Work Package 4:

Enhanced Understanding of the Actinide Atomic Structure

LISA Science Day June 17th, 2022

Klaus Wendt, JGU Mainz for EU ITN LISA

This Marie Sklodowska-Curie Action (MSCA) Innovative Training Networks (ITN) receives funding from the European Union's H2020 Framework Programme under grant agreement no. 861198

WP 4	Enhanced understanding of the actinide atomic structure	M4 – M48
Beneficiaries WP leader bold	**JGU**, UGOT (experimental) – FSU, RUG (theory)	

Description of Acxtivities

Task 1 - JGU: RIS on atoms **ESR 5 Magda**

Identification of **RIS schemes** for actinides, redetermination of **ionization potentials,** investigation of **HFS** and **IS**

Task 2 - UGOT: Studies on Negative Ions **ESR 6 Miranda**

Installation of the **GANDALPH** detector at CRIS/CERN-ISOLDE. Collinear laser photodetachment spectroscopy on **negative actinide ions**

Task 3 - FSU: Theory **ESR 13 Joseph since 12/21**

Development of **dedicated atomic structure codes** and calculations for actinide elements

Task 4 – RUG : Theory **ESR 14 Raphael**

Relativistic coupled cluster (CC) & **configuration interaction (CI)** atomic calculations of properties of **heavy & superheavy**

The Actinide Atomic Structure
Experimental Status 2022

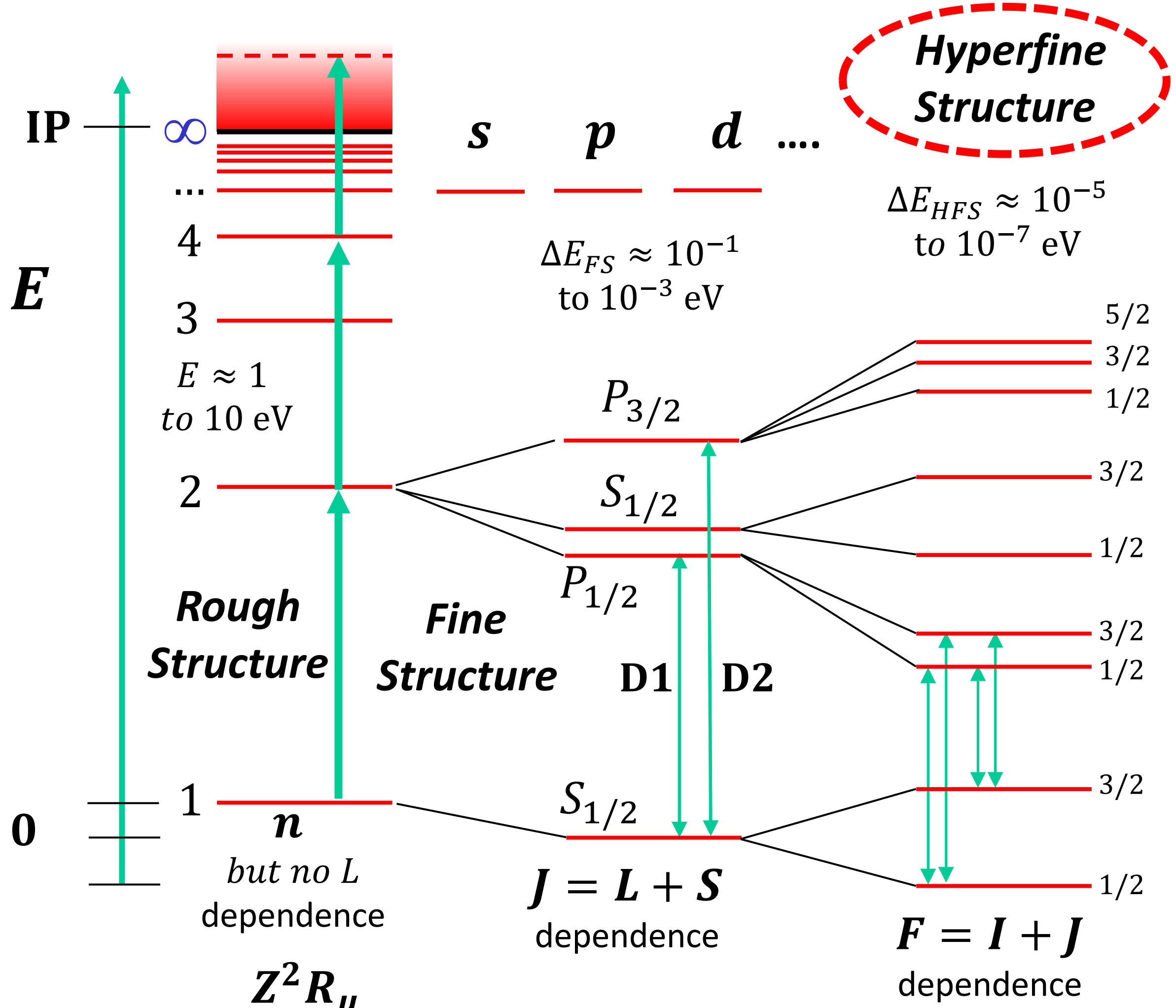
JGU (Johannes Gutenberg-Universität),
Mainz, Germany

EU ITN in Horizon 2020

Atomic Spectroscopy of the Elements --- from $_{1}$H to $_{100}$Fm

Resonance Ionization Spectroscopy on atomic structures

$$C = F(F+1) - I(I+1) - J(J+1)$$



Hyperfine Structure

$E \approx 1$ to 10 eV

$\Delta E_{FS} \approx 10^{-1}$ to 10^{-3} eV

$\Delta E_{HFS} \approx 10^{-5}$ to 10^{-7} eV

Rough Structure

n *but no L* dependence

Fine Structure

$J = L + S$ dependence

$F = I + J$ dependence

$$E_n \sim \mathrm{IP} - \frac{Z^2 R_\mu}{n^2}$$

≈ 1-5 GHz

~ 10 MHz

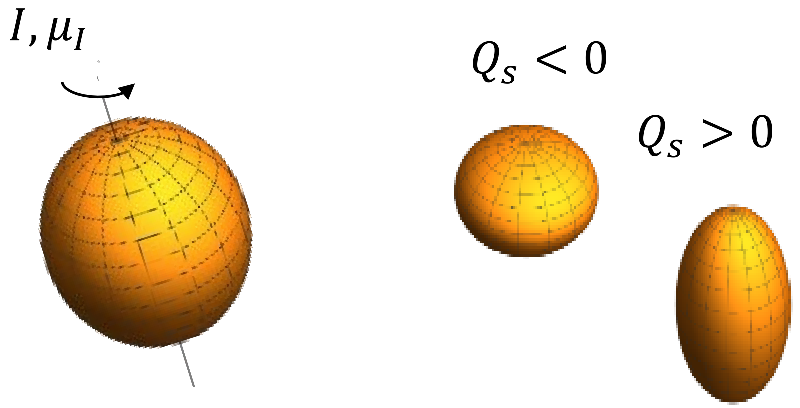
$$\Delta E_H = \Delta E_\mu + \Delta E_Q$$

$$= A\,\frac{C}{2} + B\,\frac{3\,(C+1) - 2I(I+1)J(J+1)}{8\,I\,(2I-1)J(2J-1)}$$

Magnetic dipole & Electric quadrupol

moment of the atomic nucleus

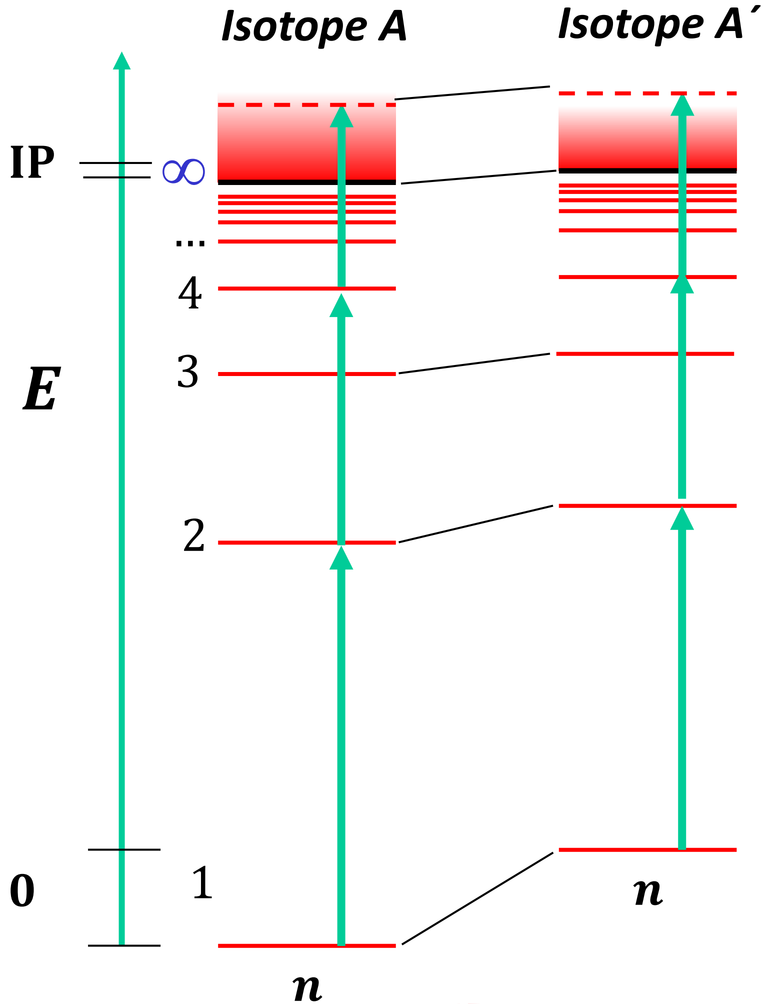
$$A = \frac{\mu_I \overline{H(0)}}{IJ} \qquad B = eQ_s \left\langle \frac{\partial^2 \phi}{\partial z^2} \right\rangle_{r=0}$$



→ High spectral resolution required

The **Extra:** isotope shifts in High Resolution Spectroscopy

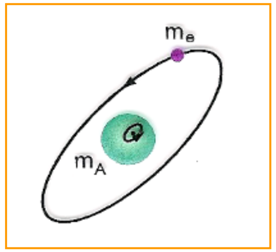
Isotope Shift

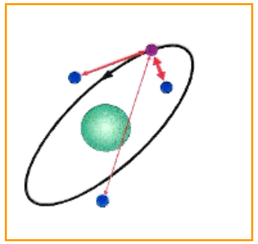


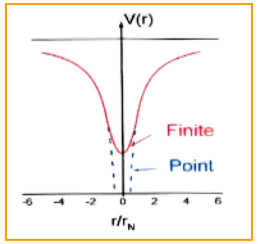
10 MHz – 1 GHz

Shift of all resonance frequencies from isotope to isotope

$$\delta\nu_{A,A'} = \nu_{A'} - \nu_{A} = \overbrace{(K_{NMS} + K_{SMS})\,\frac{m_A - m_{A'}}{m_A \cdot m_{A'}}}^{\textit{Mass shift}} + \overbrace{F_{FS}\cdot\,\delta\langle r^2\rangle_{A,A'}}^{\textit{Field shift}}$$

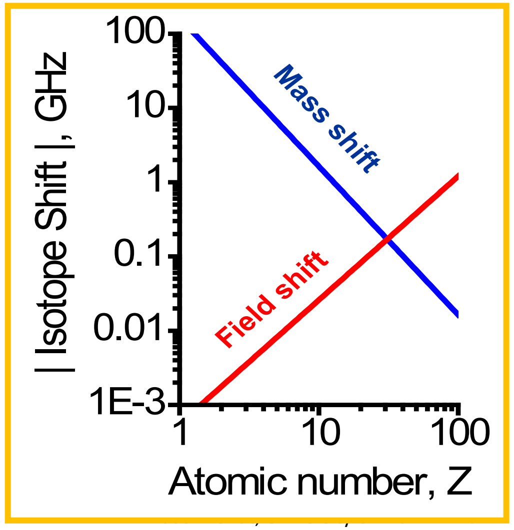






→ *Size and deformation of atomic nuclei*

→ *Highest optical isotope selectivity above 10^9*



P. Müller, B.A. Bushaw et al., Fresenius J. Anal. Chem. 370, 508-512 (2001)

IP values & open subshells of the Elements

One open valence shell

only for alkaline elements

Two open shells

alkaline earths, noble gases

& main group elements

Three open shells

transition group elements

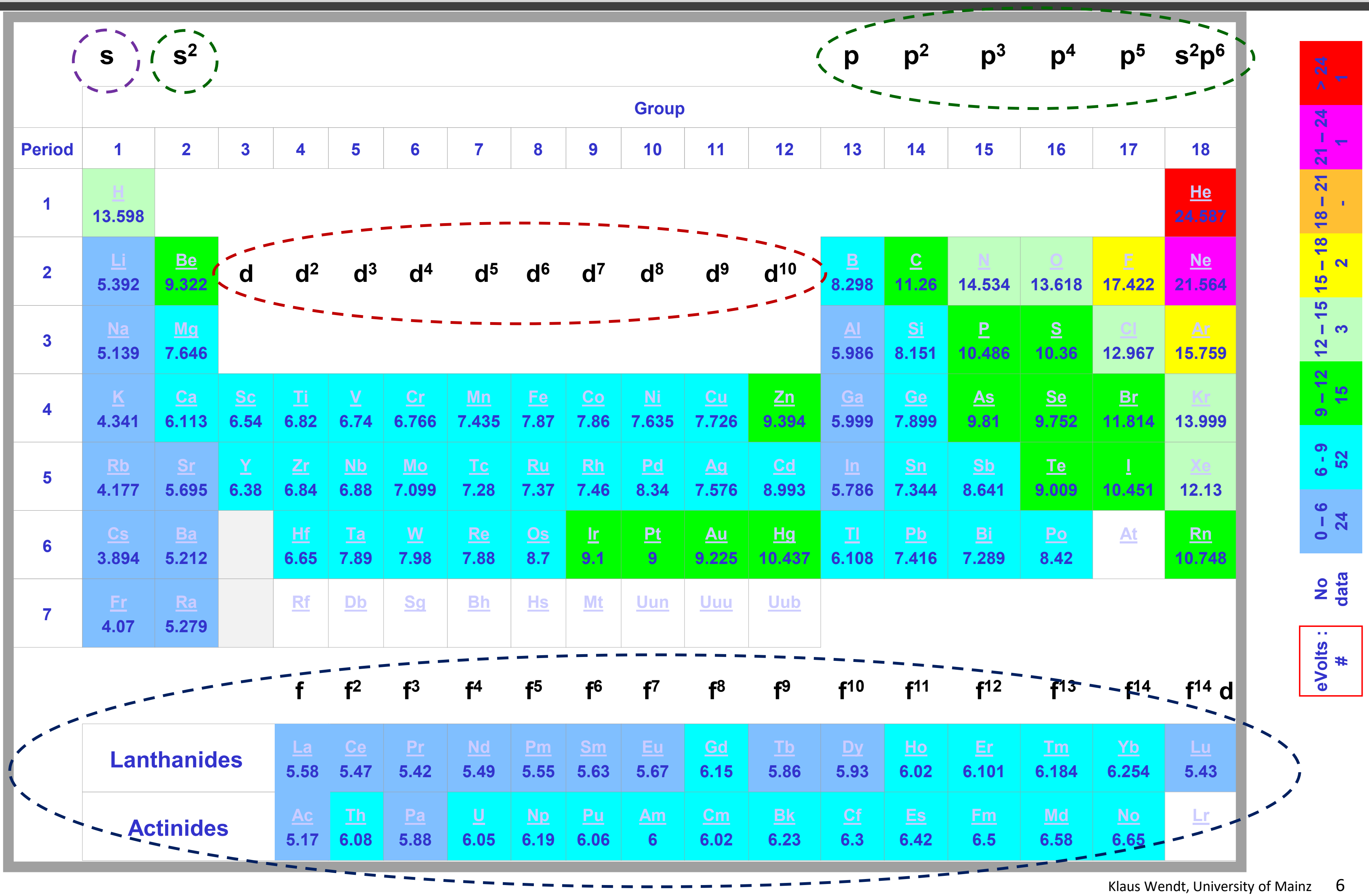
Four open shells –

lanthanide & actinides

BUT

Binding energy (IP)

neither affected nor regular



	s	s^2											p	p^2	p^3	p^4	p^5	s^2p^6
	Group																	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 13.598																	He 24.587
2	Li 5.392	Be 9.322	d	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	B 8.298	C 11.26	N 14.534	O 13.618	F 17.422	Ne 21.564
3	Na 5.139	Mg 7.646											Al 5.986	Si 8.151	P 10.486	S 10.36	Cl 12.967	Ar 15.759
4	K 4.341	Ca 6.113	Sc 6.54	Ti 6.82	V 6.74	Cr 6.766	Mn 7.435	Fe 7.87	Co 7.86	Ni 7.635	Cu 7.726	Zn 9.394	Ga 5.999	Ge 7.899	As 9.81	Se 9.752	Br 11.814	Kr 13.999
5	Rb 4.177	Sr 5.695	Y 6.38	Zr 6.84	Nb 6.88	Mo 7.099	Tc 7.28	Ru 7.37	Rh 7.46	Pd 8.34	Ag 7.576	Cd 8.993	In 5.786	Sn 7.344	Sb 8.641	Te 9.009	I 10.451	Xe 12.13
6	Cs 3.894	Ba 5.212		Hf 6.65	Ta 7.89	W 7.98	Re 7.88	Os 8.7	Ir 9.1	Pt 9	Au 9.225	Hg 10.437	Tl 6.108	Pb 7.416	Bi 7.289	Po 8.42	At	Rn 10.748
7	Fr 4.07	Ra 5.279		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
				f	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}	f^{14} d
Lanthanides				La 5.58	Ce 5.47	Pr 5.42	Nd 5.49	Pm 5.55	Sm 5.63	Eu 5.67	Gd 6.15	Tb 5.86	Dy 5.93	Ho 6.02	Er 6.101	Tm 6.184	Yb 6.254	Lu 5.43
Actinides				Ac 5.17	Th 6.08	Pa 5.88	U 6.05	Np 6.19	Pu 6.06	Am 6	Cm 6.02	Bk 6.23	Cf 6.3	Es 6.42	Fm 6.5	Md 6.58	No 6.65	Lr

eVolts :	#
No	data
0 – 6	24
6 - 9	52
9 – 12	15
12 – 15	3
15 – 18	2
18 – 21	-
21 – 24	1
> 24	1

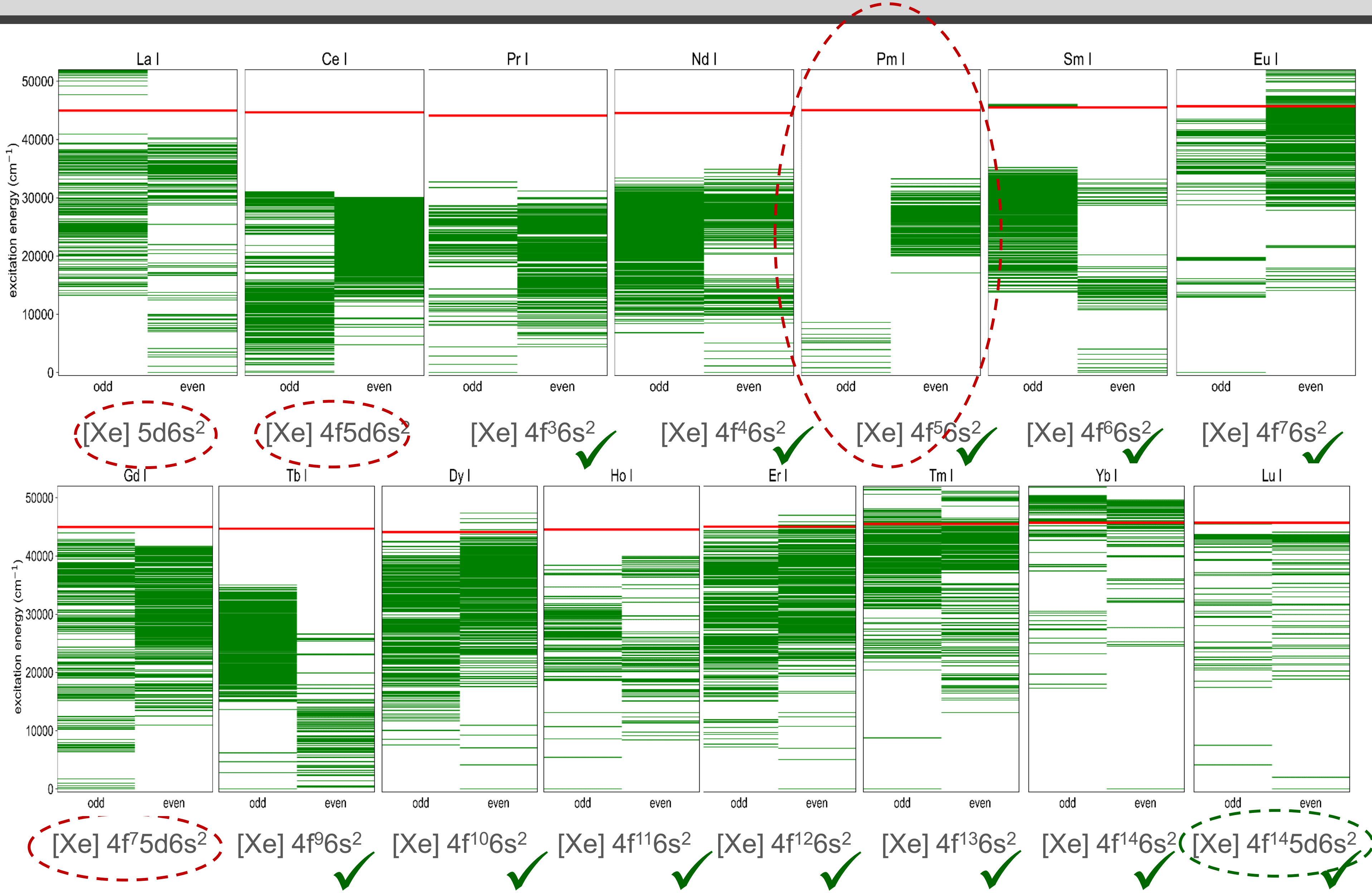
Complex Atoms: Ground States & Level Schemes of Lanthanides

Lanthanide atoms (rather) **regularly** fill the **4f^n** shell sequentially

- **5d** electron mixed in -
(**3** out of 15
at empty and half filled shell)

Ground state configurations obey the **3 Hund´s rules** for the lowest energy level:

1. Max. multiplicity 2S+1
2. Largest orbital L
3. Lowest total J = L+S



[Xe] $5d6s^2$ | [Xe] $4f5d6s^2$ | [Xe] $4f^36s^2$ ✓ | [Xe] $4f^46s^2$ ✓ | [Xe] $4f^56s^2$ ✓ | [Xe] $4f^66s^2$ ✓ | [Xe] $4f^76s^2$ ✓

[Xe] $4f^75d6s^2$ | [Xe] $4f^96s^2$ ✓ | [Xe] $4f^{10}6s^2$ ✓ | [Xe] $4f^{11}6s^2$ ✓ | [Xe] $4f^{12}6s^2$ ✓ | [Xe] $4f^{13}6s^2$ ✓ | [Xe] $4f^{14}6s^2$ ✓ | [Xe] $4f^{14}5d6s^2$ ✓

More Complex Atoms : Ground States & Levels of Actinides

Free **actinide** atoms do **NOT** fill the **5f^n** shell sequentially

-1 to 2 **6d** electrons mixed in (for **6** out of 15)
(all the lighter ones & half-filled f shell)

→

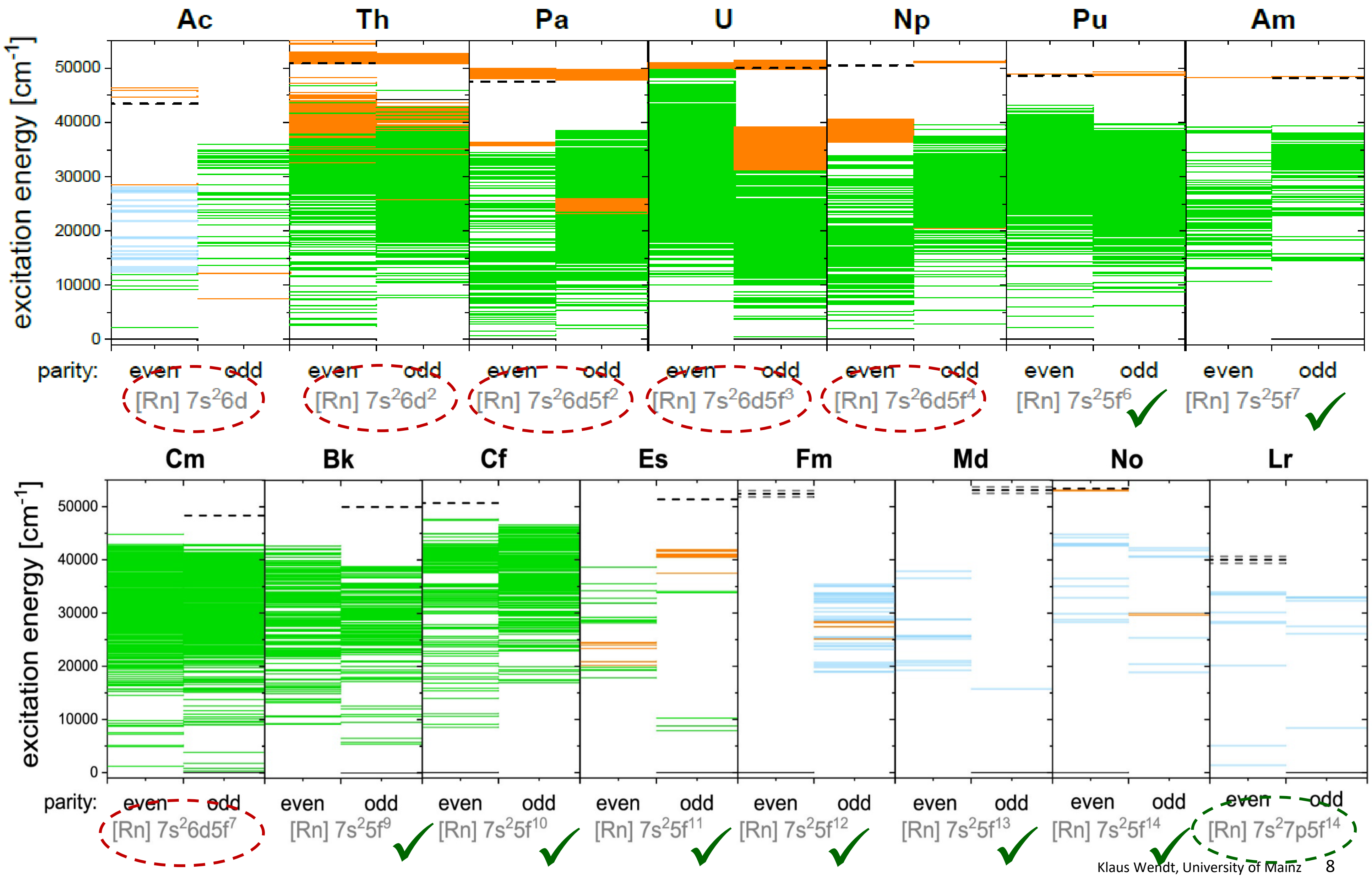
Ground and excited levels not clearly assignable
(only total angular momentum J)

-

strong configurations mixing
→ quantum chaos

-

Orange levels newly studied

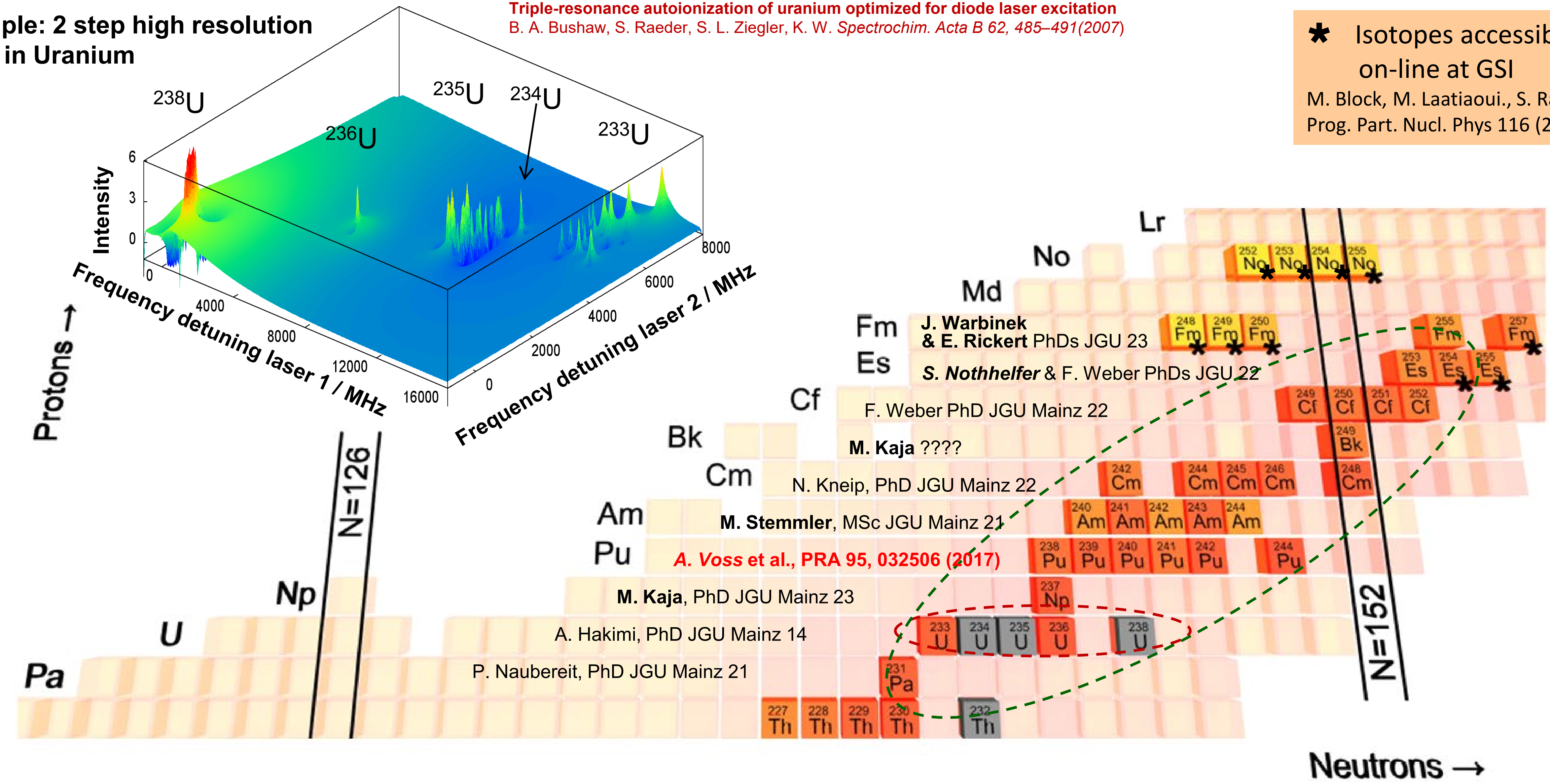


Off-line and on-line accessible Isotopes in the Actinides

Example: 2 step high resolution RIMS in Uranium

Triple-resonance autoionization of uranium optimized for diode laser excitation
B. A. Bushaw, S. Raeder, S. L. Ziegler, K. W. *Spectrochim. Acta B 62, 485–491(2007)*

* Isotopes accessible on-line at GSI
M. Block, M. Laatiaoui., S. Raeder
Prog. Part. Nucl. Phys 116 (2021)



J. Warbinek & **E. Rickert** PhDs JGU 23

S. Nothhelfer & F. Weber PhDs JGU 22

F. Weber PhD JGU Mainz 22

M. Kaja ????

N. Kneip, PhD JGU Mainz 22

M. Stemmler, MSc JGU Mainz 21

A. Voss **et al., PRA 95, 032506 (2017)**

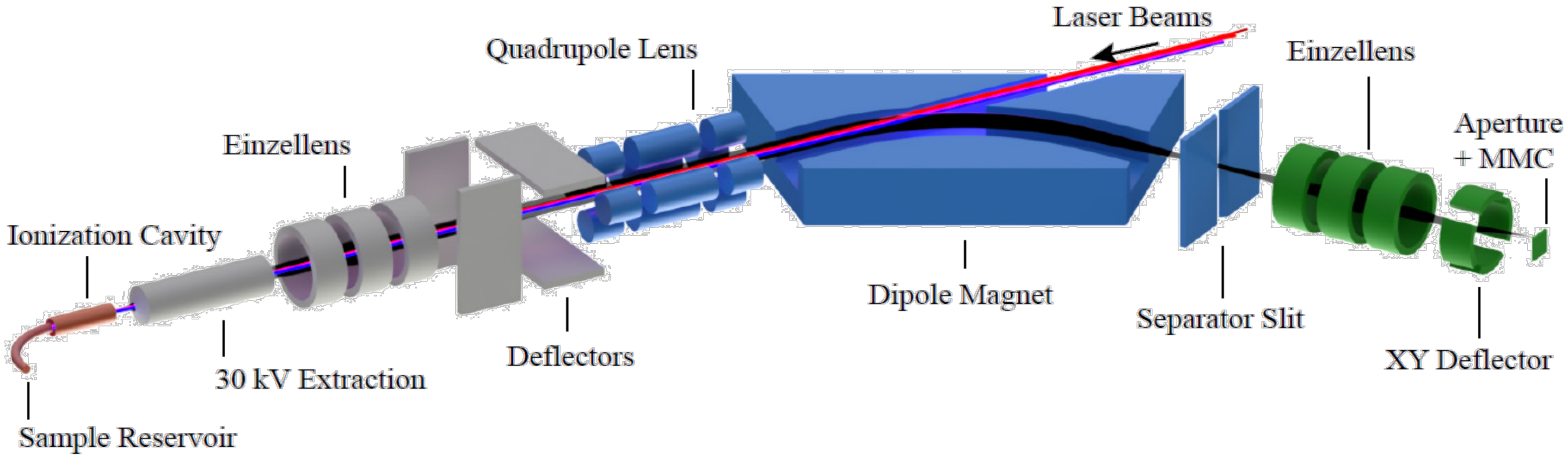
M. Kaja, PhD JGU Mainz 23

A. Hakimi, PhD JGU Mainz 14

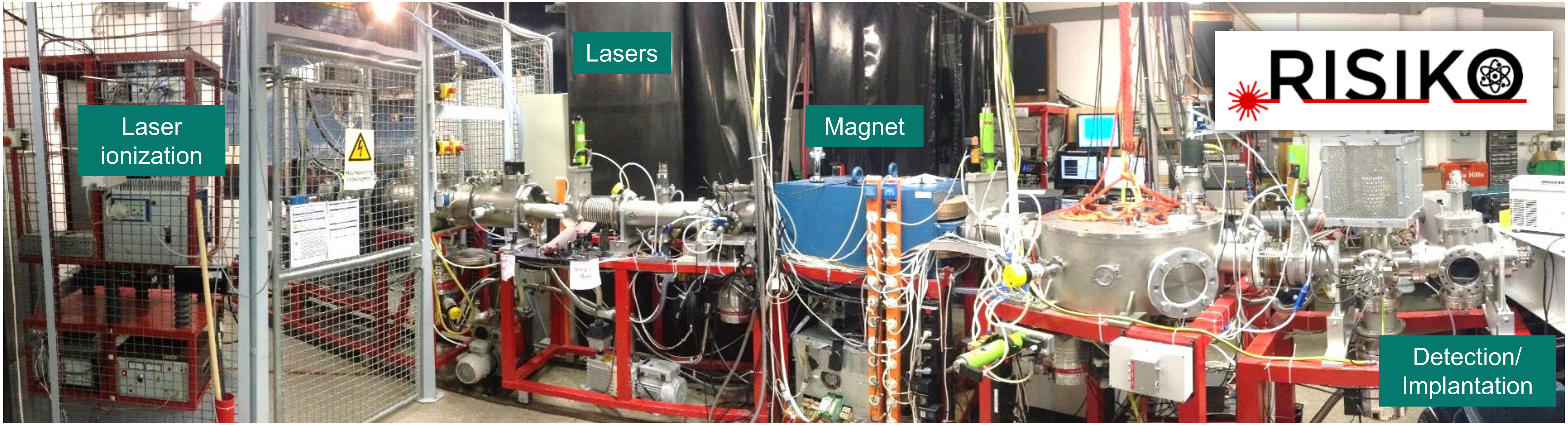
P. Naubereit, PhD JGU Mainz 21

Production of Actinides at ORNL High Flux Reactor: S.M. Robinson et al., Radiochim. Acta 2020; 108(9): 737–746

The **RISIKO** – RILIS development tool & off-line **RIB** facility



Optimum development tool for on-line laser ion sources and RIMS analytics

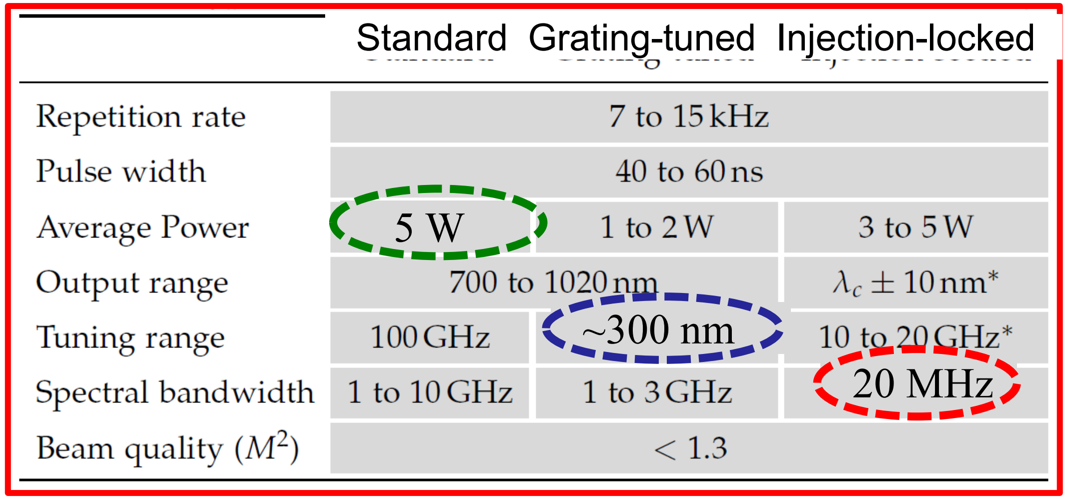


The laser family: pulsed, powerful & narrow-bandwidth for RIMS

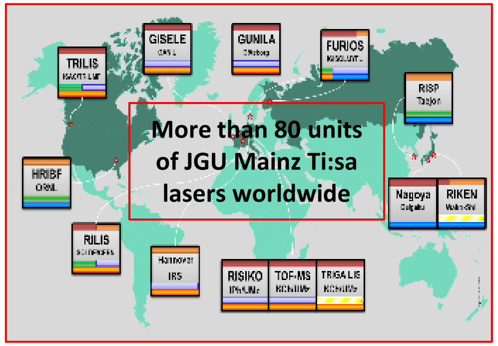
Custom-built Ti:sa laser cavities for pulsed high repetition rate operation

R. Horn, PhD. JGU 2003

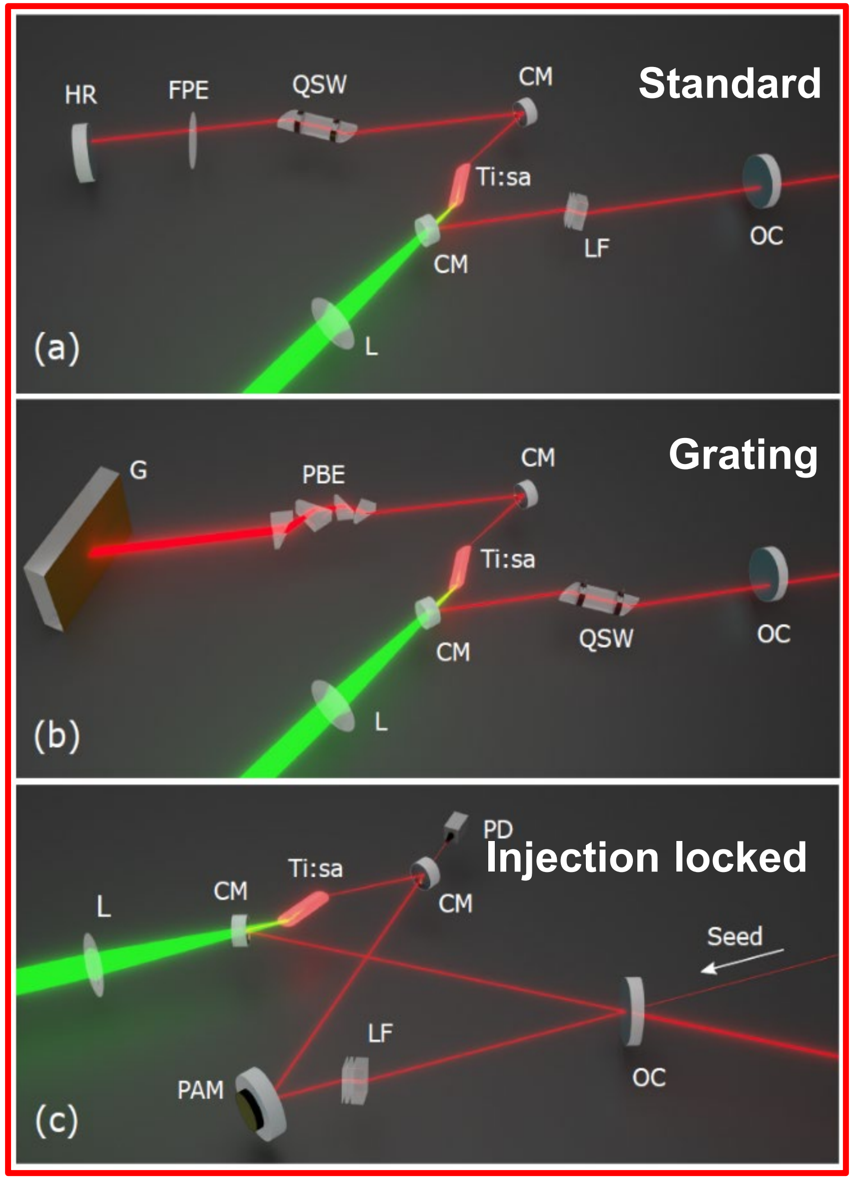
- Three different designs - tailored for
  - High power (standard laser) → efficiency
  - Fast continuous wide-range scanning (via grating) → quasi-simultaneous multi element analysis
  - Narrowband operation (injection-locked laser) → high resolution
- Resonator internal SHG for blue and single pass THG or FHG for UV



	Standard	Grating-tuned	Injection-locked
Repetition rate	7 to 15 kHz		
Pulse width	40 to 60 ns		
Average Power	5 W	1 to 2 W	3 to 5 W
Output range	700 to 1020 nm		$\lambda_c \pm 10$ nm*
Tuning range	100 GHz	~300 nm	10 to 20 GHz*
Spectral bandwidth	1 to 10 GHz	1 to 3 GHz	20 MHz
Beam quality (M^2)	< 1.3		

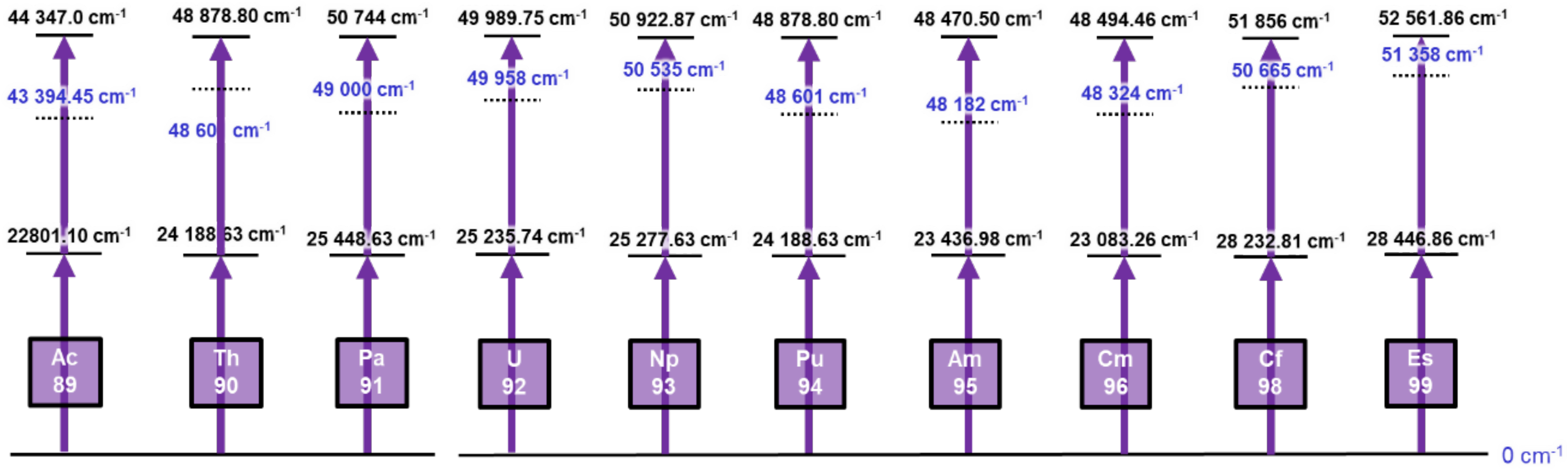


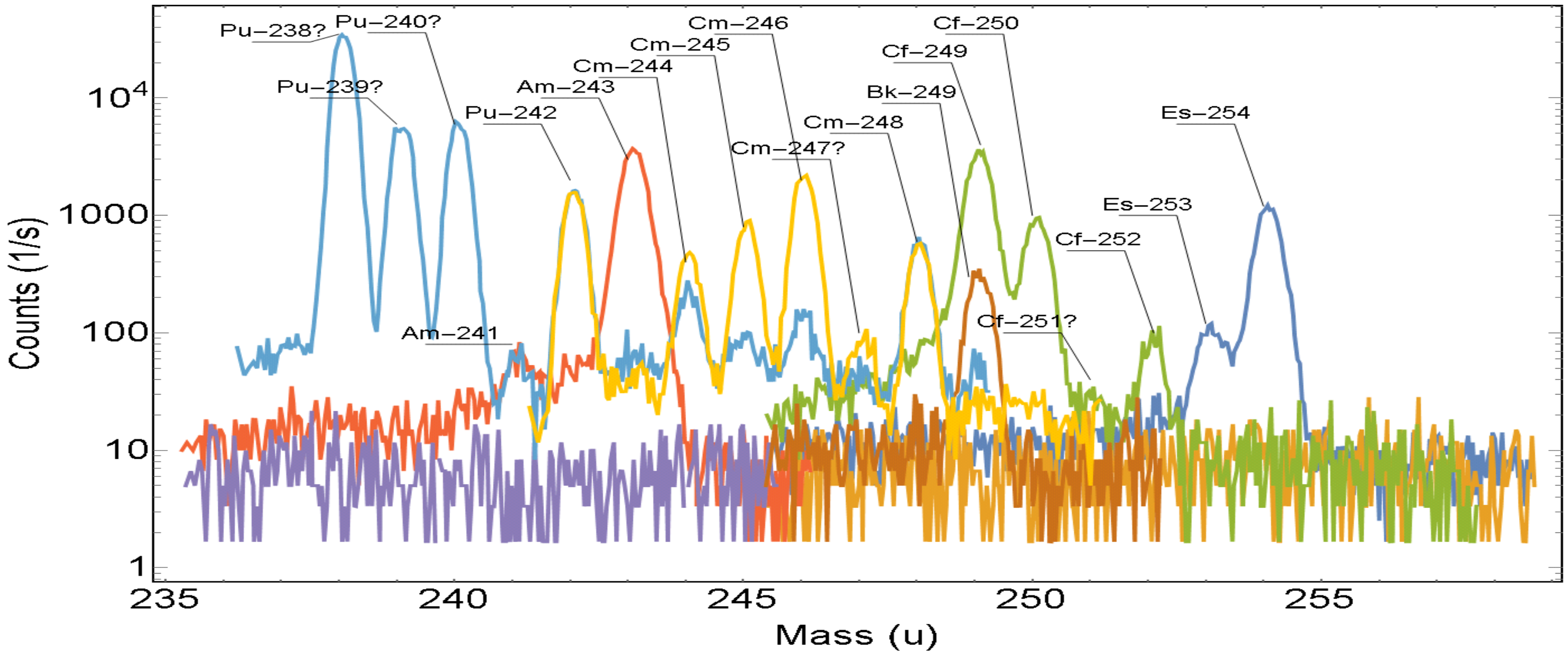
More than 80 units of JGU Mainz Ti:sa lasers worldwide



Characterization of a pulsed injection-locked Ti:sapphire laser and its application to HR RIMS of copper
V. Sonnenschein, I.D. Moore, S. Raeder, M. Reponen, H. Tomita, K. W. *Laser Physics 27, 085701 (2017)*

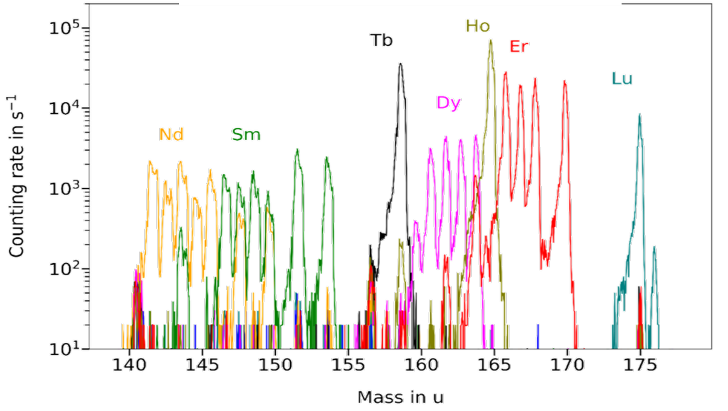
Multielement RIMS on Actinides





- Simple & efficient two-step RIS
- Rapid access to each individual element taken from isoelectronic REEs

F. Weber , MSc JGU al., in preparation



→ Fast full sample characterization

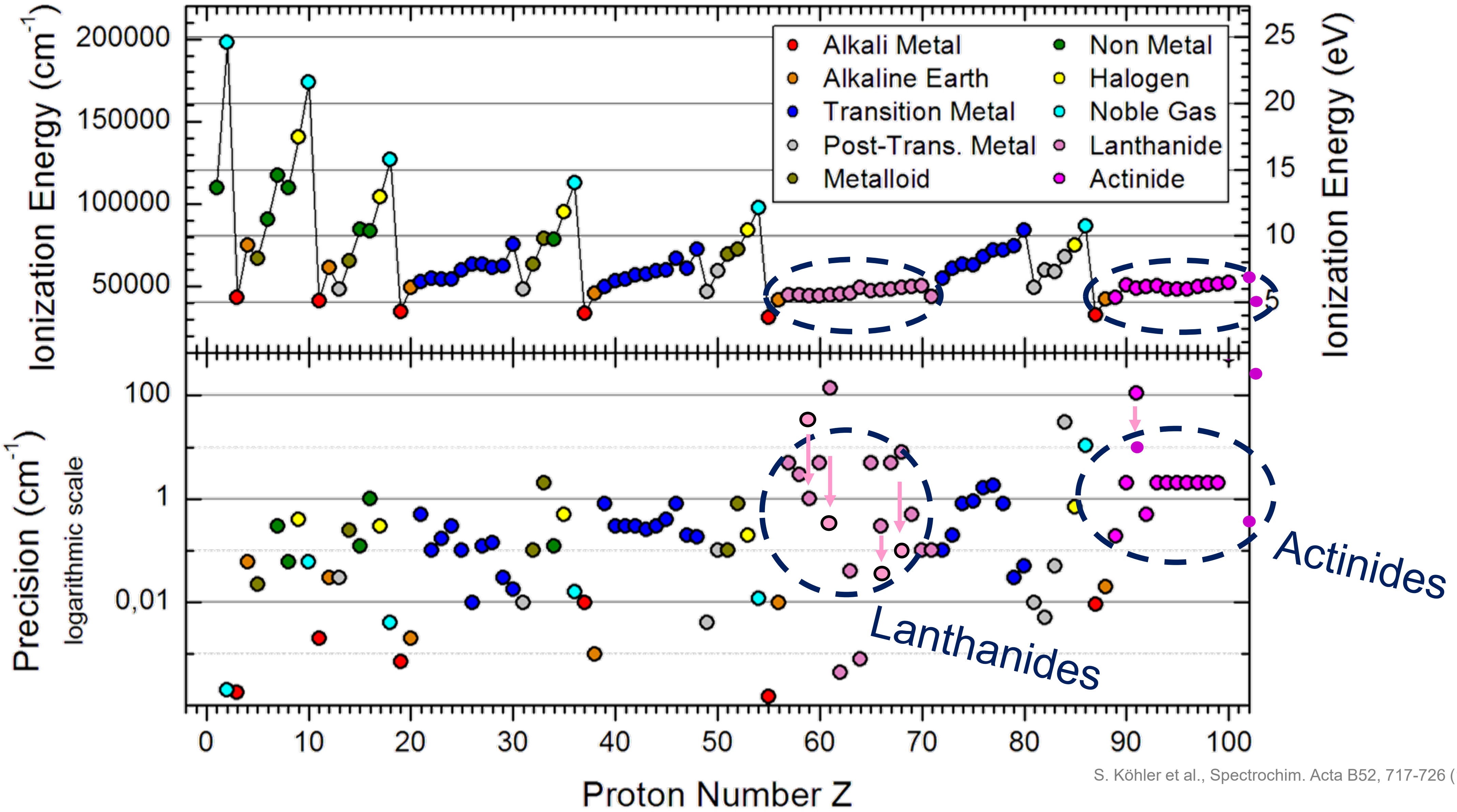
→ Isobar-free, low-background isotope ratio determination

→ Laser spectroscopy in mixed sample

→ Ultratrace analysis & fundamentals studies

Exclusive sample obtained from ORNL (J. Etzold)

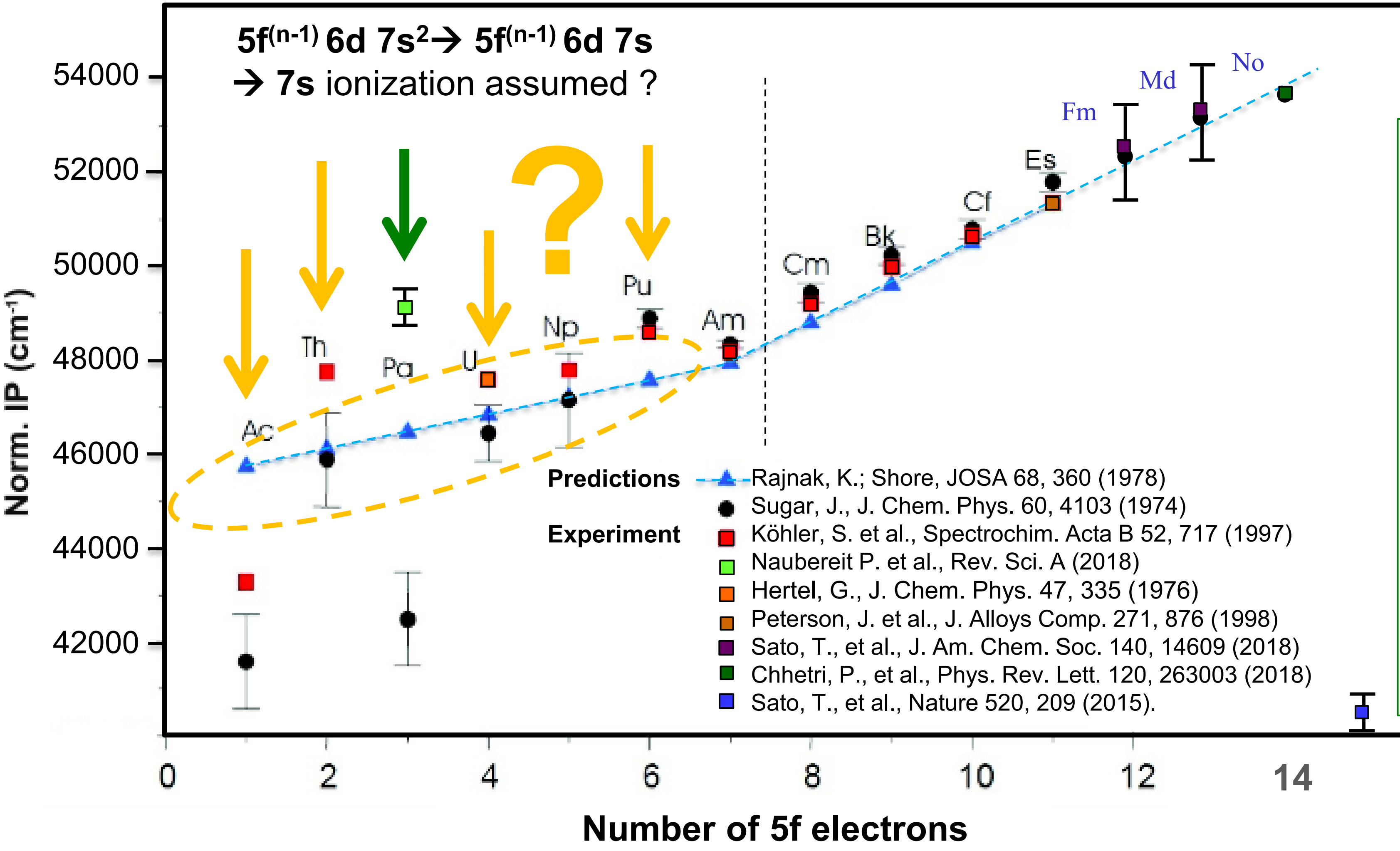
Ionization Potentials and Errors



S. Köhler et al., Spectrochim. Acta B52, 717-726 (1997)

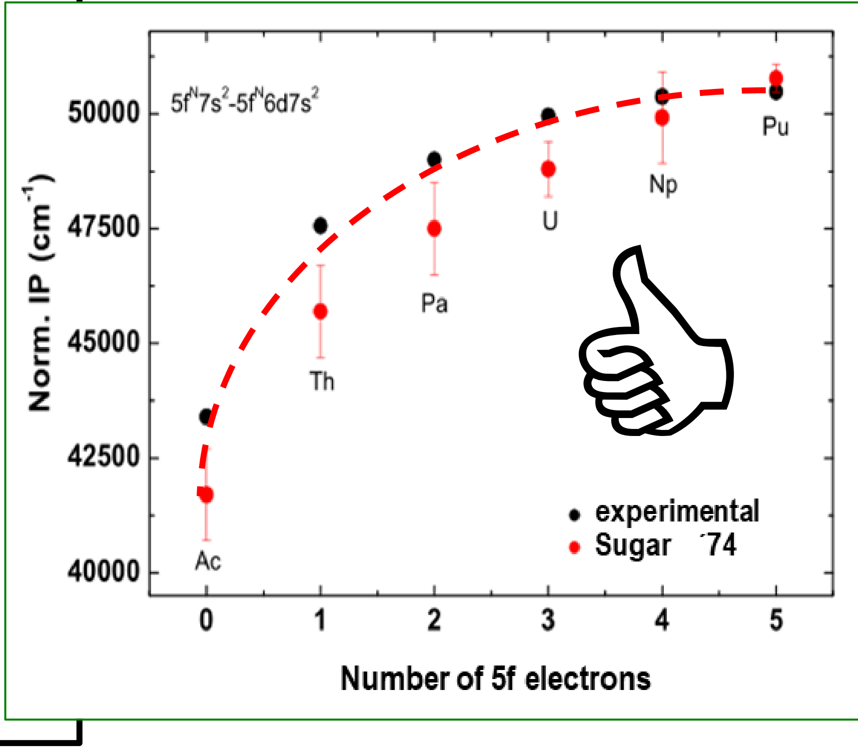
Knowledge on the IP´s of the Actinides today

Regular trend of **5f^n 6d 7s^2 → 5f^n 6d 7s ionization above** - - - unpronounced behaviour **below** half-filled **5f shell**



5f$^{(n-1)}$ 6d 7s^2 → 5f$^{(n-1)}$ 6d 7s
→ **7s** ionization assumed ?

5f$^{(n-1)}$ 6d 7s^2 → 5f$^{(n-1)}$ 7s^2
→ **6d** ionization valid !



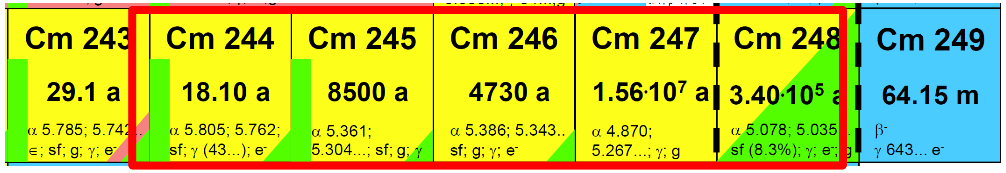
K. W. et al., Hyperfine Interact **227,** 55 (2017)

Low and high resolution spectroscopy in $_{96}$Curium

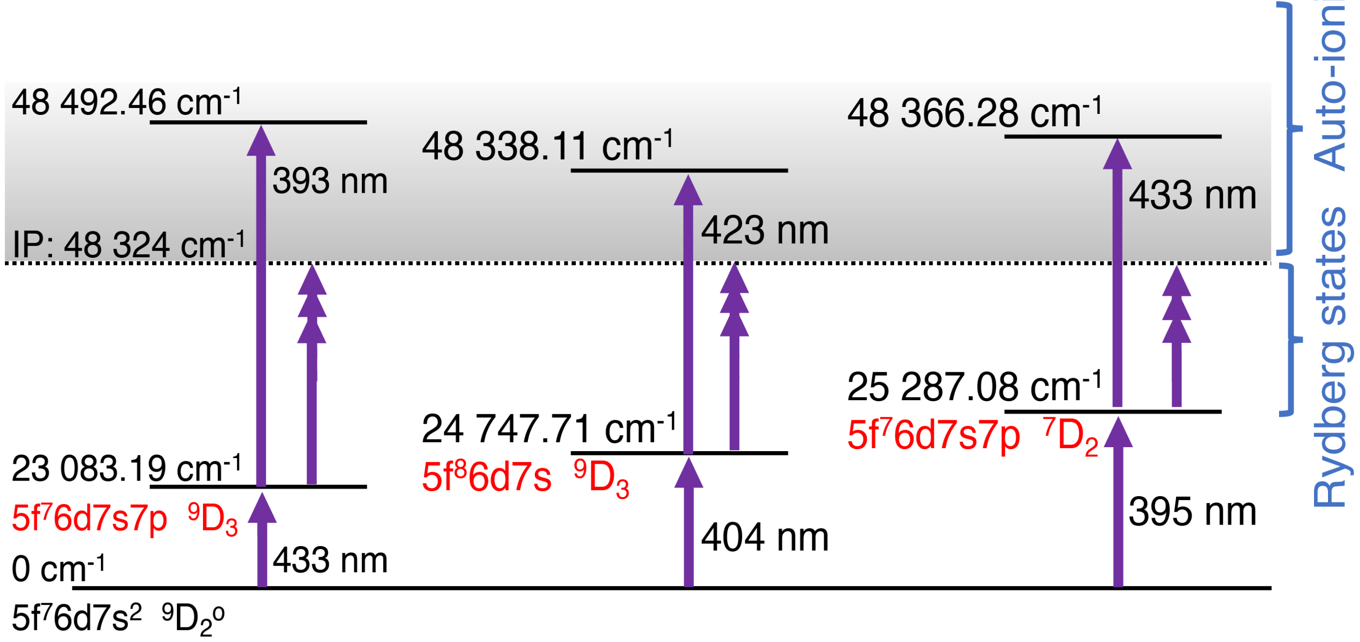
Auto-ionizing states & Rydberg analysis

- Characterization of first excitation states (FES)
- Identification of 3 different ionization schemes
- IP determination by Rydberg analysis
- Verification by field ionization
- High resolution spectroscopy on HFS & IS

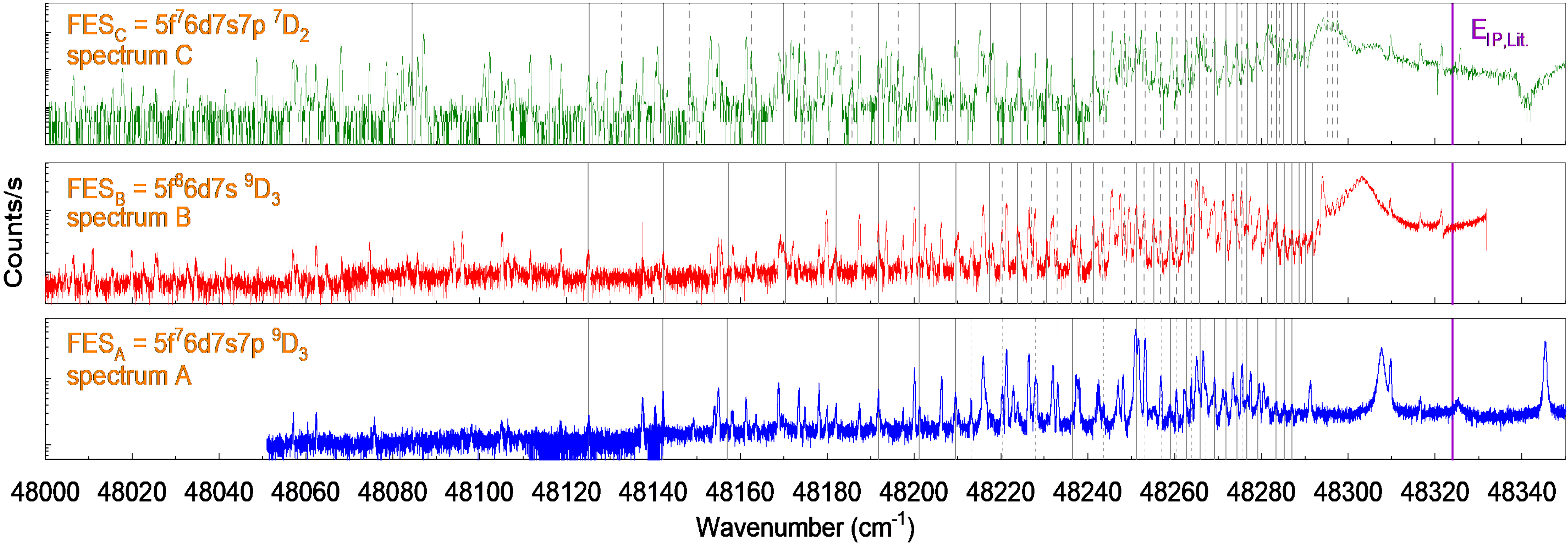
PhD Thesis of Nina Kneip & to be published



Cm 243	Cm 244	Cm 245	Cm 246	Cm 247	Cm 248	Cm 249
29.1 a	18.10 a	8500 a	4730 a	$1.56 \cdot 10^7$ a	$3.40 \cdot 10^5$ a	64.15 m
α 5.785; 5.742 ∊; sf; g; γ; e^-	α 5.805; 5.762; sf; γ (43...); e^-	α 5.361; 5.304...; sf; g; γ	α 5.386; 5.343.. sf; g; γ; e^-	α 4.870; 5.267...; γ; g	α 5.078; 5.035 sf (8.3%); γ; e^-; g	β^- γ 643... e^-



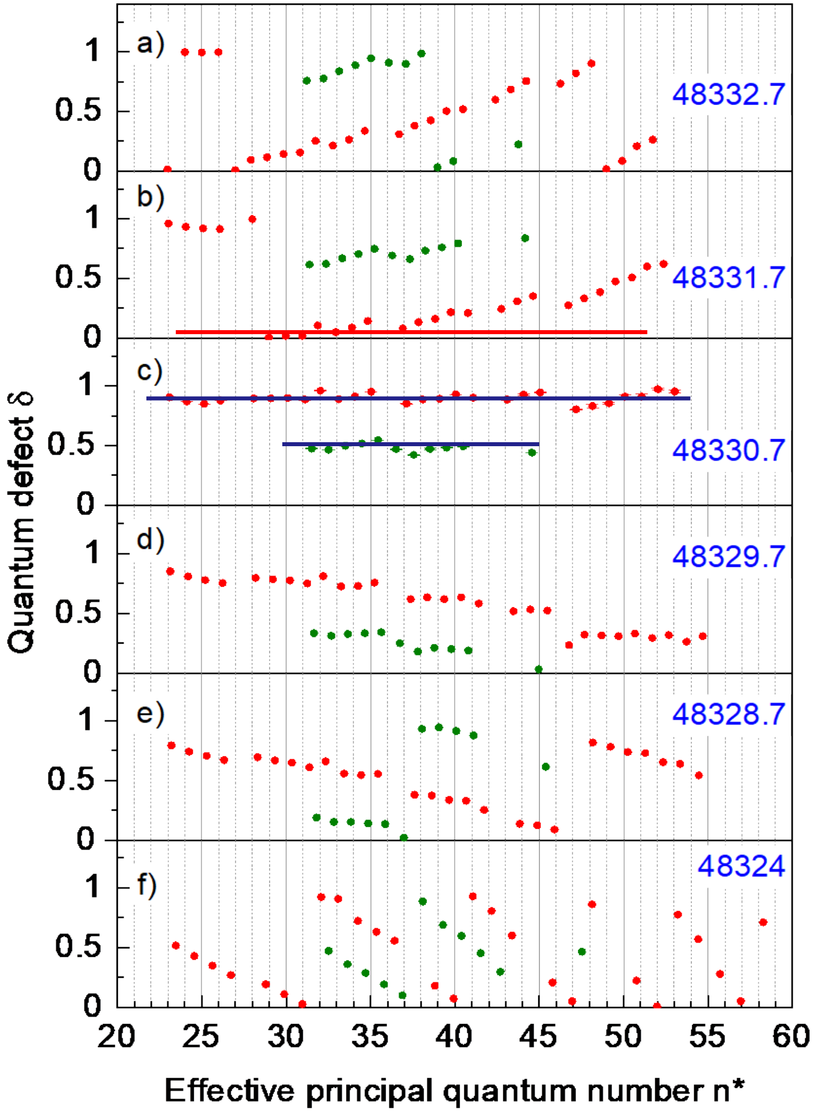
High lying & Rydberg states in Curium



Investigation of the Rydberg spectrum A, B and C

- Spectral scan range 400 cm^{-1}
- High state density below the ionization potential showing systematic structures

Rydberg analysis for IP determination



Rydberg Ritz formula:

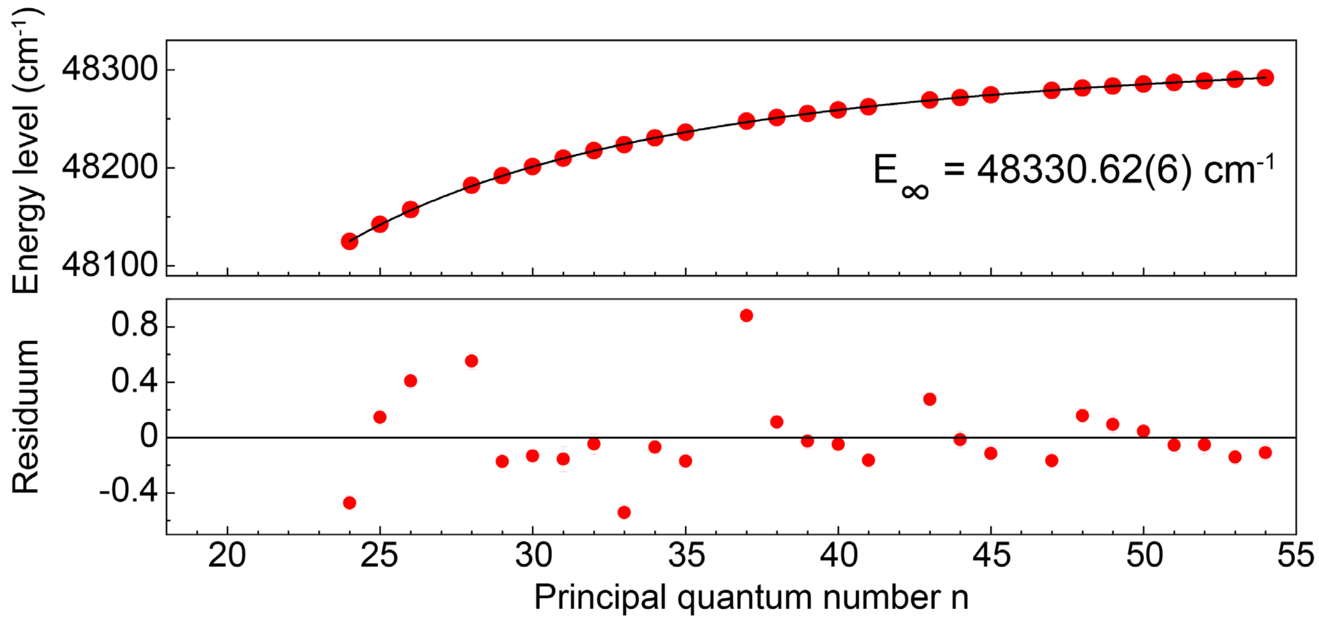
$$E_n = E_{\mathrm{IP}} - \frac{R_\mu}{(n-\delta(n))^2} = E_{\mathrm{IP}} - \frac{R_\mu}{(n^*)^2}$$

$$\rightarrow \quad n^* = \frac{R_\mu}{E_{\mathrm{IP}} - E_n}$$

E_n	measured energy level	δ	quantum defect
E_{IP}	ionization potential	n	principal quantum number
R_μ	Rydberg constant	n^*	effective principal quantum number

This work

Köhler et al.:
48324(2) cm^{-1}



Rydberg Ritz fit [1]

n^* against δ for first IP estimation [1]

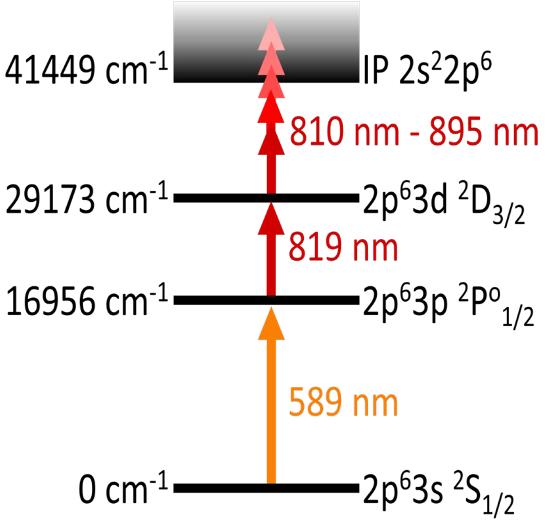
Precision of IP Determination: Rydberg Convergences in Na

Test in $_{11}$Sodium

wide range laser scan

for > 1000 cm^{-1} in TES

around the expected IP



41449 cm^{-1} IP $2s^22p^6$

810 nm - 895 nm

29173 cm^{-1} $2p^63d\ ^2D_{3/2}$

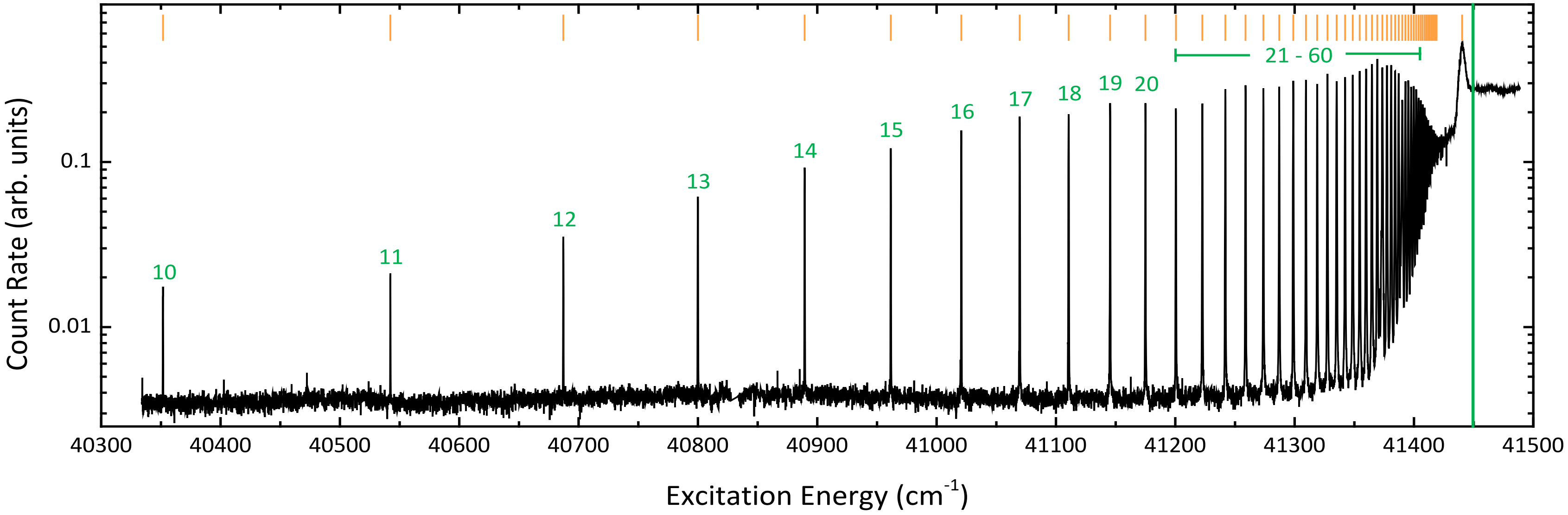
819 nm

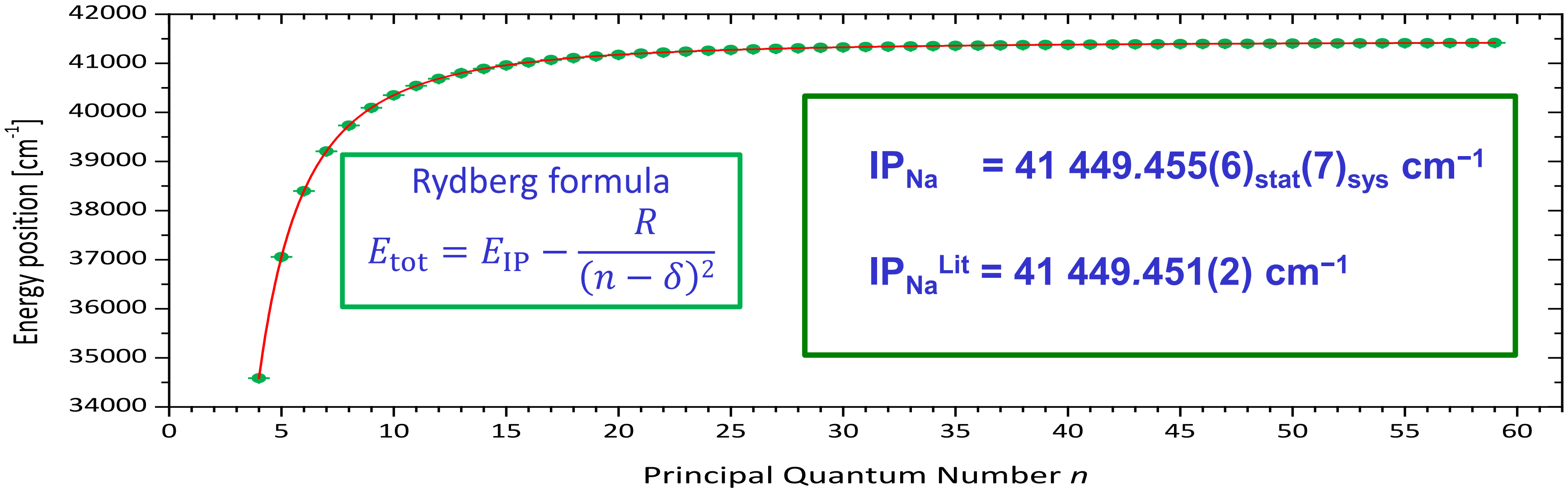
16956 cm^{-1} $2p^63p\ ^2P^o_{1/2}$

589 nm

0 cm^{-1} $2p^63s\ ^2S_{1/2}$

…an optimum situation…





Rydberg formula

$$E_{\text{tot}} = E_{\text{IP}} - \frac{R}{(n-\delta)^2}$$

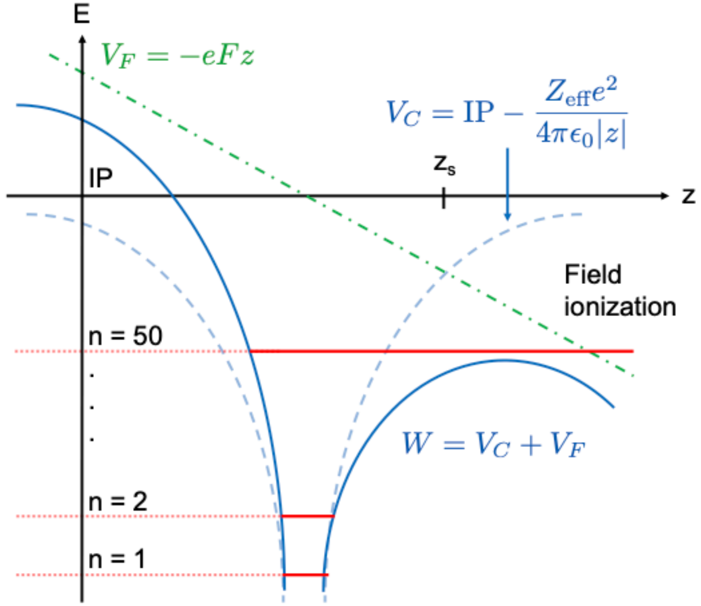
$\mathbf{IP_{Na} = 41\,449.455(6)_{stat}(7)_{sys}\ cm^{-1}}$

$\mathbf{IP_{Na}^{Lit} = 41\,449.451(2)\ cm^{-1}}$

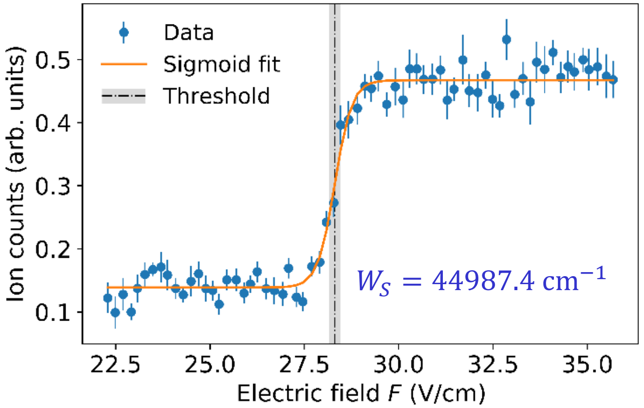
[7] P. Naubereit et al., *Phys. Rev. A*, **93**, 052518 (2016)

Redetermination by Field Ionization

Test on the Quasi-Actinide Element Pm (isoelectronic to Np)

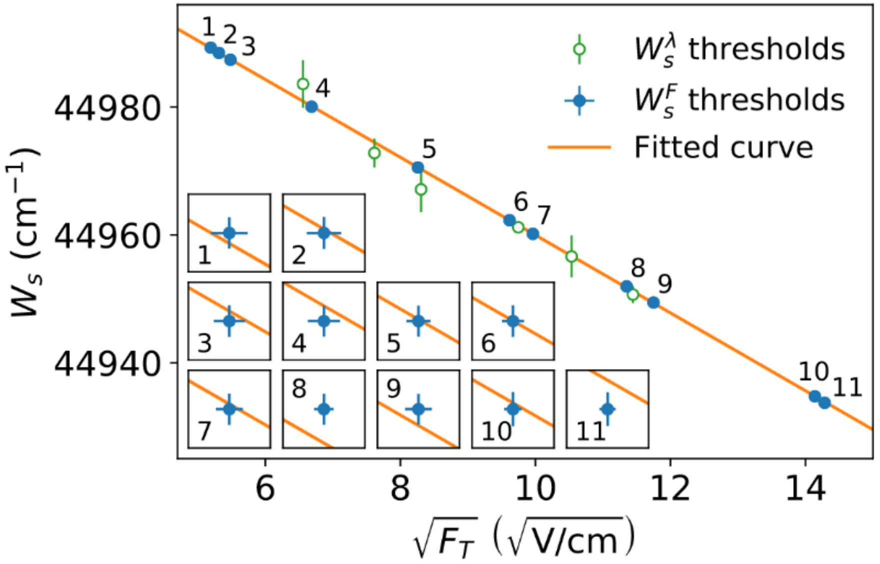


Saddle-Point Model

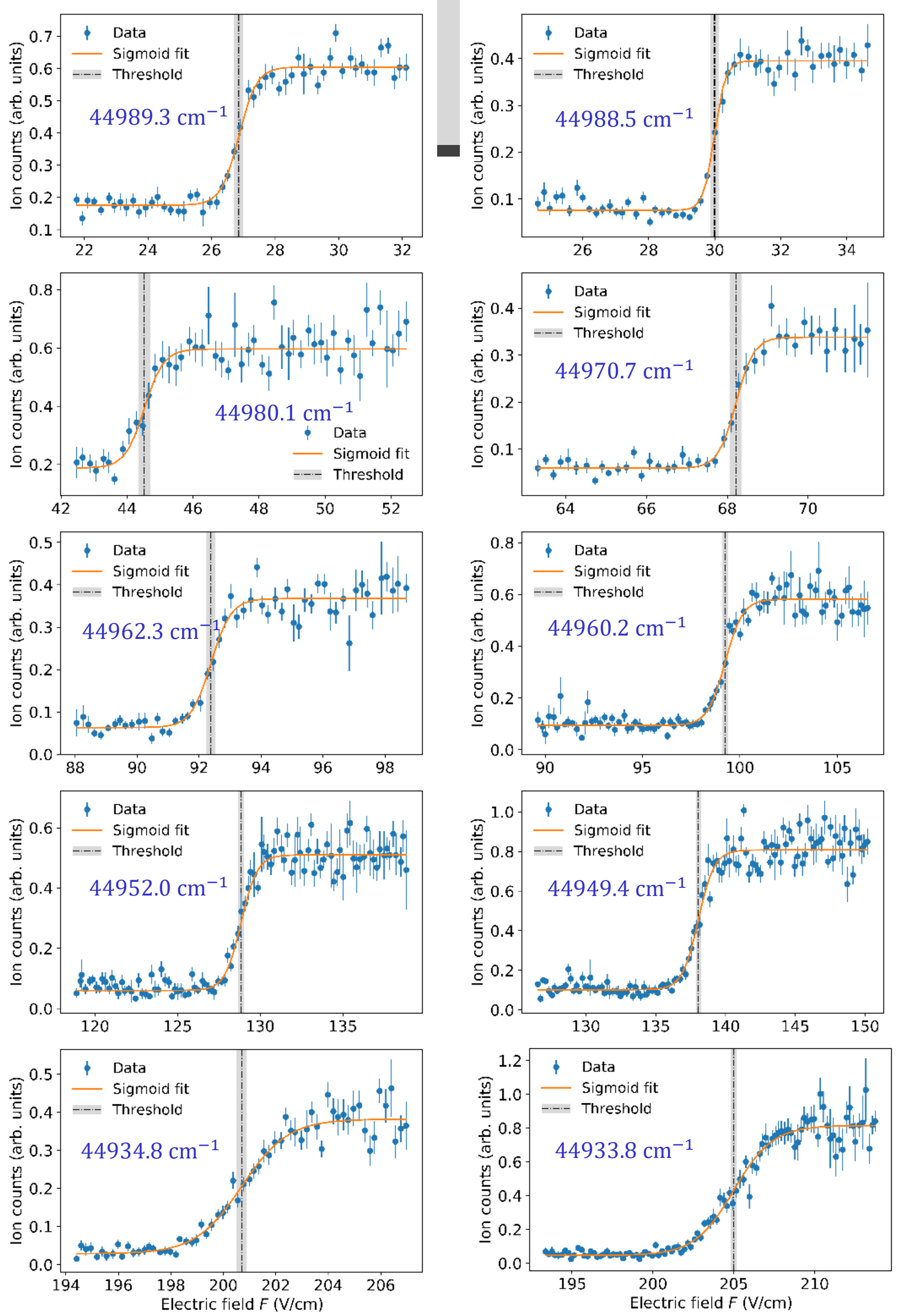


Result

$\rightarrow \mathbf{IP_{Pm} = 45020.8(3)\ cm^{-1}}$



D. Studer et al., PRA **99**, *062513 (2019)*

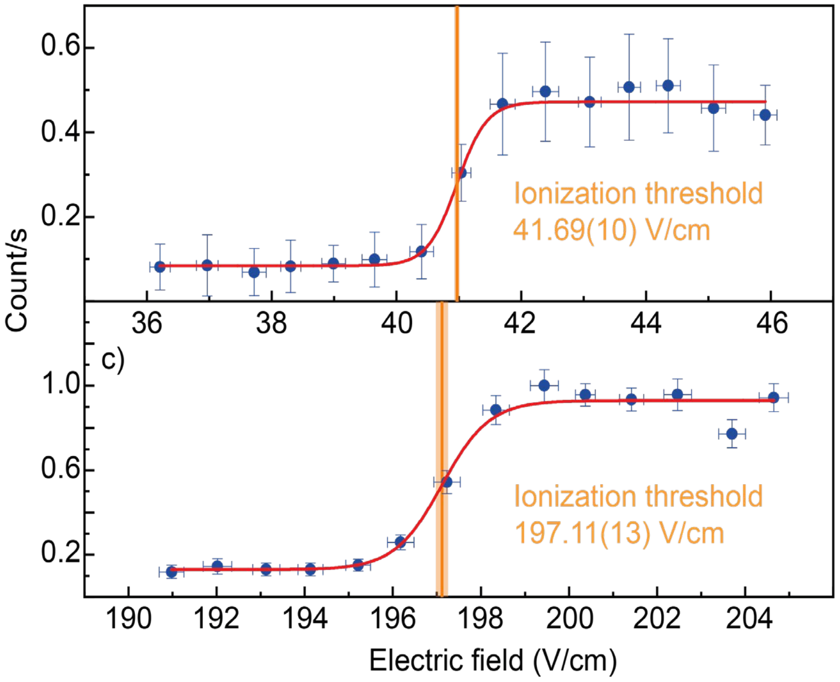


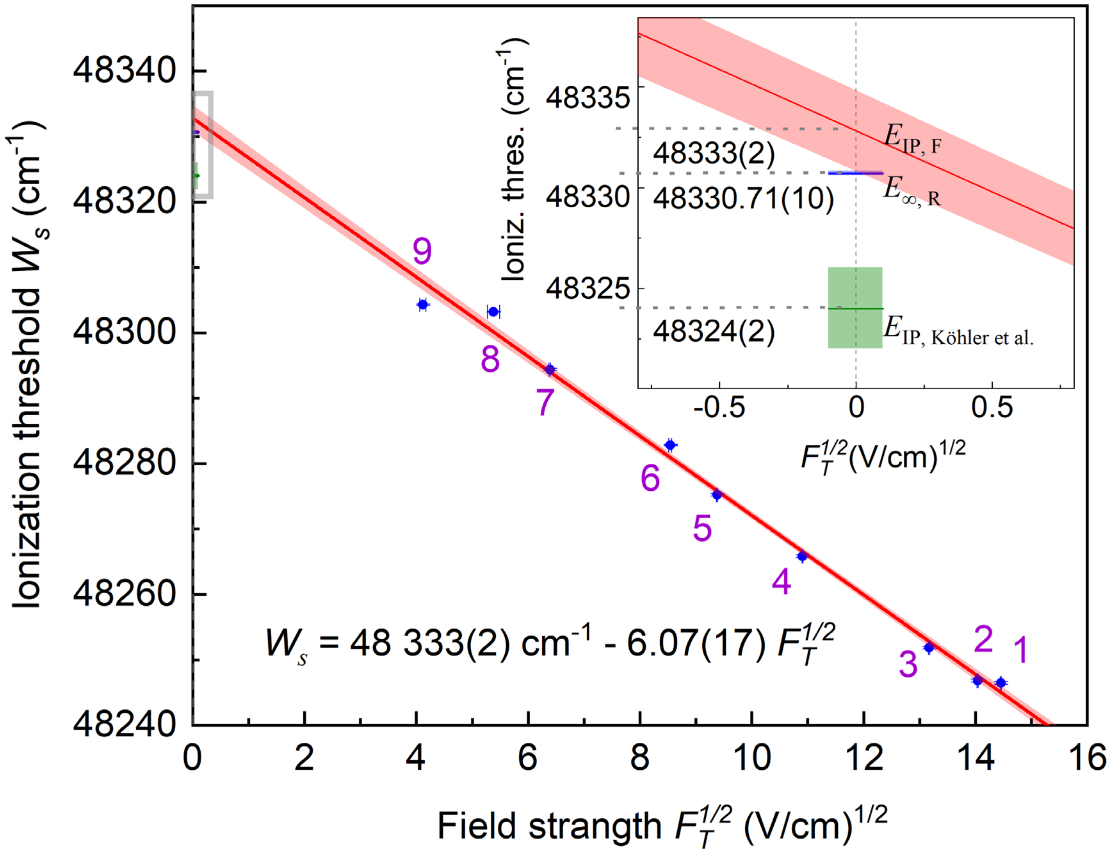
Ionization potential of Curium via field ionization

- Assignment of states not required
- Perfectly suited for IP extraction of complex atoms (actinides)

$$W_s = E_{\mathrm{IP}} - 2\sqrt{\frac{Z_{\mathrm{eff}} e^3 F}{4\pi\epsilon_0}}$$

W_s : saddle point
Z_{eff} : effective charge
V_C : Coulomb potential
V_F : electric potential

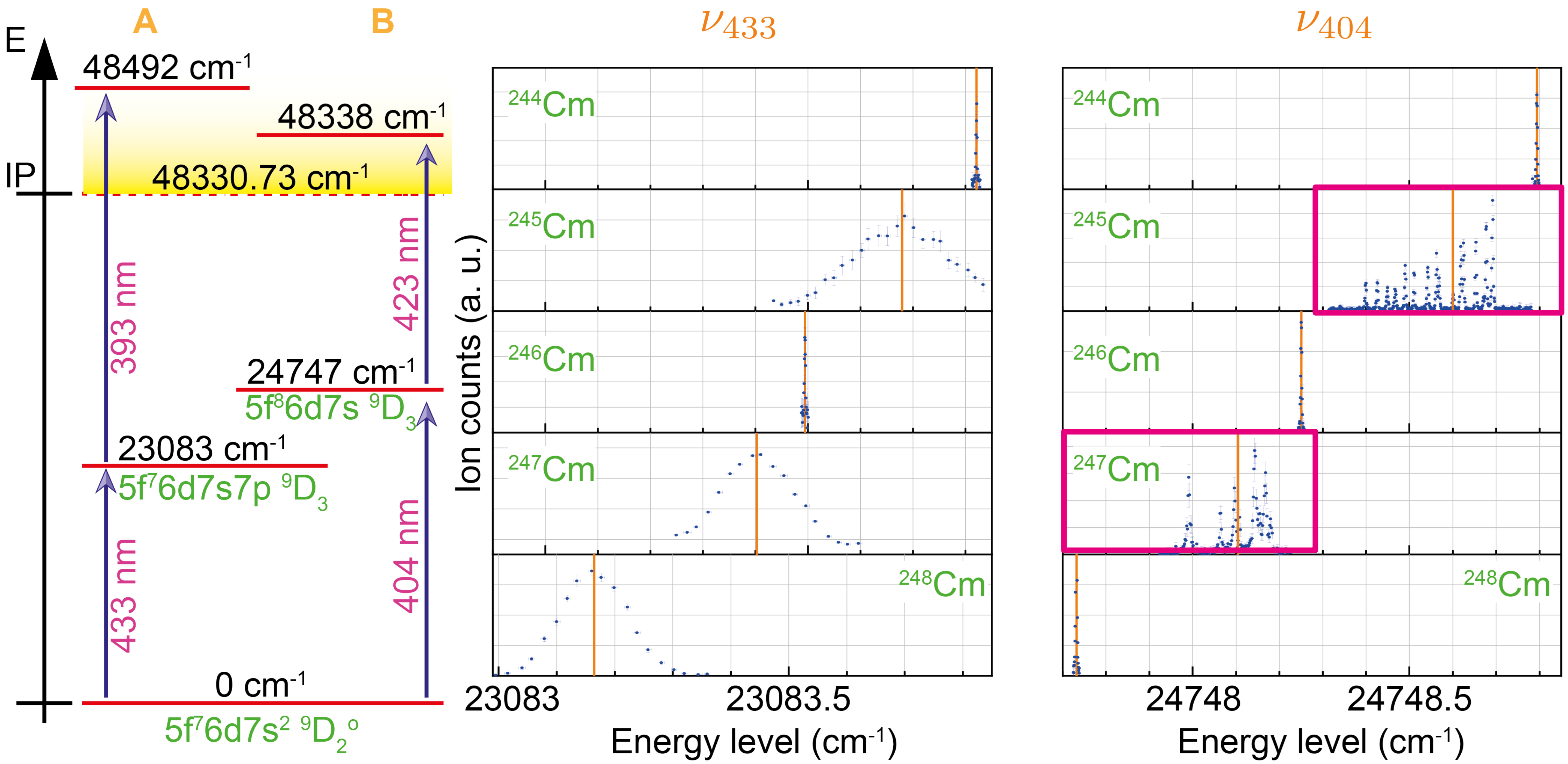




Overview of measured ionization thresholds [1]

[1] N. Kneip et al., in preparation (2022).

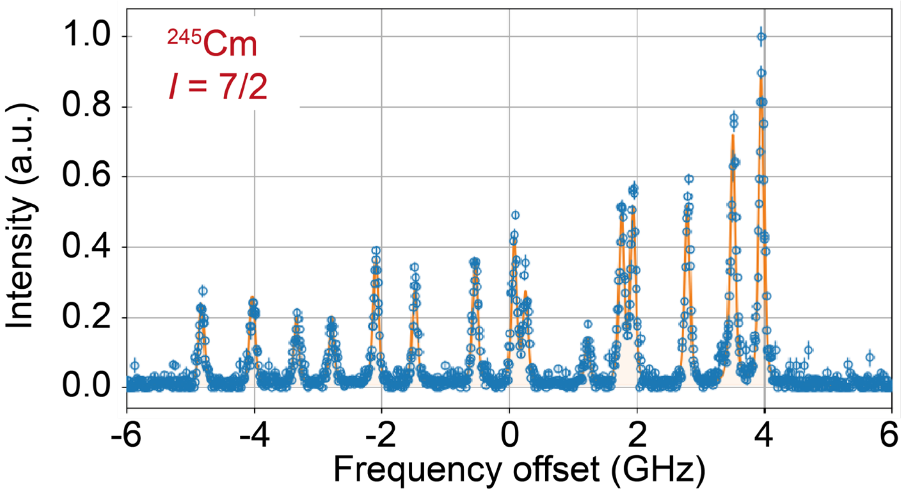
High-resolution measurements of isotope shift

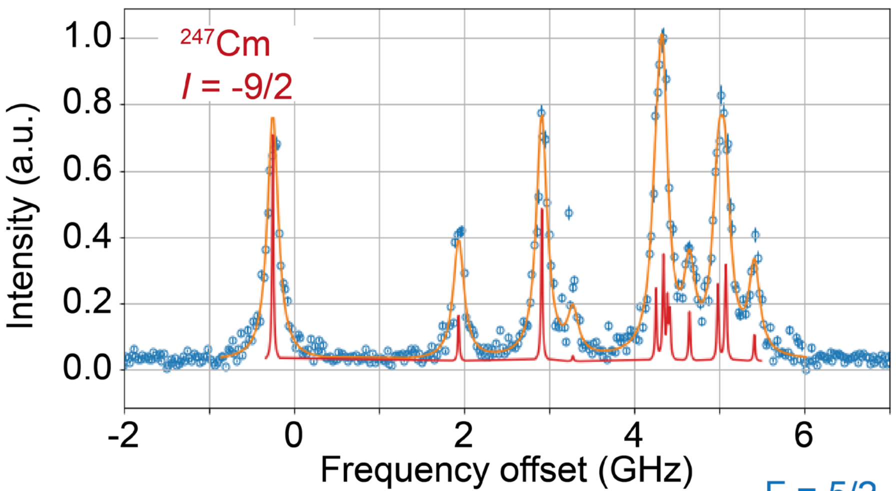


Profiles and isotope shifts of the 23083 cm^{-1} and 24747 cm^{-1} FES

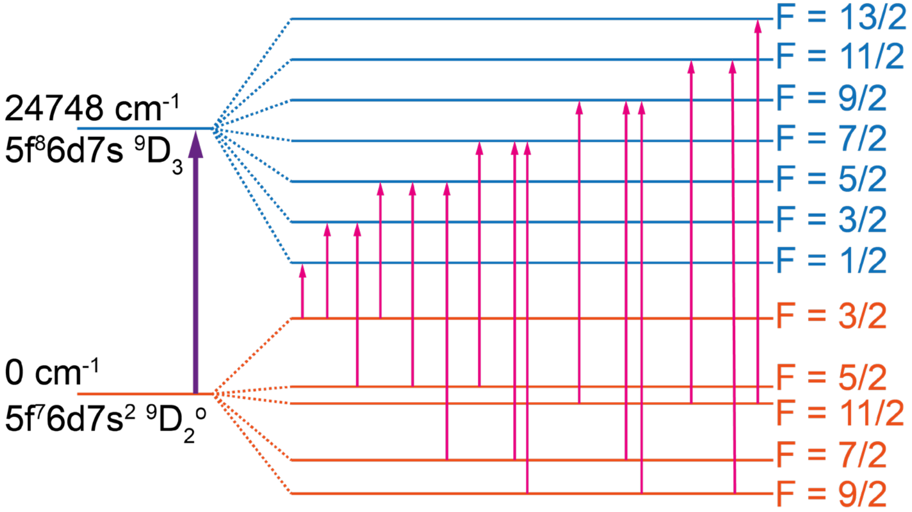
III. High-resolution of HFS in ^{245}Cm and ^{247}Cm

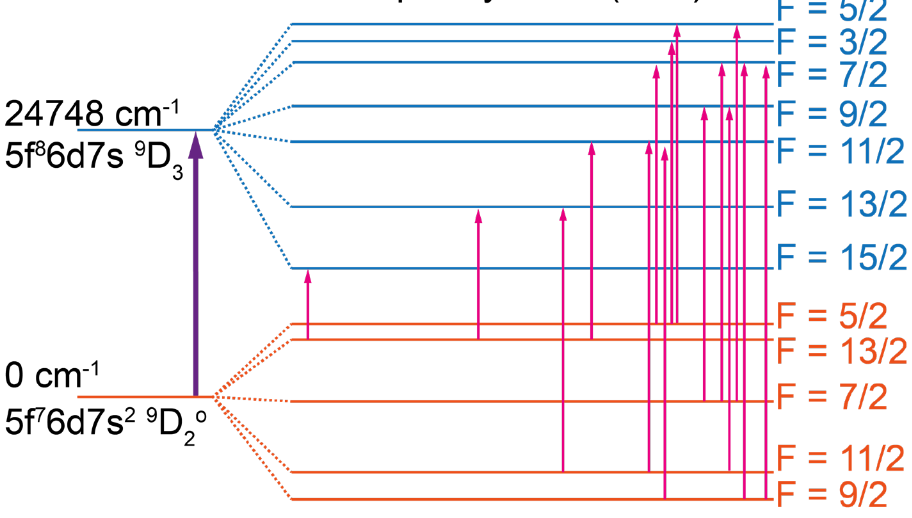
3.2 x 10^{12} atoms





1.9 x 10^{11} atoms





Cm isotope	$\mathcal{A}^l$ (MHz)	$\mathcal{A}^u$ (MHz)	$\mathcal{B}l$ (MHz)	$\mathcal{B}^u$ (MHz)
245	−22.72(14)	311.56(15)	1421(2)	−1862.44(91)
247	15.31(93)	−170.88(24)	1618(14)	−2168(14)

A and B factor from hyperfine structure fit

Conclusion and Outlook

Laser spectroscopy along the series of actinides and beyond

→ lot of work has been done and still

→ it´s a big challenges for state-of-the-art atomic (and nuclear physics)

Atomic spectroscopic data of high relevance,

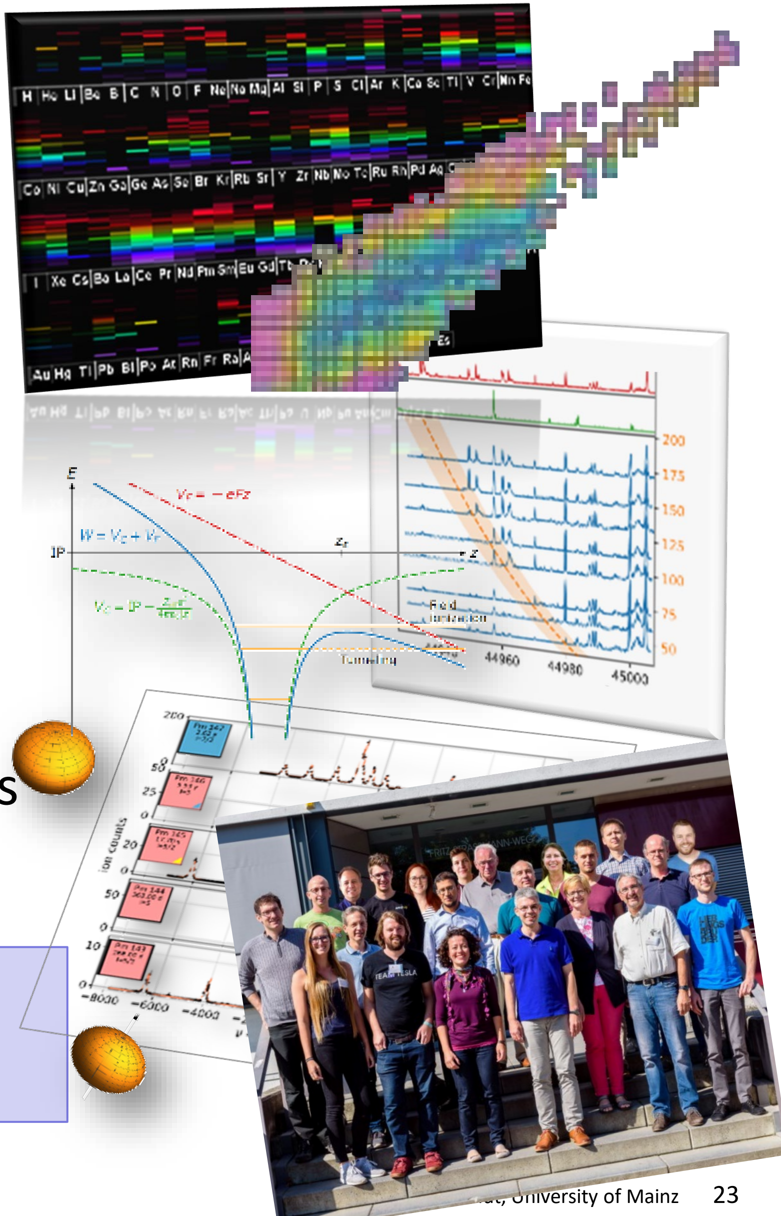
→ i.e. the nuclear clock, nuclear medicine or ultra trace analysis

Access ensured for specific isotopes & isotopic sequences from Ac to Fm

→ on-line more isotopes and even further

Theory support mandatory for analysis of atomic (and nuclear) structures

→ fruitful exchange just at the start….



Thanks to the funding agencies: BMBF 05P18UMCIA, EU ITN LISA, to all members of the teams and to you for your attention…