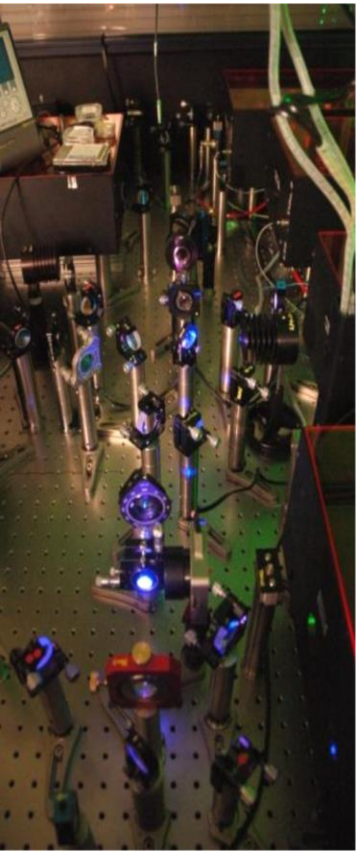


Laser Ion Sources

-

quantitative considerations and analytical applications of resonance ionization

Klaus D.A. Wendt and the LARISSA Collaboration

WG Quantum, Institute of Physics, Johannes Gutenberg-University Mainz, D-55099 Mainz, Germany
E-mail: Klaus.Wendt@uni-mainz.de

in collaboration with

Institut für Kernchemie, Universität Mainz and
PNNL, Richland, ORNL, Oak Ridge, USA - ISAC, TRIUMF, Vancouver, Canada - University of Nagoya, JAERI, Tokai-Mura, Japan -
- JYFL, Jyväskylä, Finnland - Chalmers University, Göteborg, Schweden - GANIL, Caen, Frankreich - ISOLDE, CERN, Geneva, Schweiz -

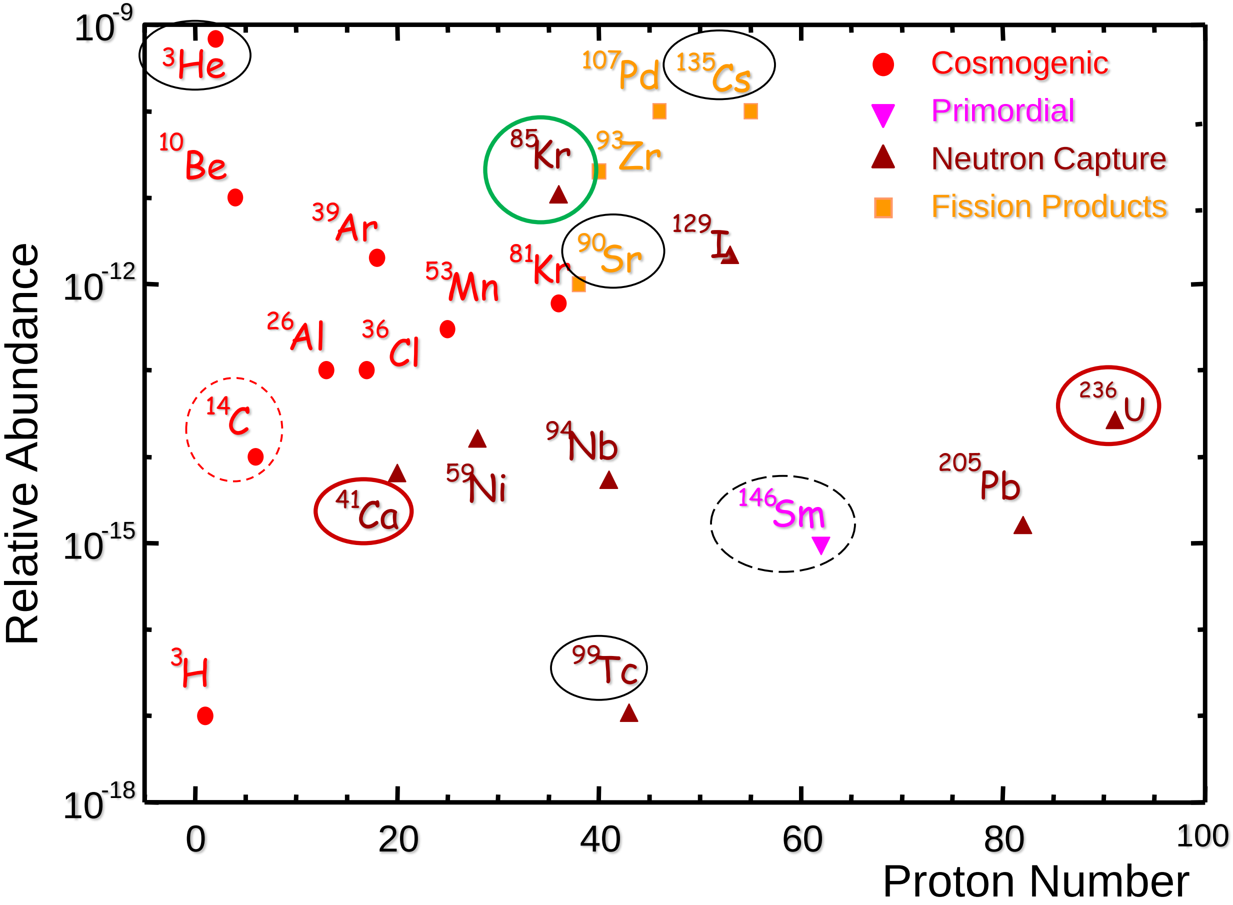
Outline

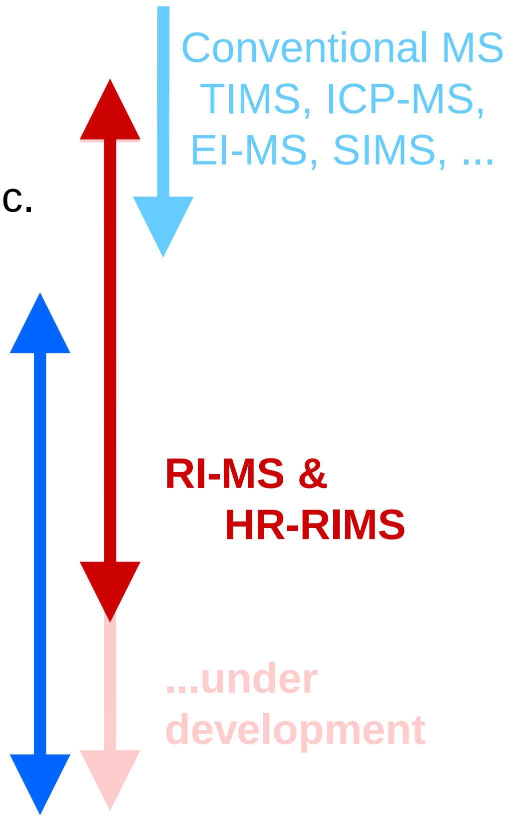
- Motivation: Access to Exotic Isotopes through Quantum Optics
  – off-line (not on-line) on long-lived natural and anthropogenic species
- Theory: Multi-Step Excitation Processes in Atomic Systems
  – Benefits, drawbacks & limitations of light-atom interactions
- Experimental & Applications:
  - HR-RIMS – for isotope selective coherent atomic spectroscopy
  - Analytics – high-tech physics for low level chemistry & radioprotecion
  - (Laser AMS – isobar selection at accelerators for radiodating)
- Exclusion: On-line Laser Ion Sources and related physics
  – Hot cavity or gas cell technology (-- Bruce Marsh or Iain Moore)
- Outlook & Summary
  – Laser (tunable ones) applications at accelerators (smaller ones)

Motivation

Natural Ultra Trace Isotopes & Detection Techniques

- Abundance below 10^{-9} of neighboring isotopes
- High surplus of elemental and/or molecular isobars
- Inaccessibility by conventional detection, i.e. radiometric or mass spec.





Conventional MS
TIMS, ICP-MS,
EI-MS, SIMS, ...

**RI-MS &
HR-RIMS**

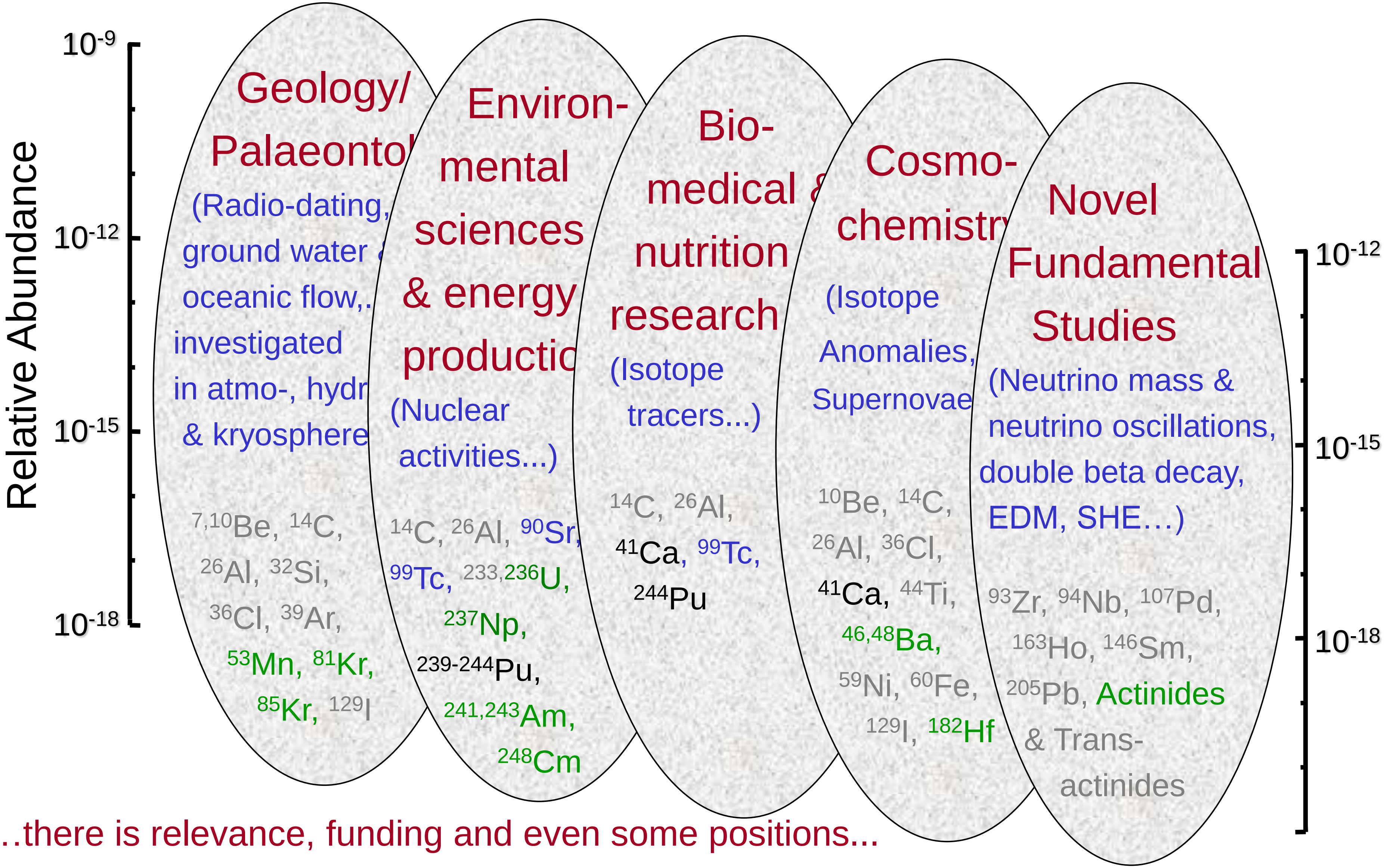
**...under
development**

**AMS (Accelerator
Mass Spectrometry)**

QO technique for the future:
ATTA- Atom Trap Trace Analysis

RI in Ultra Trace Isotope Research

…to solve important questions in the humonguously wild field of applied research in...



Geology/ Palaeontol
(Radio-dating, ground water oceanic flow,.. investigated in atmo-, hydr & kryosphere
^{7,10}Be, ^{14}C, ^{26}Al, ^{32}Si, ^{36}Cl, ^{39}Ar, ^{53}Mn, ^{81}Kr, ^{85}Kr, ^{129}I

Environ-mental sciences & energy productio
(Nuclear activities...)
^{14}C, ^{26}Al, ^{90}Sr, ^{99}Tc, ^{233,236}U, ^{237}Np, $^{239-244}$Pu, ^{241,243}Am, ^{248}Cm

Bio-medical nutrition research
(Isotope tracers...)
^{14}C, ^{26}Al, ^{41}Ca, ^{99}Tc, ^{244}Pu

Cosmo-chemistr
(Isotope Anomalies, Supernovae
^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{44}Ti, ^{46,48}Ba, ^{59}Ni, ^{60}Fe, ^{129}I, ^{182}Hf

Novel Fundamental Studies
(Neutrino mass & neutrino oscillations, double beta decay, EDM, SHE…)
^{93}Zr, ^{94}Nb, ^{107}Pd, ^{163}Ho, ^{146}Sm, ^{205}Pb, Actinides & Trans-actinides

…there is relevance, funding and even some positions...

Ex 1: Efficiency of RI - Detection of ^{81}Kr & ^{85}Kr

Measuring ^{81,85}Kr in Polar Ice by RIMS

1. Degas the ice (10^{27} Molecules) 10^{23} Molecules

2. Kryogenic rare gase extraction

10^{17} Kr + 5×10^{4} ^{81}Kr

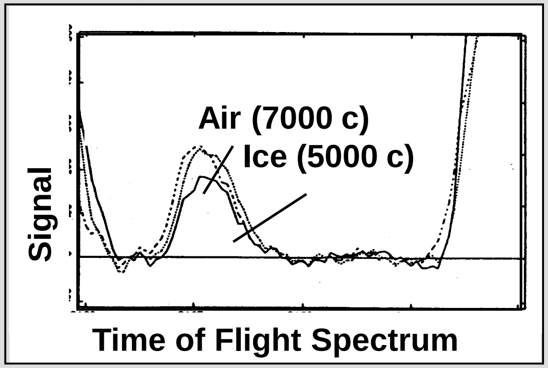
3. First preenrichment in a velocity filter

4×10^{11} Kr + 1.5×10^{4} ^{81}Kr

4. Second preenrichment in a quadrupole filter

3×10^{6} Kr + 6×10^{3} ^{81}Kr

5. Closed system RI-TOF Analysis → 5×10^{3} Counts



Selectivity:

> 10^{13}

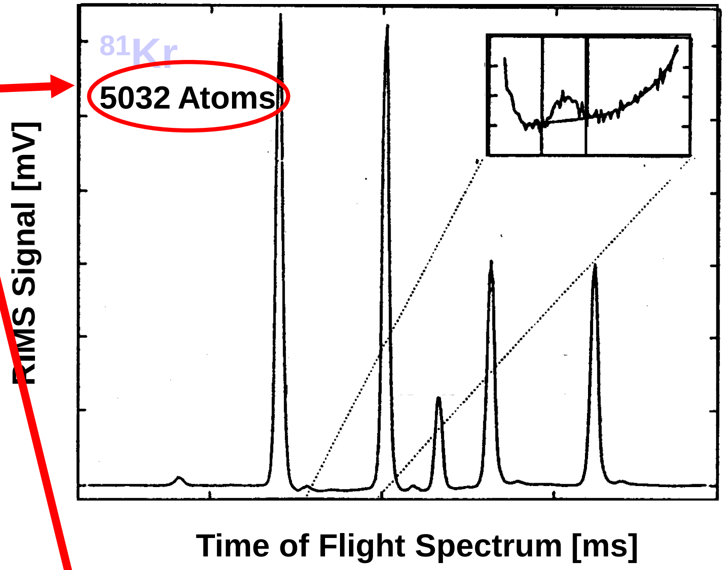
Efficiency:

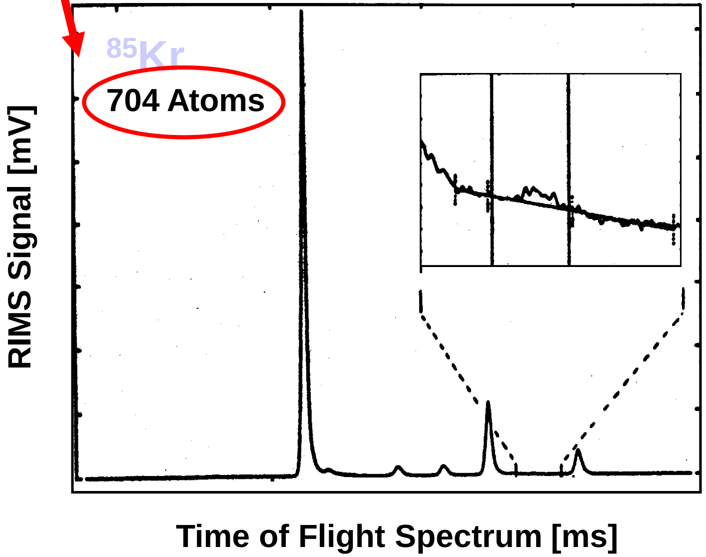
> 10^{-2}

Age of Antartic Ice:

$116(24) \times 10^{3}$ years

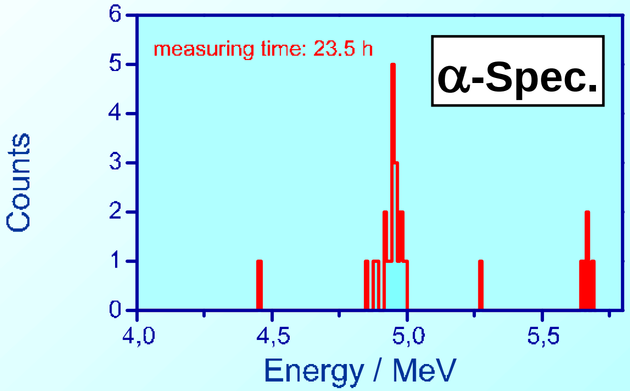
† B. Lehmann, Appl. Geochemistry 6, 419 (1991)

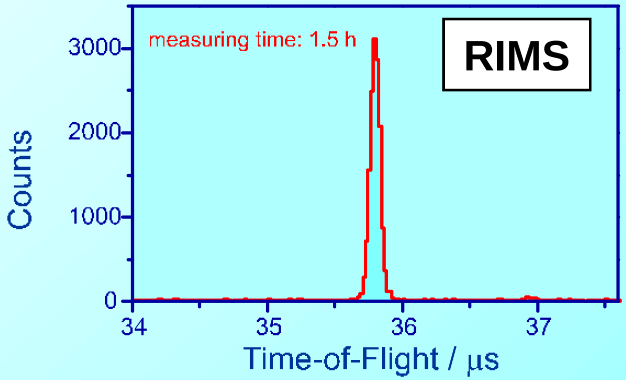


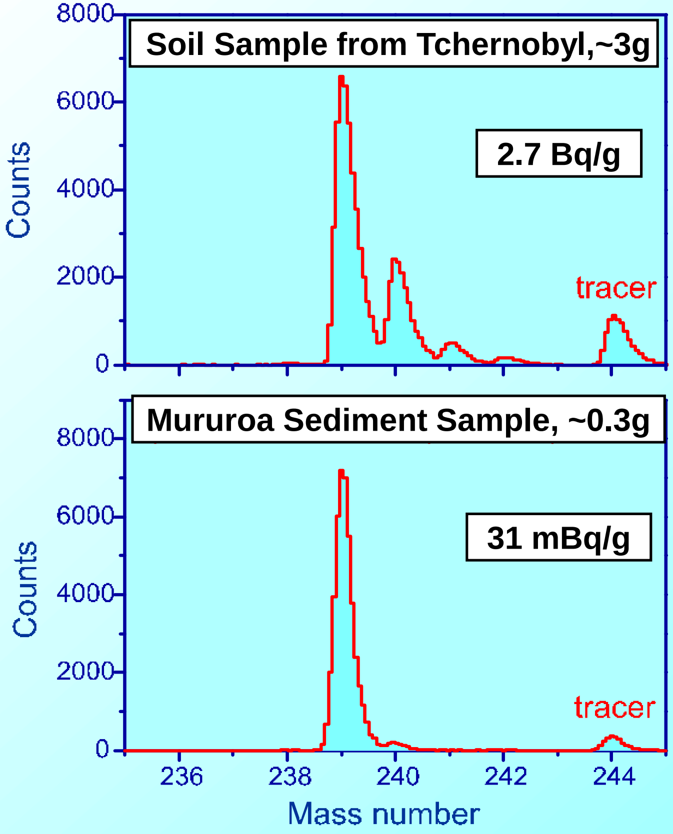


Ex 2: Sensitivity of RI – Determination of Pu

Univ. Mainz – KCh – Phys Collaboration







Efficiency and Measuring Time

Sample of 10^9 atoms of ^{239}Pu (~ 4 mBq)

α -Spec.: 20 Counts / 24 hours

RIMS : 15000 Counts / 1.5 hours

RIMS - Time-of-Flight Spectra of Pu

Determination of - overall content

- isotopic composition

Full suppression of isobars UH, UH$_2$, others

Efficiency, Sensitivity & LOD: Actinides

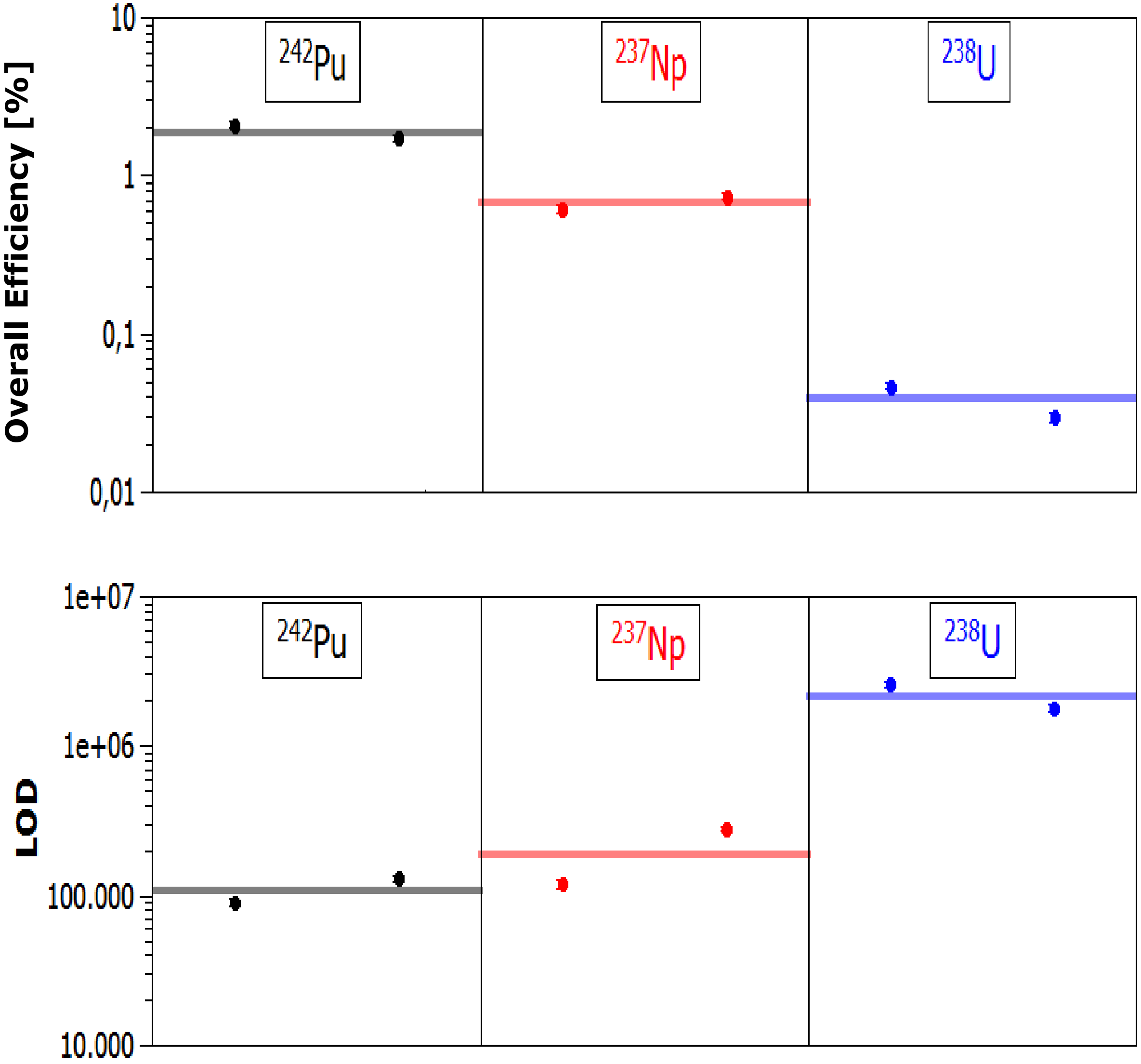
Overall Efficiency

Plutonium	1,9(3) %
Neptunium	0,7(1) %
Uranium	0,04(1) %

Detection Level(LOD$_{3\sigma}$)

Plutonium	1,1(3) ·10^5
Neptunium	1,9(11)·10^5
Uranium	22,0(60)·10^5
	[atoms/sample]

→ corresponds to radioactive contaminations well below mBq (measured in a medium transmission qms – further enhancement expected)



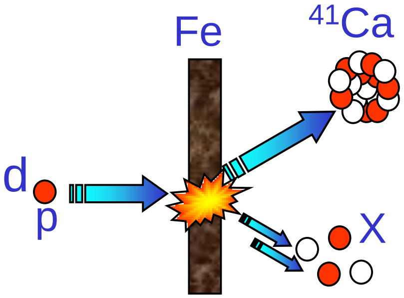
Diploma thesis Michael Franzmann 2013

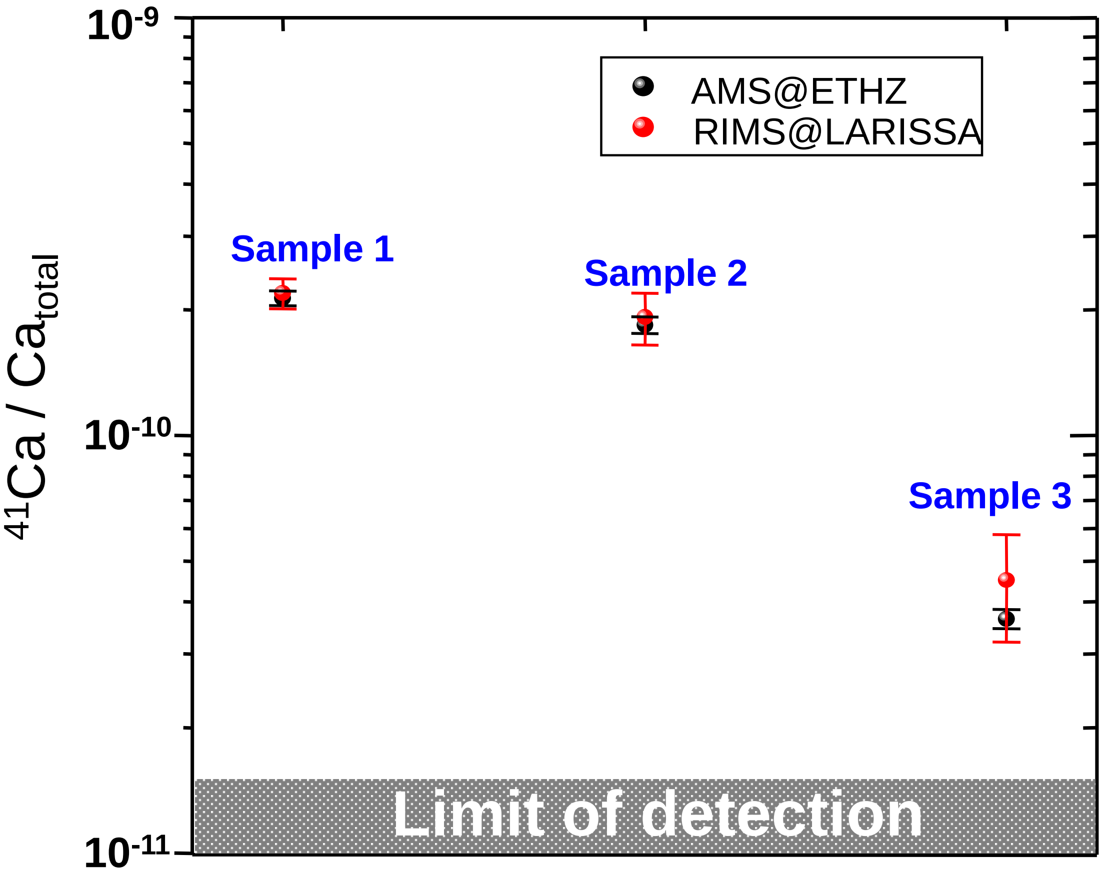
Isotopic Selectivity of RI: ^{41}Ca Determination

Astrophysics – Cosmochemistry - Nucleosynthesis

Cross section determination of proton induced spallation reactions

p(Fe,X)^{41}Ca in an artificial meteorite at PSI accelerator, Switzerland





#	RIMS (x 10^{-12})	AMS (x 10^{-12})	δ RIMS/AMS
1	219(18)	213,3(85)	2,7 %
2	192(27)	184,0(85)	4,4 %
3	45(13)	36,4(19)	23,6 %

additional important applications in biomed. & nutrition research e.g. for osteoporosis prevention and in-vivo calcium-kinetics

Ch. Geppert, P. Müller, K. W., Ch. Schnabel, H.-A. Synal, **NIMB** 229/3, 519 (2005)

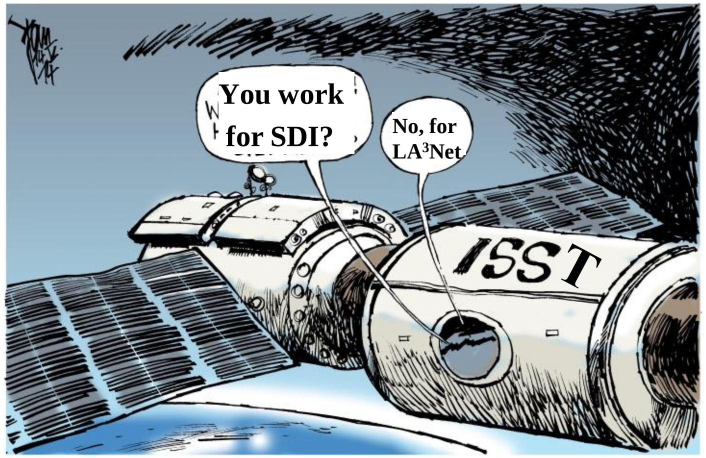
Resonance Ionization Laser Ion Sources

Preconditions for RILIS in general – for ultra trace determination

	Q uantifiability
U niversality	U niversality
S electivity	S electivity
E fficiency	sE ensitivity
R eliability	R eproducability
…from Bit to Q-bit …	… from USER to Q-USER…

Resonance Ionization Laser Ion Sources

Preconditions for operation of the lasers in analytical RIS



I ntensity

S pectral: position and width

S patial: size and overlap of beams

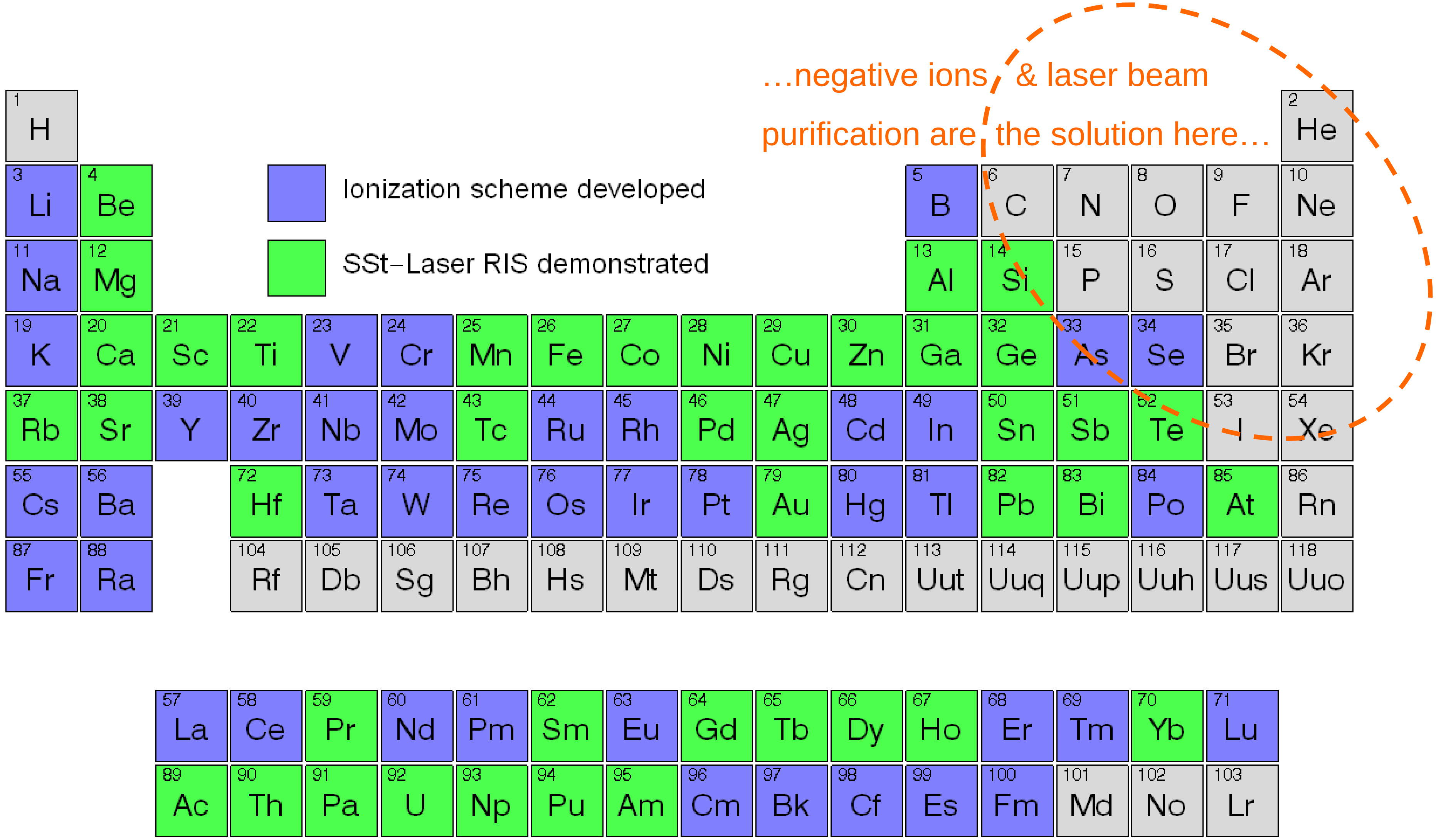
T emporal: synchronization and length of pulses

→ Must Match the Mission !

…for ultra trace determination these laser parameters must be properly monitored or even actively controlled !

Universality of RI: Accessibility of (almost) all Elements

Resonance ionization schemes are developed and tested for most elements



…negative ions & laser beam purification are the solution here…

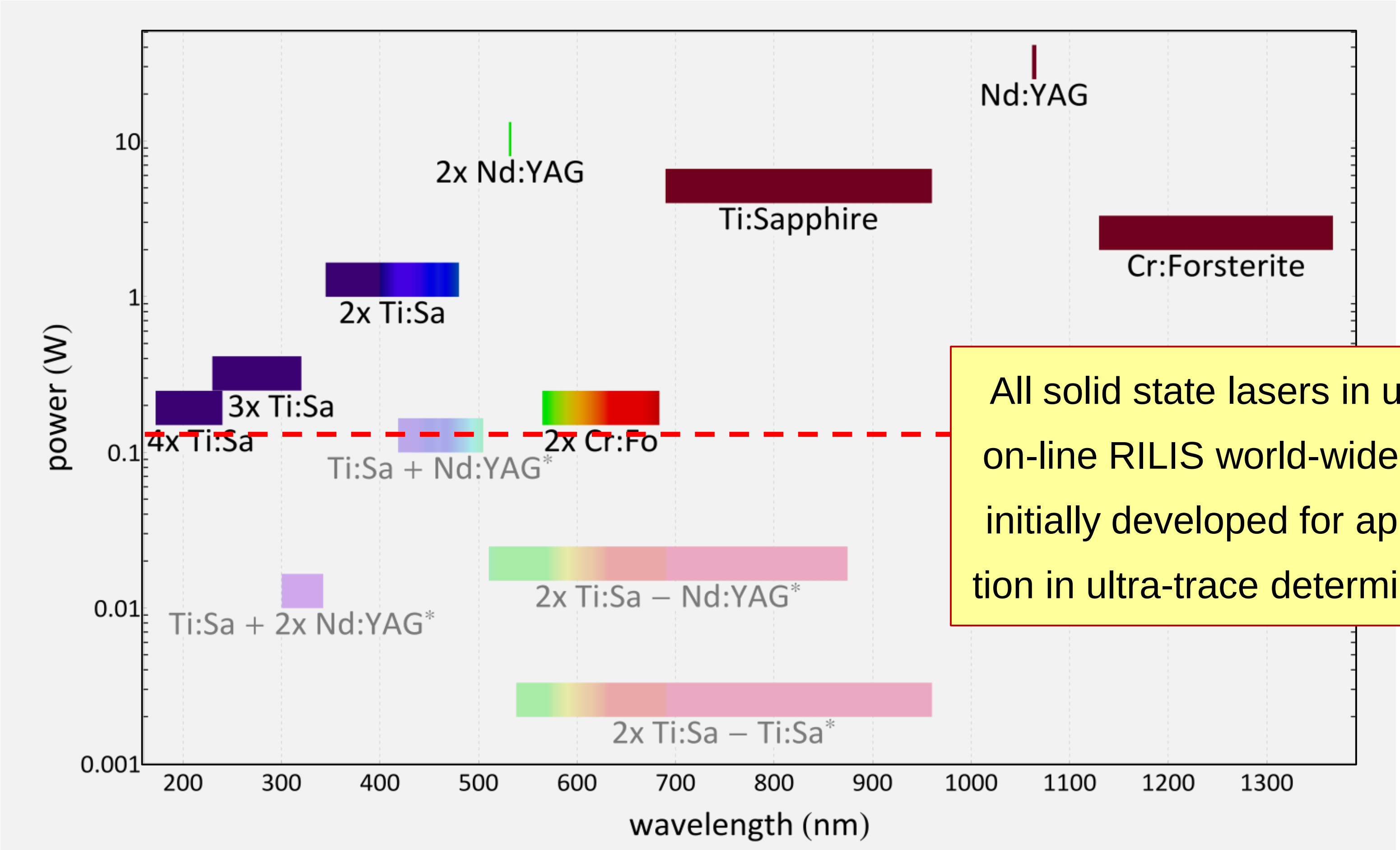
🟦 Ionization scheme developed

🟩 SSt–Laser RIS demonstrated

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Universality: Tunable Lasers (SSTL´s) for RIS

Average power and tuning range (pulsed, high repetition rate ~ 10 kHz)

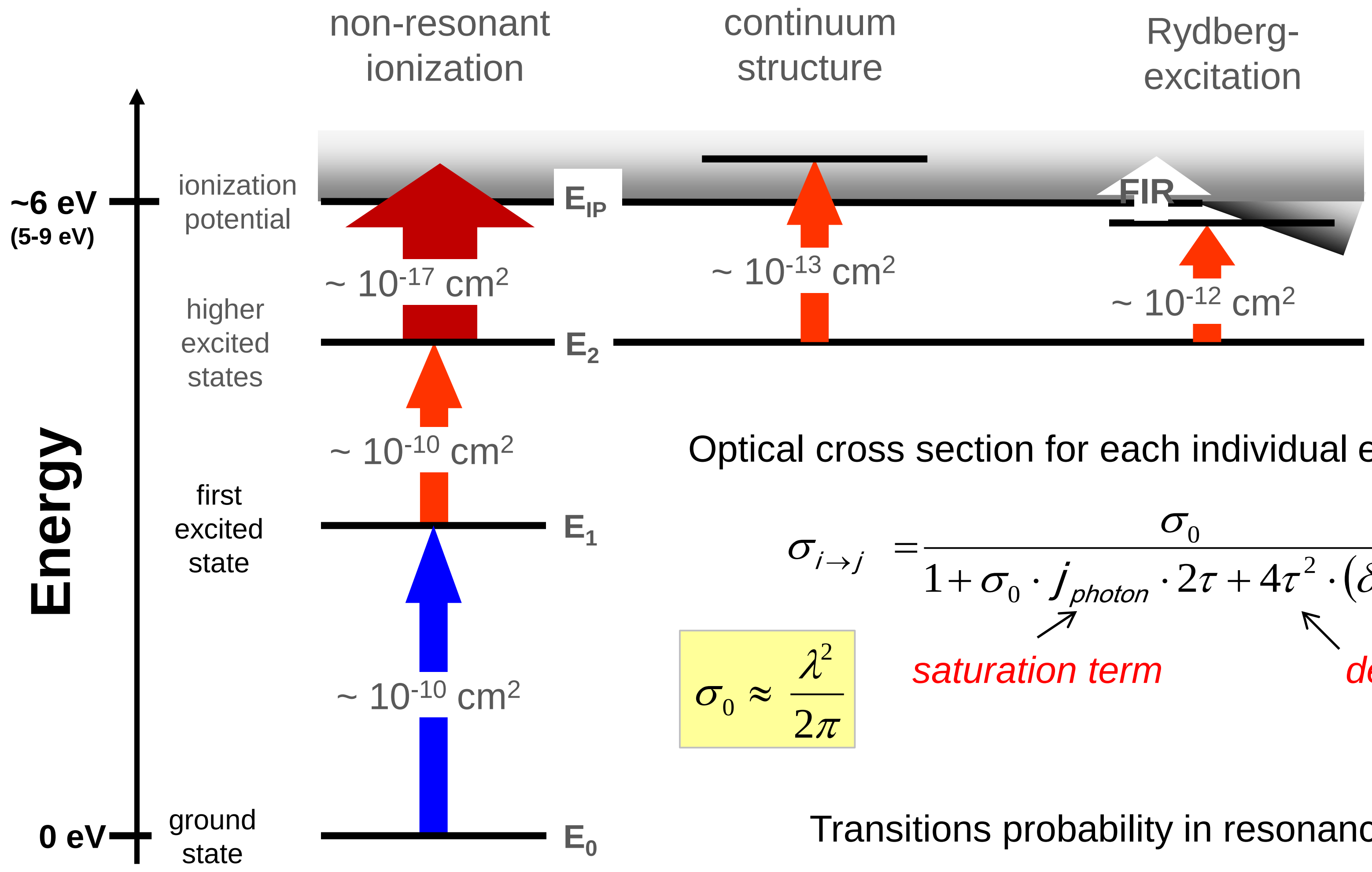


All solid state lasers in use at on-line RILIS world-wide were initially developed for application in ultra-trace determination

Spectal coverage from UV to IR – high rep rate & output power – well controlled line width

→Universal applicability for multi-step RI in ultra-trace analysis & on-line RIB production

Efficiency of RI – Multi-Step Laser Excitation



Ionization via
- Black Body Rad.
- IR Lasers
- Collisions
- Electrical Field

Optical cross section for each individual excitation step

$$\sigma_{i\to j} = \frac{\sigma_0}{1+\sigma_0 \cdot \underset{\nearrow}{j_{photon}} \cdot 2\tau + 4\tau^2 \cdot \underset{\nwarrow}{(\delta\omega)^2}}$$

saturation term *detuning term*

$$\sigma_0 \approx \frac{\lambda^2}{2\pi}$$

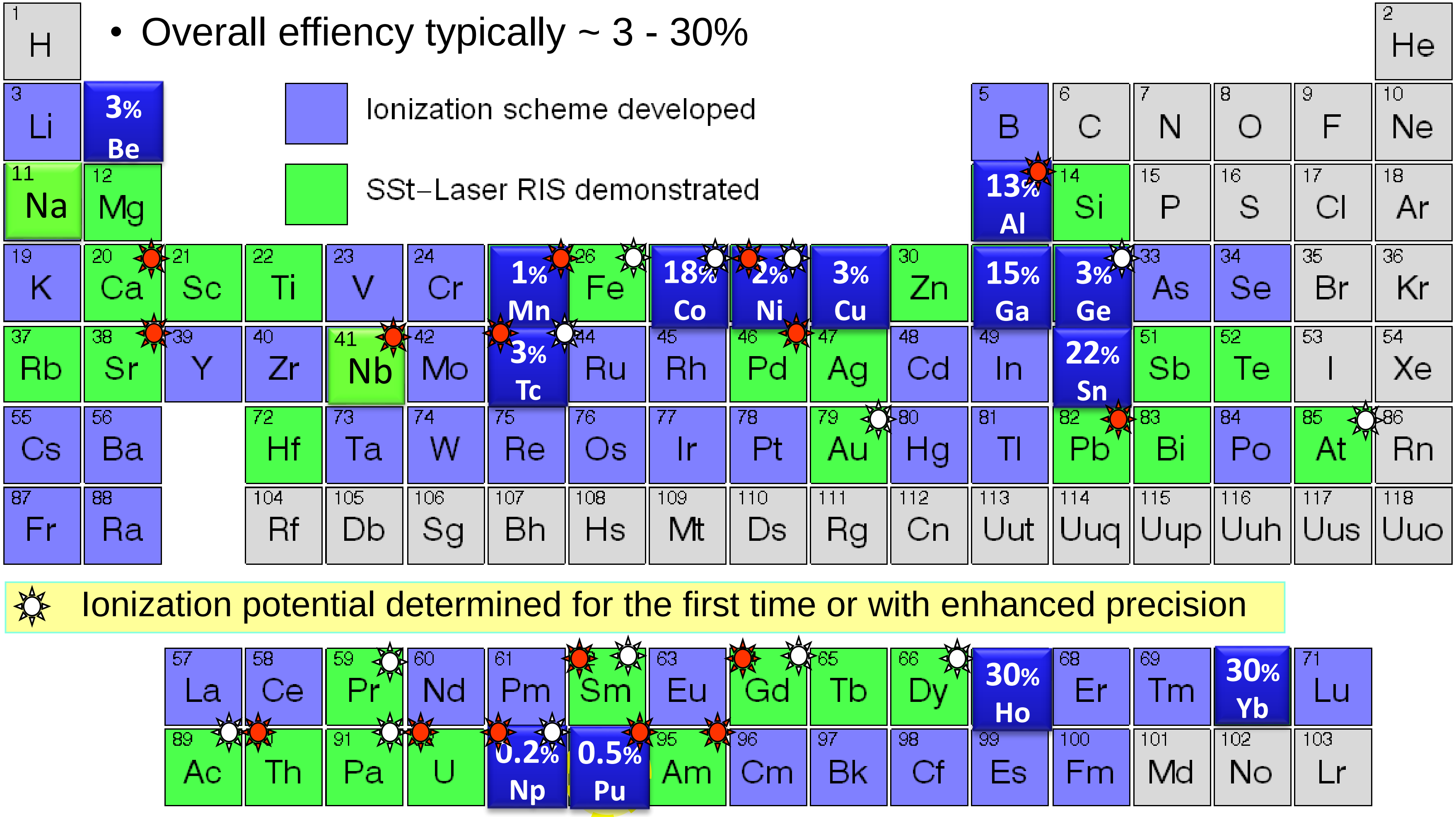
Transitions probability in resonance

$$W_{i\to j} = 1 - e^{-\sigma_{i\to j}\cdot t_{\text{int}}\cdot n_\gamma} \cong \sigma_{i\to j}\cdot t_{\text{int}}\cdot n_\gamma \quad \to \quad 1$$

$$t_{\text{int}} \approx 10\,\mu s \;\cap\; n_\gamma \geq 10^{17} \to I_{Sat} \approx 10mW$$

RI Efficiency and Analytical Relevance

- 45 elements accessible in analytical (& on-line) RILIS, ~ 40 others possible
- Overall effiency typically ~ 3 - 30%



🟦 Ionization scheme developed

🟩 SSt–Laser RIS demonstrated

1 H																	2 He
🟦 3 Li	3% Be											🟦 5 B	6 C	7 N	8 O	9 F	10 Ne
🟩 11 Na	🟩 12 Mg											13% Al	🟩 14 Si	15 P	16 S	17 Cl	18 Ar
🟦 19 K	🟩 20 Ca	🟩 21 Sc	🟩 22 Ti	🟦 23 V	🟦 24 Cr	1% Mn	🟩 26 Fe	18% Co	2% Ni	3% Cu	🟩 30 Zn	15% Ga	3% Ge	🟦 33 As	🟦 34 Se	🟦 35 Br	🟦 36 Kr
🟩 37 Rb	🟩 38 Sr	🟦 39 Y	🟦 40 Zr	🟩 41 Nb	🟦 42 Mo	3% Tc	🟦 44 Ru	🟦 45 Rh	🟩 46 Pd	🟩 47 Ag	🟦 48 Cd	🟦 49 In	22% Sn	🟩 51 Sb	🟩 52 Te	🟦 53 I	🟦 54 Xe
🟦 55 Cs	🟦 56 Ba		🟩 72 Hf	🟦 73 Ta	🟦 74 W	🟦 75 Re	🟦 76 Os	🟦 77 Ir	🟦 78 Pt	🟩 79 Au	🟦 80 Hg	🟦 81 Tl	🟩 82 Pb	🟩 83 Bi	🟦 84 Po	🟩 85 At	🟦 86 Rn
🟦 87 Fr	🟦 88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
		🟦 57 La	🟦 58 Ce	🟩 59 Pr	🟦 60 Nd	🟦 61 Pm	🟩 Sm	🟦 63 Eu	🟩 Gd	🟩 65 Tb	🟩 66 Dy	30% Ho	🟦 68 Er	🟦 69 Tm	30% Yb	🟦 71 Lu	
		🟩 89 Ac	🟩 Th	🟩 91 Pa	🟩 U	0.2% Np	0.5% Pu	🟩 95 Am	🟦 96 Cm	🟦 97 Bk	🟦 98 Cf	🟦 99 Es	100 Fm	101 Md	102 No	103 Lr	

☼ Ionization potential determined for the first time or with enhanced precision

✹ Analytical relevance: ultra trace isotope determination on long-lived radio-isotopes

Outline

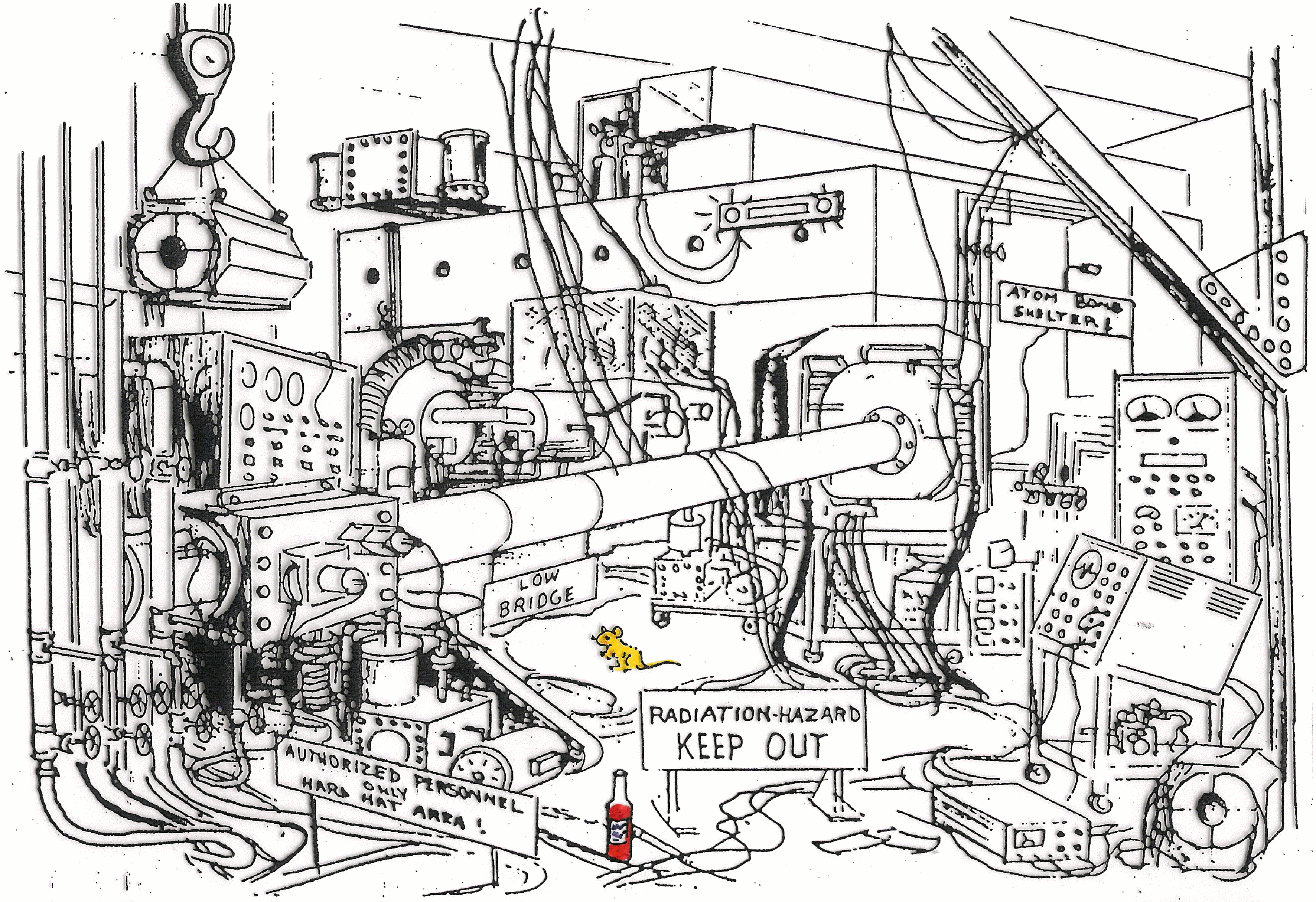
- Motivation: Access to Exotic Isotopes through Quantum Optics
  – off-line (not on-line) on long-lived natural and anthropogenic species
- Theory: Multi-Step Excitation Processes in Atomic Systems
  – benefits, drawbacks & limitations of light-atom interactions

INSERTION:

- Experimental Realization & Applications:
  - HR-RIMS – for isotope selective coherent atomic spectroscopy
  - Analytics – high-tech physics for low level chemistry & radioprotecion
  - (Laser AMS – isobar selection at accelerators for radiodating)
- Exclusion: On-line Laser Ion Sources and related physics
  – Hot cavity or gas cell technology (-- Bruce Marsh or Iain Moore)
- Outlook & Summary

The typical on-line RILIS

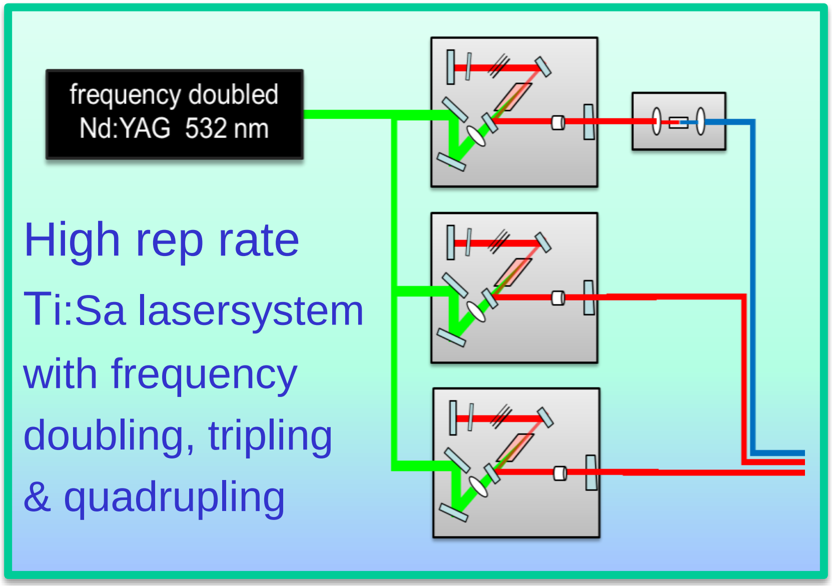
(…at any large research facility worldwide)



LARISSA - Laboratory for All the Really Indispensable Studies in Selective Analytics (...you never thought someone would ever really do!)

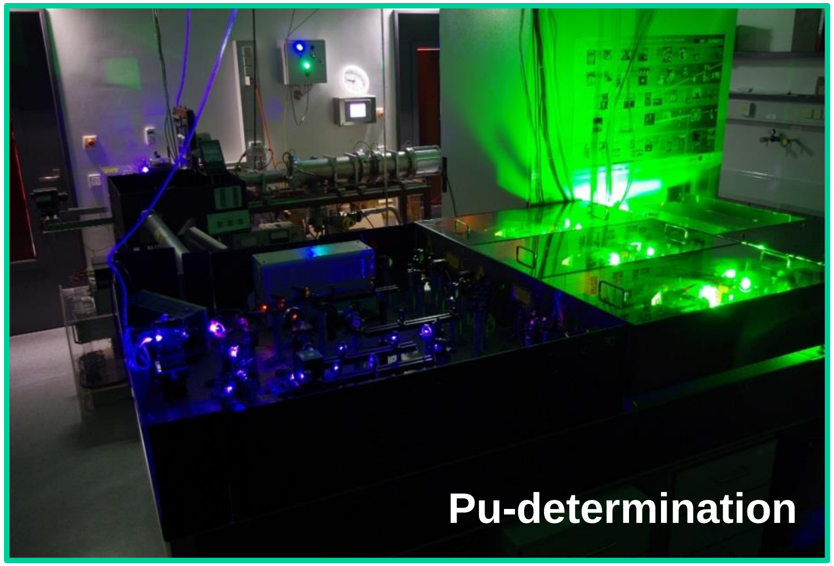
A1) The RI laser system at Mainz

for analytics, atomic spectroscopy & scheme development

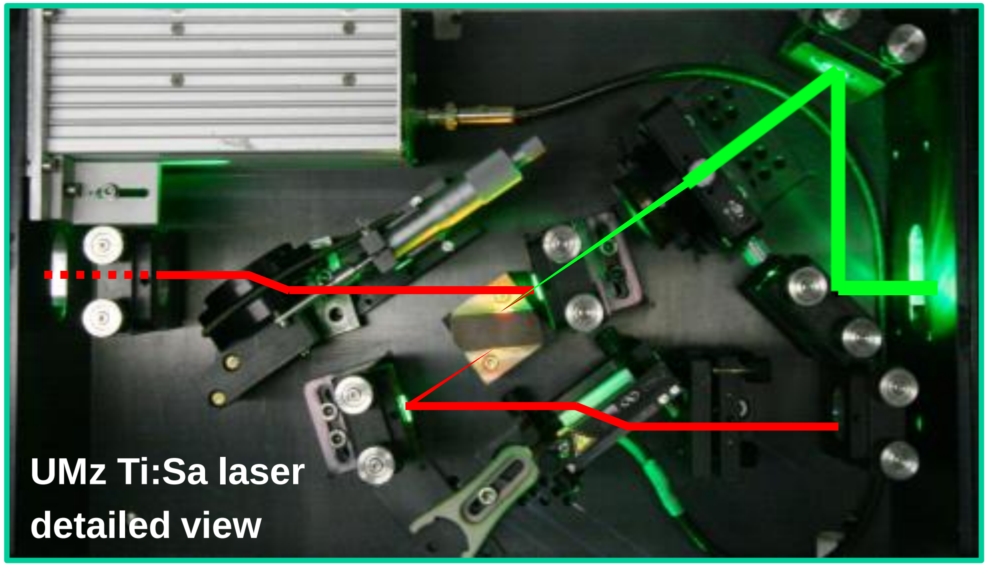


High rep rate Ti:Sa lasersystem with frequency doubling, tripling & quadrupling

LARISSA-lab for laser development and spectroscopy

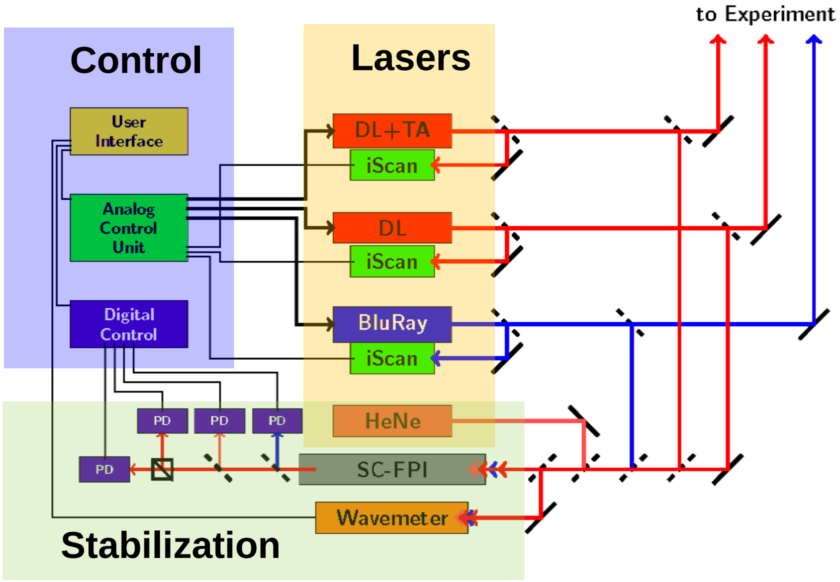


Pu-determination



UMz Ti:Sa laser detailed view

A2) The High Resolution (HR)-RI laser system

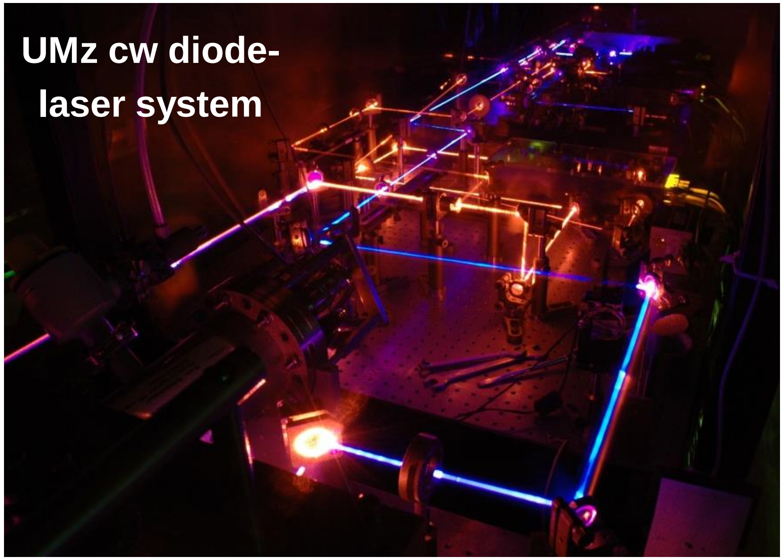


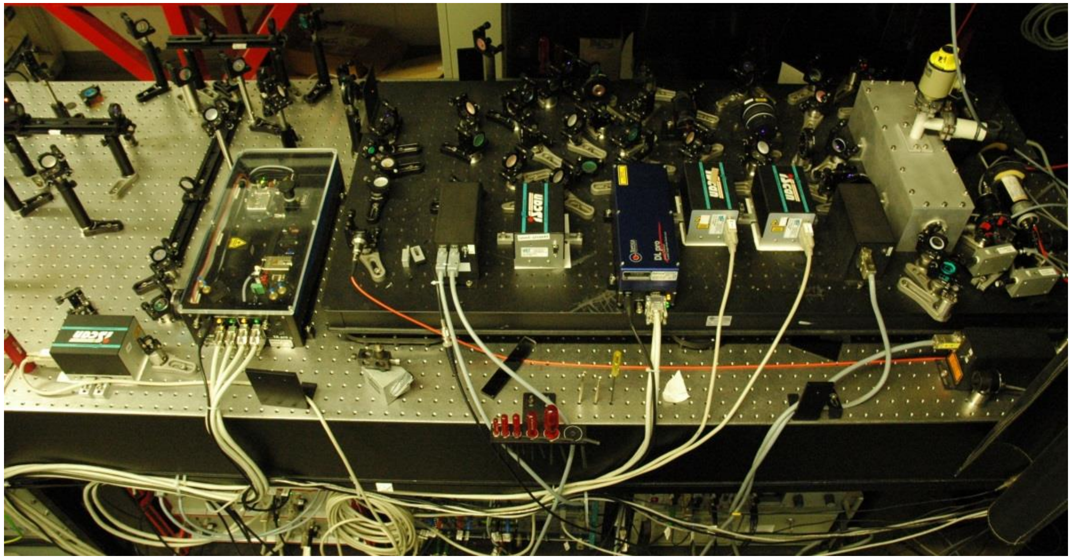
Continuous wave diode-laser system

for high resolution isotope selective RI

- tunability around 405, 755-790, 810-870 nm
- active frequency stabilization ~1 MHz
- reproducible frequency jumps up to 10 GHz

  for isotope ratio measurements (quantification)





B1) The Accelerators for RI

Magnetic sector-field Mass Spec

30 - 60 kV two stage acceleration voltage

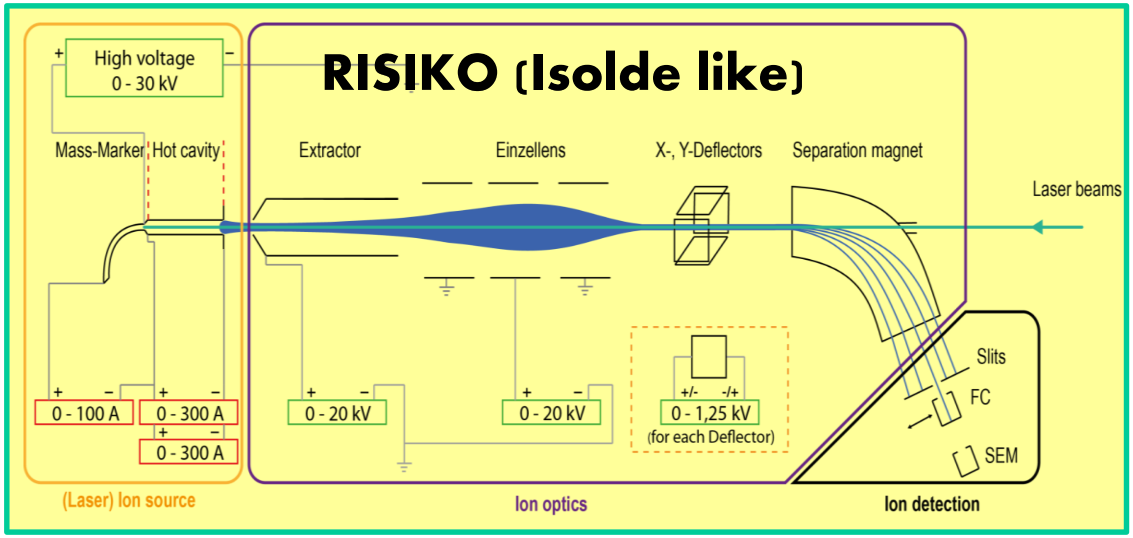
60° double focussing separator magnet

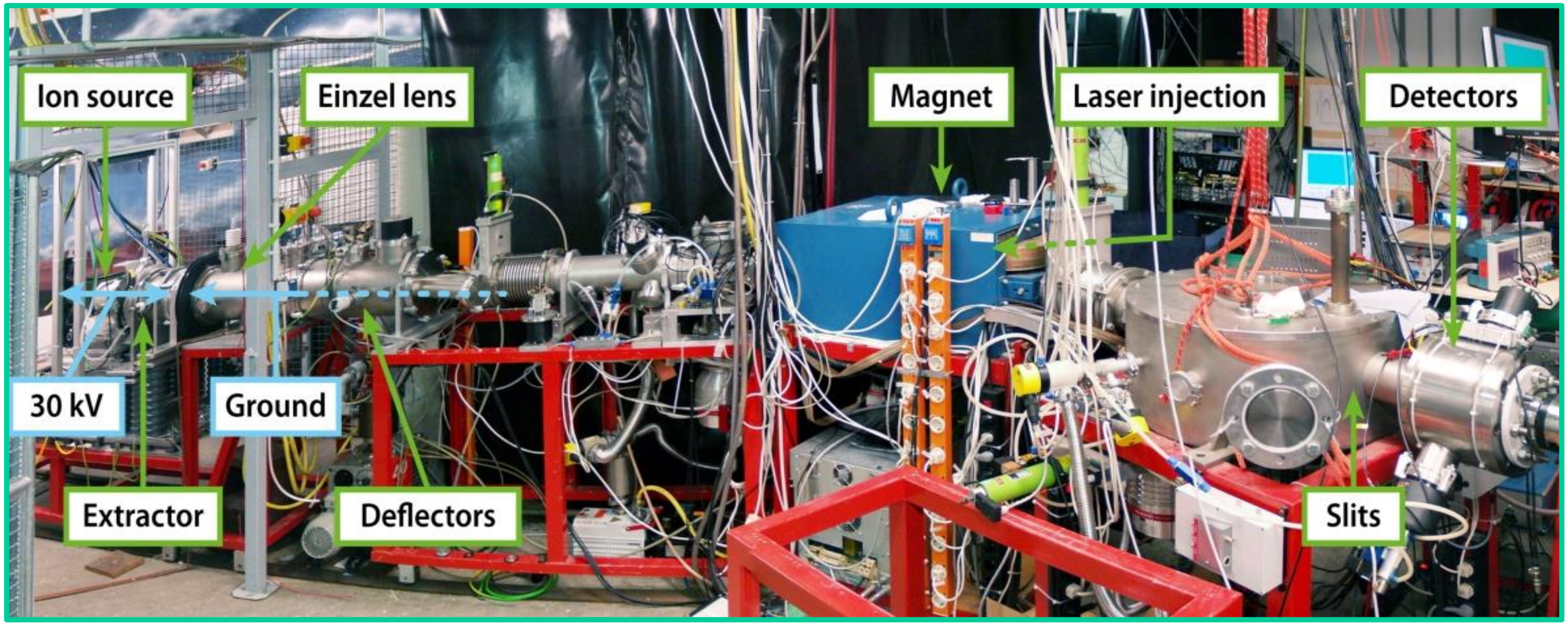
Mass resolution: $\frac{m}{\Delta m} = 500 - 1000$

Isotopic abundance sensitivity $S_{m\pm1} \approx 10^4$

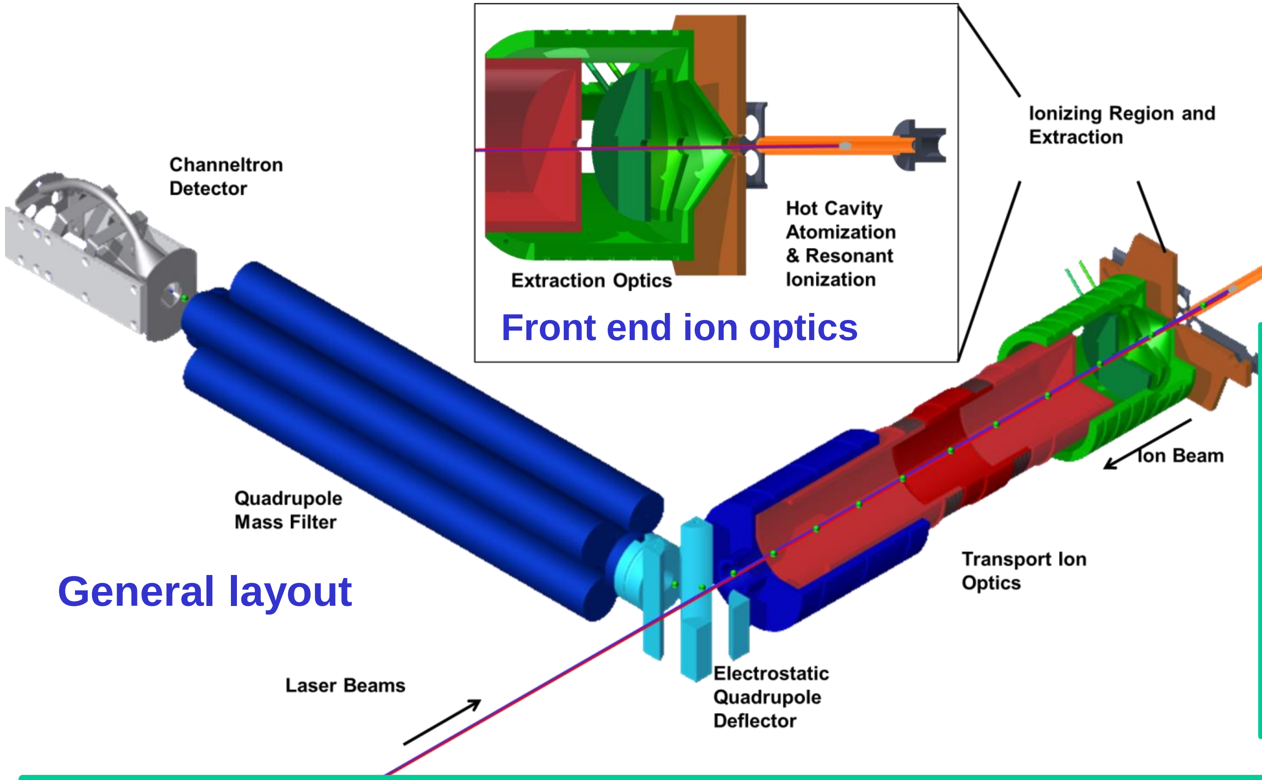
…in use for laser ion source development

& laser isotope enrichment



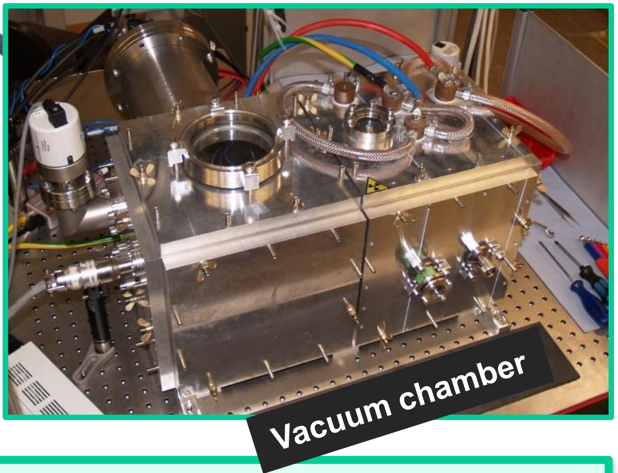


B2) The Accelerators for RI



General layout

Graphite furnace atomizer



Vacuum chamber

Low-energy accelerator and mass spectrometer MABU

100 V acceleration voltage

Graphite atom beam source, dc qadrupole bender and radiofrequency quadrupole mass filter

mass resolution: $\frac{m}{\Delta m} \approx 200$ isotopic abundance sensitivity: $S_{m\pm1} \approx 10^3 - 10^8$

…used for analytics and mid to high resolution atomic spectroscopy

B3) The Accelerators at Mainz

Time-of-flight - mass spectrometer

4 kV acceleration voltage

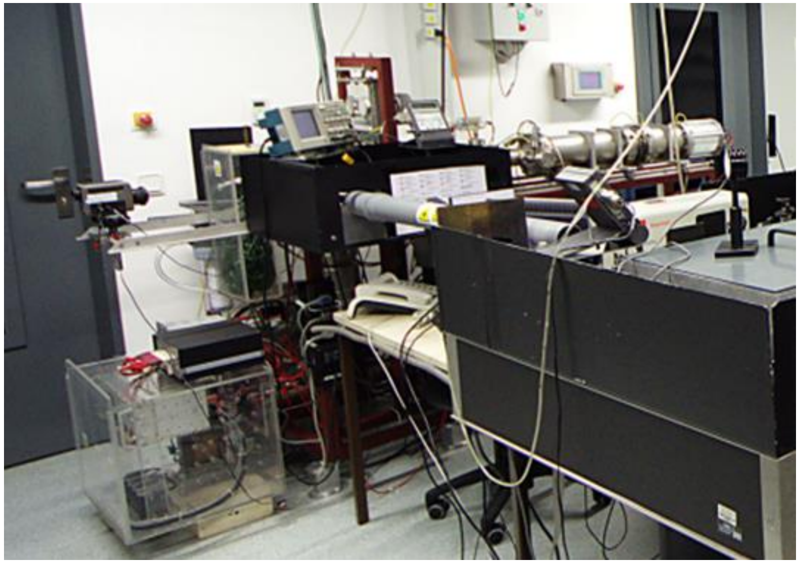
mass resolution $\frac{m}{\Delta m} \approx 600$

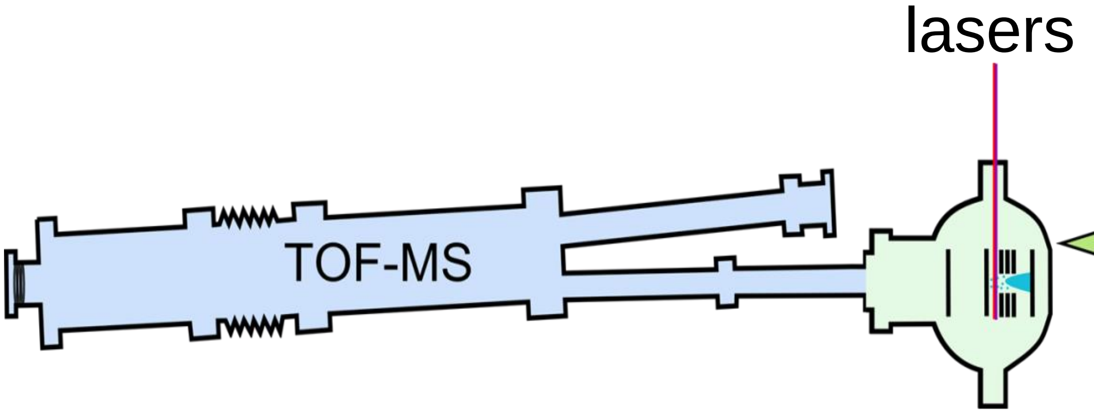
isotopic abundance sensitivity

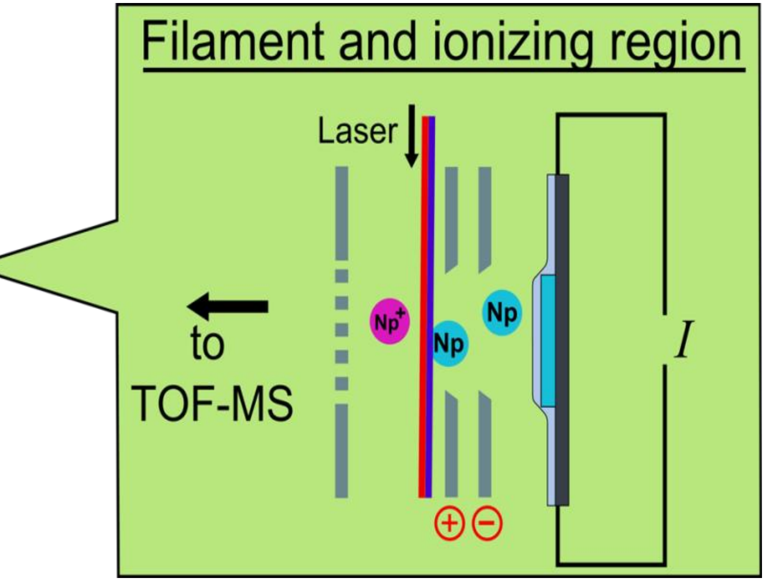
$$S_{m-1} \approx 50000 \quad S_{m+1} \approx 300$$

installed in controlled nuclear chemical laboratory

→ used for analytical measurements on actinides







Optimized for complete sample evaporation and atomization as well as background suppression

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  - HR-RIMS – for isotope selective coherent atomic spectroscopy
  - Analytics – high-tech physics for low level chemistry & radioprotecion
  - (Laser AMS – isobar selection at accelerators for radiodating

- Theory: Multi-Step Excitation Processes in Atomic Systems

  – benefits, drawbacks & limitations of light-atom interactions

- Exclusion: On-line Laser Ion Sources and related physics

  – Hot cavity or gas cell technology (-- Bruce Marsh or Iain Moore)

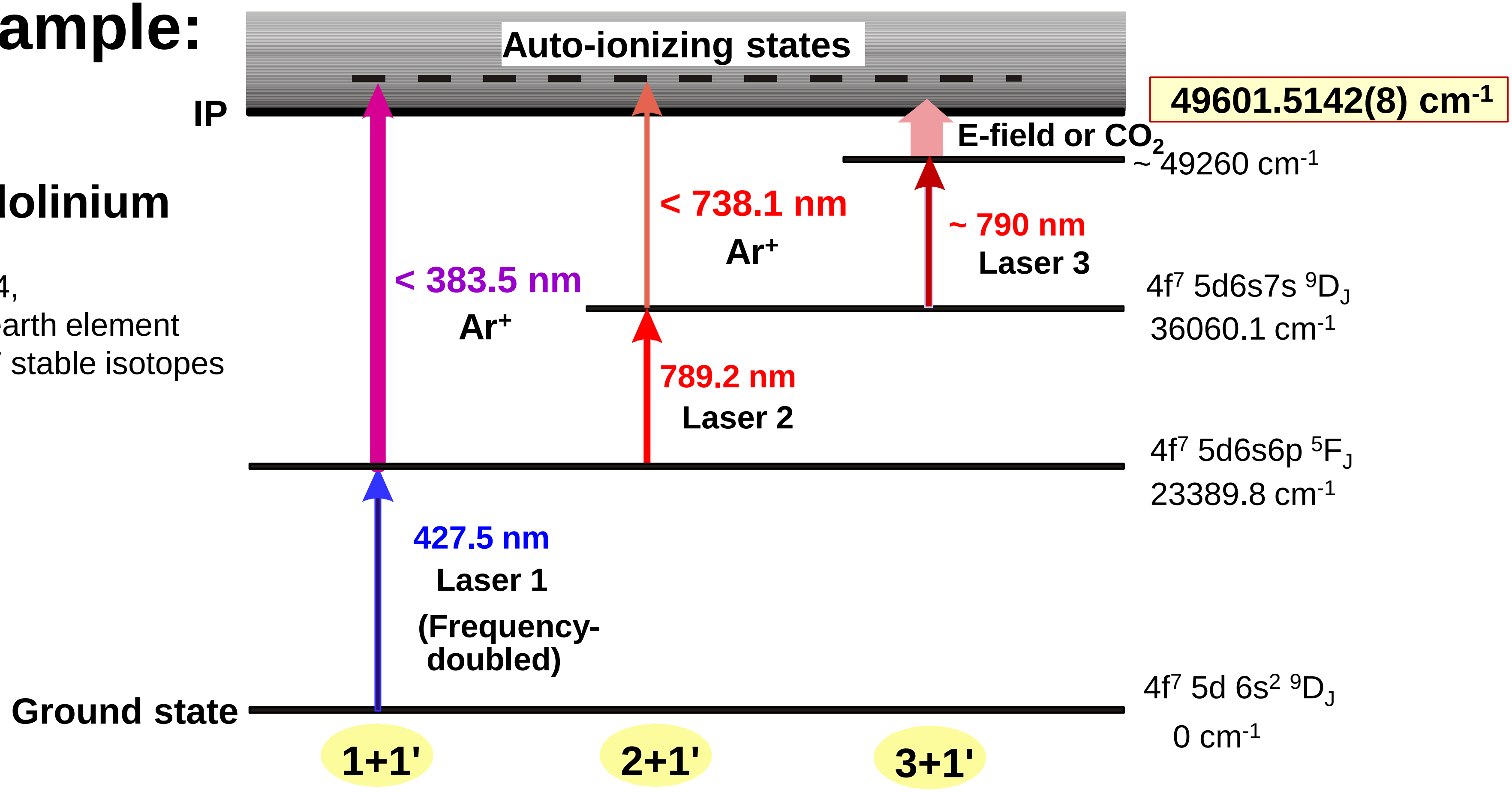
- Outlook & Summary

Development of RI schemes for Analytics

Example:

Gadolinium

Z = 64,
rare earth element
with 7 stable isotopes



Auto-ionizing states

IP

49601.5142(8) cm^{-1}

E-field or CO$_2$

~ 49260 cm^{-1}

< 738.1 nm
Ar$^+$

~ 790 nm
Laser 3

< 383.5 nm
Ar$^+$

4f^7 5d6s7s ^9D_J
36060.1 cm^{-1}

789.2 nm
Laser 2

4f^7 5d6s6p ^5F_J
23389.8 cm^{-1}

427.5 nm
Laser 1
(Frequency-doubled)

Ground state

4f^7 5d 6s^2 ^9D_J
0 cm^{-1}

1+1'

2+1'

3+1'

HR-Spectroscopy: K. Blaum, B.A. Bushaw, Ch. Geppert, P. Müller, W. Nörtershäuser, A. Schmitt, K. W., Eur. Phys. J. D 11, 37 (2000)

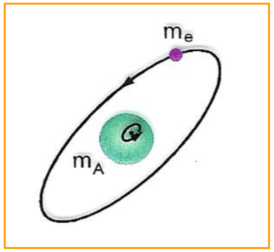
Analytics: K. Blaum, Ch. Geppert, W.G. Schreiber, J.G. Hengstler, P. Müller, W. Nörtershäuser, K. W. and B.A. Bushaw, ABC 372, 759 (2002)

Determination of the IP: B. A. Bushaw, K. Blaum and W. Nörtershäuser, Phys. Rev. A 67, 022508 (2003)

Narrow auto-ionizing states: B.A. Bushaw, W. Nörtershäuser, K. Blaum, K. W., Spectrochim. Acta B58, 1083 (2003)

Basics of High Resolution Laser Spectroscopy

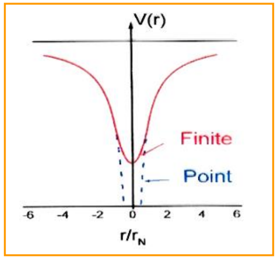
Isotope effects = influences of the atomic nucleus:



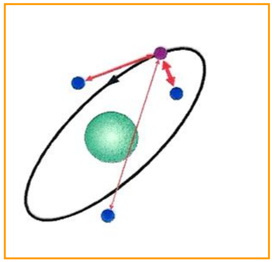
$$H\Psi = E\Psi$$

$$\downarrow$$

$$\sum_{i=1}^{N} \frac{-\hbar^2}{2m}\nabla^2 \longleftarrow U + V \longrightarrow V(\vec{r}_1\vec{s}_1, \vec{r}_2\vec{s}_2 \ldots \vec{r}_n\vec{s}_n)$$



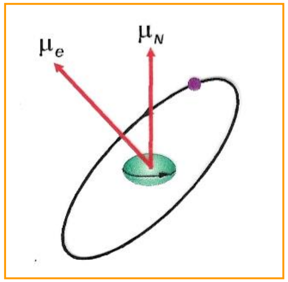
$$\frac{\vec{p}^{\,2}}{2\mu} = \sum \frac{\vec{p}_i^{\,2}}{2\mu} + \sum_i \sum_{j>i} \frac{\vec{p}_i \cdot \vec{p}_j}{\mu}$$



$$V_{Ze} + \underline{V_{Is} + V_{I\ell}} + \underbrace{V_{ee} + V_{s\ell} + V_{ss} + V_{ll}}_{\textit{pure electronic}}$$

Normal Mass Shift **Specific Mass Shift** **Isomer or Field Shift** **Hyperfine Structure**

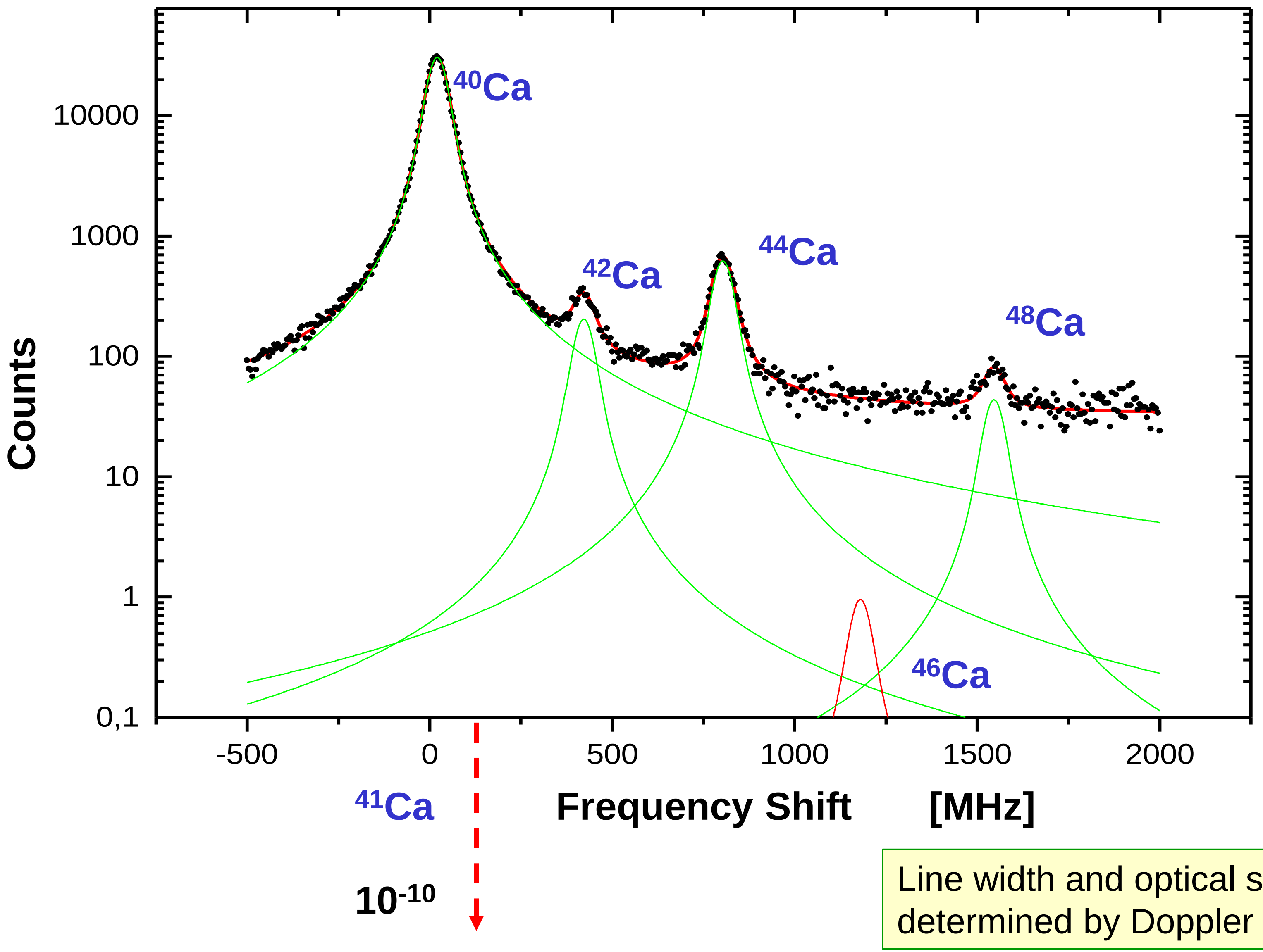
$$\Delta\nu_{ij}^{AA'} = \nu_{ij}^{0} \frac{m_e}{m_p} \frac{(A-A')}{AA'} + C_{ij}\nu_{ij}^{0} \frac{(A-A')}{AA'} + \frac{\pi a_0^3}{Z} \Delta|\Psi(0)|^2 f(Z)\left[\delta\langle r^2\rangle^{AA'} + C_1\delta\langle r^4\rangle^{AA'} + \ldots\right]$$

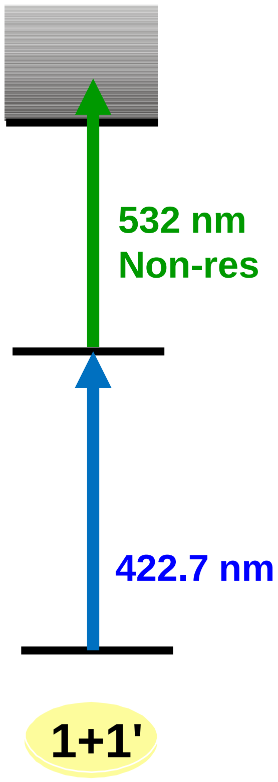


$$\Delta\nu_{IS} = (M_N + M_S)\frac{(A-A')}{AA'} + F\delta\langle r^2\rangle^{AA'}$$

…line splittings and shifts
in the 10-100 MHz range

Experimental: Isotope Shift in 2-level RI in Ca



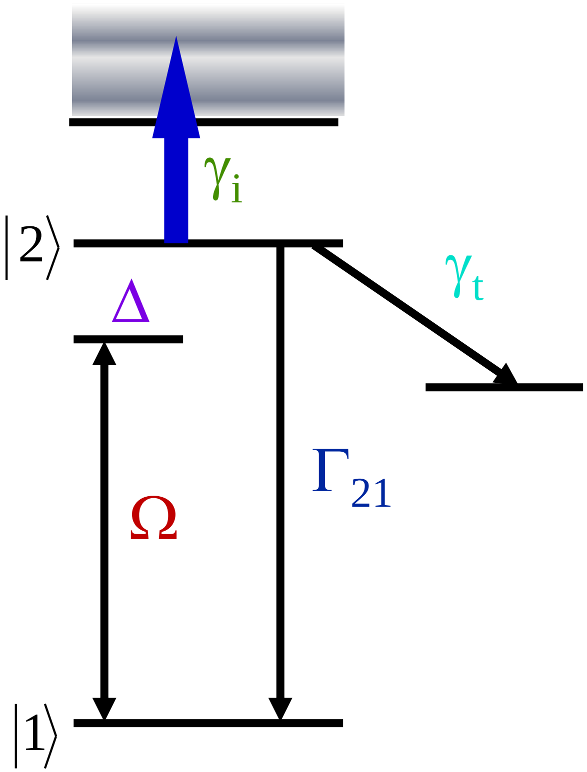


Line width and optical selectivity determined by Doppler broadening

Theory: Resonance Ionization in a 2-Level System

Description of RI through time evolution of the density matrix elements

(includes coherences in contrast to simple rate equation model)



Coherent Excitation Process

$$\left.\begin{aligned}\dot{\rho}_{11} &= \underbrace{2\,\Gamma_{21}\,\rho_{22}}_{\text{spontanous decay}} + \underbrace{i\,G\,\rho_{21} - i\,G^{*}\rho_{12}}_{\text{induced transitions}}\\ \dot{\rho}_{22} &= -2\,(\,\Gamma_{21} + \gamma_i + \gamma_t\,)\,\rho_{22} - i\,G\rho_{21} + i\,G^{*}\rho_{12}\end{aligned}\right\}\ \text{Population}$$

$$\left.\begin{aligned}\dot{\rho}_{21} &= \left[\ i\,\Delta - (\,\Gamma_{21} + \gamma_i + \gamma_t\,)\,\right]\rho_{21} - \ i\,G^{*}(\rho_{22} - \rho_{11})\\ \dot{\rho}_{12} &= \left[-\ i\,\Delta - (\,\Gamma_{21} + \gamma_i + \gamma_t\,)\,\right]\rho_{12} + i\,G\,(\rho_{22} - \rho_{11})\end{aligned}\right\}\ \text{Coherence}$$

$$\left.\begin{aligned}\dot{N}_i &= 2\,\gamma_i\,\rho_{22}\\ \dot{N}_t &= 2\,\gamma_t\,\rho_{22}\end{aligned}\right\}\ \text{Loss Rate and Ionization}$$

Laser Parameter:
Rabi-Frequency

$$G_j = \frac{\Omega_j^{*}}{2} = \frac{\mu E_0}{2\hbar} = \sqrt{\frac{3A_{mn}I\lambda^3}{8\pi hc}}$$

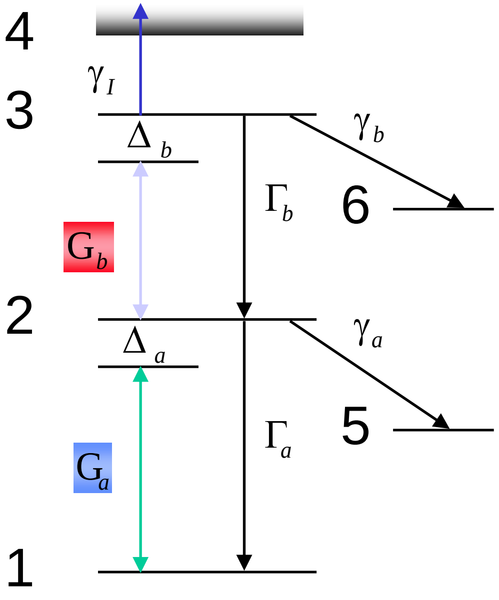
Atomic Parameters:
Transition probability - given by Einstein A factor

$$\Gamma_j = \frac{A_{nm}}{2}$$

Theory: Resonance Ionization in the 3-Level System

Density Matrix Formalism for 2 step coherent excitation:

….from 6 to 12 coupled differential equations….



$$G_j = \frac{\Omega_j^*}{2} = \frac{\mu E_0}{2\hbar} = \sqrt{\frac{3A_{mn}I\lambda^3}{8\pi hc}}$$

$$\Gamma_j = \frac{A_{nm}}{2}$$

$$\dot{\rho}_{11} = \mathrm{i}G_a\rho_{21} - \mathrm{i}G_a^*\rho_{21} + 2\Gamma_a\rho_{22}$$

$$\dot{\rho}_{22} = \mathrm{i}G_b\rho_{32} - \mathrm{i}G_a\rho_{21} + \mathrm{i}G_a^*\rho_{12} - \mathrm{i}G_b^*\rho_{23} + 2\Gamma_b\rho_{33} - 2(\Gamma_a + \gamma_a)\rho_{22}$$

$$\dot{\rho}_{33} = \mathrm{i}G_b^*\rho_{23} - \mathrm{i}G_b\rho_{32} - 2(\Gamma_b + \gamma_b + \gamma_I)\rho_{33}$$

$$\dot{\rho}_{32} = \left[\mathrm{i}\Delta_\mathrm{b} - (\Gamma_a + \Gamma_b + \gamma_a + \gamma_b + \gamma_I)\right]\rho_{32} - \mathrm{i}G_b^*(\rho_{33} - \rho_{22}) - \mathrm{i}G_a\rho_{31}$$

$$\dot{\rho}_{23} = \left[-\mathrm{i}\Delta_\mathrm{b} - (\Gamma_a + \Gamma_b + \gamma_a + \gamma_b + \gamma_I)\right]\rho_{23} + \mathrm{i}G_b(\rho_{33} - \rho_{22}) - \mathrm{i}G_a^*\rho_{13}$$

$$\dot{\rho}_{31} = \left[\mathrm{i}(\Delta_\mathrm{a} + \Delta_\mathrm{b}) - (\Gamma_b + \gamma_b + \gamma_I)\right]\rho_{31} + \mathrm{i}G_b^*\rho_{21} - \mathrm{i}G_a^*\rho_{32}$$

$$\dot{\rho}_{13} = \left[-\mathrm{i}(\Delta_\mathrm{a} + \Delta_\mathrm{b}) - (\Gamma_b + \gamma_b + \gamma_I)\right]\rho_{13} - \mathrm{i}G_b\rho_{12} + \mathrm{i}G_a\rho_{23}$$

$$\dot{\rho}_{21} = \left[\mathrm{i}\Delta_\mathrm{a} - (\Gamma_a + \gamma_a)\right]\rho_{21} - \mathrm{i}G_a^*(\rho_{22} - \rho_{11}) + \mathrm{i}G_b\rho_{31}$$

$$\dot{\rho}_{12} = \left[-\mathrm{i}\Delta_\mathrm{a} - (\Gamma_a + \gamma_a)\right]\rho_{12} + \mathrm{i}G_a(\rho_{22} - \rho_{11}) + \mathrm{i}G_b^*\rho_{13}$$

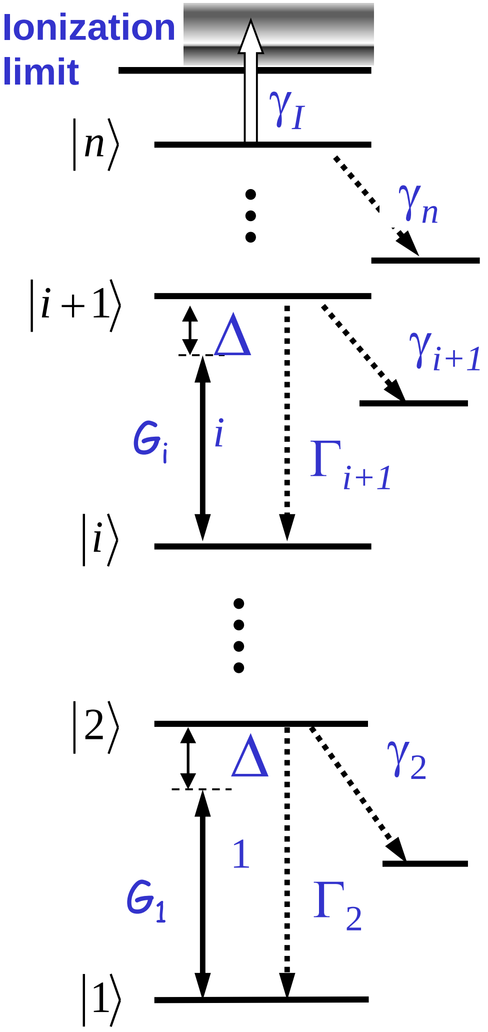
$$\dot{\rho}_{44} = 2\gamma_I\rho_{33}$$

$$\dot{\rho}_{55} = 2\gamma_a\rho_{22}$$

$$\dot{\rho}_{66} = 2\gamma_b\rho_{33}$$

Generalization for n-state Resonance Excitation

N-state RI : the generalized density matrix equations → (2n+n!) equations



$$\frac{d}{dt}\rho_{jk}\Big|_{j\ge k} = \left(i\cdot\sum_{\ell=k}^{j\text{-}1}\Delta_\ell - \Gamma_j - \gamma_j - \Gamma_k - \gamma_k \right)\cdot\rho_{jk} + 2\,\Gamma_{k+1}\cdot\rho_{k+1,\,k+1}\cdot\delta_{jk}$$

$$- i\cdot G_{k-1}\cdot\rho_{j,k-1} - G_k^*\cdot\rho_{j,k+1} + G_{j-1}^*\cdot\rho_{j-1,k} + i\cdot G_j\cdot\rho_{j+1,k}$$

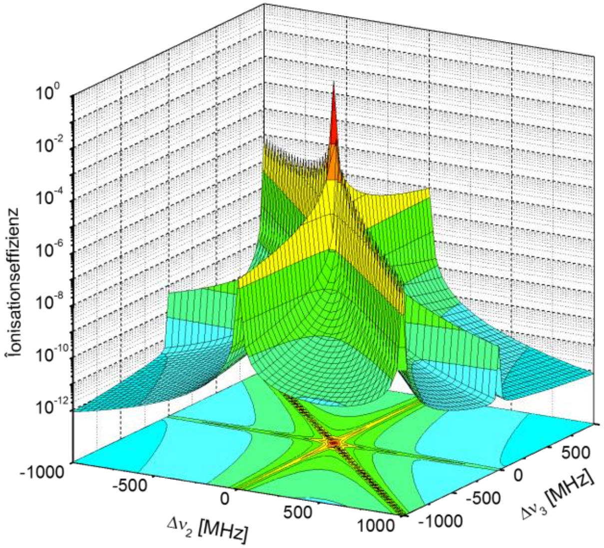
$$\frac{d}{dt}\rho_{jk}\Big|_{j<k} = \frac{d}{dt}\rho^*_{kj}$$

j = k → Populations

j ≠ k → Coherences

γ → Loss Rates

Ionization : $\dot{\rho}_I = 2\,\gamma_I\cdot\rho_{nn}$ $\gamma_I = \dfrac{\sigma_{PI}\cdot I}{h\nu}$



Atomic Parameters:

Decay rates

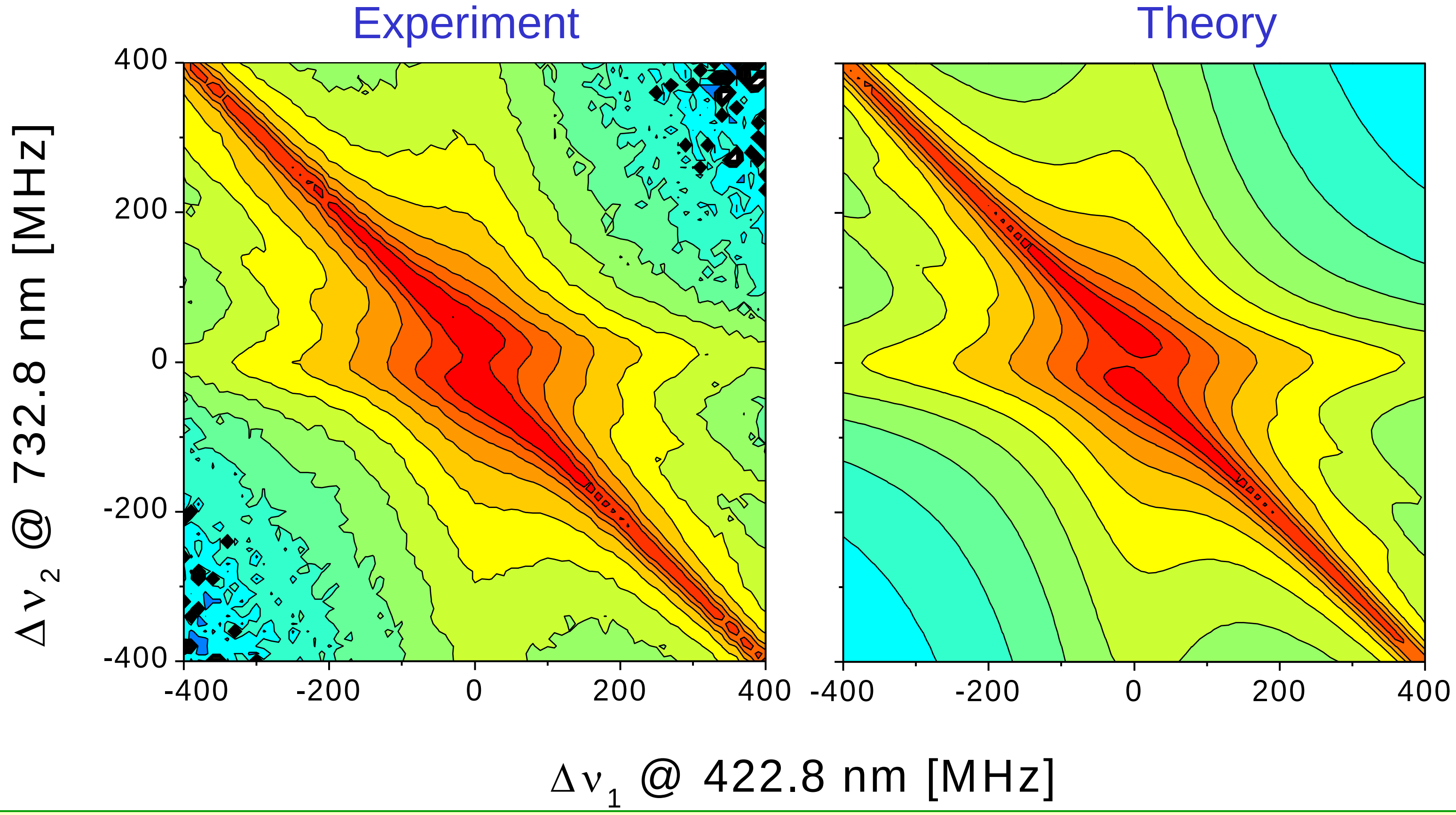
$\Gamma_{internal}, \gamma_{external}$

Rabi frequencies

$$G_j = \frac{\Omega}{2} = \sqrt{\frac{3A_{j+1,j}\,I_j\,\lambda_j^3}{8\pi hc}}$$

Ionization cross section $\sigma_{PhotoIon}$

Comparison: Ab-initio Peak Profile ←→ Experiment



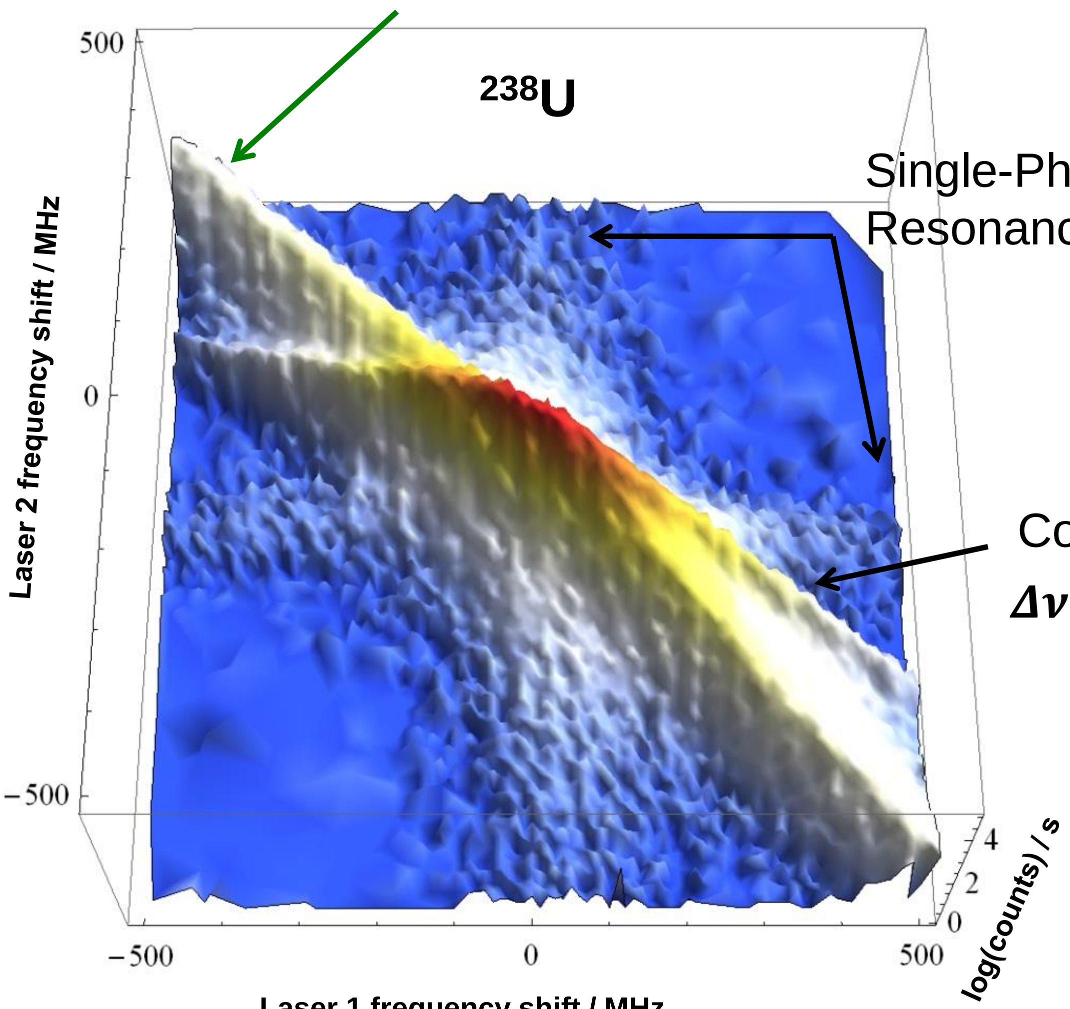
Procedure: Simulation considers experimental conditions via numerivcal convolution over
– the velocity & angle distributions of the atomic beam & – the laser beam shape

Result: complex experimental line shape including ac-Stark effect from laser field is properly reproduced → Prediction of achievable optical selectivity & efficiency

Limitation: atomic parameters must be known for all transitions

Experimental Coherent Multi-Step RI Profile

Coherent Two-Photon Sum: $\Delta\nu_1 + \Delta\nu_2 = 0$



Single-Photon Resonances

Doppler Compensation:

$$\Delta\nu_1 + \frac{\lambda_1}{\lambda_2}\Delta\nu_2 = 0$$

789.255 nm

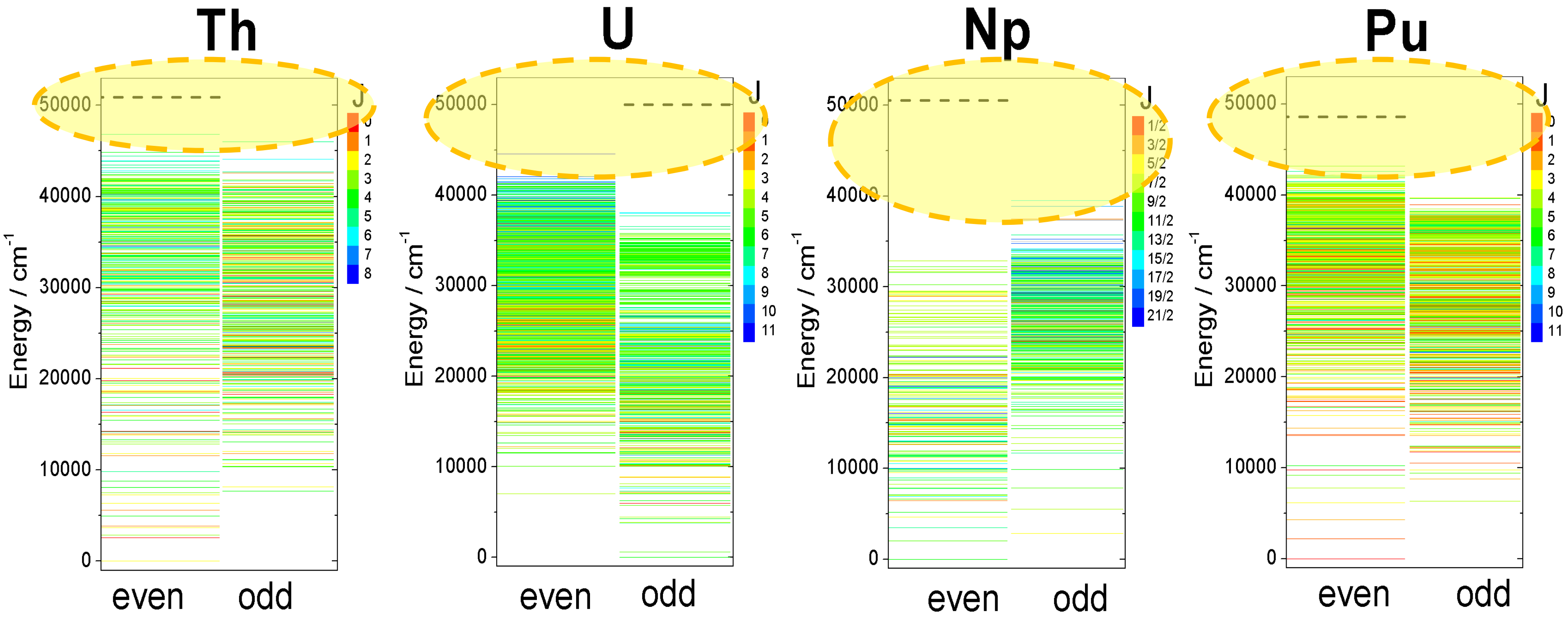
404.389 nm

Uranium Analytics:

facing the actinide (and lanthanide) problem

→ No atomic parameters known

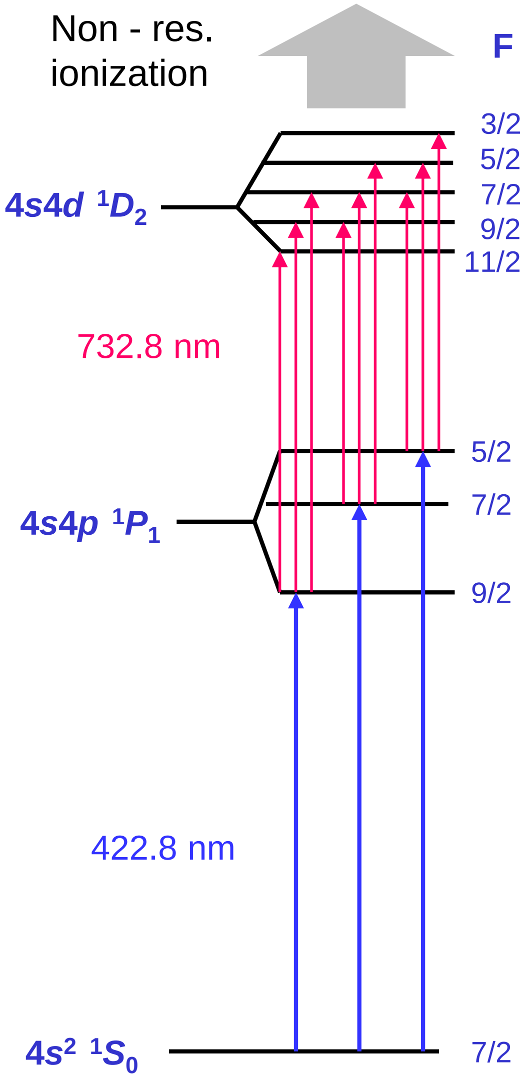
Complexity and Gaps in Actinide Schemes



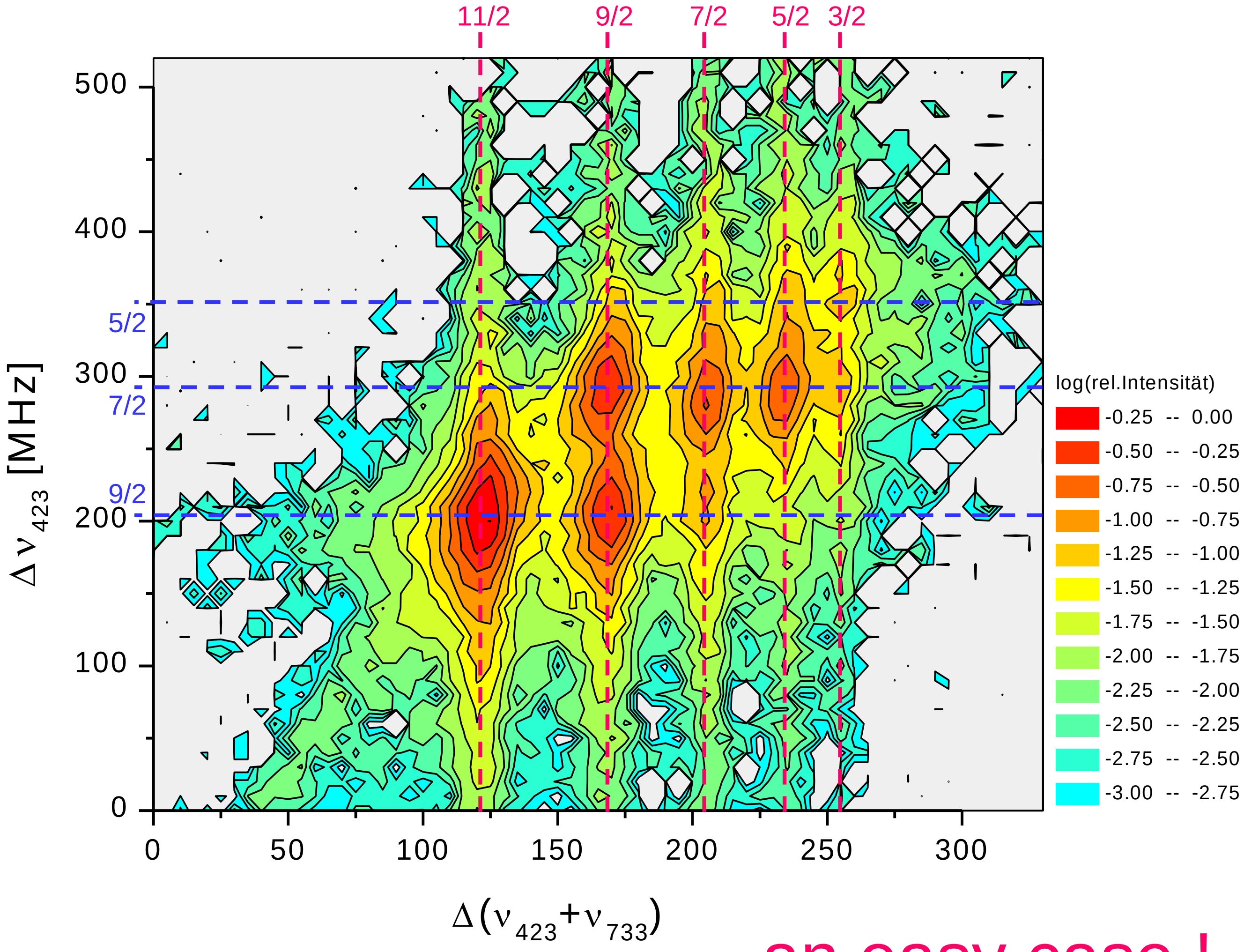
- Up to **4 open valence shells** → rich and highly complex level schemes
- Missing information above **~ 40 000 cm^{-1}** – higher actinides even less known
- No **Rydberg levels,** no continuum structure, no **auto-ionizing (AI)** states known
- Very limited information **on configuration assignments** or **transition strengths**

Data: Blaise J., Wyart J.F. (1992)

Even worse: Consideration of Hyperfine Structure

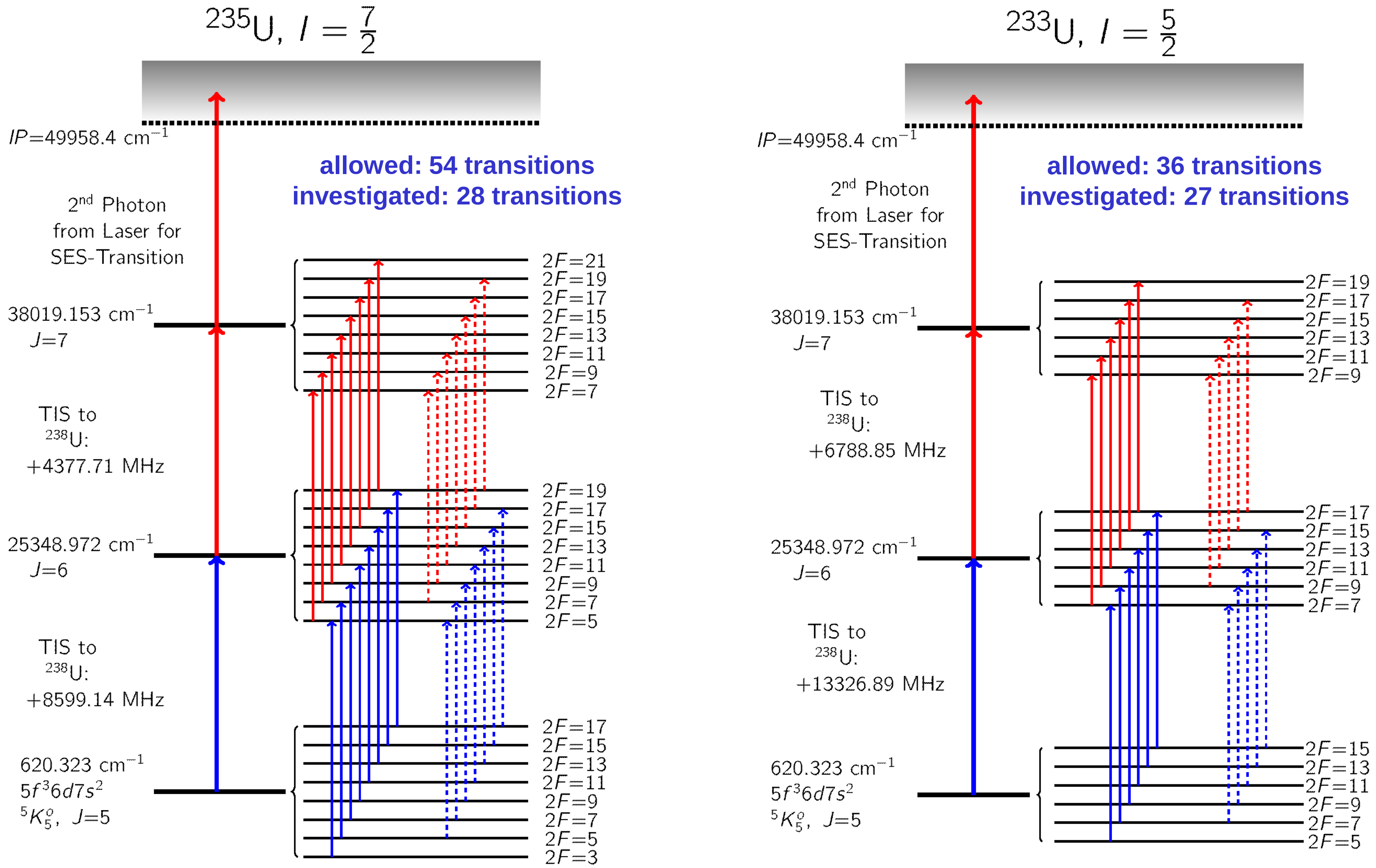


Example: ^{43}Ca as test and reference for ^{41}Ca



..an easy case !

HR-RI Hyperfine Structure Studies in Uranium



allowed: 54 transitions
investigated: 28 transitions

allowed: 36 transitions
investigated: 27 transitions

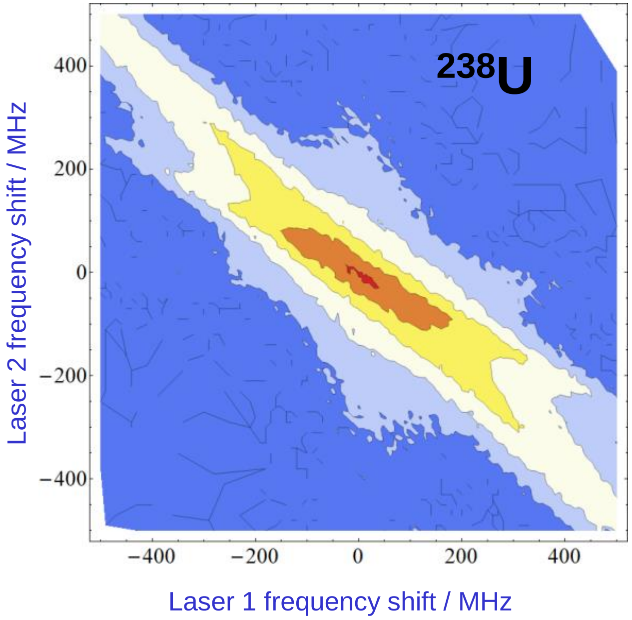
ΔF=+1 **ΔF=0**

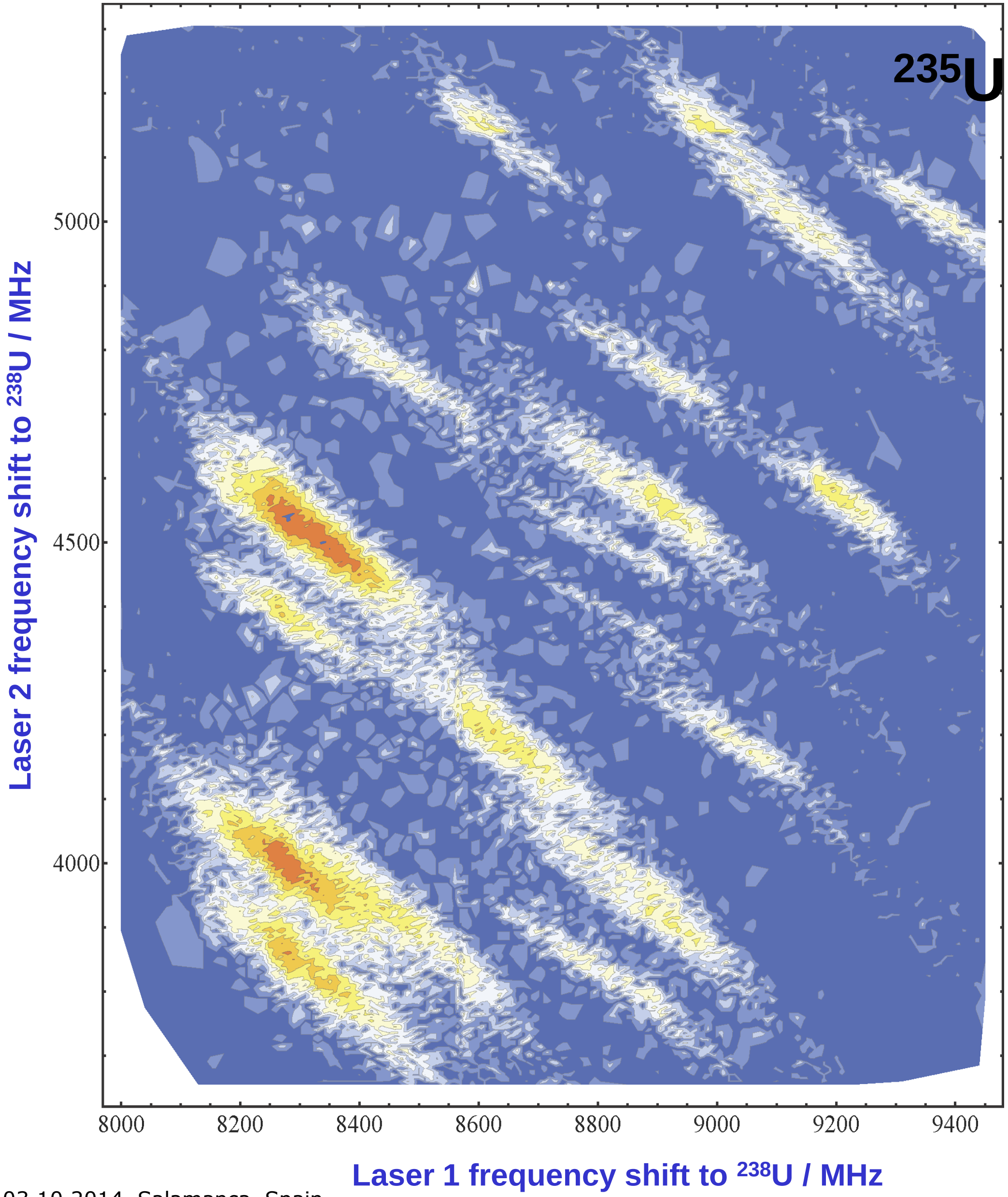
ΔF= -1
too weak for evaluation

ΔF=+1 **ΔF=0**

Frequency Map of ^{235}U

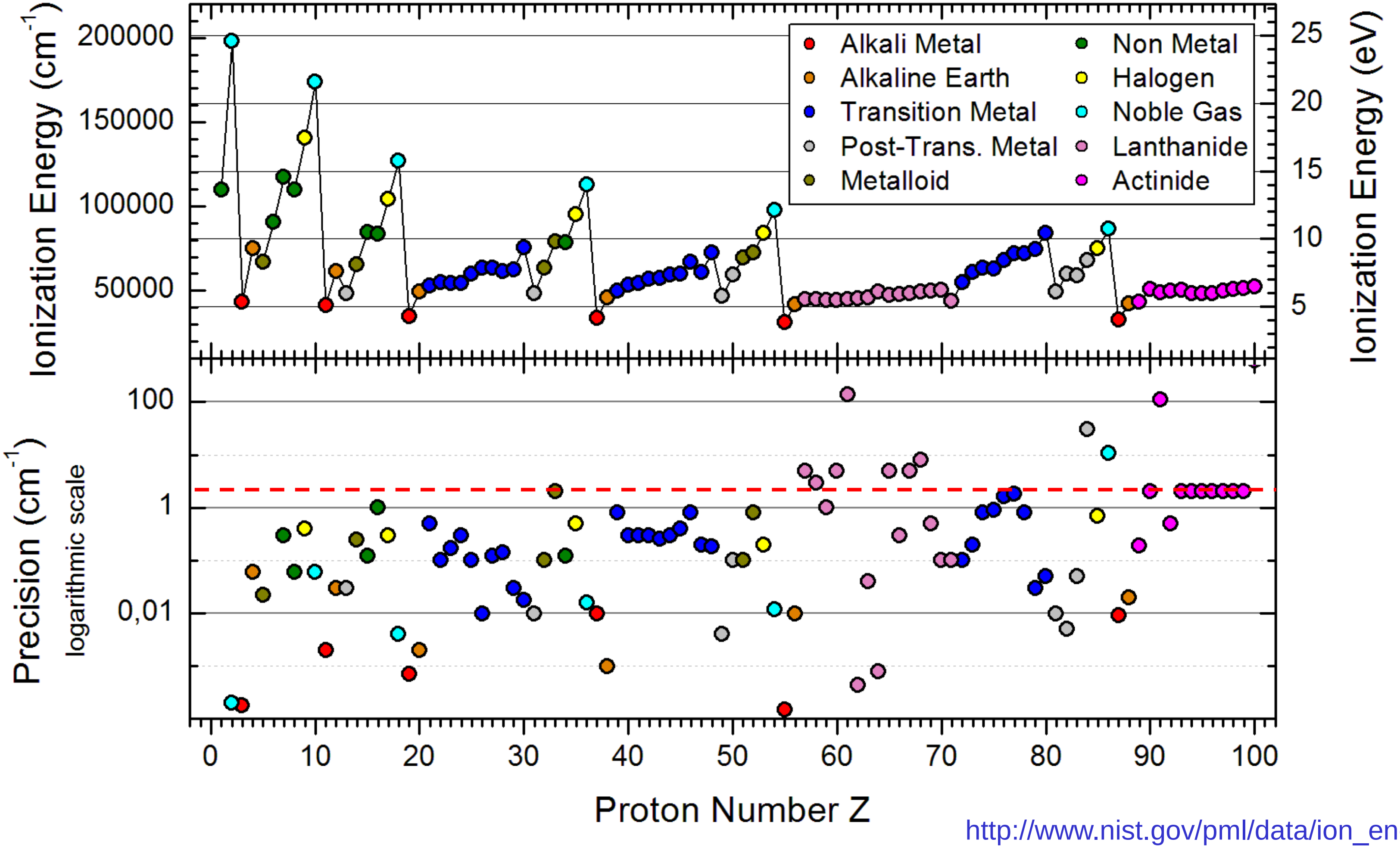
Separation of spectrally overlapping components in one dimension via the second dimension in the 2dim. frequency space





Another problem for laser analytics:

the Knowledge of Ionization Potentials

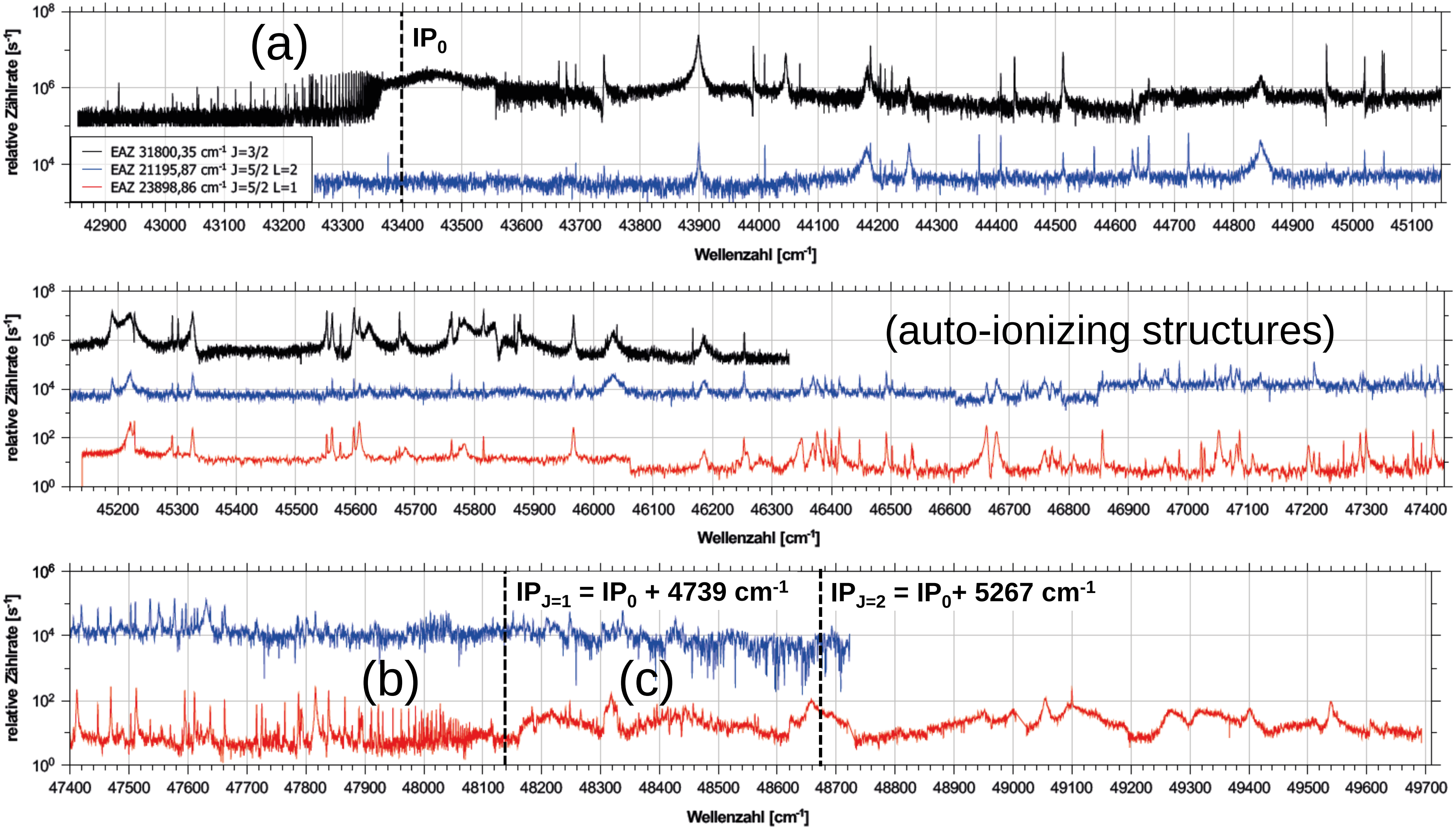


http://www.nist.gov/pml/data/ion_energy.cfm

- Experimental data on the most fundamental atomic quantity **IP** are almost entirely available

  (except for the two all radioactive „Pr“ elements, the four heaviest actinides with Z > 100 and „SHE“s)
- Precision of data varying between 10^{-4} - 10^{2} cm^{-1} (only data more precise than ~1 cm^{-1} is meaningful)

Raw data: Third excitation step in Ac



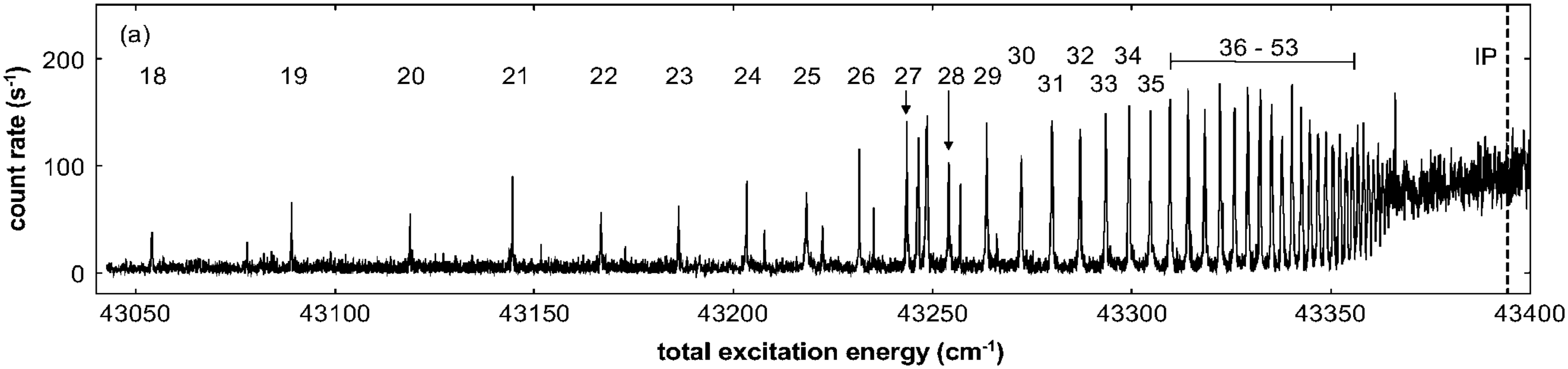
(auto-ionizing structures)

$IP_{J=1} = IP_0 + 4739\ cm^{-1}$

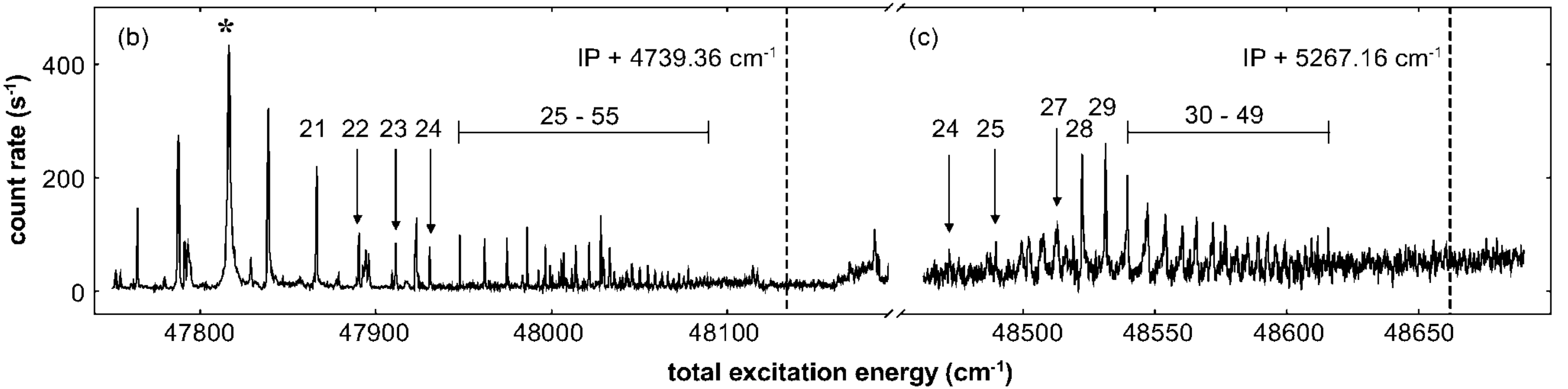
$IP_{J=2} = IP_0 + 5267\ cm^{-1}$

Rydberg and AI level spectroscopy in Ac

Series of Rydberg-levels converging to the first IP of Actinium

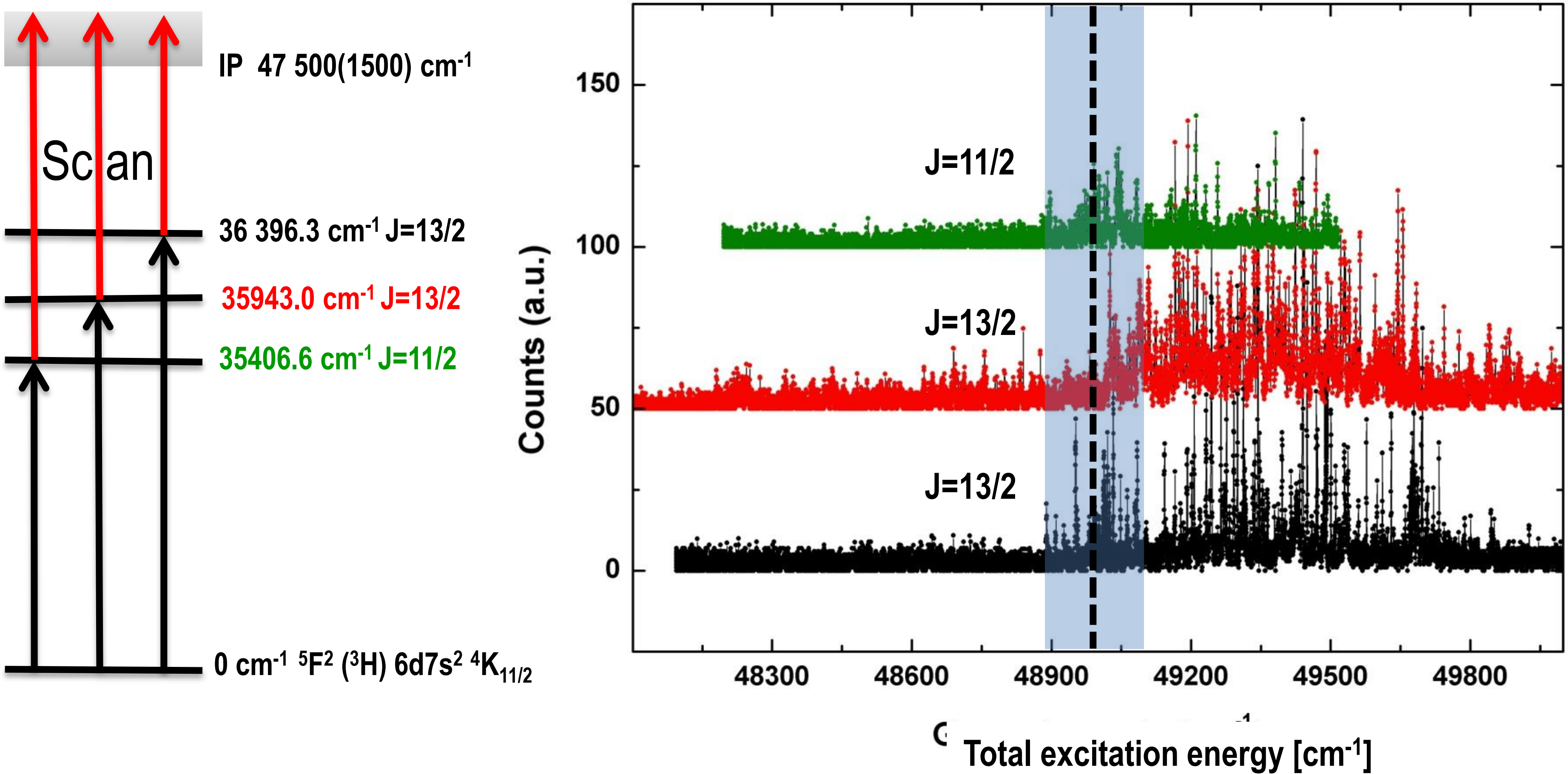


Two series of auto-ionizing Rydberg-levels converging to excited states in Ac II



… towards the IP of Protactinium (Pa)

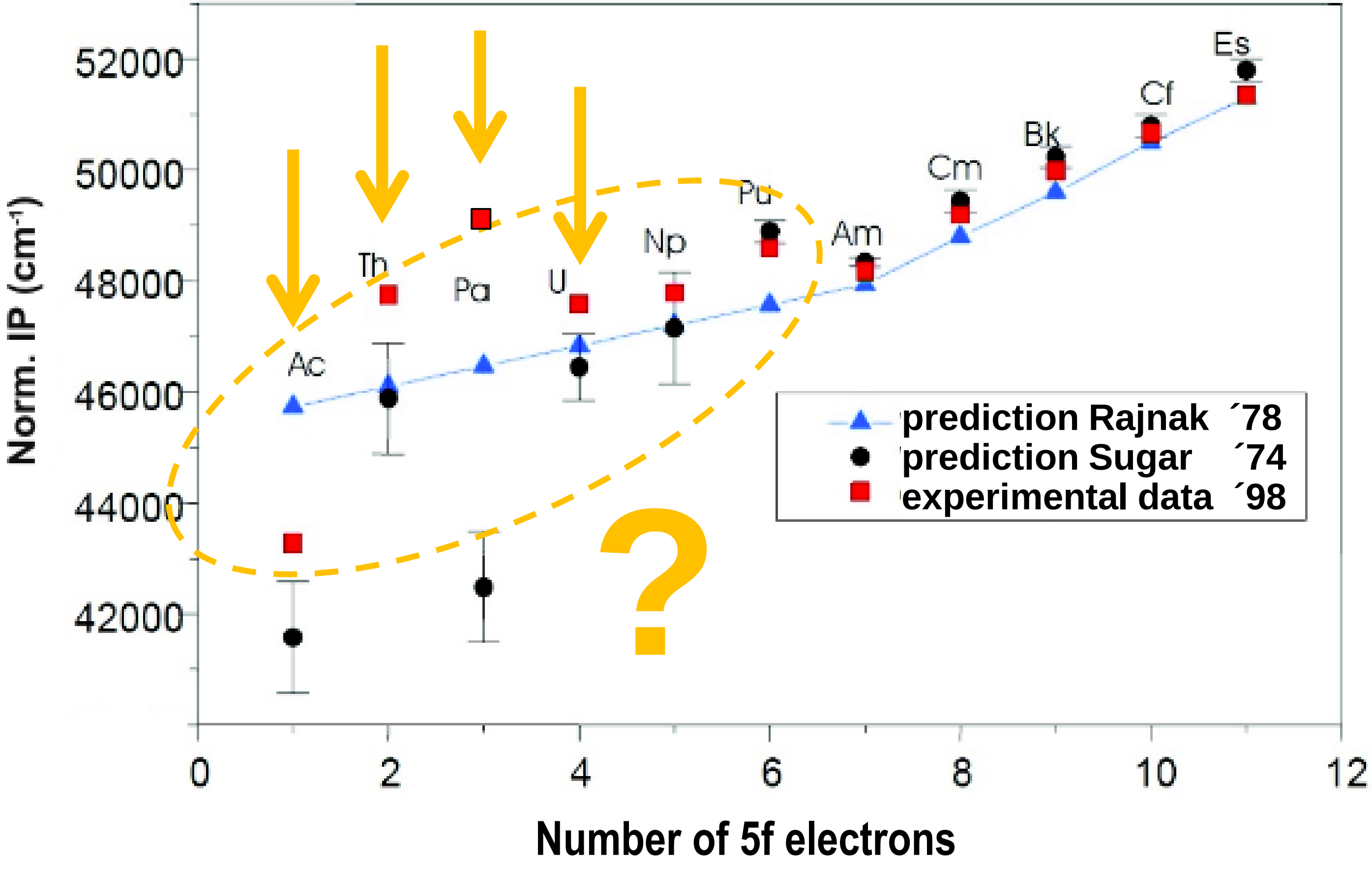
- **Evaporation** & **atomization** of Pa very inefficient due to unfavorable **chemical** behaviour
- **Ionization onset** observed – **but no Rydberg levels** present (?) – very rich **AI** spectrum
- Vague preliminary result: **IP_{Pa}= 49 000(110) cm^{-1}** from comparison to other actinides



Ionization Potentials of the Actinides

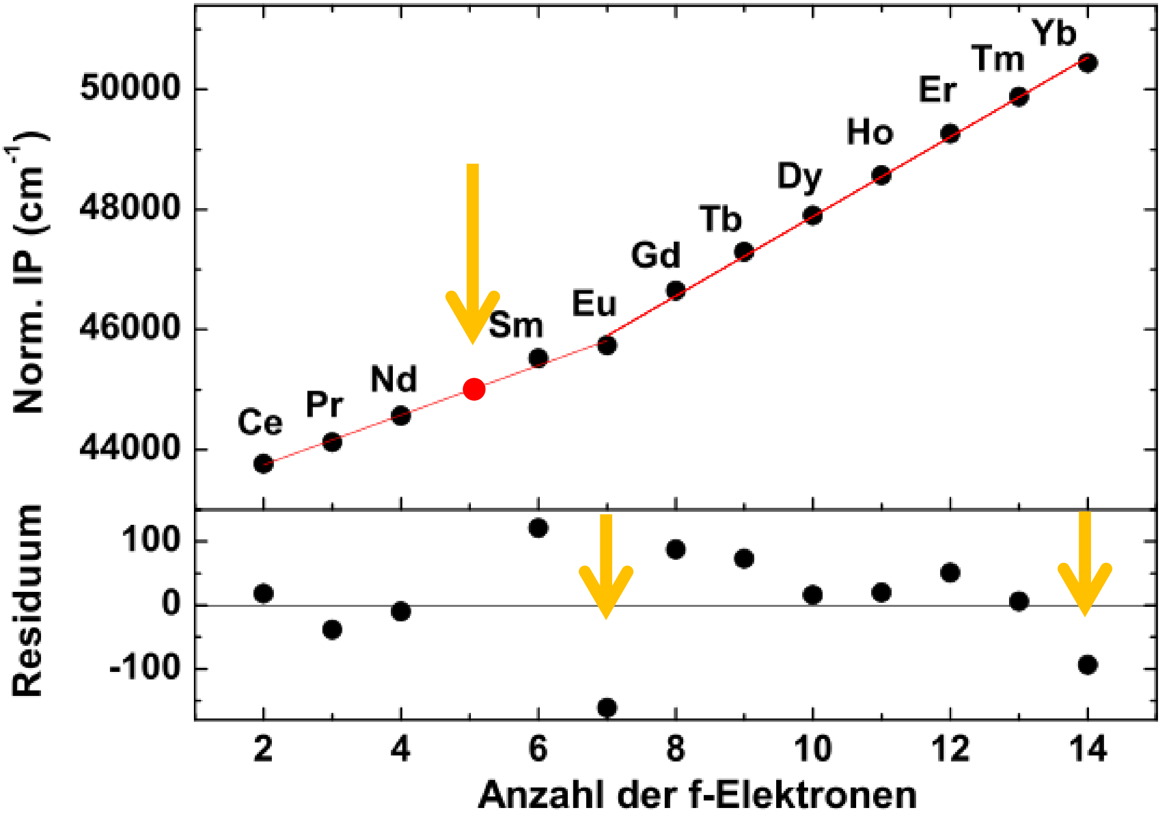
- Values normalized to most logical ionization process of **$5f^{N}7s^{2} \rightarrow 5f^{N}7s$**
- Regular trend above, but unclear behaviour below the half-filled f shell
- Systematic deviations from predictions for at least 4 light actinide elements Ac, Th, Pa, U

?



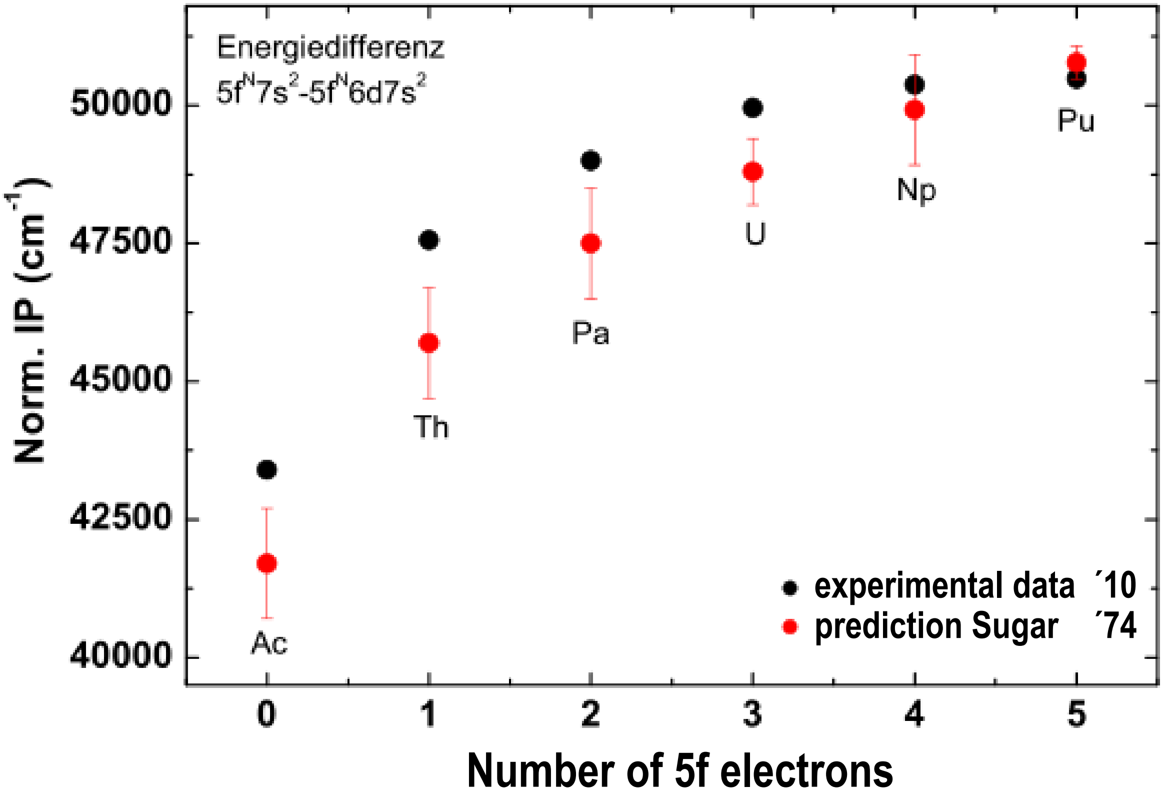
Iso-electronic Sequence of IPs in Lanthanides

- IP values normalized to **$4f^{N}6s^{2} \rightarrow 4f^{N}6s$** – expectations within $\Delta E \approx 100\ \mathrm{cm}^{-1}$ confirmed
- Theoretical prediction of **two linear slopes** – below and above **half filled shell closure**
- Extrapolation of missing IP of radioactive **Promethium** possible – **IP_{Pm}= 44 985(140) cm^{-1}**



Solution: systematics of IPs of light Actinides

- Experimental data **verified** and completed for **Actinium to Plutonium**
- New theoretical apprach: normalization to **$5f^{N-1}6d\ 7s^2 \rightarrow 5f^{N-1}\ 7s^2$** (instead of $5f^N\ 7s^2 \rightarrow 5f^N\ 7s$)
- **Smooth** trend generated, only slight discrepancy to theoretical predictions [Sug74]
- Obvious non-linear behavior explained by relativistic compression of high Z electron orbits



Outline

- Motivation: Access to Exotic Isotopes through Quantum Optics
  – off-line (not on-line) on long-lived natural and anthropogenic species
- Theory: Multi-Step Excitation Processes in Atomic Systems
  – benefits, drawbacks & limitations of light-atom interactions
- Experimental & Applications:
  - HR-RIMS – for isotope selective coherent atomic spectroscopy
  - Back to Analytics
    – high-tech physics for low level chemistry & radioprotecion
  - (Laser AMS – isobar selection at accelerators for radiodating
    → postponed to LA3NET conference in Mallorca)
- Outlook & Summary

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Pu Analysis Fukushima Reactor Desaster

Samples, taken at Minamisoma, Prefecture Fukushima,

~3 months after desaster, dust and soil from a nearby parking lot

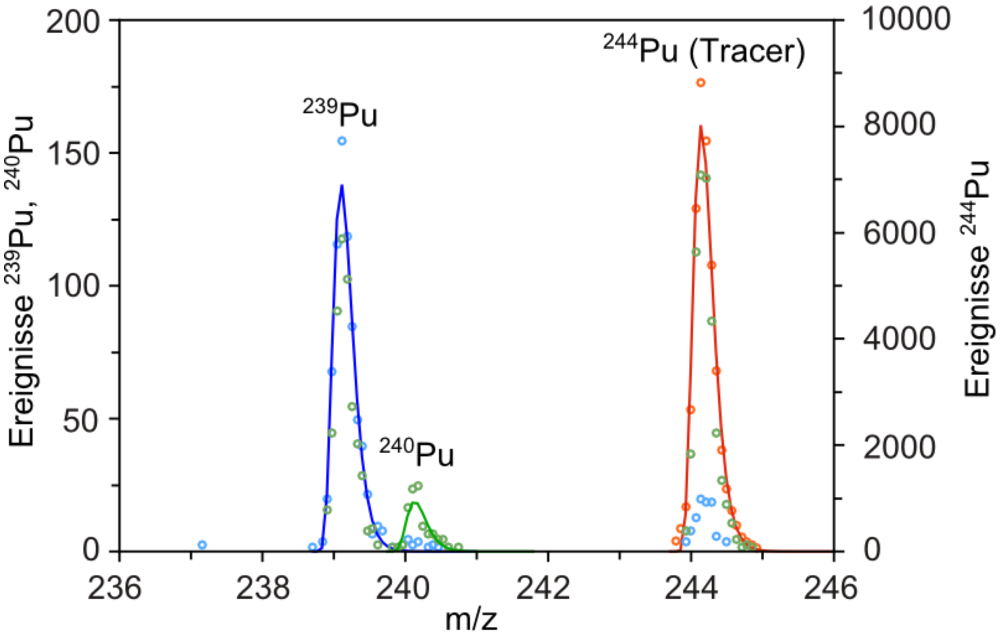
	^{239}Pu	^{240}Pu
Atoms / g sample	$1{,}2 \cdot 10^8$	$1{,}7 \cdot 10^7$
Overall Content	~ 50 fg / g	~ 7 fg / g
Activity Level	~ 160 µBq / g	~ 90 µBq / g

Low level Pu Concentration!

Identification of Origin:

^{240}Pu/^{239}Pu = 0,14

Signature of fallout Pu - indication for reactor Pu on this low level not detectable!

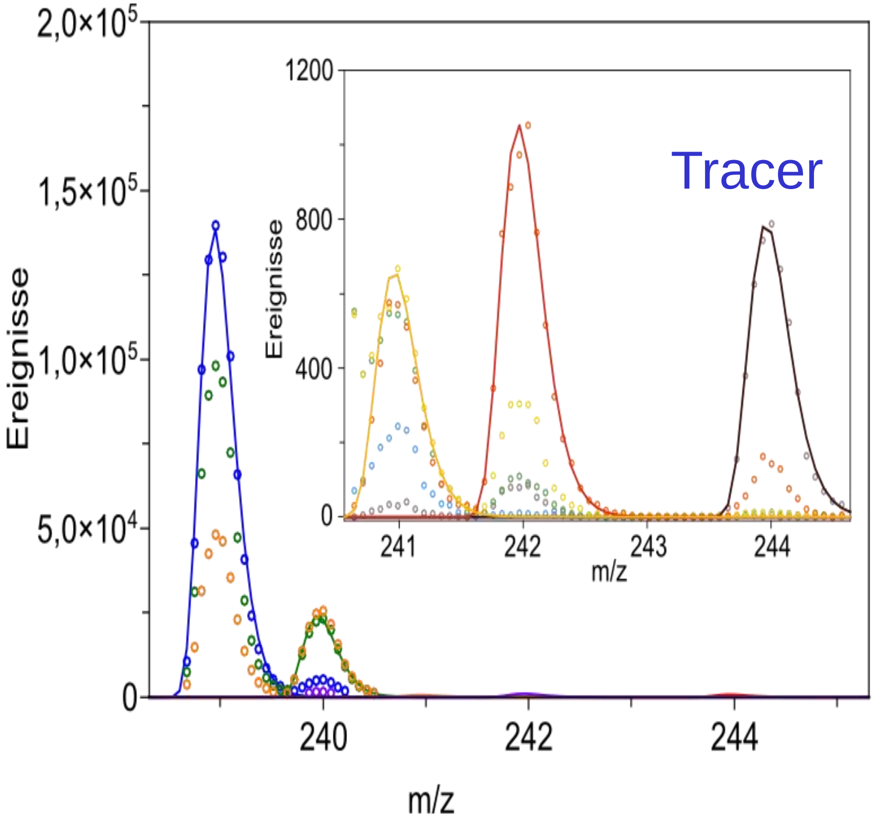


Pu Analysis of Sellafield river bed

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Atoms / g	$3{,}4\cdot10^{9}$	$3{,}8\cdot10^{12}$	$6{,}5\cdot10^{11}$	$1{,}8\cdot10^{10}$	$2{,}9\cdot10^{10}$
Overall content	1 pg / g	2 ng / g	300 pg / g	7 pg / g	10 pg / g

	measured	Cooper et al., 2000
^{238}Pu/^{239}Pu	$8.9\text{x}10^{-4}$	$1.2\text{x}10^{-3}$
^{240}Pu/^{239}Pu	0.17	0.18
^{241}Pu/^{239}Pu	$4.73\text{x}10^{-3}$	$4.86\text{x}10^{-3}$*
^{242}Pu/^{239}Pu	$7.6\text{x}10^{-3}$	$5.3\text{x}10^{-3}$

* ^{241}Pu-Content corrected for 1.1.2013



Determination of Pu - Mixture

$Pu_{\text{reactor}} / Pu_{\text{fallout}}$ = 20 % / 80 %

Conclusion and Outlook

- Resonance Ionization serves as a most selective & universal tool in ultra-trace analytics of radiotoxic isotopes

- Laser systems & accelerators (=mass spectrometers) must be well adapted to the individual task

- Optical spectroscopy on actinides (& lanthanides) is highly relevant to push theory and to refine data & experiments

- Theoretical support for conclusive interpretation of complex atomic spectra today is still a challenge and open

Thank you for your attention...