | – | 48291.70(16) | – |

### 6 Conclusion

Two-step RIS was applied for sensitive atomic spectroscopy of curium ($Z = 96$), using minuscule samples in the ng range. Three different FES were used to investi-
Table 5  Measured Rydberg resonances of spectra A, B and C. The principal quantum number is given for each energy level. Series assignment was according to Fano et al. [25], in this case as a $s$-series. The uncertainties include the fit errors as well as the systematic and statistical errors (c.f. Ch. 4).

| n  | $E_A$ (cm$^{-1}$) | $E_B$ (cm$^{-1}$) | $E_C$ (cm$^{-1}$) |
|----|-----------------|-----------------|-----------------|
| $s$-series |
| 29 | –               | –               | 48132.70(15)    |
| 30 | –               | –               | 48148.30(18)    |
| 31 | –               | –               | 48162.51(16)    |
| 32 | –               | –               | 48174.84(15)    |
| 33 | –               | –               | 48185.65(20)    |
| 34 | –               | –               | –               |
| 35 | –               | –               | –               |
| 36 | 48213.18(15)    | –               | –               |
| 37 | –               | 48220.28(15)    | –               |
| 38 | 48227.98(15)    | 48227.02(15)    | –               |
| 39 | 48233.11(14)    | 48232.92(16)    | –               |
| 40 | –               | 48238.41(16)    | –               |
| 41 | 48243.69(20)    | 48243.34(14)    | 48243.67(17)    |
| 42 | –               | 48248.46(15)    | –               |
| 43 | 48253.15(14)    | 48252.98(15)    | 48253.23(16)    |
| 44 | 48256.93(15)    | 48256.77(16)    | 48256.77(20)    |
| 45 | 48260.51(14)    | 48260.43(16)    | –               |
| 46 | 48263.90(16)    | 48263.82(15)    | 48263.82(15)    |
| 47 | 48267.26(19)    | –               | –               |
| 48 | –               | –               | –               |
| 49 | –               | –               | –               |
| 50 | –               | –               | –               |
| 51 | –               | –               | –               |
| 52 | –               | –               | –               |
| 53 | –               | –               | 48282.34(17)    |
| 54 | –               | –               | 48284.12(15)    |
| 55 | –               | –               | –               |
| 56 | –               | –               | –               |
| 57 | –               | –               | –               |
| 58 | –               | –               | –               |
| 59 | –               | –               | –               |
| 60 | –               | –               | –               |
| 61 | –               | –               | 48295.30(16)    |
| 62 | –               | –               | 48296.41(16)    |
| 63 | –               | –               | 48297.50(15)    |

Within all three excitation schemes, in total six Rydberg series were identified and were assigned to a $d$-series in the range of $n = 25$ – $57$ and a $s$-series with $n = 29$ – $63$. Based on these Rydberg convergences, an IP value of $E_{\text{IP,R}} = 48330.68(12)$cm$^{-1}$ was determined. FI was used as a complementary and independent method to determine the IP by using the saddle point method. The ionization threshold was determined for eight energy levels below the IP, resulting in an IP value of $E_{\text{IP,FI}}$ with 48333(2)cm$^{-1}$. The results of this work, as well as the previous literature value, are shown in Table 3. As expected, the precision of the Rydberg analysis is one order of magnitude higher than the one of FI determination.

Considering the combined uncertainties of $E_{\text{IP,R}}$ and $E_{\text{IP,FI}}$, the two values are in good agreement. Finally, the IP was determined by the weighted average of both values as $E_{\text{IP,av.}}$ to be $48330.68(16)$cm$^{-1}$. The good agreement between the two independent measurement methods gives us confidence in our results, which we propose as a correction to the Köhler et al. value [15].

**Author contributions**

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**References**

1. G.T. Seaborg, Science 104, 379-386 (1946), https://www.science.org/doi/10.1126/science.104.2704.379
2. R. A. James Isotopes of the New Element, Curium (Atomic No. 96) (PhD. thesis, University of California, 1948), https://escholarship.org/uc/item/9zt6g894
3. Gregg J. Lumetta, et al. “Curium.” The chemistry of the actinide and transactinide elements. Springer, Dordrecht, 1397-1443 (2008), https://link.springer.com/content/pdf/10.1007/1-4020-3598-5_9.pdf
4. A. Habibi et al., Radioanal. Nucl. Chem. 329, 545–554 (2021), https://doi.org/10.1007/s10967-021-07751-7
5. E. Hom et al., Radioanal. Nucl. Chem. 252, 211–214 (2002). https://doi.org/10.1023/A:1015786431984
6. D. Gorietti et al., Radioanal. Nucl. Chem. 314, 1785–1792 (2017). https://doi.org/10.1007/s10967-017-5553-y
7. H. Bosco et al., Hyperfine Interact. 241, 1–8 (2020). https://doi.org/10.1007/s10751-020-1696-2
8. M. Franzmann et al., Anal. Spectrom. 33, 730–737 (2018). https://doi.org/10.1039/C7JA00423K
9. N. Kneip et al., Hyperfine Interact. 241, 1–7 (2020). https://doi.org/10.1007/s10751-020-01712-4
10. S. Raeder et al., Radiochim. Acta 107, 645–652 (2019). https://doi.org/10.1515/ract-2019-0001
11. L.R. Morss et al., The chemistry of the actinide and transactinide elements (Springer, Dordrecht, 2008)
12. E. F. Worden et al., J. Opt. Soc. Am., 66, 109–121 (1976) https://opg.optica.org/josa/abstract.cfm?URI=josa-66-2-109
13. E. F. Worden et al., At. Data Nucl. Data Tables 18, 459–495 (1976). https://doi.org/10.1016/0092-640X(76)90014-0
14. J. Sugar, J. Chem. Phys. 60, 4103 (1974). https://doi.org/10.1063/1.1680874
15. S. Köhler et al., Spectrochim. Acta B 52, 717–726 (1997). https://doi.org/10.1016/S0584-8547(96)01670-9
16. T. Kieck et al., Nucl. Instrum. Methods Phys. Res., B 945, 1–10 (2019). https://doi.org/10.1016/j.nima.2019.162602
17. K. Zhang et al., PRL 125, 7–14 (2020). https://doi.org/10.1103/PhysRevLett.125.073001
18. A. Teigelhöfer et al., Hyperfine Interact. 196, 161–168 (2010). https://doi.org/10.1007/s10751-010-0171-x
19. A. Sonnenschein et al., Hyperfine Interact. 227, 113–123 (2014). https://doi.org/10.1007/s10751-013-1000-9
20. D. Studer et al., Phys. Rev. A 99, 1–8 (2019). https://doi.org/10.1103/PhysRevA.99.062513
21. E.F. Worden, J.G. Conway, J. Opt. Soc. Am 66, 109–121 (1976). https://doi.org/10.1364/JOSA.66.000109
22. J. Blaise, J.-F. Wyart, Energy levels and atomic spectra (Tables Internationales de Constantes, Paris, 1992)
23. H. Bosco et al., Sci. Adv. 7, 1–8 (2021). https://doi.org/10.1126/sciadv.abj1175
24. W. Ritz, Annalen der Physik 317, 444–446 (1903)
25. U. Fano et al., Rev. Mod. Phys. 48, 49–68 (1976). https://doi.org/10.1103/RevModPhys.48.49
26. M.G. Littman et al., Phys. Rev. Lett. 41, 103–107 (1978). https://doi.org/10.1103/PhysRevLett.41.103
27. B.H. Bransden et al., Physics of atoms and molecules (Prentice Hall, Harlow, 2003)
28. R. F. Martin, Clin. Chem. 46, 100–104 (2000). https://academic.oup.com/clinchem/article/46/1/100/5670706