Laser Spectroscopy along the Series of Actinide Elements

–

A Rewarding Challenge

→ Uncovering the Atomic Structure at the Upper Rim of the Nuclear Chart ←

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Research Interests in Exotic Element & Isotope Physics


https://www.deviantart.com/okapienarts/art/**Exotic-Element-Icon**-718895183

Structures and Properties
of Complex **Atomic** Systems,
Quantum Chaos

Nuclear Matter,
Nucleosynthesis Pathways
and **Astrophysics**

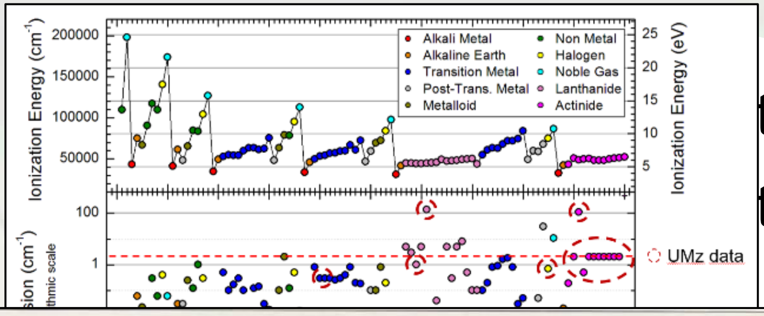
Fundamental Questions
and **Precision Physics**,
i.e. Neutrino Mass

Medical Radioisotopes
for Diagnostics and Theraphy

Transactinides and
Super Heavy Elements

Laser-based
Ultra-Trace Analytics of
Radiotoxic Species

Research Interests in Exotic Element & Isotope Physics



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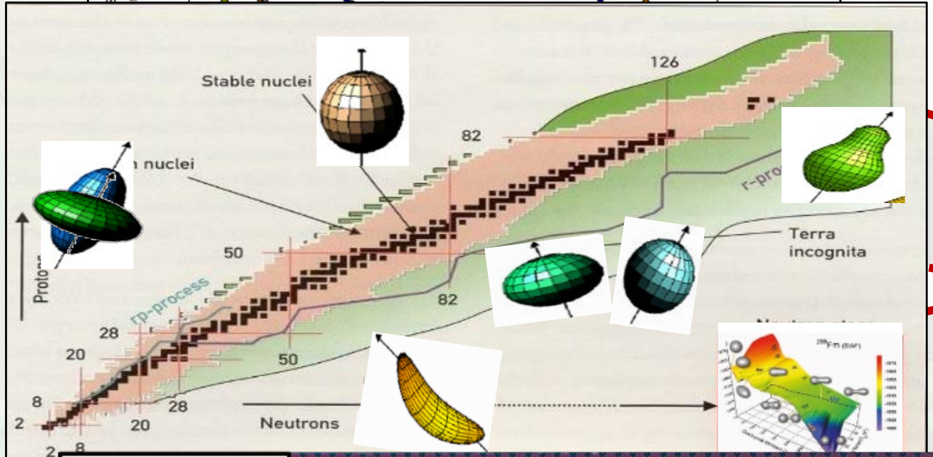
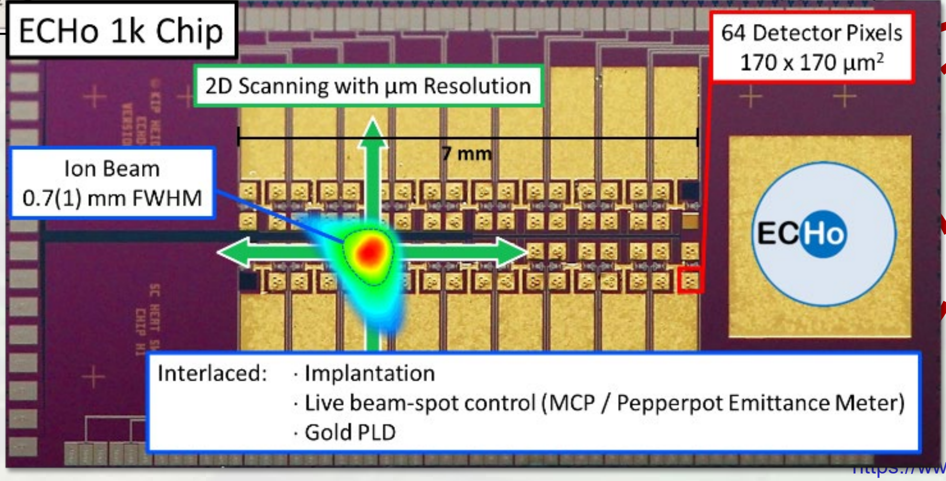


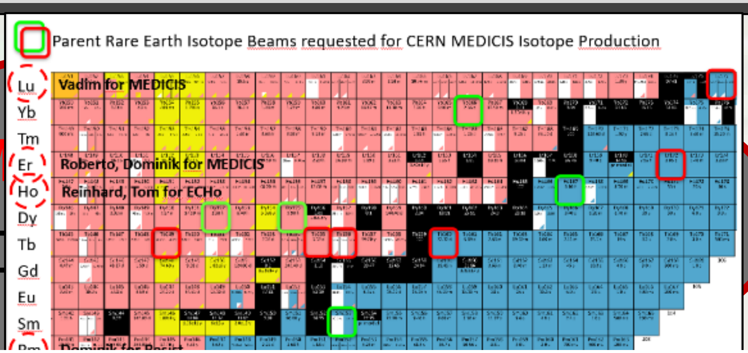


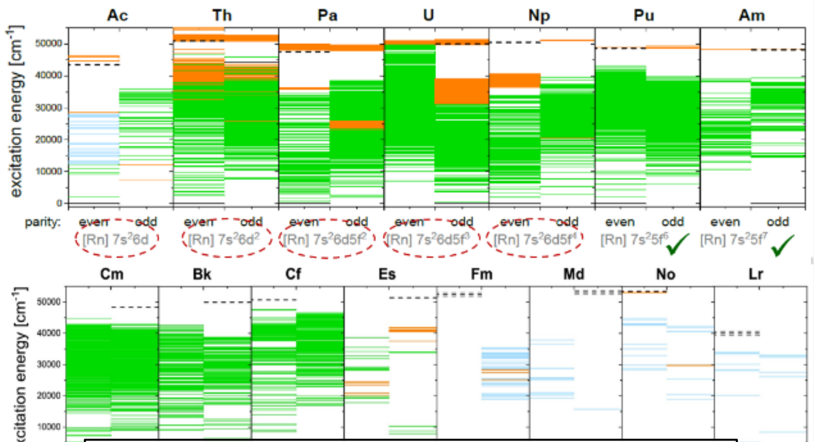
M

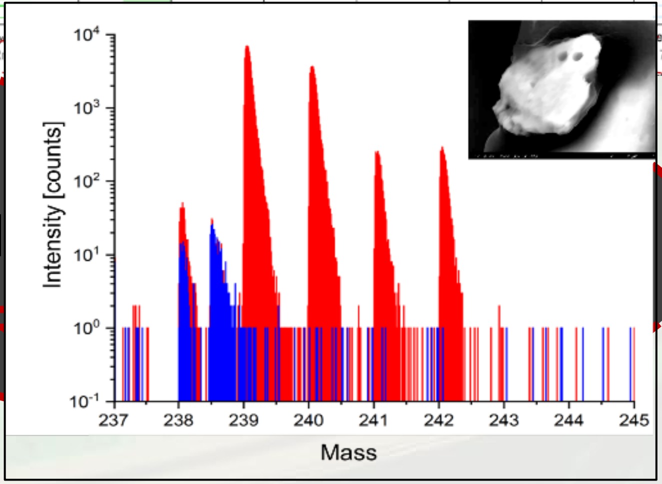
for D

Ul

F







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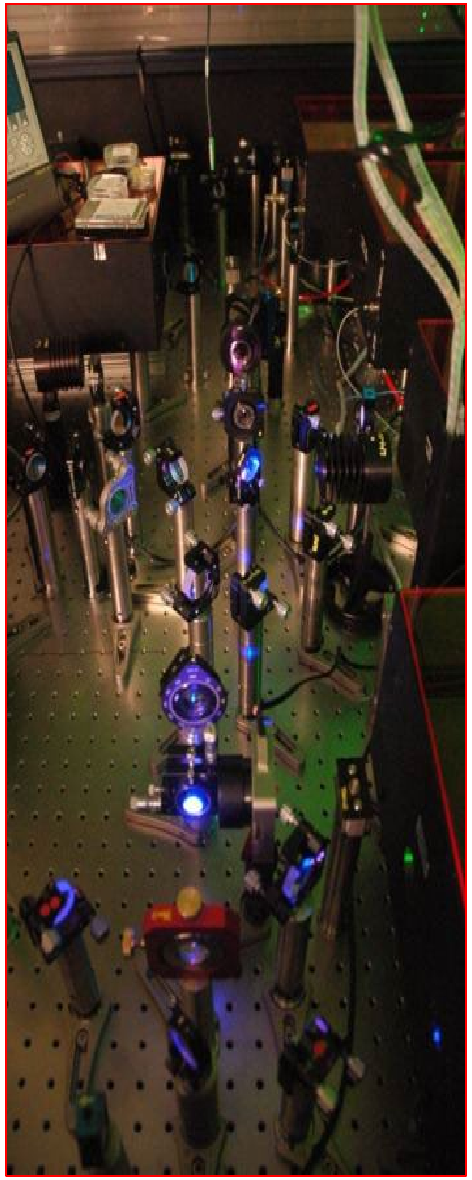
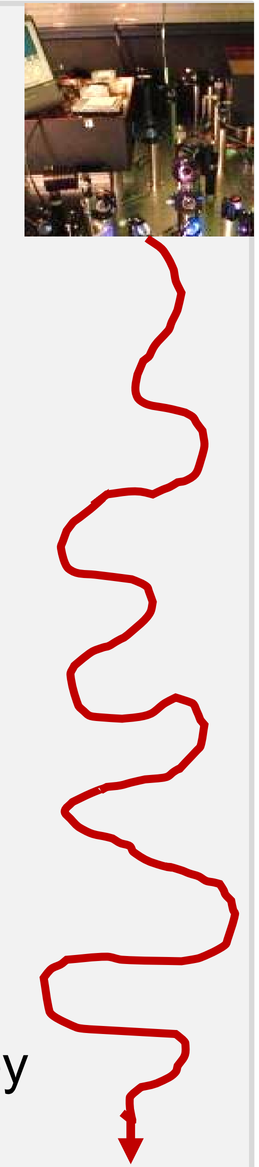
Outline



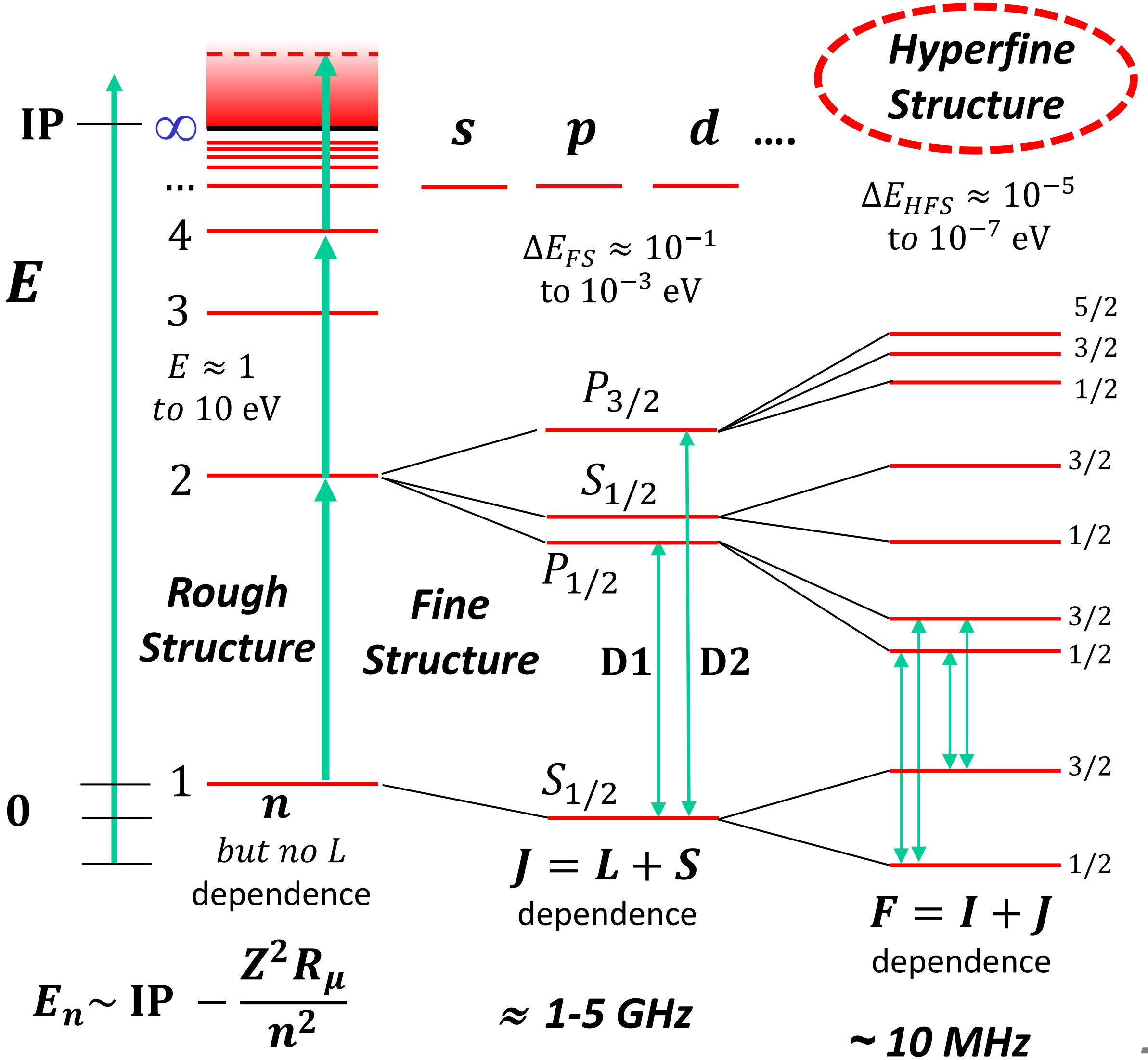


- **Motivation** – atomic and nuclear structure from laser spectroscopy
- **Theoretical** – some aspects on (actinide) atomic systems
  - – e.g. why sodium is not an actinide
- **Experimental** – laser spectroscopy within the actinides
- **Results** – looking at data on level schemes, IPs and more
- **Summary and Outlook**
  - – a look into the dazzling future of actinide spectroscopy

On the Atomic Spectroscopy of the Elements --- from $_1$H to $_{100}$Fm

Resonance Ionization Spectroscopy on atomic structures

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



Rough Structure

n but no L dependence

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

Fine Structure

$J = L + S$ dependence

≈ 1-5 GHz

$F = I + J$ dependence

~ 10 MHz

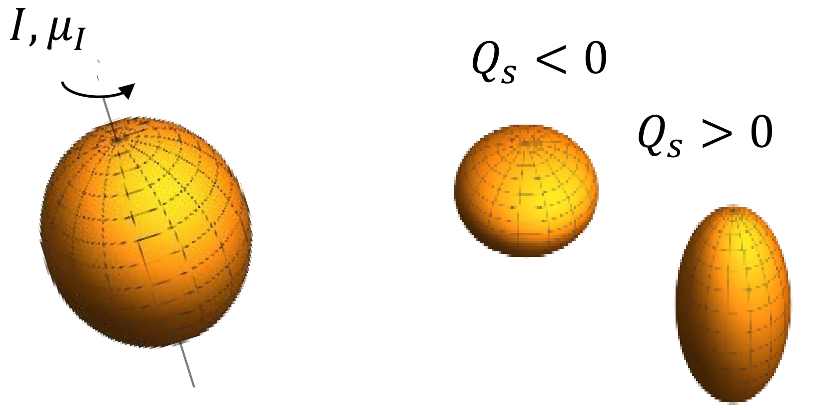
$$\Delta E_H = \Delta E_\mu + \Delta E_Q$$

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

Magnetic dipole & Electric quadrupol

moment of the atomic nucleus

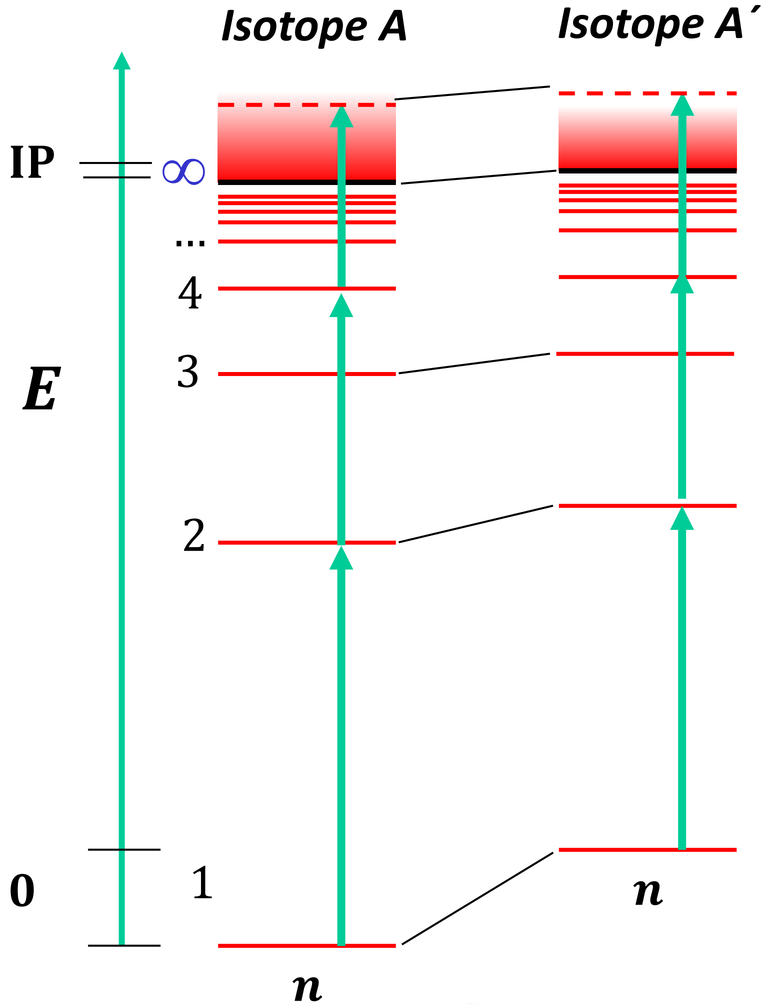
$$A = \frac{\mu_I \overline{H(0)}}{IJ} \qquad B = eQ_s \left\langle \frac{\partial^2 \phi}{\partial z^2} \right\rangle_{r=0}$$



→ High spectral resolution required

The **Extra**: Isotope Selection in High Resolution Spectroscopy

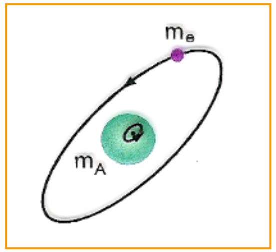
Isotope Shift

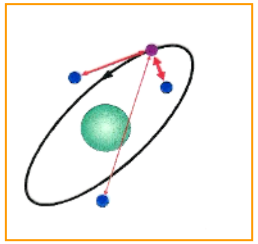


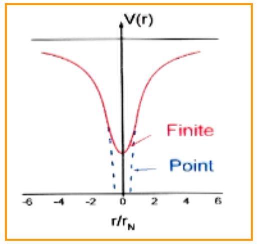
10 MHz – 1 GHz

Shift of all resonance frequencies from isotope to isotope

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



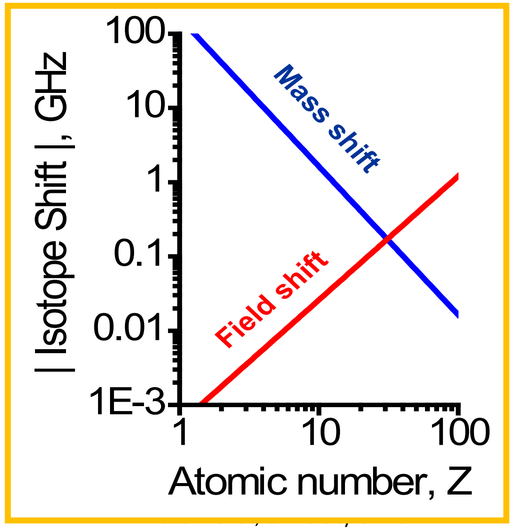




→ *Highest optical isotope selectivity above 10^9*

→ *Size and deformation of the atomic nucleus*

→ Odd isotopes: additional hyperfine structure splitting



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

Atomic Structure of the Elements: IP values & open subshells

One open valence shell

only for alkaline elements

Two open shells

alkaline earths, noble gases

& main group elements

Three open shells

transition group elements

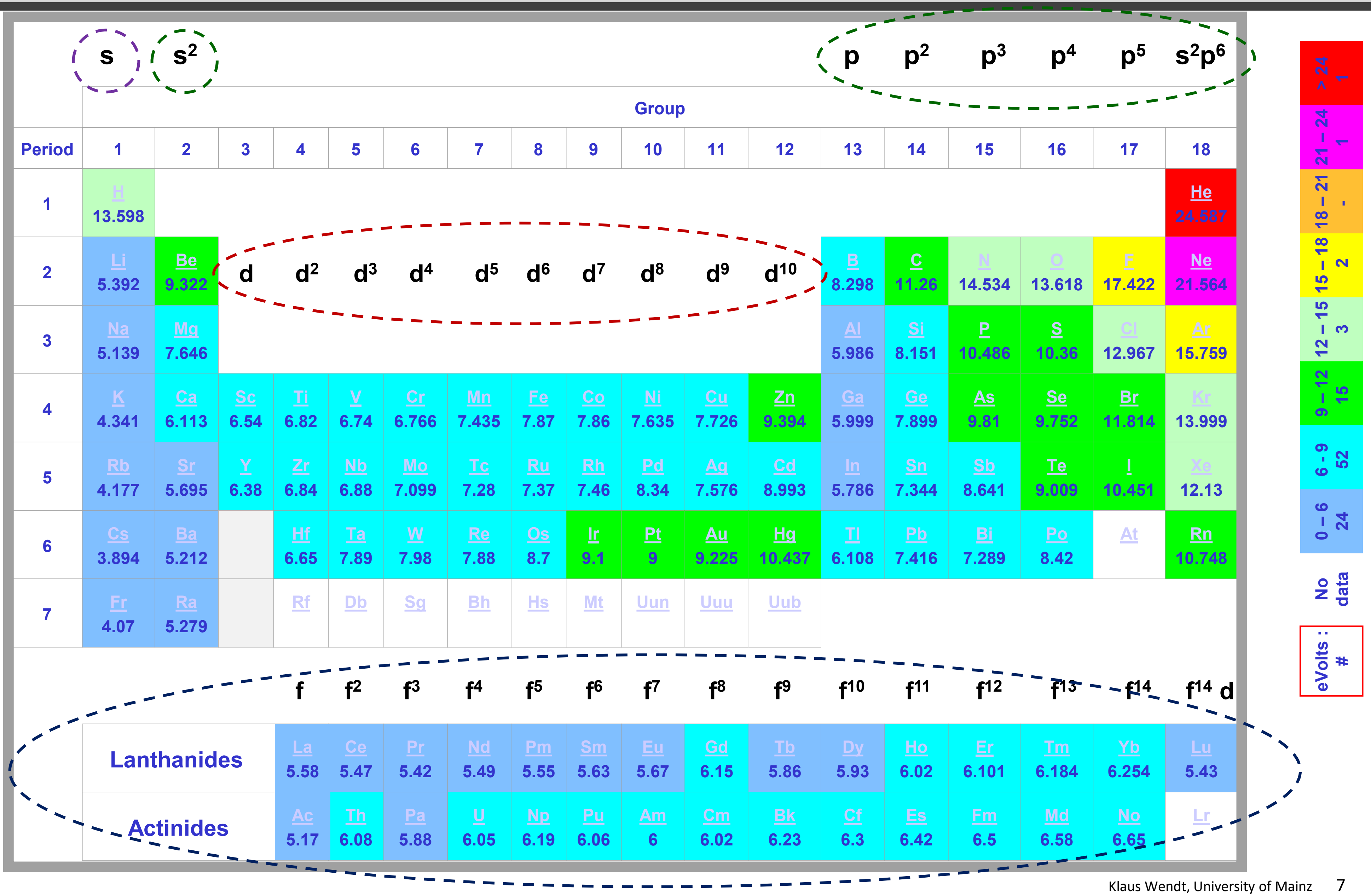
Four open shells –

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 :	#
🟥	> 24	1
🟪	21 – 24	1
🟧	18 – 21	-
🟨	15 – 18	2
🟩	12 – 15	3
🟩	9 – 12	15
🟦	6 - 9	52
🟦	0 – 6	24
	No data	

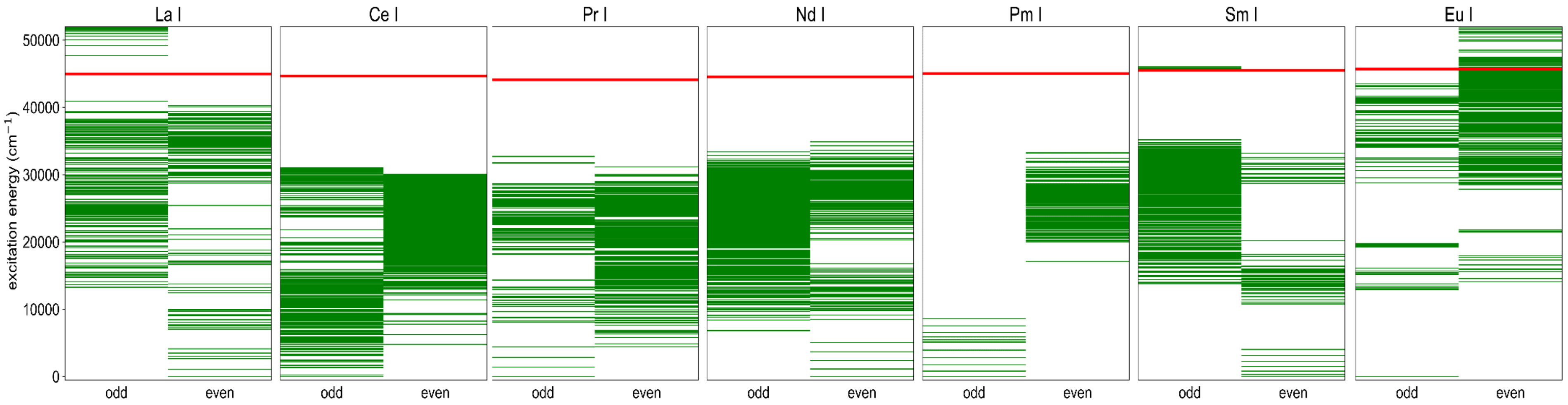
Complex Atoms: Ground States & Level Schemes of Lanthanides

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

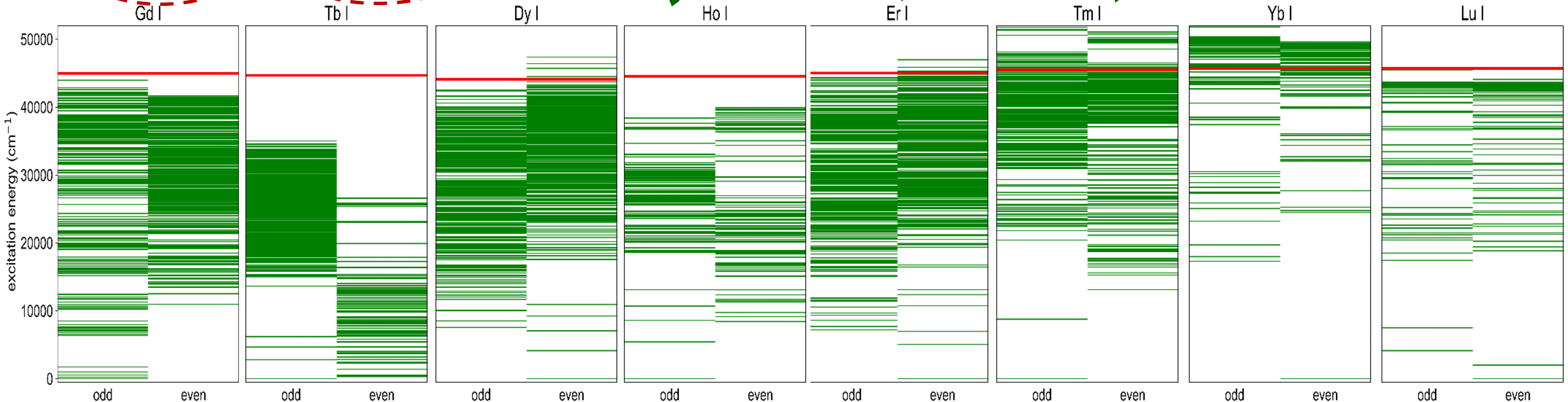
\- **5d** electron mixed in -
(3 out of 15
at empty and half filled shell)

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^{3}6s^2 ✓ | [Xe] 4f^{4}6s^2 ✓ | [Xe] 4f^{5}6s^2 ✓ | [Xe] 4f^{6}6s^2 ✓ | [Xe] 4f^{7}6s^2 ✓



[Xe] 4f^{7}5d6s^2 | [Xe] 4f^{9}6s^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 the 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)

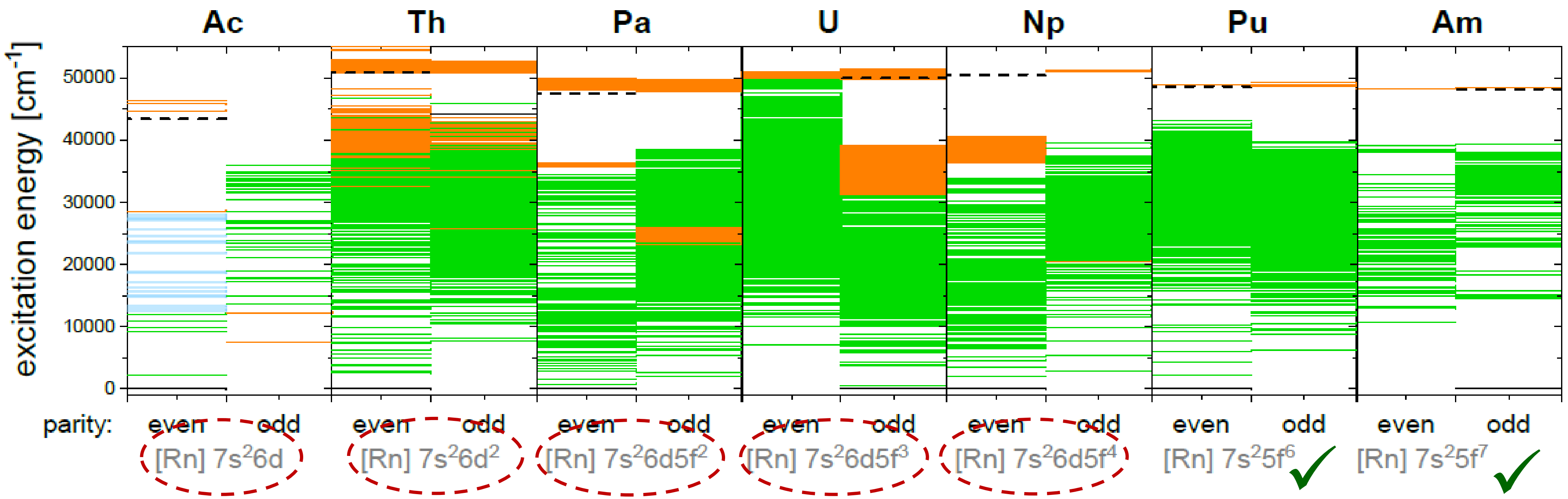
-

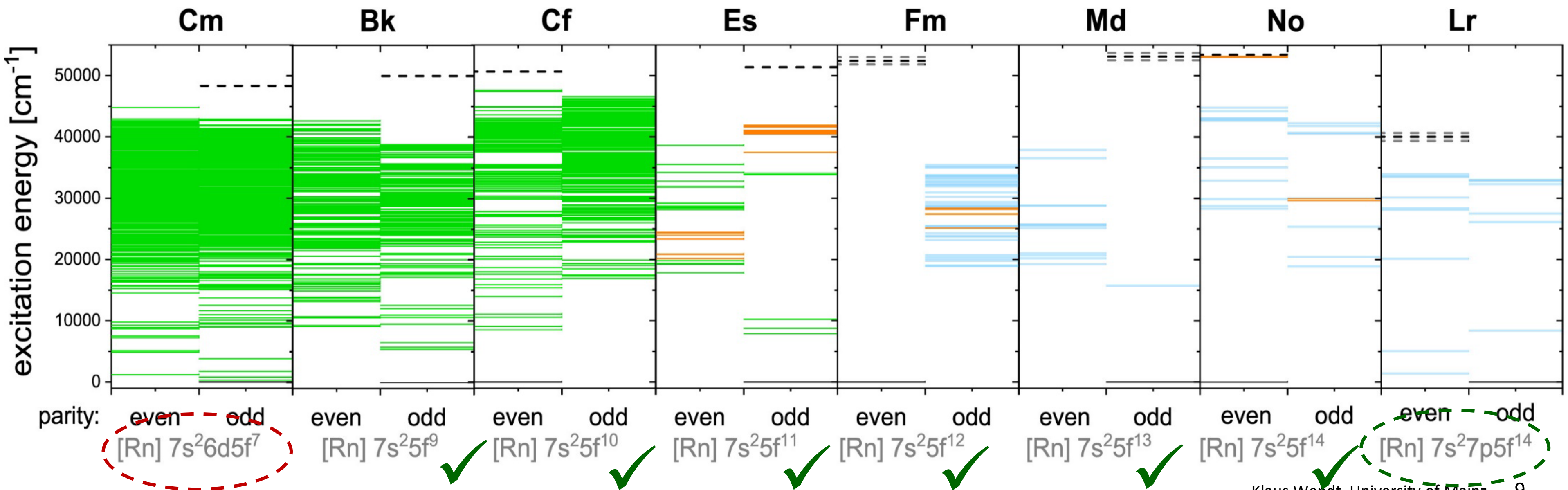
strong configurations mixing

→ quantum chaos

-

Orange levels newly studied



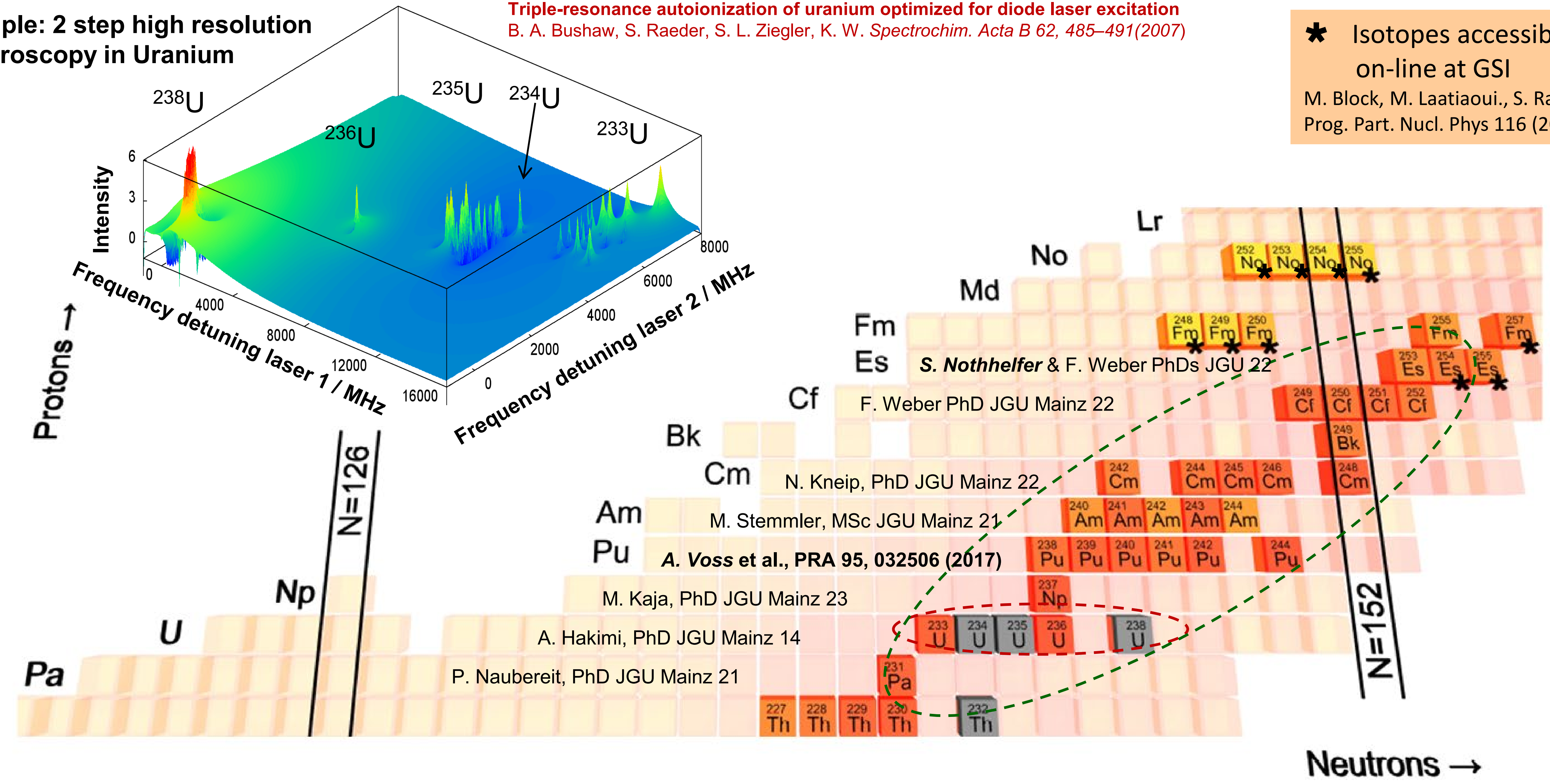


Off-line and on-line accessible Isotopes in the Actinides

Example: 2 step high resolution spectroscopy 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)



S. Nothhelfer & F. Weber PhDs JGU 22

F. Weber PhD JGU Mainz 22

N. Kneip, PhD JGU Mainz 22

M. Stemmler, MSc JGU Mainz 21

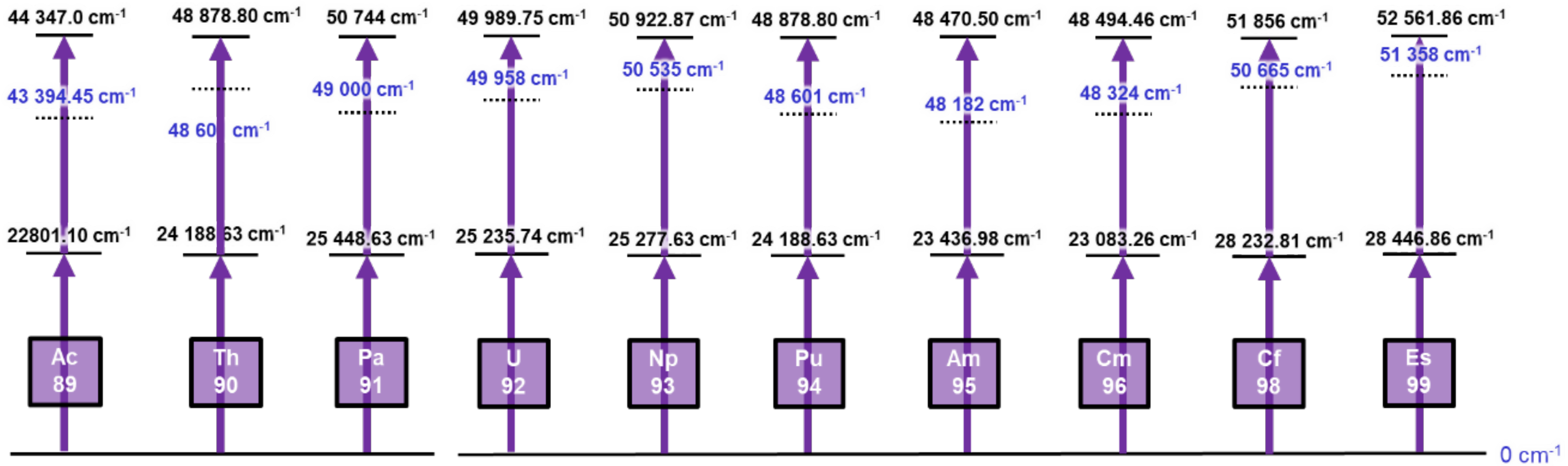
***A. Voss* et al., PRA 95, 032506 (2017)**

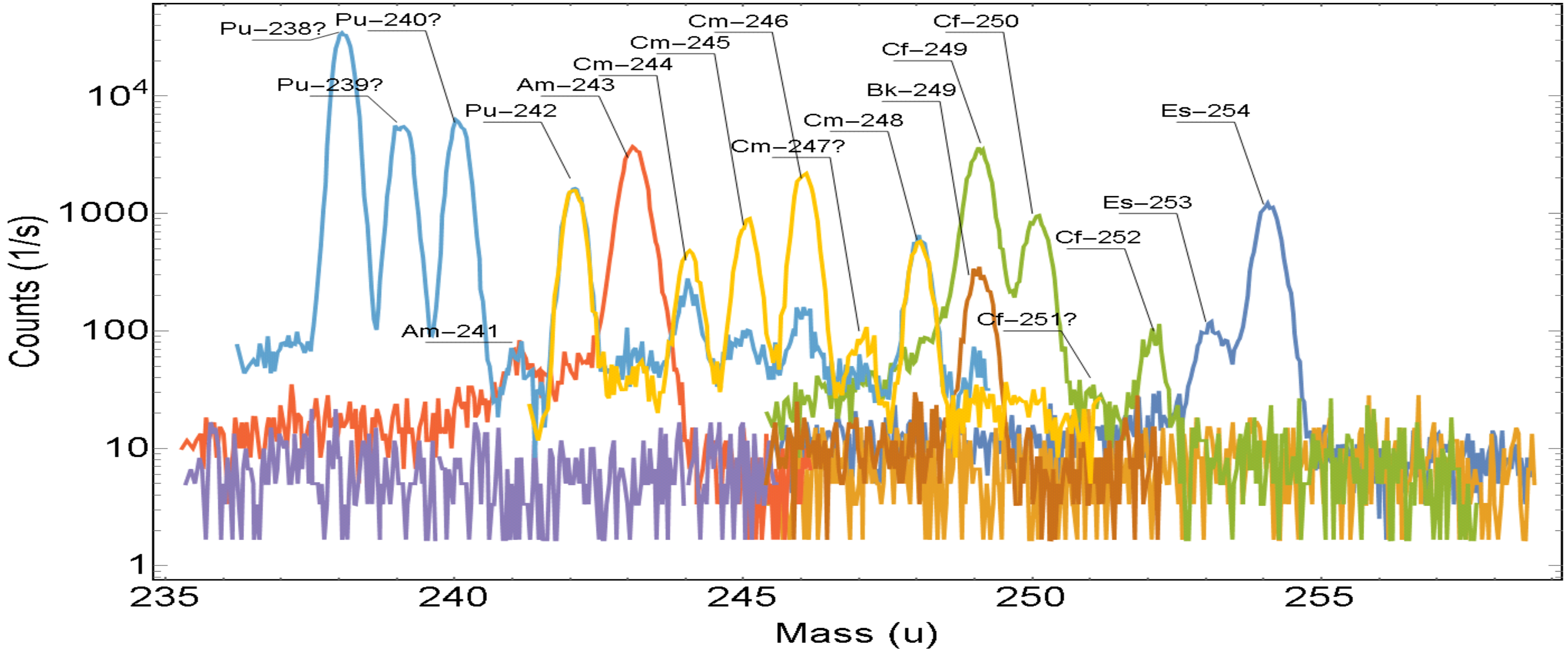
M. Kaja, PhD JGU Mainz 23

A. Hakimi, PhD JGU Mainz 14

P. Naubereit, PhD JGU Mainz 21

Multielement Actinide RIMS for Full Sample Characterization





- Simple & efficient two-step RIS
- Rapid access to individual element developed in isoelectronic REEs

→ Fast full sample characterization

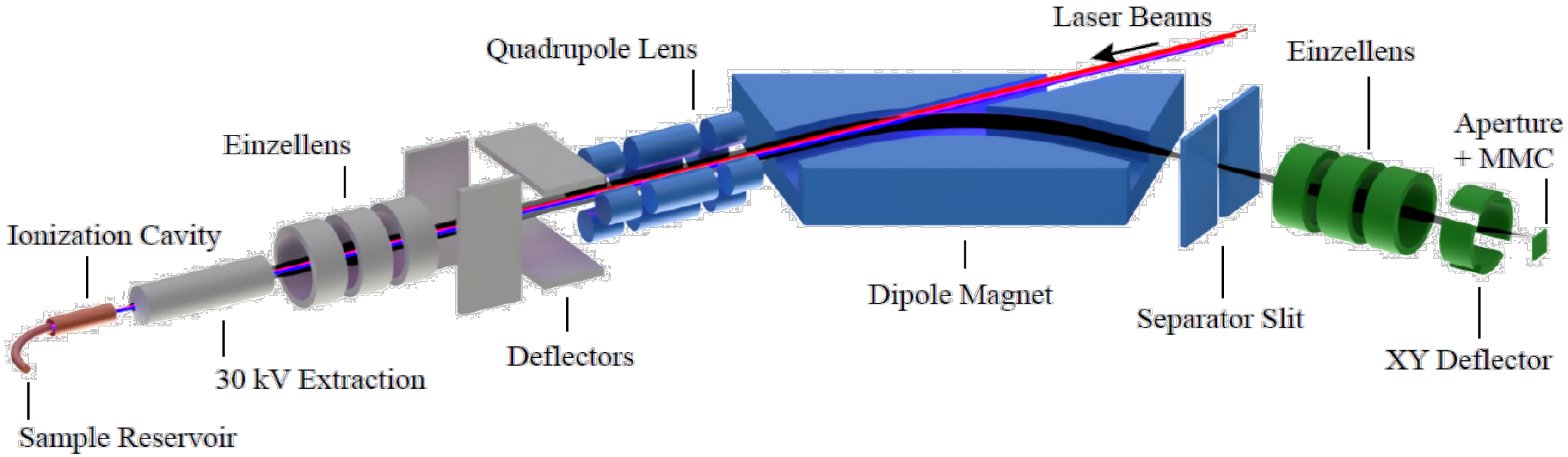
→ Isobar-free, low-background isotope ratio determination

→ Laser spectroscopy in mixed sample

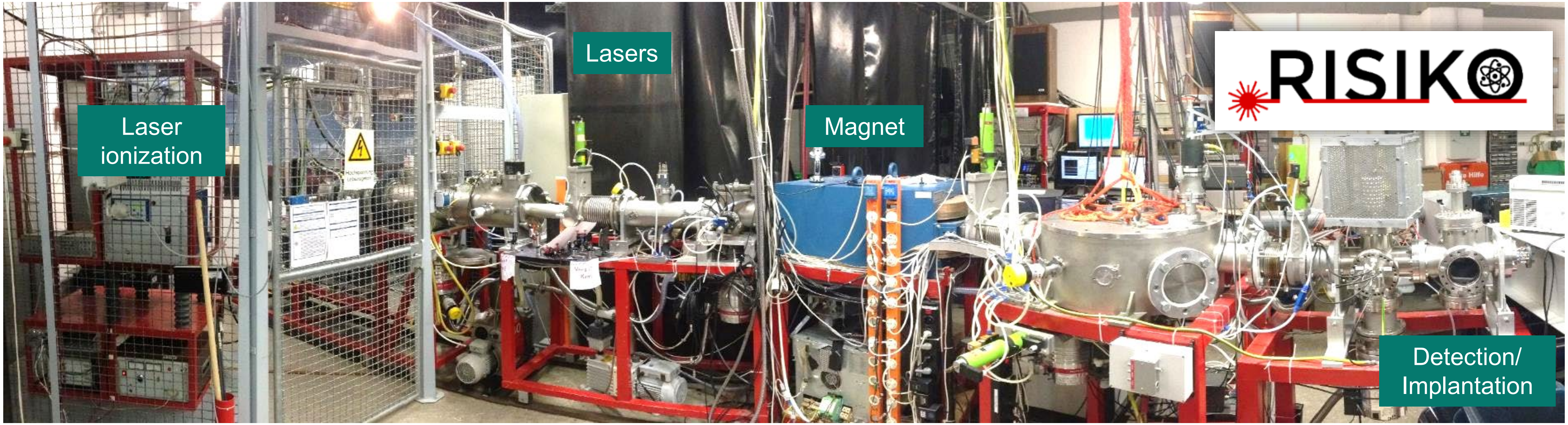
→ Ultratrace analysis & fundamentals studies

Exclusive sample obtained from ORNL (J. Etzold)

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



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



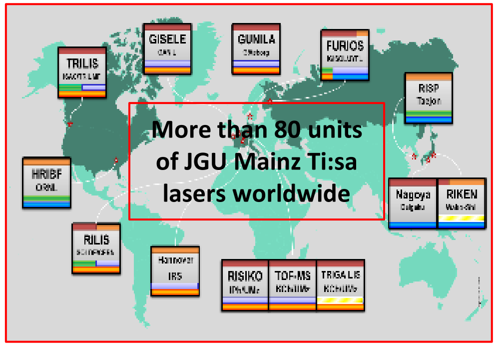
The laser family: pulsed, powerful & narrow-bandwidth for RIMS

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

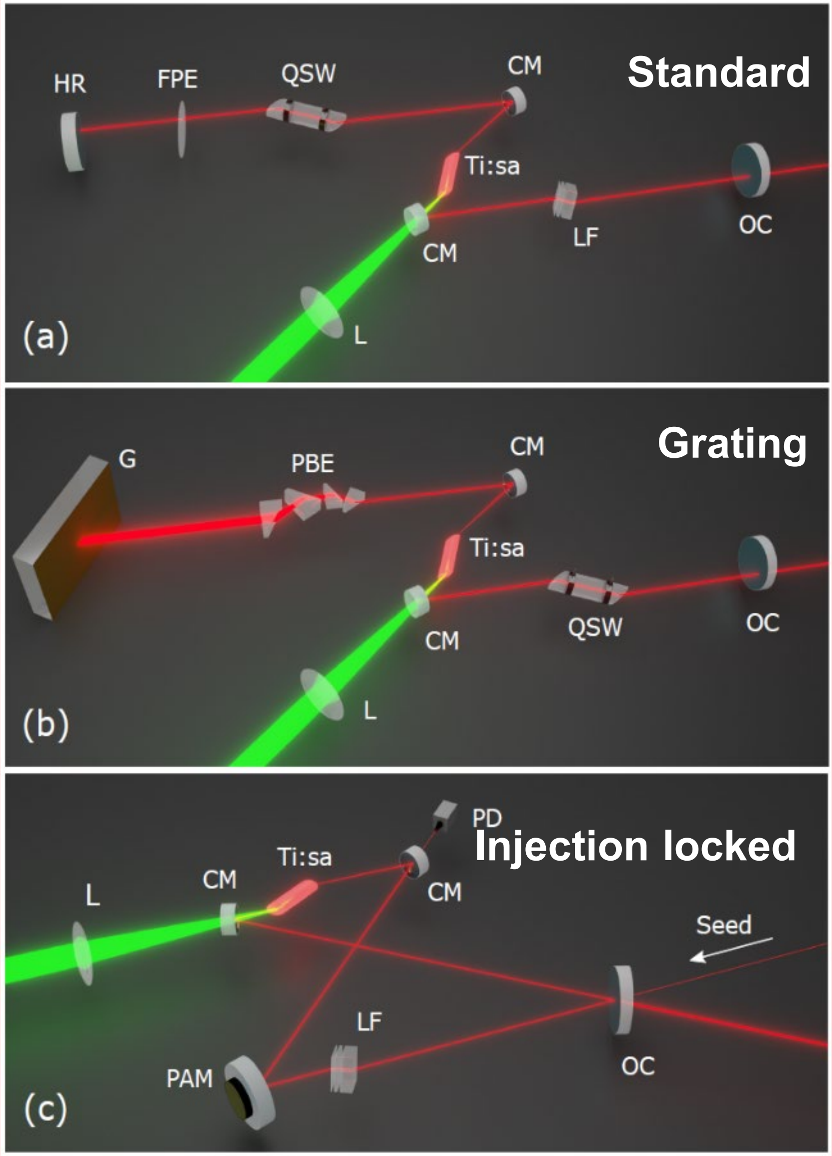
R. Horn, PhD. JGU 2003

- 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		

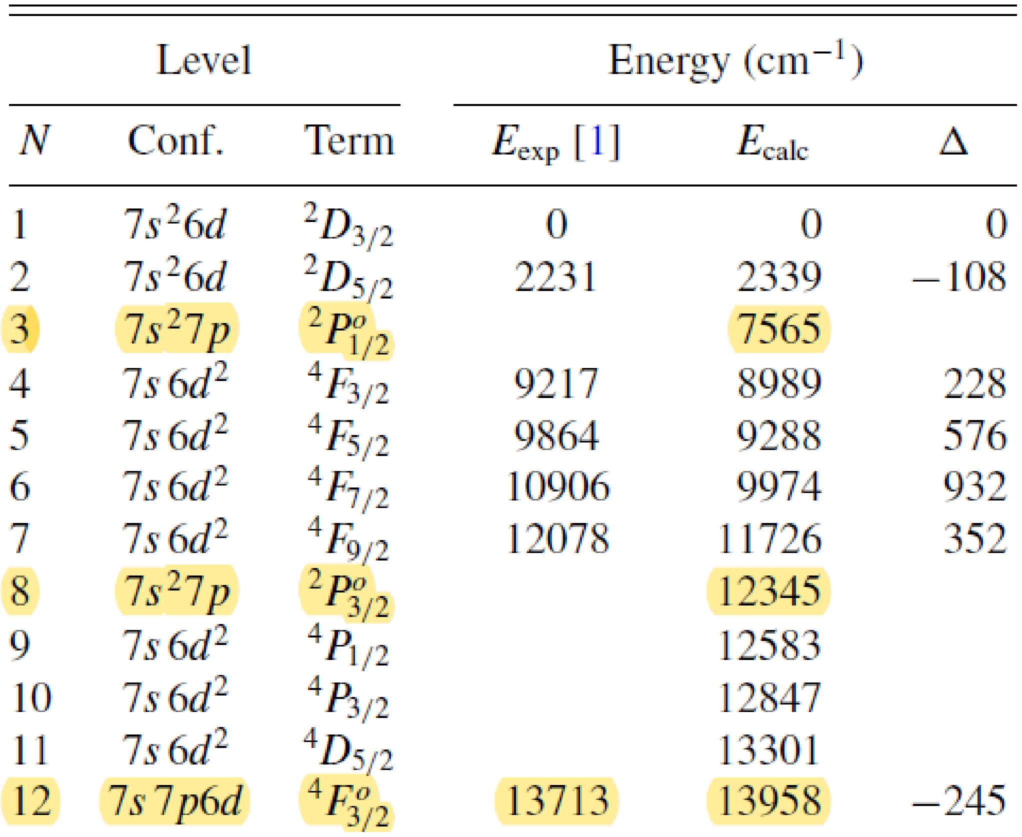


More than 80 units of JGU Mainz Ti:sa lasers worldwide



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)*

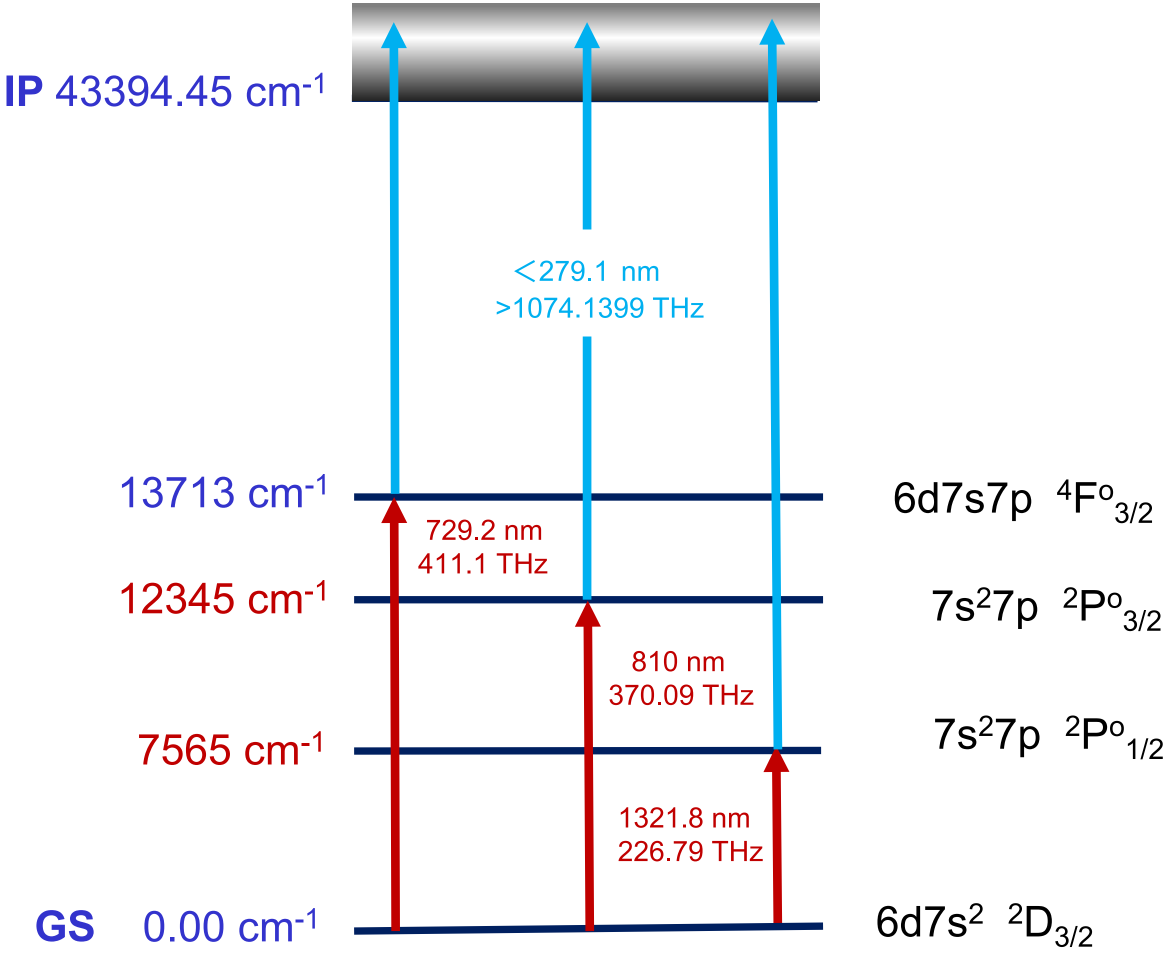
Atomic Physics: Search for Missing **Low Lying** Levels in Actinium



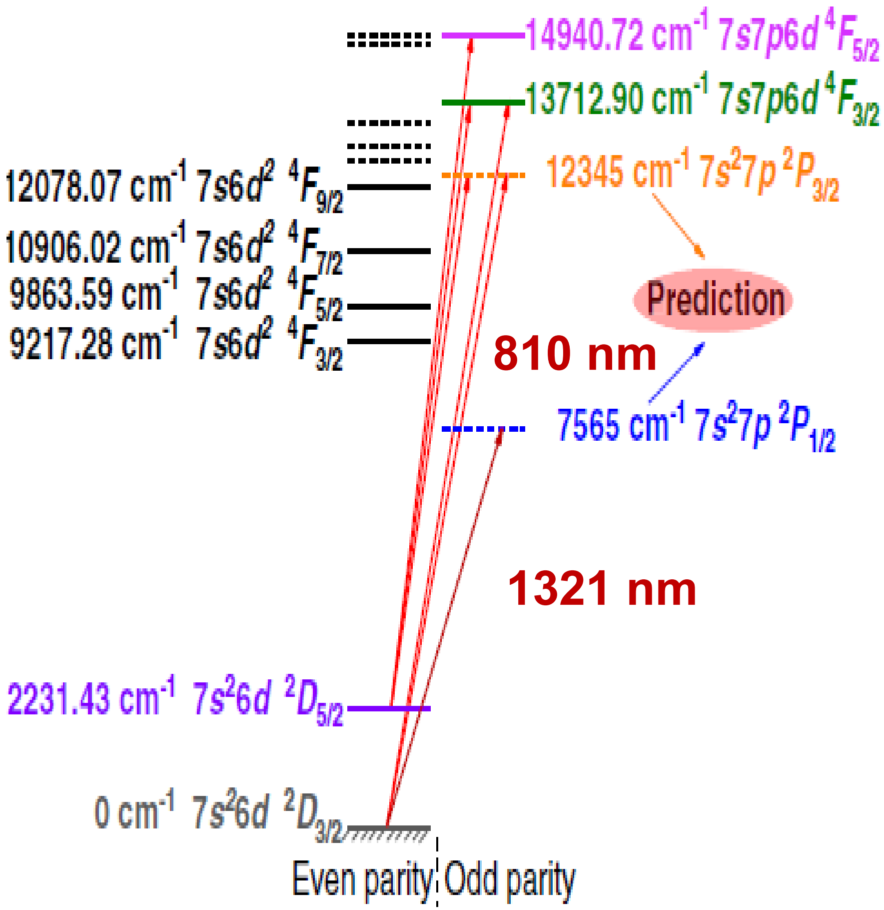
Level			Energy (cm^{-1})		
N	Conf.	Term	$E_{\rm exp}$ [1]	$E_{\rm calc}$	Δ
1	$7s^26d$	$^2D_{3/2}$	0	0	0
2	$7s^26d$	$^2D_{5/2}$	2231	2339	−108
3	$7s^27p$	$^2P^o_{1/2}$		7565	
4	$7s\,6d^2$	$^4F_{3/2}$	9217	8989	228
5	$7s\,6d^2$	$^4F_{5/2}$	9864	9288	576
6	$7s\,6d^2$	$^4F_{7/2}$	10906	9974	932
7	$7s\,6d^2$	$^4F_{9/2}$	12078	11726	352
8	$7s^27p$	$^2P^o_{3/2}$		12345	
9	$7s\,6d^2$	$^4P_{1/2}$		12583	
10	$7s\,6d^2$	$^4P_{3/2}$		12847	
11	$7s\,6d^2$	$^4D_{5/2}$		13301	
12	$7s\,7p6d$	$^4F^o_{3/2}$	13713	13958	−245

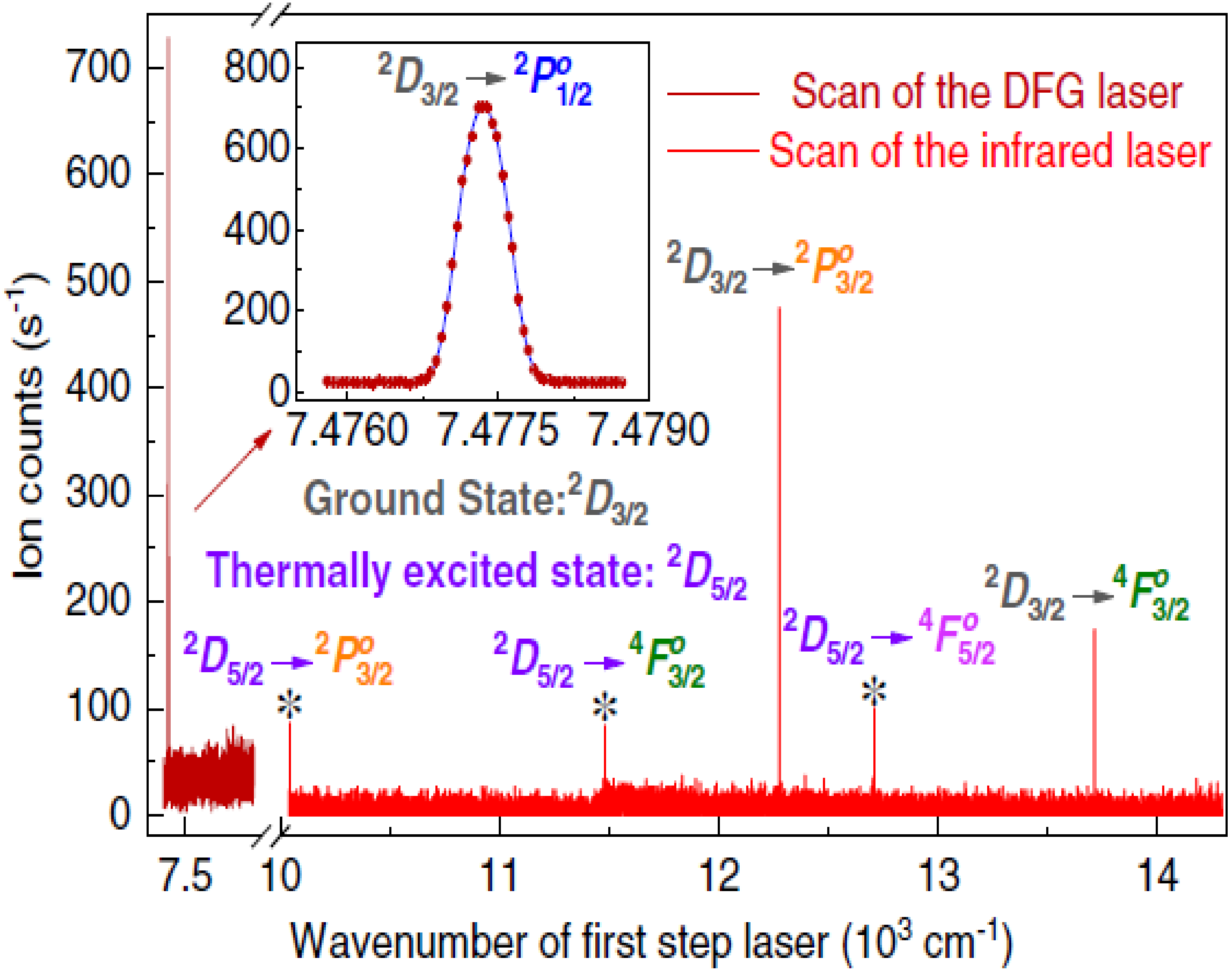
Excitation energies and g factors
for the lowest states of Actinium

V. A. Dzuba, V. V. Flambaum, et al., Phys. Rev. A **100**, 022504 (2019)



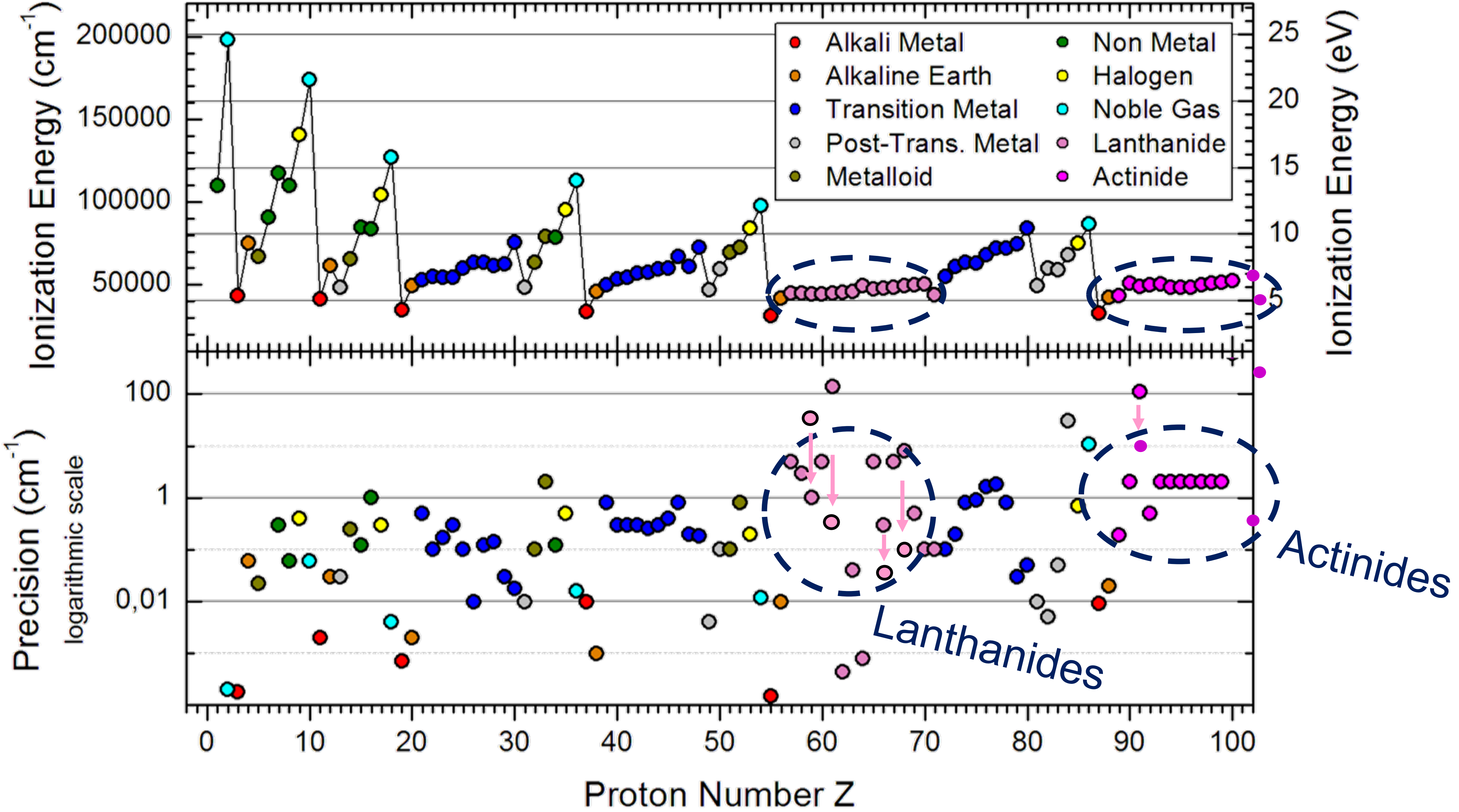
Spectroscopic Observation of the D1, D2-like Transistions in Ac I





K. Zhang, D. Budker et al., PRL 125, 073001 (2020)

Studies on the Ionization Potentials by RIMS



Lanthanides

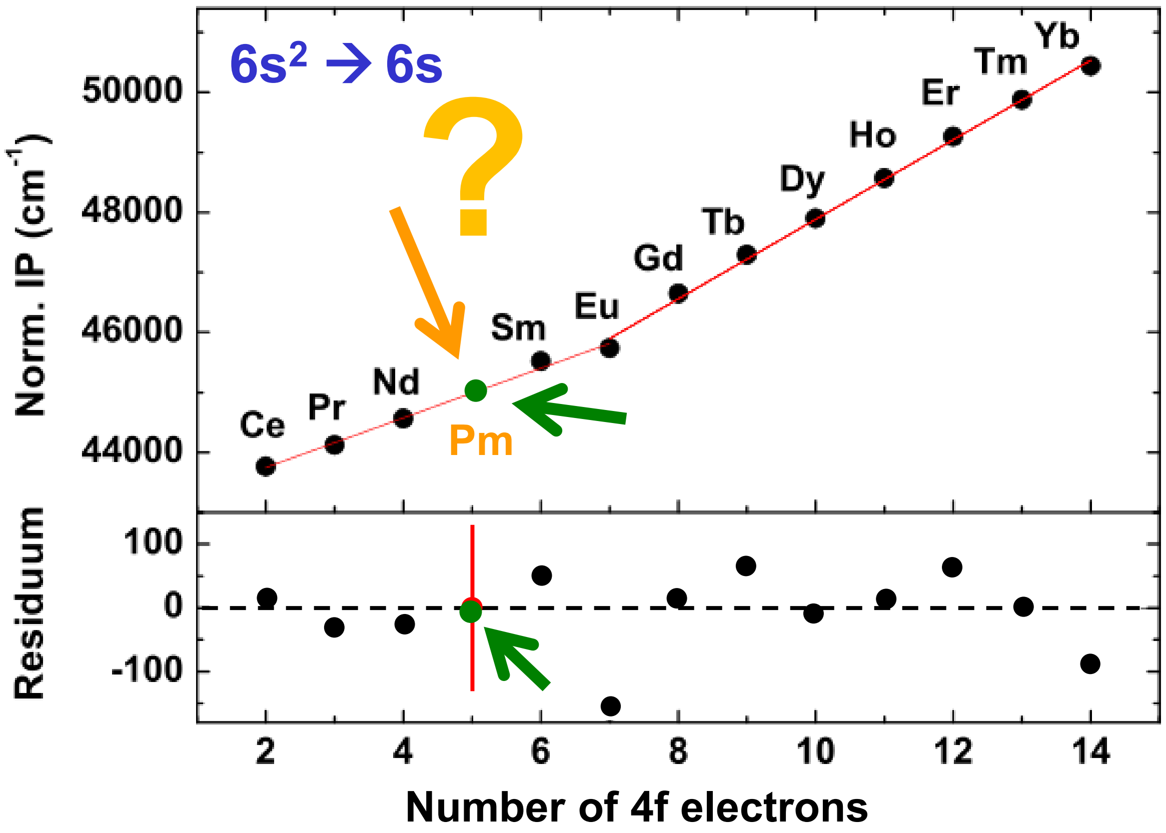
Actinides

Do we understand the IP´s in the (Iso-electronic) Lanthanides ?

- Simple theoretical prediction: **two linear slopes** – below & above **half filled shell closure**

E.F. Worden et al., JOSA **68**, 52 (1978)

- Expectations fulfilled within $\Delta E \approx 100\ \mathrm{cm}^{-1}$ – one values normalized for Ce to s-electron removal



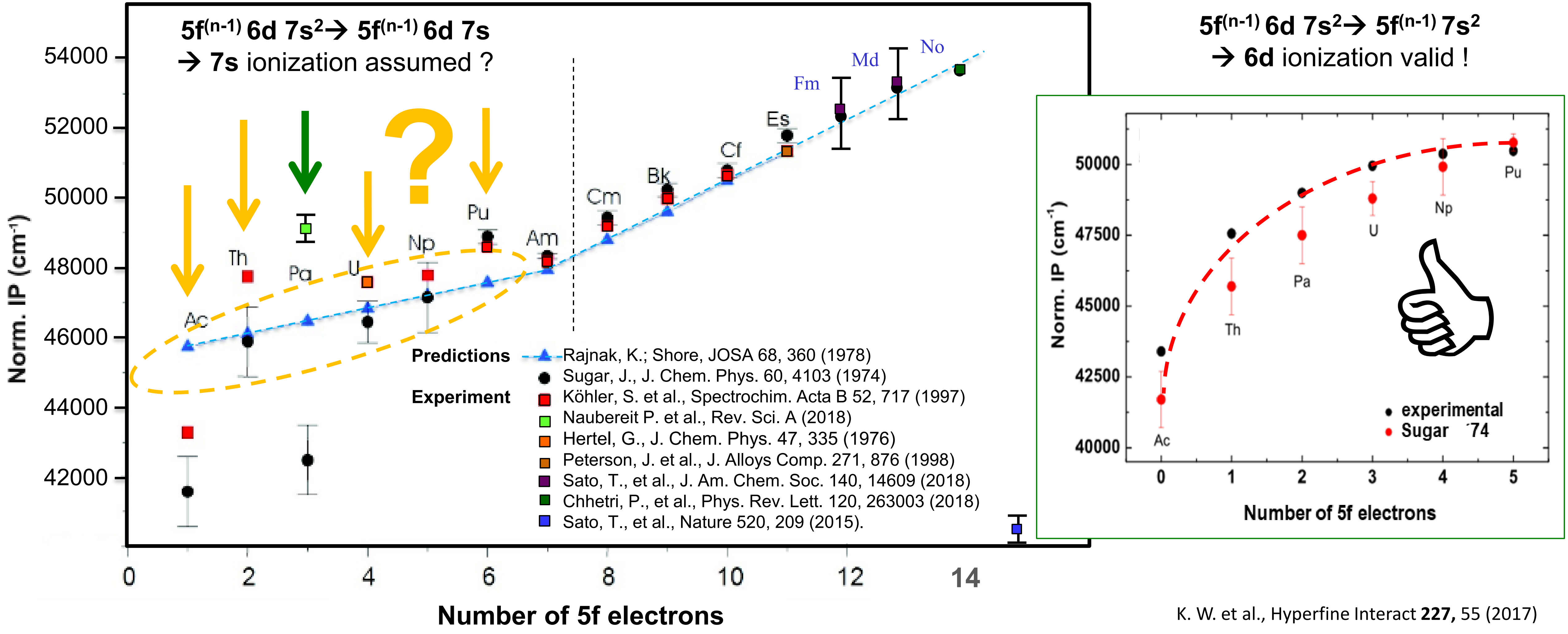
…a good starting point for the actinides…

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

D. Studer et al., Phys. Rev**. A 99**, 062513 (2019)

Knowledge on the IP´s of the Actinides today

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



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

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

Predictions ▲ Rajnak, K.; Shore, JOSA 68, 360 (1978)

● Sugar, J., J. Chem. Phys. 60, 4103 (1974)

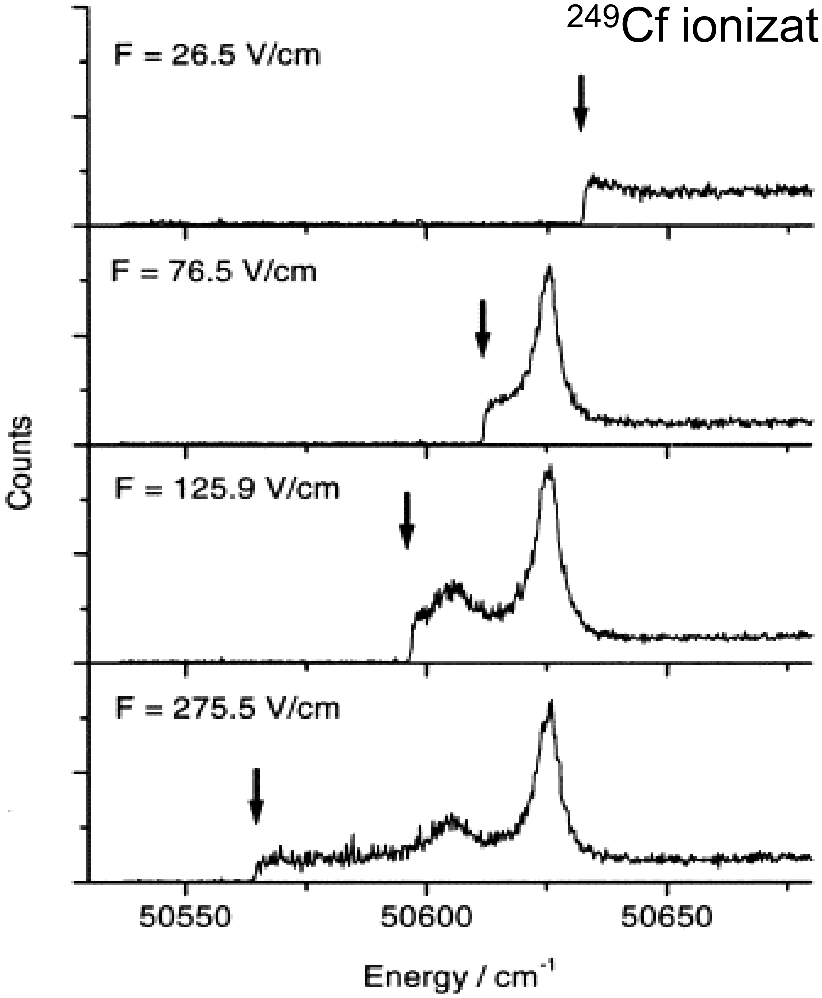
Experiment 🟥 Köhler, S. et al., Spectrochim. Acta B 52, 717 (1997)
🟩 Naubereit P. et al., Rev. Sci. A (2018)
🟧 Hertel, G., J. Chem. Phys. 47, 335 (1976)
🟫 Peterson, J. et al., J. Alloys Comp. 271, 876 (1998)
🟪 Sato, T., et al., J. Am. Chem. Soc. 140, 14609 (2018)
🟩 Chhetri, P., et al., Phys. Rev. Lett. 120, 263003 (2018)
🟦 Sato, T., et al., Nature 520, 209 (2015).

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

IP Determination via Field Ionization in the 1980ties

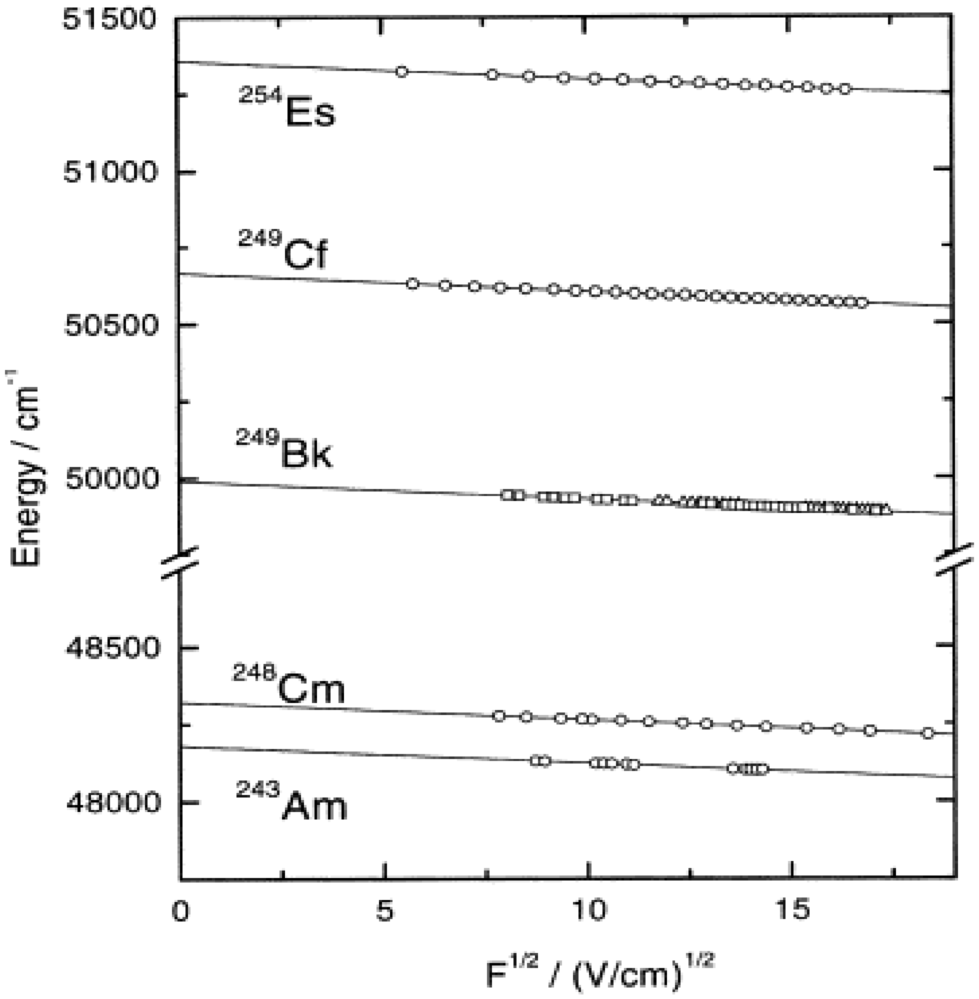
Ionization threshold as function of field strength --- extrapolation to zero field for 6 actinides

^{249}Cf ionization rate



Saddle-Point Model

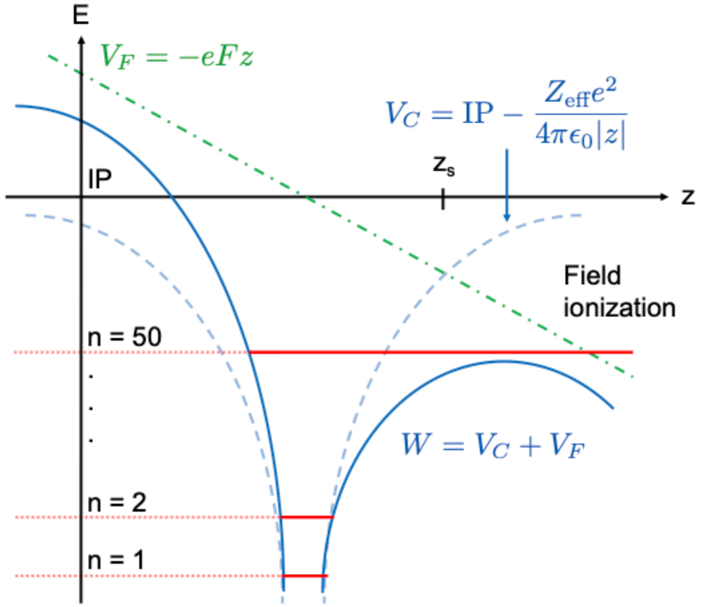
$$W_s(F) = \mathrm{IP} - 2\sqrt{\frac{Z_{\mathrm{eff}} e^3}{4\pi\epsilon_o}}\sqrt{F}$$



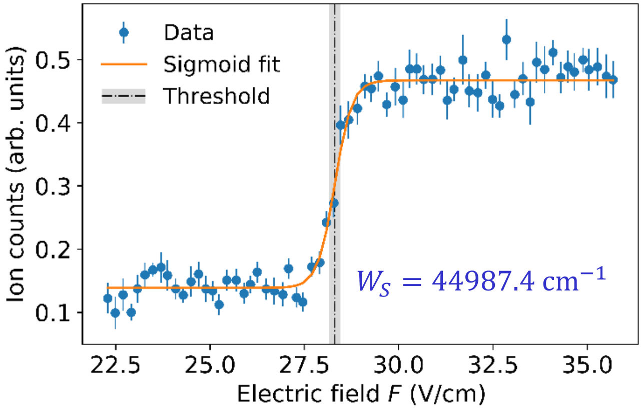
N. Erdmann et al., Journal Alloys Comp, 271-273, 837-840 (1998)

Redetermination via Field Ionization Today

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

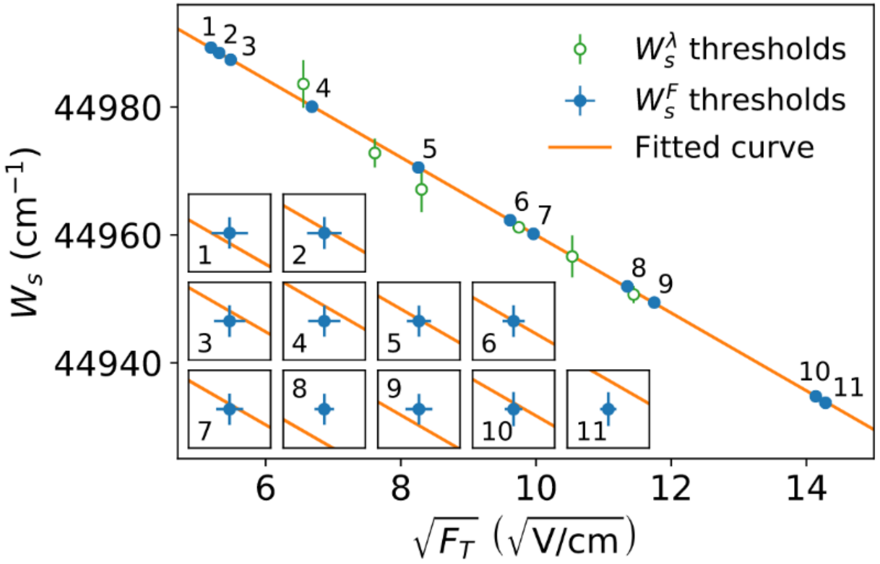


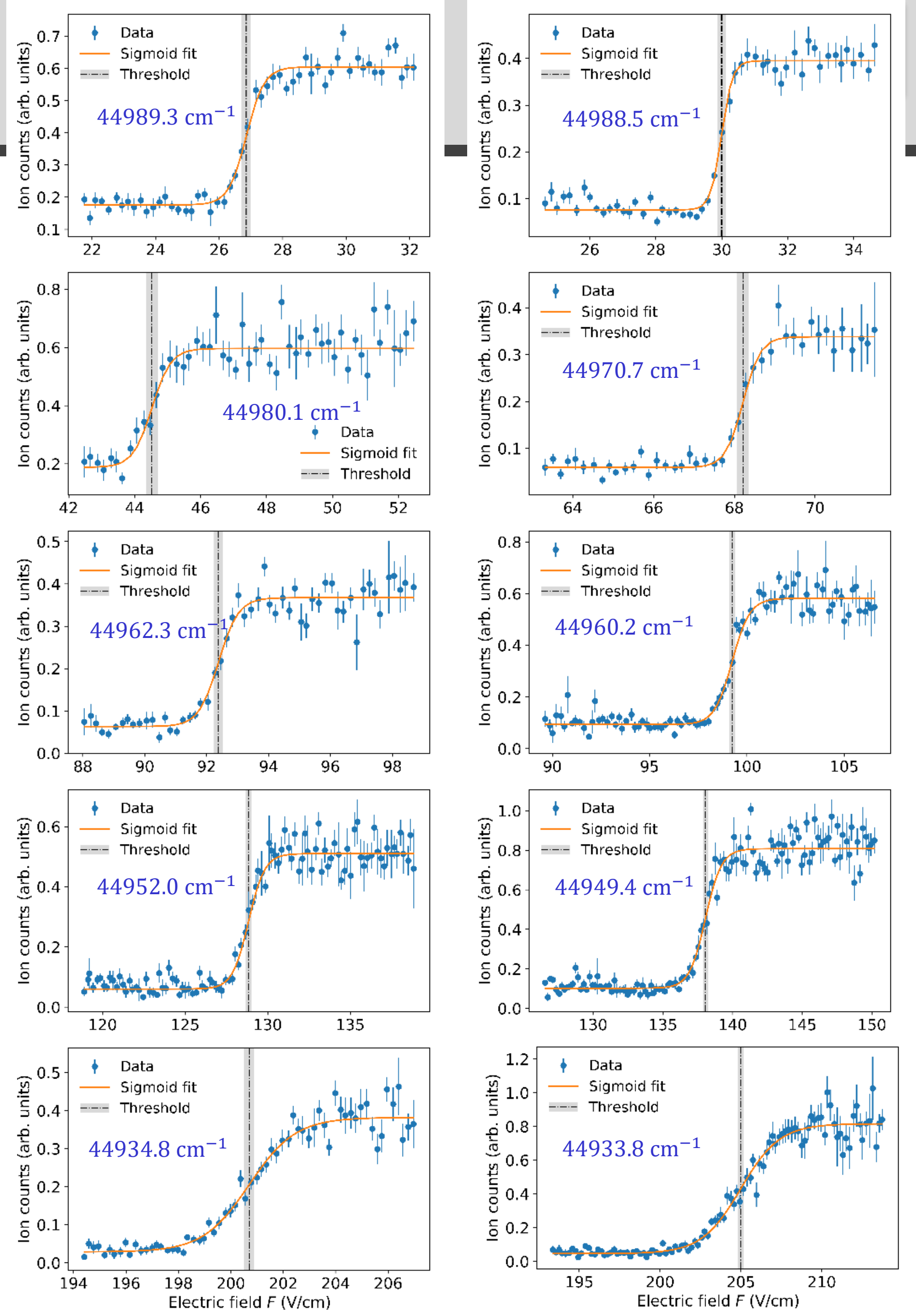
Saddle-Point Model



Result

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





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

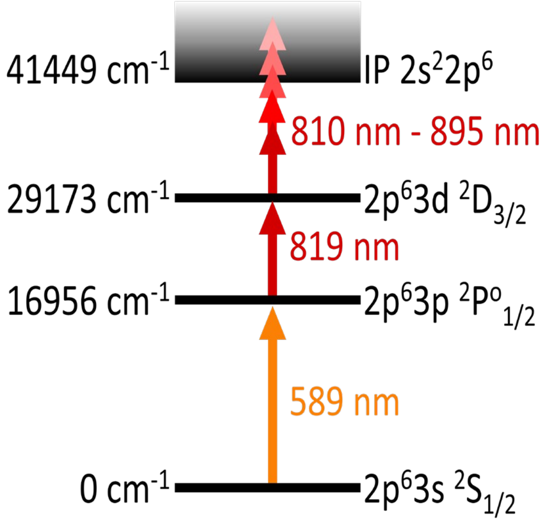
Higher Precision in IP Determination: Rydberg Convergences

Test in $_{11}$Sodium

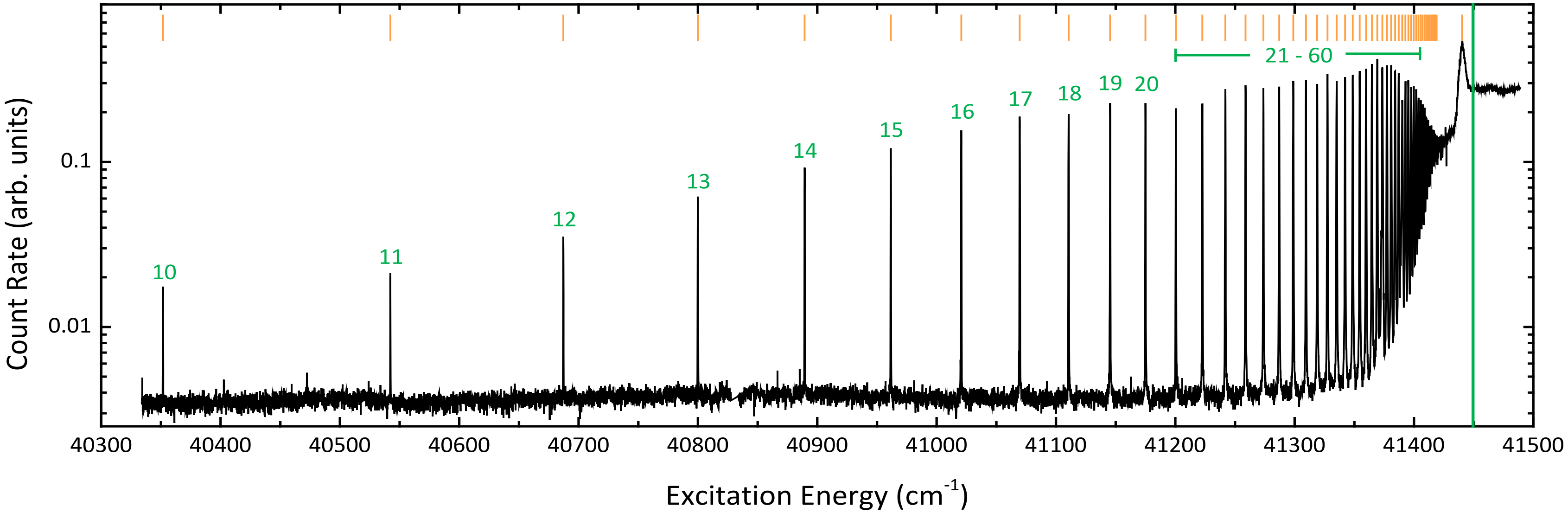
wide range laser scan

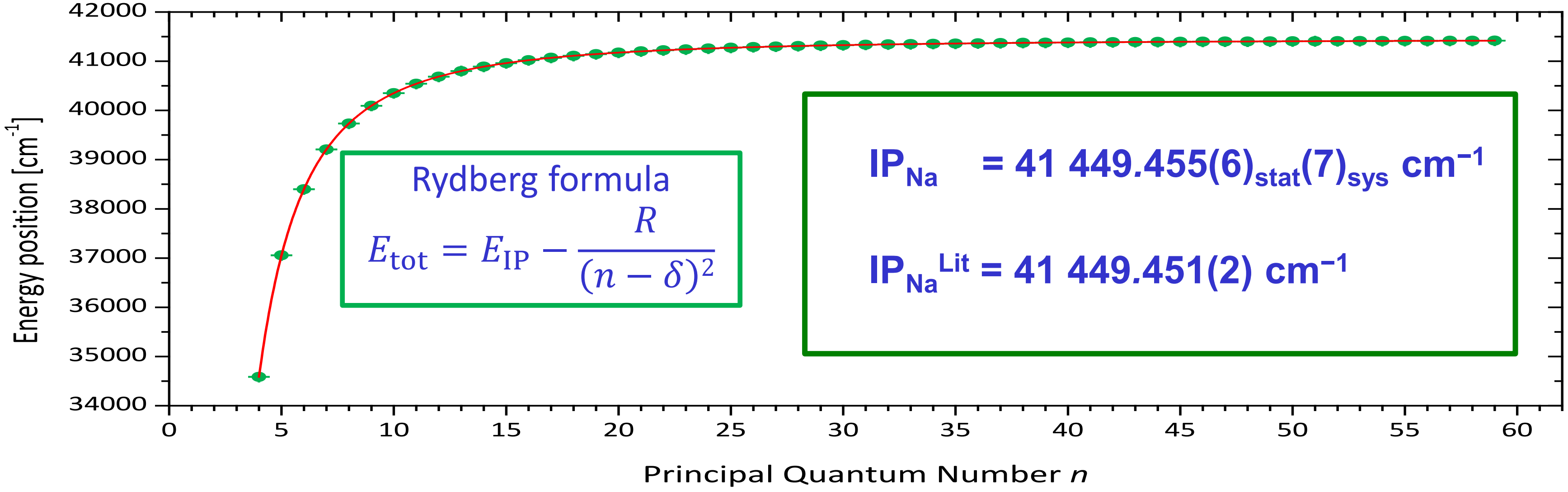
for > 1000 cm^{-1} in TES

around the expected IP



…an optimum situation…





Rydberg formula

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

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

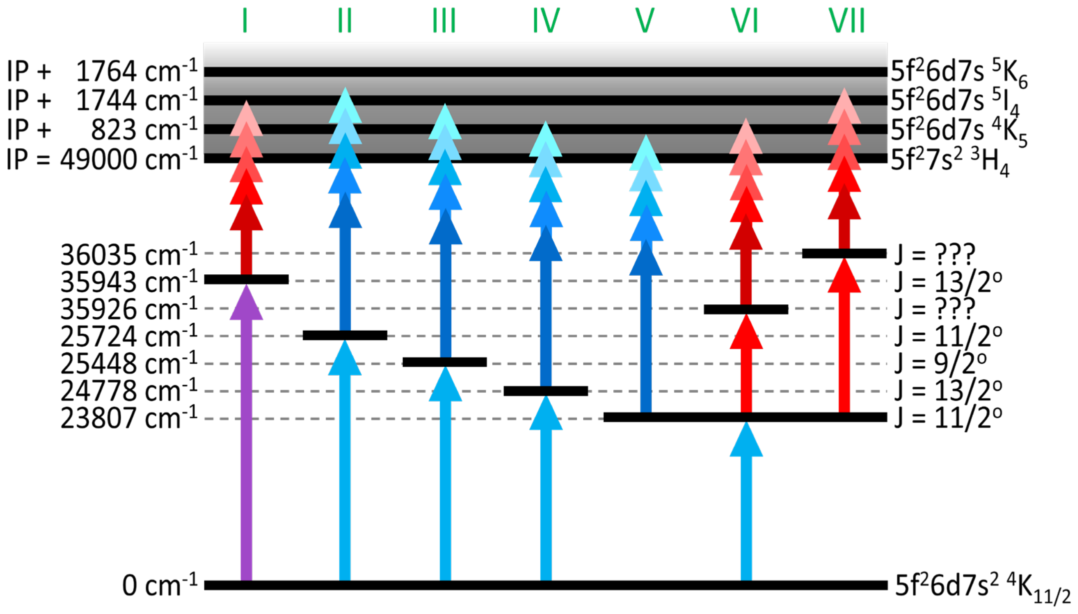
IP_{Na}^{Lit} = 41 449.451(2) cm^{-1}

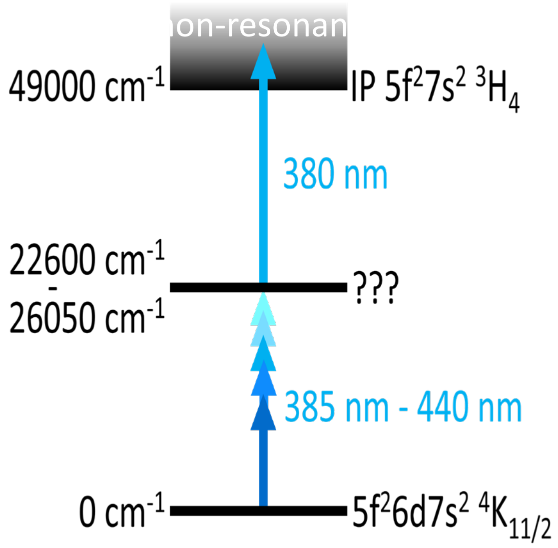
[7] P. Naubereit et al., *Phys. Rev. A*, **93**, 052518 (2016)

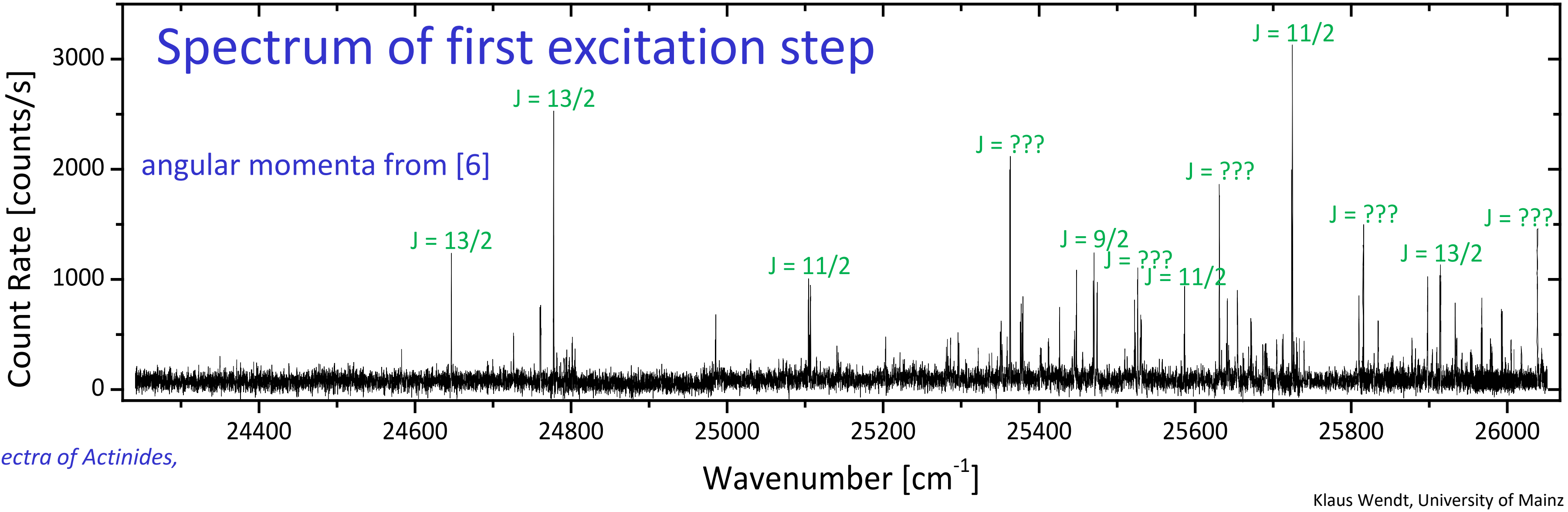
Application in $_{91}$Protactinium?

Step 1: Search for suitable first excited states (FES)

- scan the first laser in a broad wavelength range
- set a powerful second laser at an energy well above the IP for non-resonant ionization
- scan laser 2 (or 3) across the IP range to find Rydberg levels



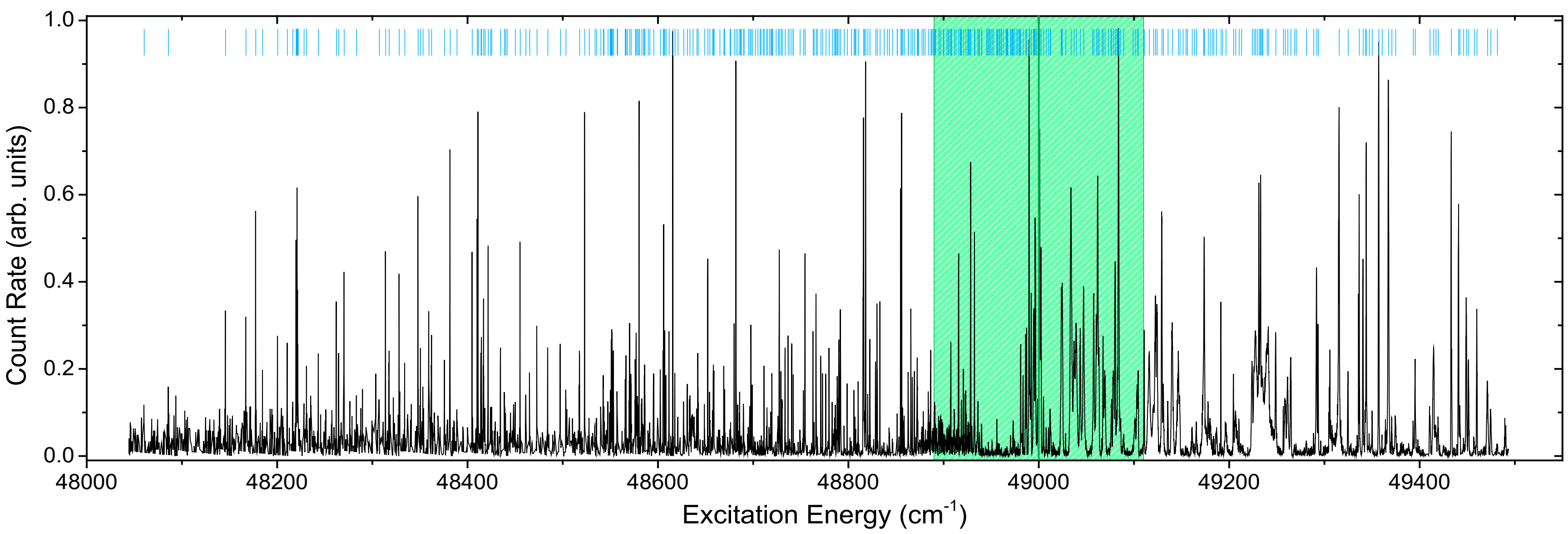



Spectrum of first excitation step

angular momenta from [6]

[6] J. Blaise, J.-F. Wyart, *Energy Levels and Atomic Spectra of Actinides,*

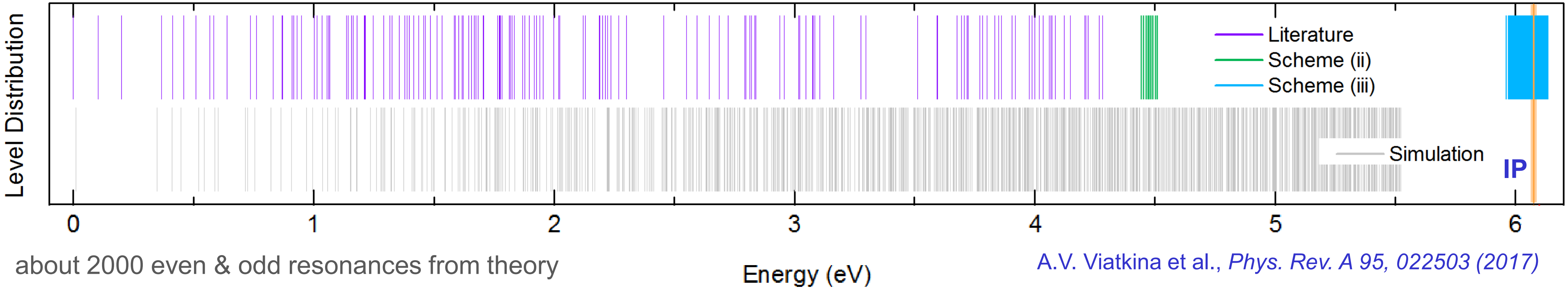
Step 2: Higher Excited Level Search in Protactinium



Scheme	Energy range	Parity	# Level	Range of J's
(i)	3.0 eV - 3.2 eV	Odd	88	7/2 - 13/2
(ii) 🟩	4.4 eV - 4.5 eV	Even	28	9/2 - 13/2
(iii) 🟦	6.0 eV - 6.1 eV	Even	423	9/2 - 13/2
(iv)	6.1 eV - 6.3 eV	Even	74	7/2 - 11/2
(v)	6.0 eV - 6.1 eV	Even	70	11/2 - 15/2
(vi)	6.0 eV - 6.1 eV	Even	187	9/2 - 13/2
(vii)	5.9 eV - 6.1 eV	Odd	472	7/2 - 15/2
(viii)	6.0 eV - 6.2 eV	Odd	233	9/2 - 13/2
Literature	0.0 eV - 4.3 eV	Even	156	3/2 - 17/2
Literature	0.2 eV - 4.8 eV	Odd	494	3/2 - 17/2
Simulation	0.0 eV - 5.5 eV	Even	989	1/2 - 19/2
Simulation	1.0 eV - 5.1 eV	Odd	989	1/2 - 19/2

156 even and 494 odd resonances from literature

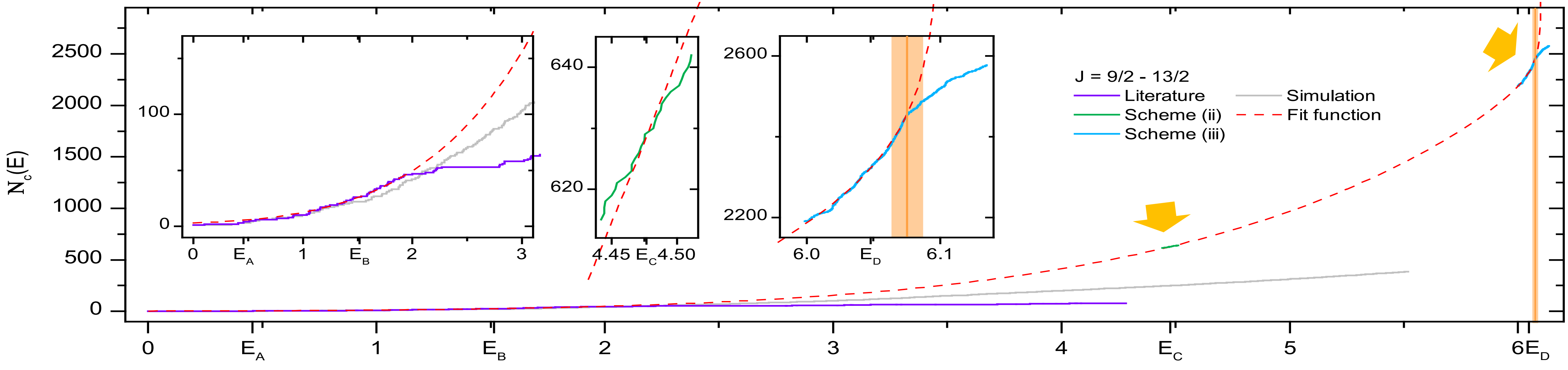
about 800 even & 800 odd resonances measured

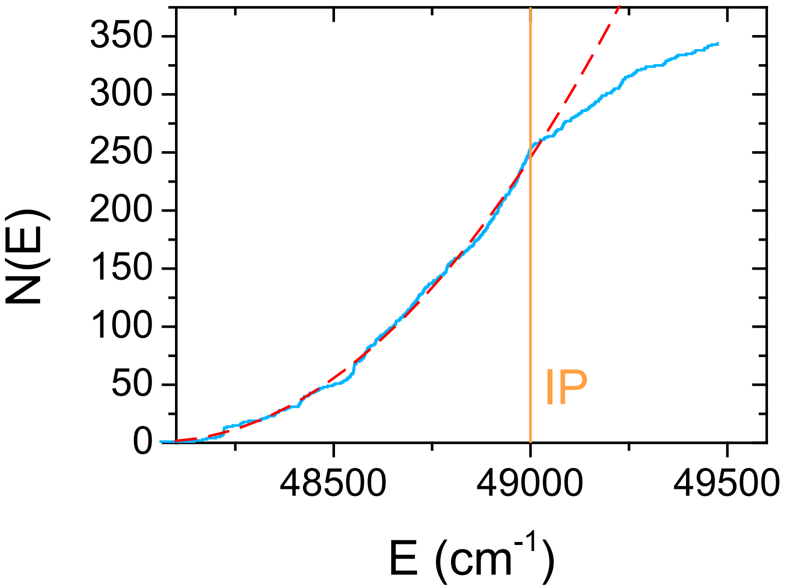


about 2000 even & odd resonances from theory

A.V. Viatkina et al., *Phys. Rev. A 95, 022503 (2017)*

Analysis of the Protactinium Spectrum by Distribution Functions





Theoretical data analysis via **1. *Level Density Collaps*** or **2. *Rydberg Correlation***

yields IP_{Pa} = 49 034 (10) cm^{-1}

IP_{Pa}^{Expect} = 49 000 (110) cm^{-1}

Excited atomic energy levels in protactinium by resonance ionization spectroscopy
P. Naubereit, T. Gottwald, D. Studer, and K. W., *PR **A 98**, 022505 (2018)*

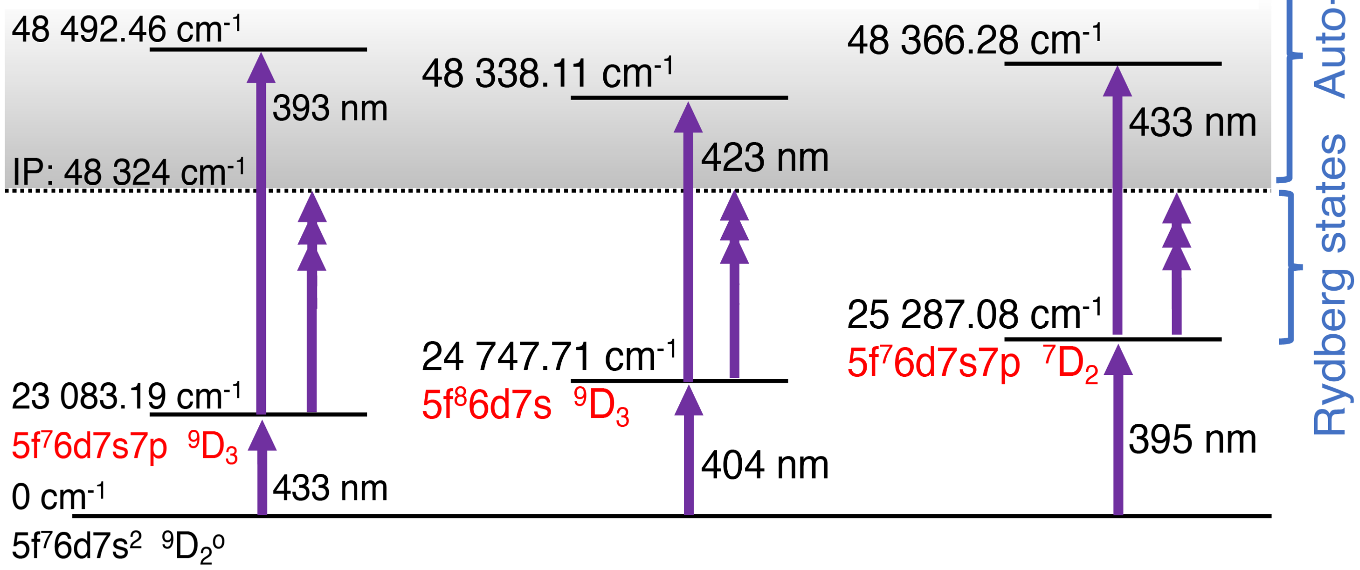
Intrinsic quantum chaos and spectral fluctuations within the protactinium atom
P. Naubereit, D. Studer, A.V. Viatkina, A. Buchleitner, B. Dietz, V.V. Flambaum, and K.W. *PR. **A 98**, 022506 (2018)*

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

Auto-ionizing states and Rydberg analysi

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... ϵ; 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⁻

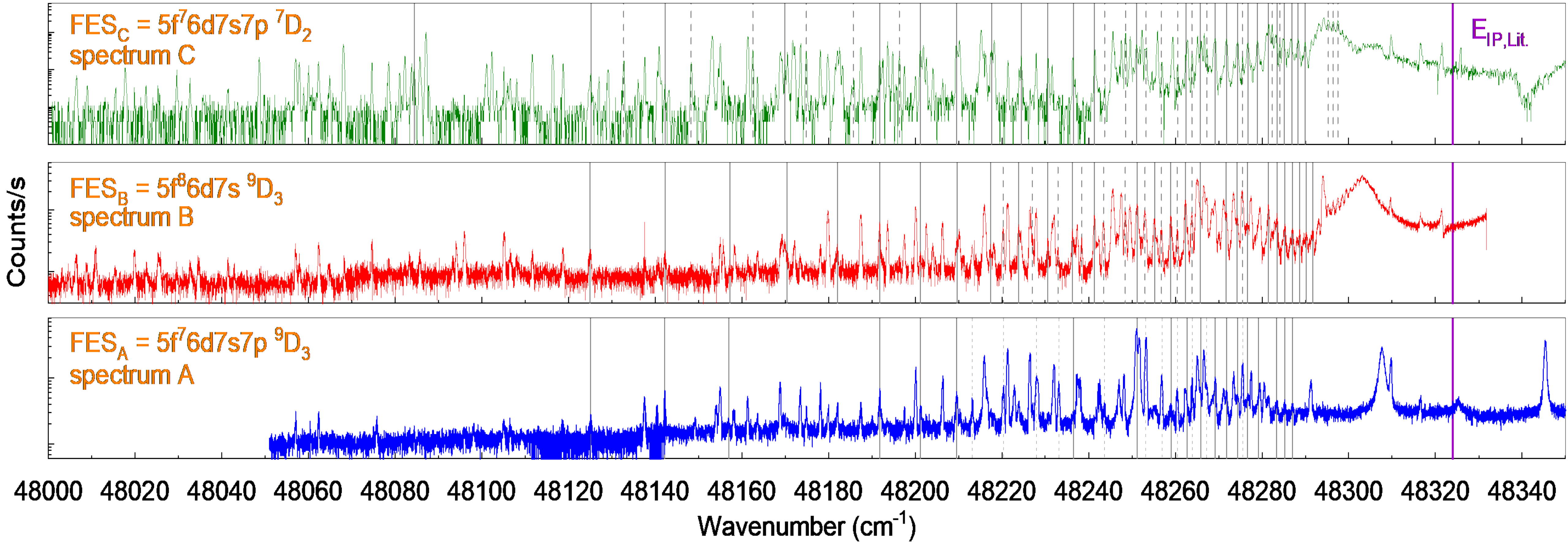
- ➢ Characterization of first excitation states (FES)
- ➢ Identification of 3 different ionization schemes
- ➢ IP determination by Rydberg analysis
- ➢ Verification by field ionization
- ➢ High resolution spectroscopy on hfs and isv



Characterization of first excitation steps

Spectroscopic investigation of spectral range above and below IP

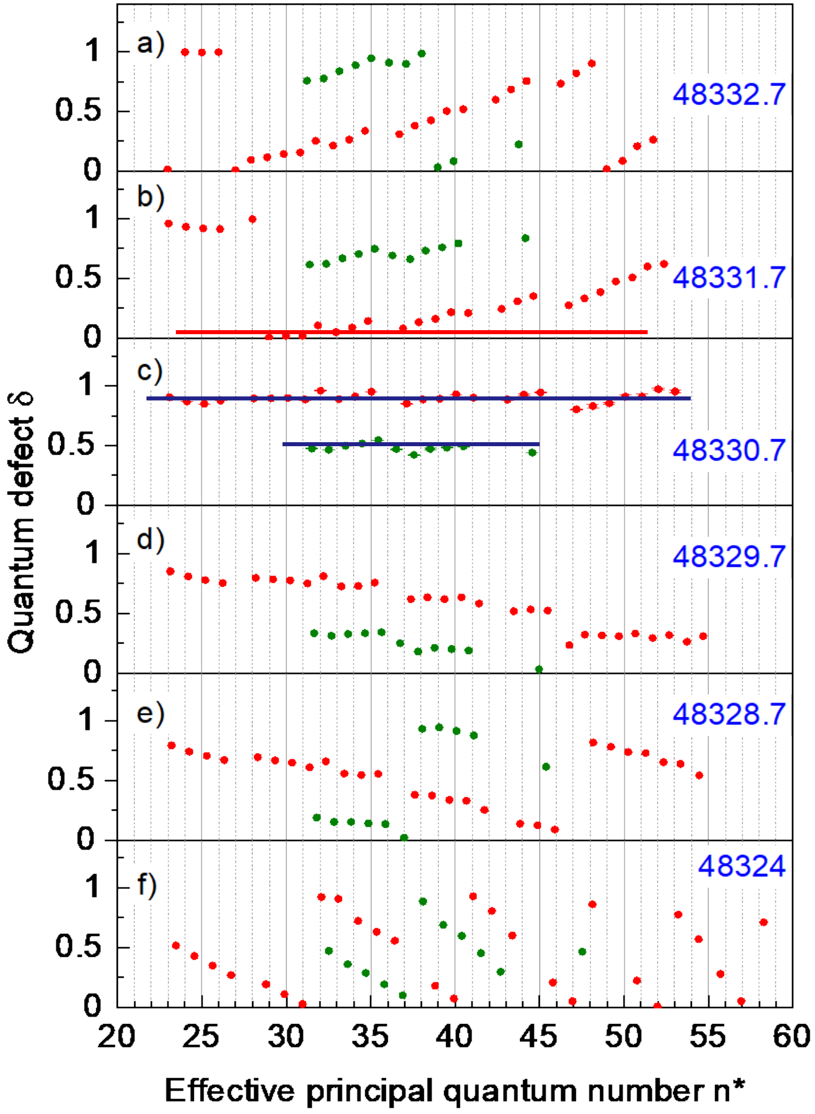
Spectroscopic investigation of Rydberg states in Curium



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



n* against δ for first IP estimation [1]

Rydberg Ritz formula:

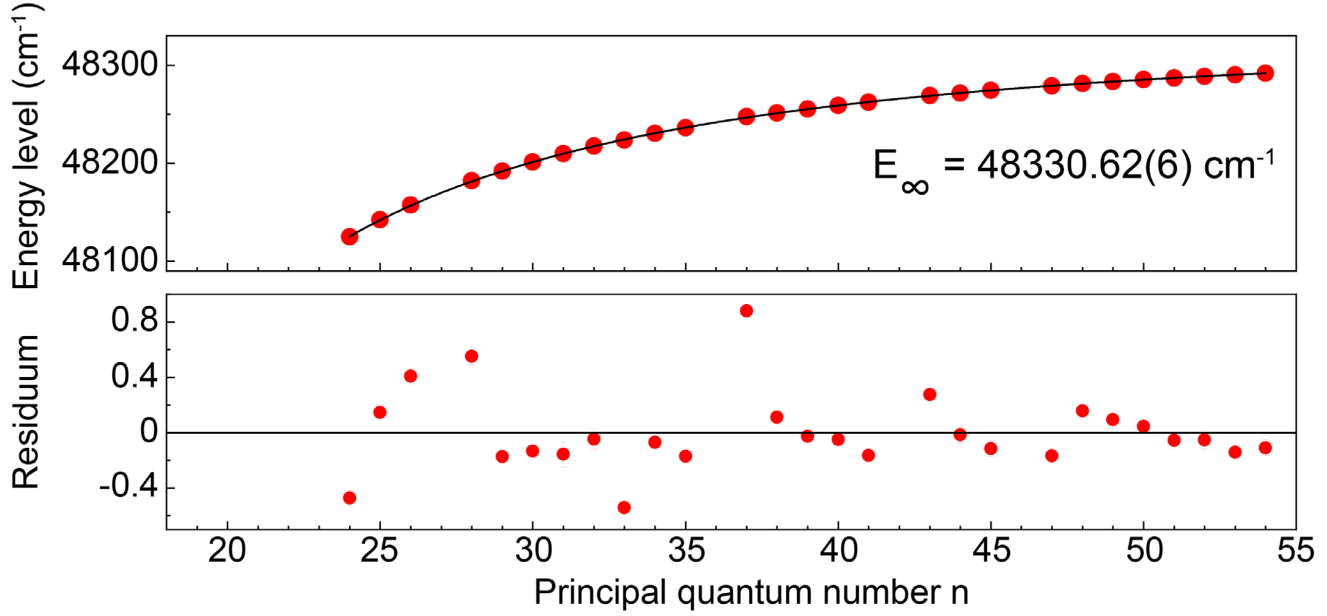
$$E_n = E_{\mathrm{IP}} - \frac{R_\mu}{(n-\delta(n))^2} = E_{\mathrm{IP}} - \frac{R_\mu}{(n^*)^2}$$

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

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]

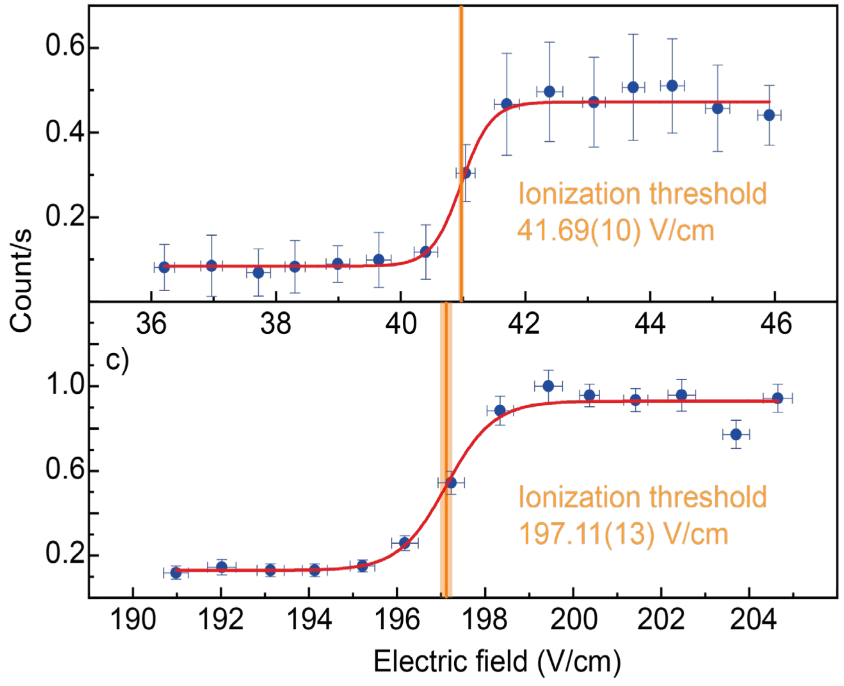
Ionization potential verification via field ionization

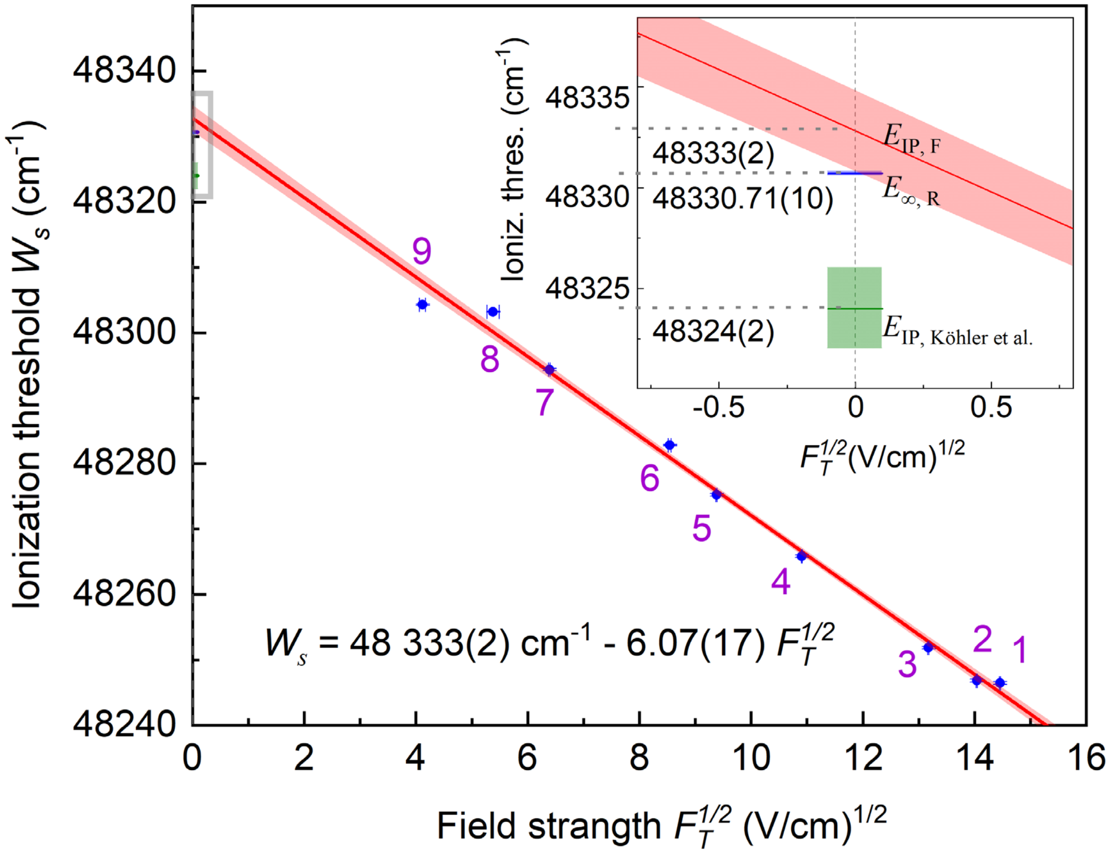
IP verification by reproduction of field ionization technique

- Assignment of specific states which are 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

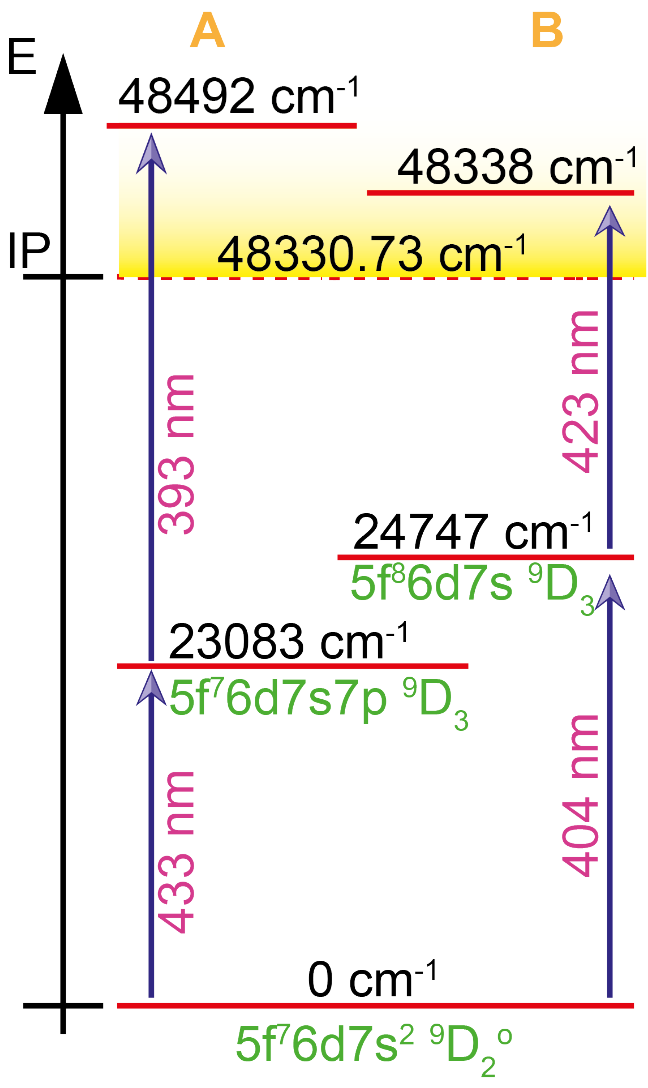


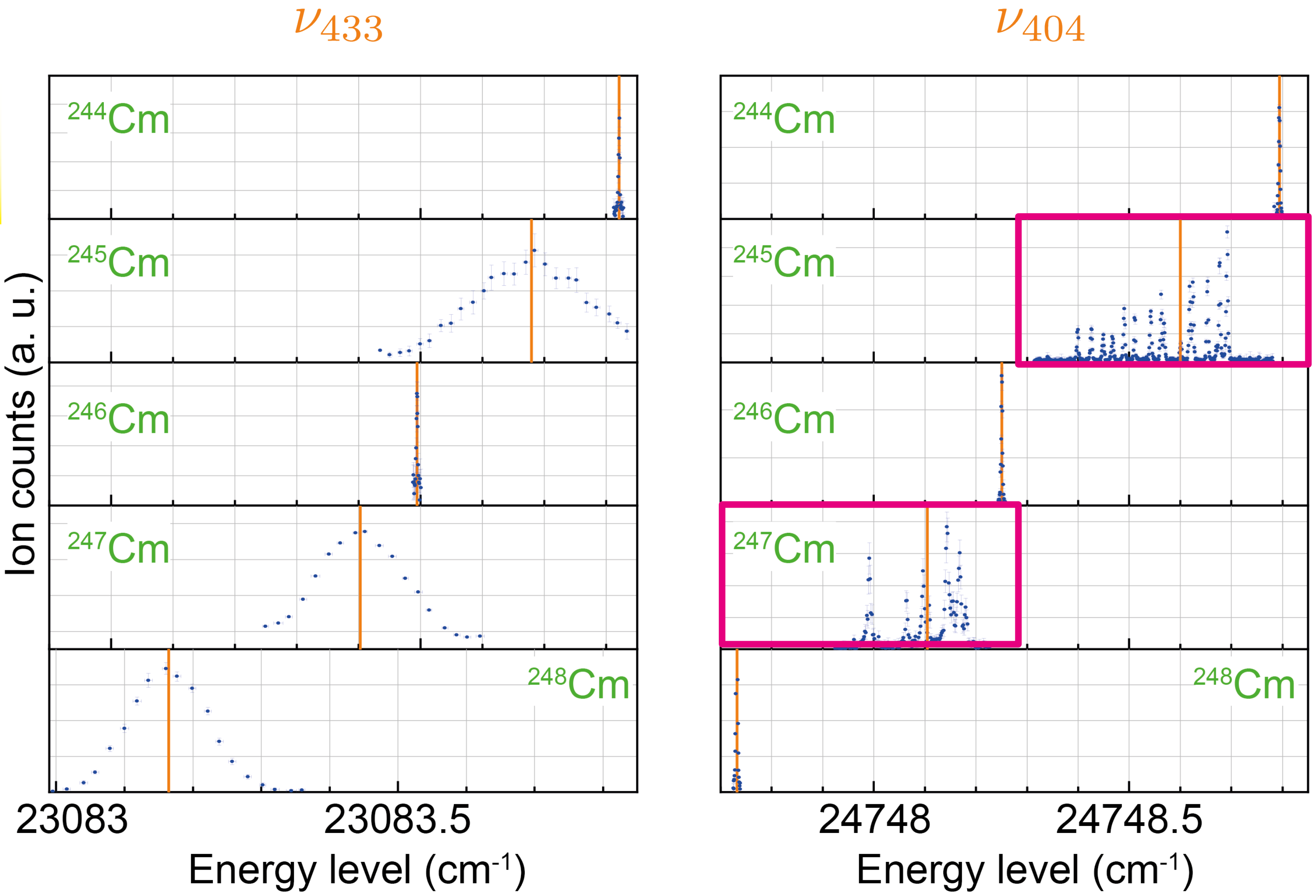


Overview of measured ionization thresholds [1]

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

High-resolution measurements of isotope shift

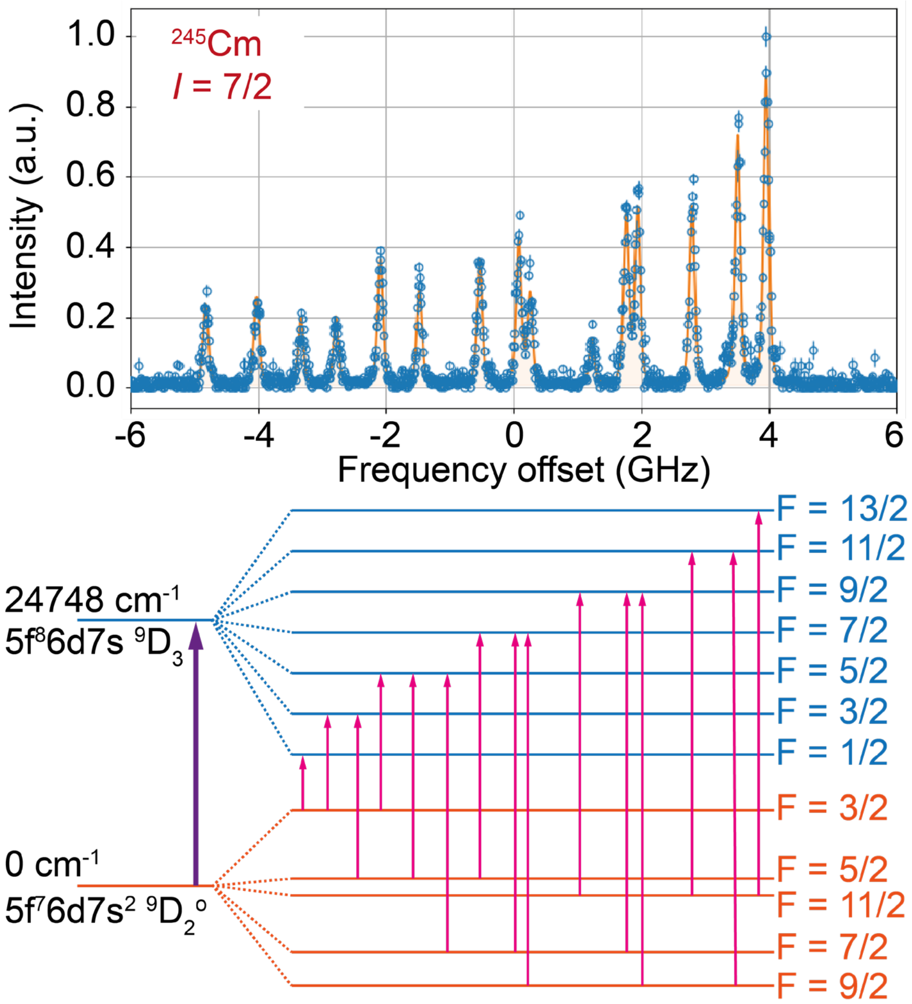


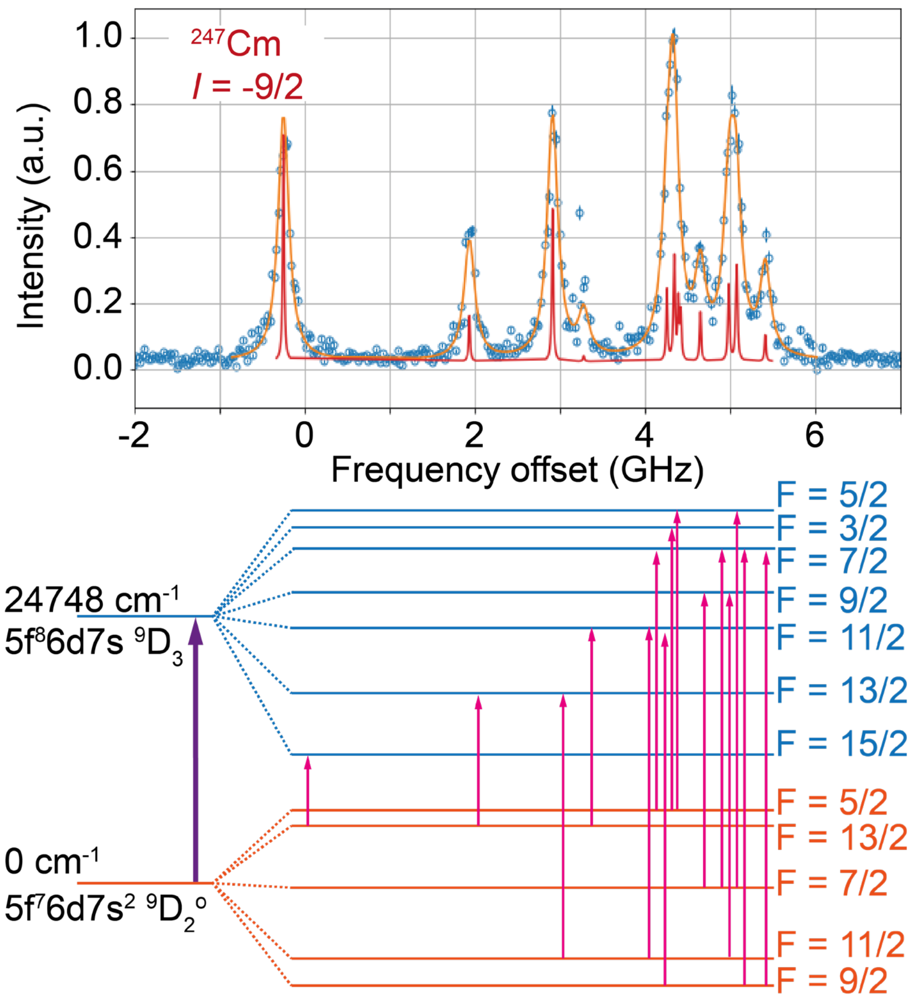


Profiles and isotope shifts of the 23083 cm^{-1} and 24747 cm^{-1} FES

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

3.2×10^{12} atoms





1.9×10^{11} atoms

A and B factor from hyperfine structure fit

Conclusion and Outlook

Laser spectroscopy along the series of actinides and beyond

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

Generation of atomic spectroscopic data of high relevance,

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

Access ensured today for specific isotopes & isotopic sequences

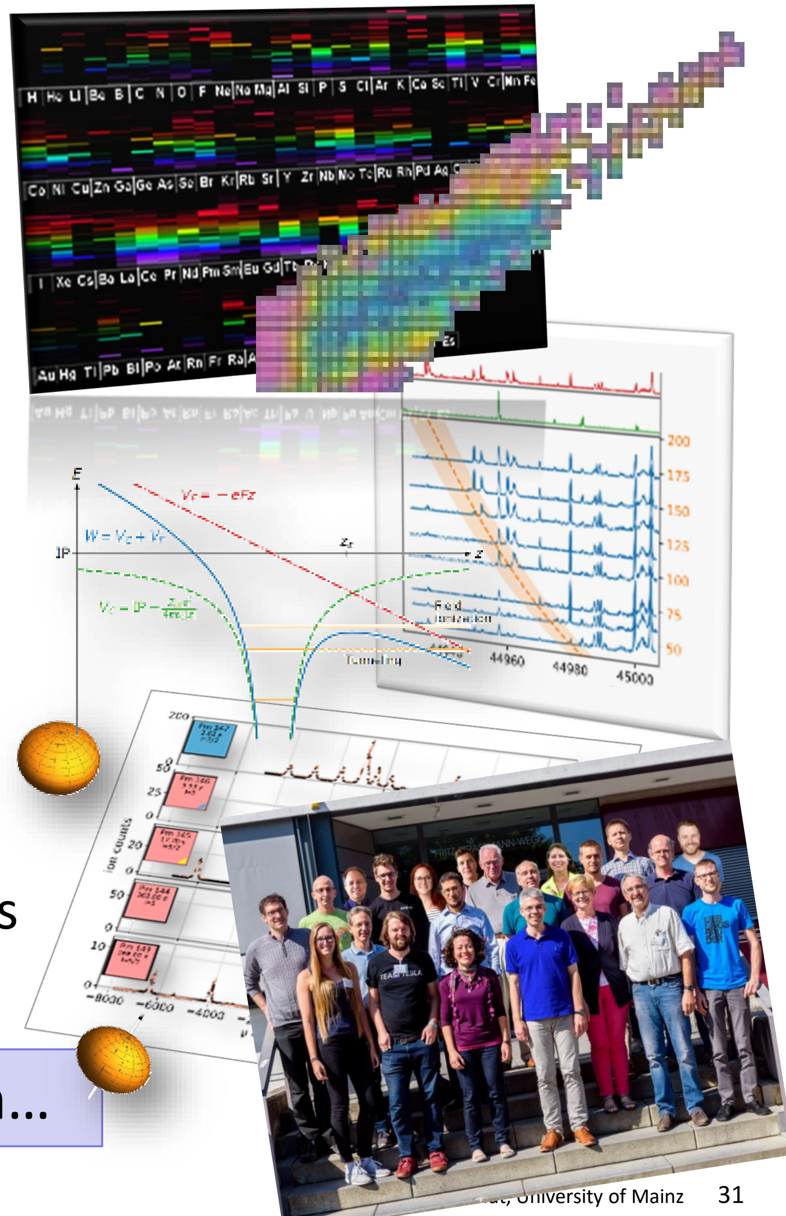
→ majority of elements from Ac up to Fm (and on-line even further)

Data collection & specifically data evaluation on-going

→ often complex and time consuming which (similarly applies to theory)

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

→ fruitful exchange just started….

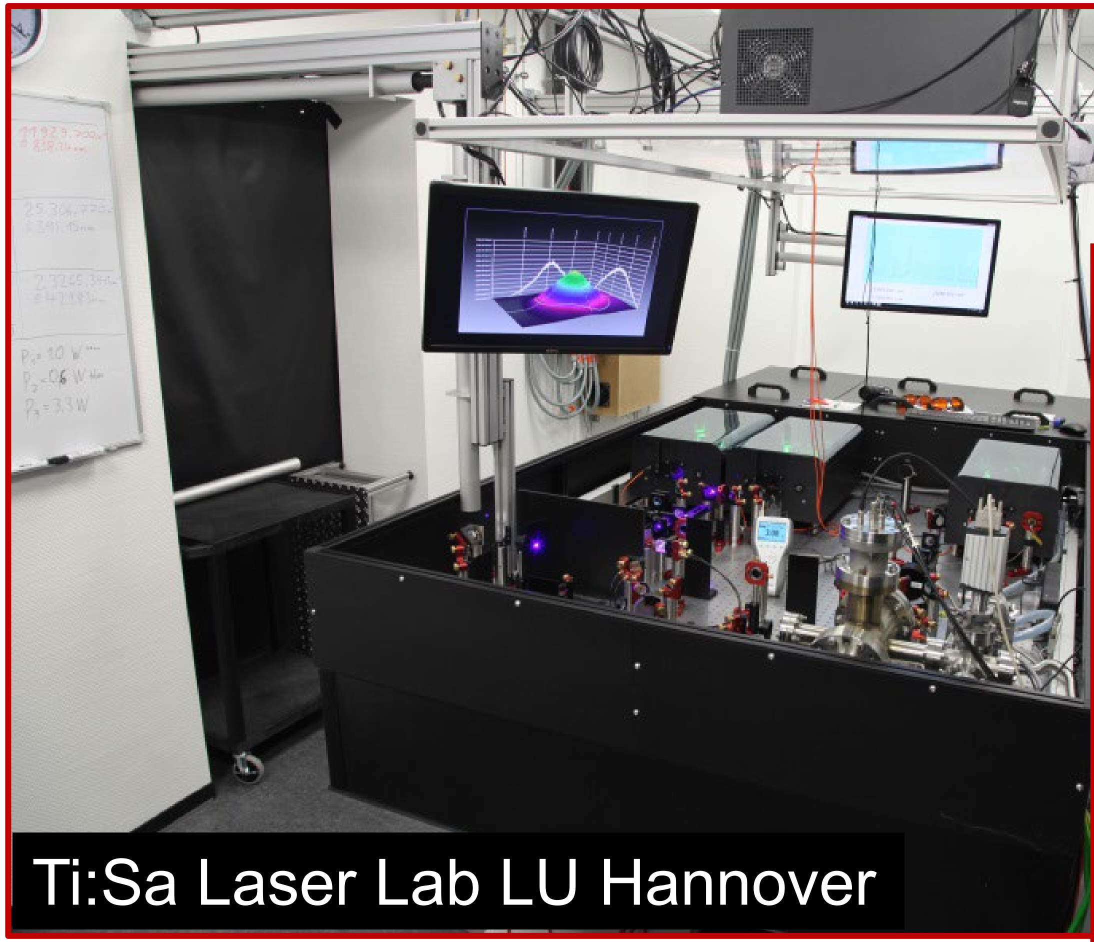


Thanks to all members of the teams and to you for your attention…

Resonant Laser SN-MS for Direct Particle Analysis at IRS LUH

SIRIUS - spatially resolved elemental selective actinide determination in particels

C. Walther, IRS-LUH, K.W., T. Reich, JGU



Ti:Sa Laser Lab LU Hannover

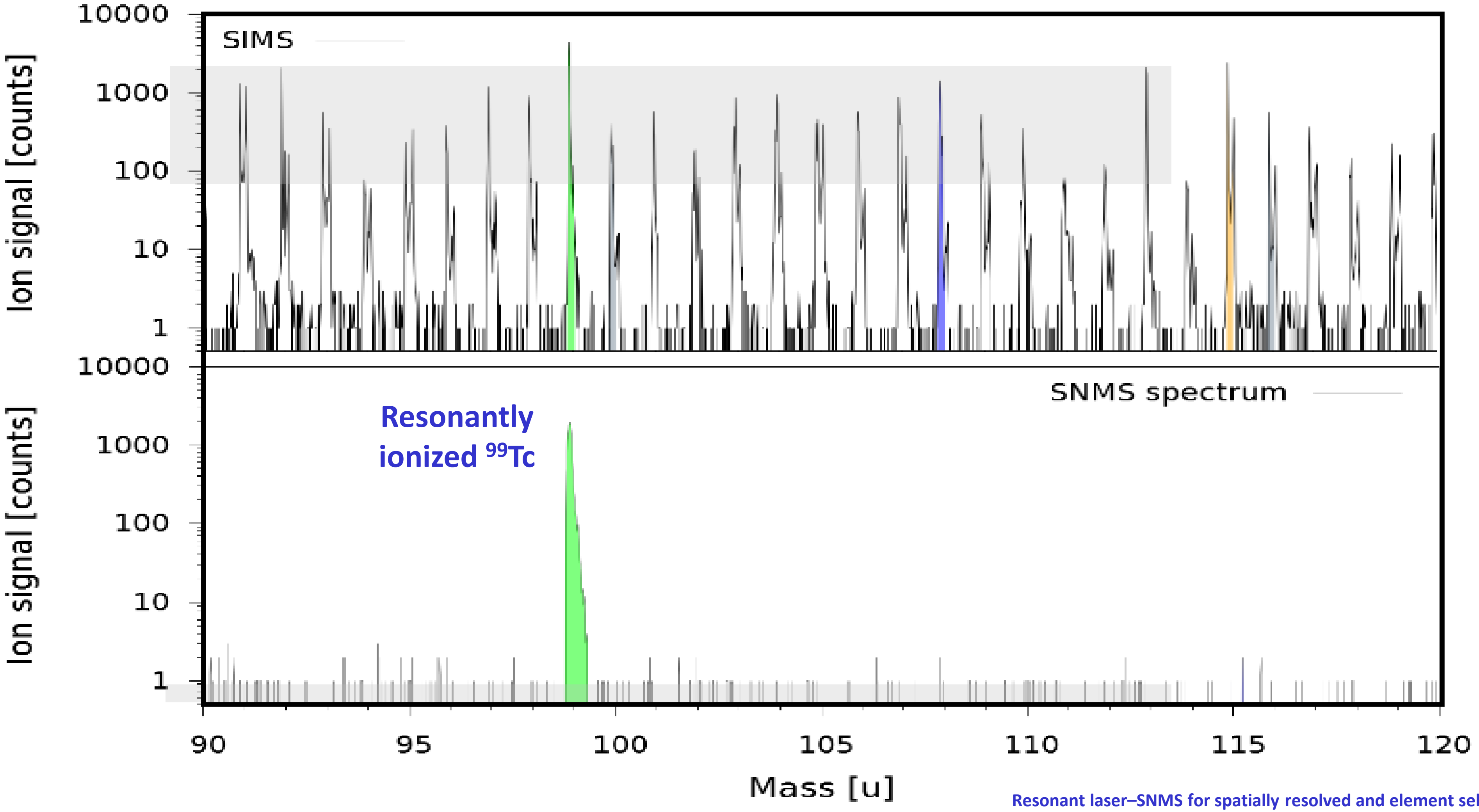
JGU Mainz Ti:Sa laser system

A new resonant Laser-SNMS system for environmental ultra-trace analysis
M. Franzmann, H. Bosco, C. Walther, K. W., IJMS 423, 27-32 (2017)

RIS – TOF-SIMS combination

Selectivity of SNMS compared to SIMS: ^{99}Tc determination

- Synthetical sample of technetium (0,2 µl with 2,8 ppm ^{99}Tc)



Resonantly ionized ^{99}Tc

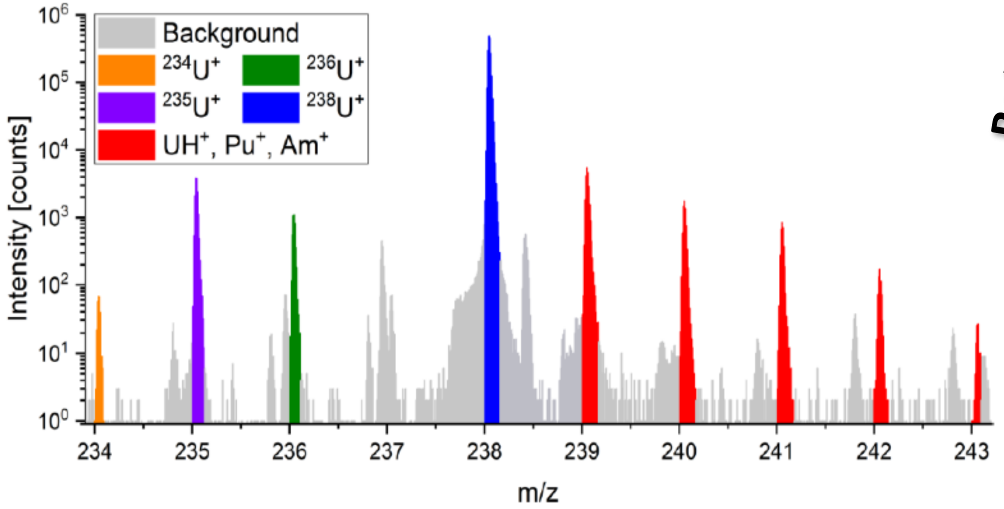
High organic background

Completely suppressed background

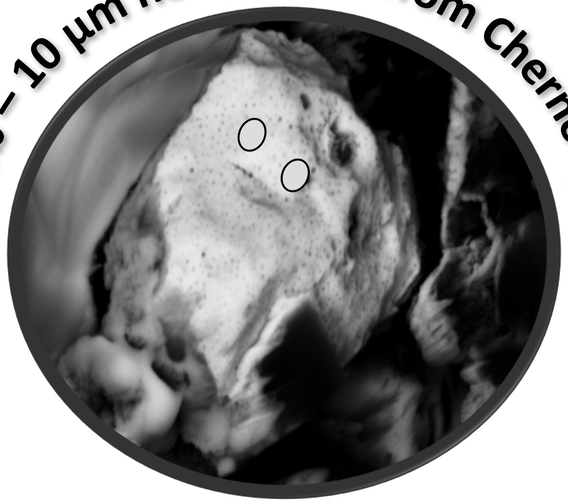
Resonant laser–SNMS for spatially resolved and element selective ultra-trace analysis of radionuclides,
M. Franzmann, H. Bosco, L. Hamann, C. Walther and K. W. *JAAS 33, 730-737 (2018)*

Element & Isotope Composition of Chernobyl Hot Particles

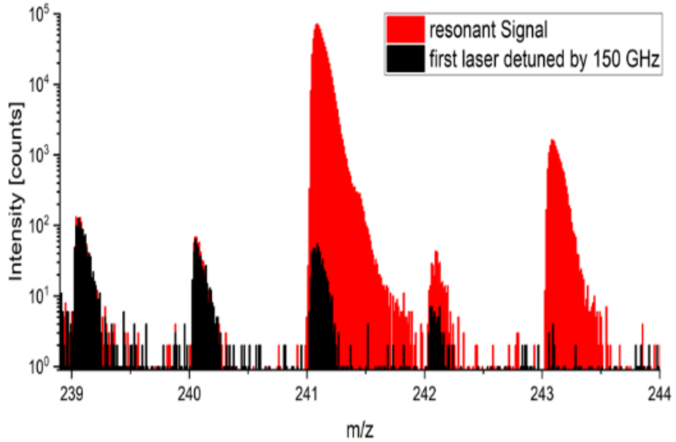
Multi-element SIMS



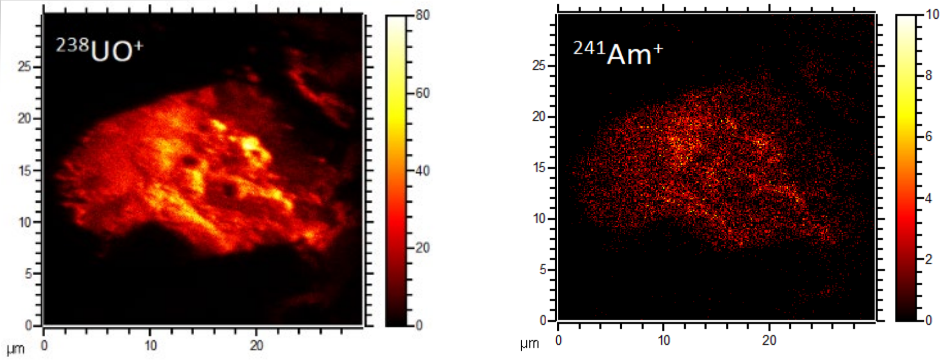
Bob – 10 µm hot particle from Chernobyl



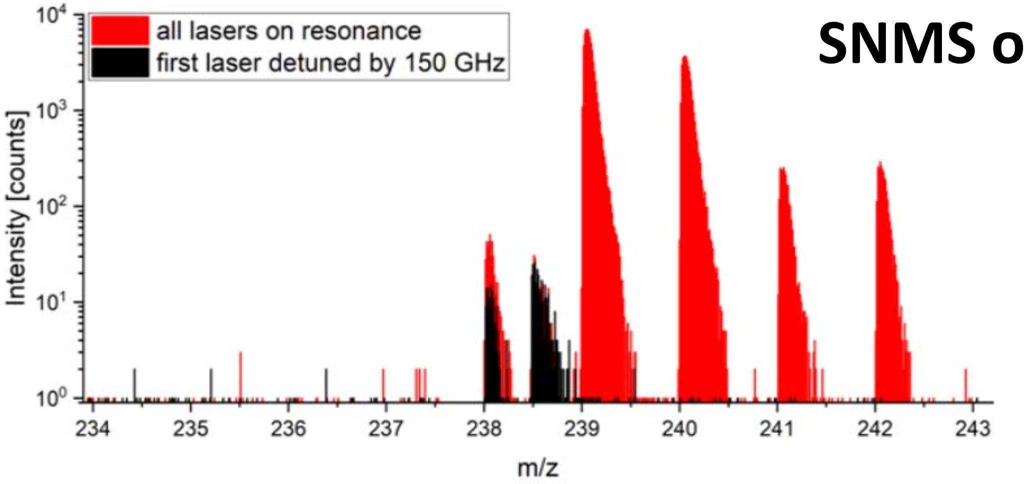
SNMS on Am



Spatial element distribution



SNMS on Pu



New horizons in micro particle forensics: Imaging ^{238}Pu and ^{242m}Am in hot-particles
H. Bosco, L. Hamann, N. Kneip, M. Raiwa, M. Weiss, K. W., C. Walther Science Adv. 7, 44 (2021)