Polarizability of Rn-like Th^{4+} from Th^{3+} High-*L* Rydberg States

M. E. Hanni
Julie A. Keele
S. R. Lundeen
Colorado State University

C. W. Fehrenbach
J. R. Macdonald Laboratory, Kansas State University

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Why study Rn-like Actinide Ions?

- Th^{4+} is the most common charge state in Thorium chemistry

- Computation of Thorium compound properties begin with the description of the free ion.

- No prior experimental observations
  - no optical spectroscopy!
  - no measurements of excited state lifetimes!
  - no measurements of the significant dynamic properties: dipole & quadrupole polarizabilities

Why study Rn-like Actinide Ions?

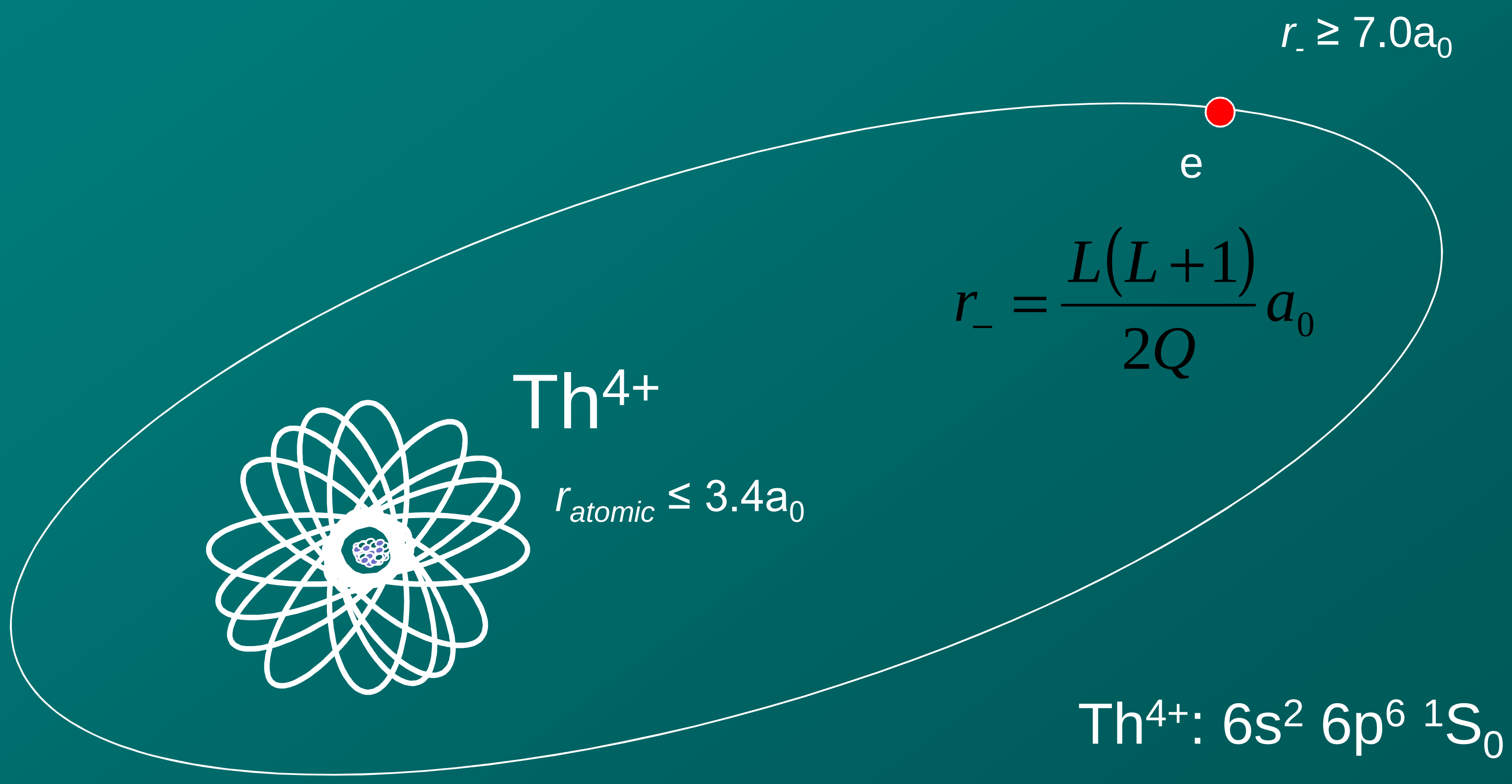
- Measurements could check existing calculations:

α_d (Th^{4+})
7.75 a.u. [1]
10.26 a.u. [2]
8.96 a.u. [3]
7.699 a.u. [4]

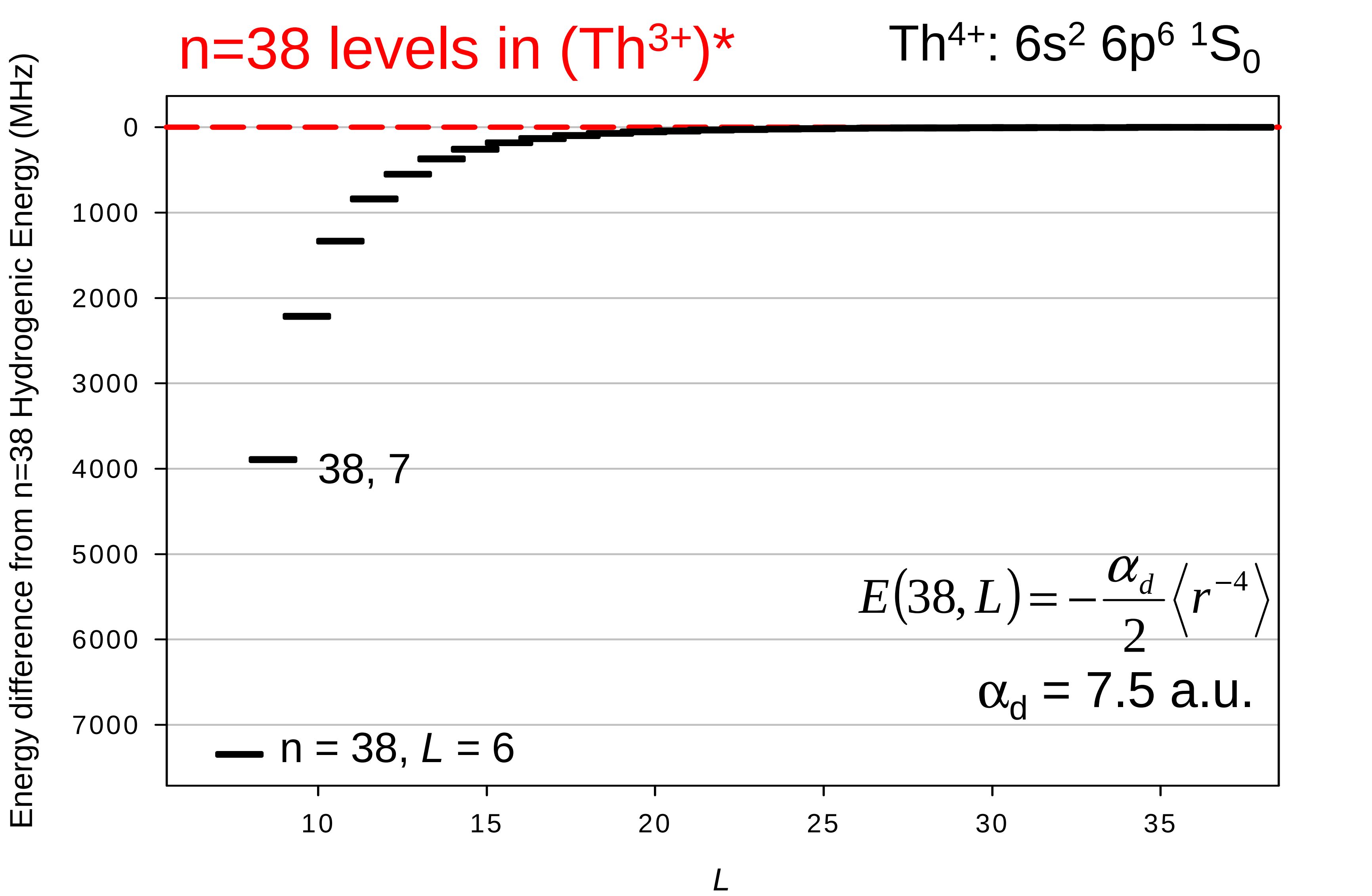
[1] U. I. Safronova, W. R. Johnson, M. S. Safronova, Phys Rev A **76**, 042604 (2007).
[2] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).
[3] A. Derevianko, *private communication*, (2010).
[4] A. Borschevsky and P. Schwerdtfeger, *private communication*, (2010).

High-L Rydberg Fine Structure: What can it teach us?

A non-penetrating high-L Rydberg electron acts as a sensitive probe of an ion's long-range interactions, giving <u>measurements</u> of the ion properties that control those interactions.

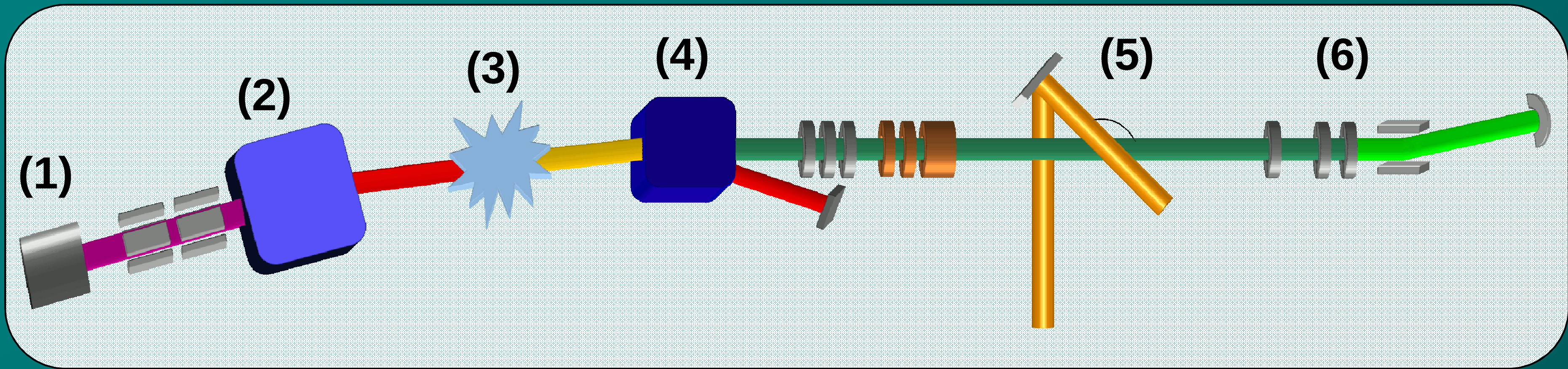


What's a Typical Pattern?



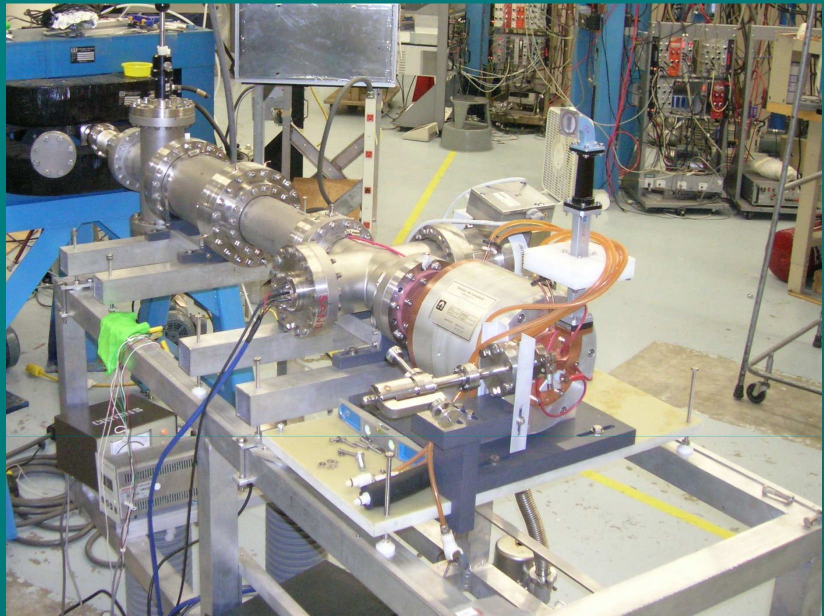
How can we SEE the pattern?

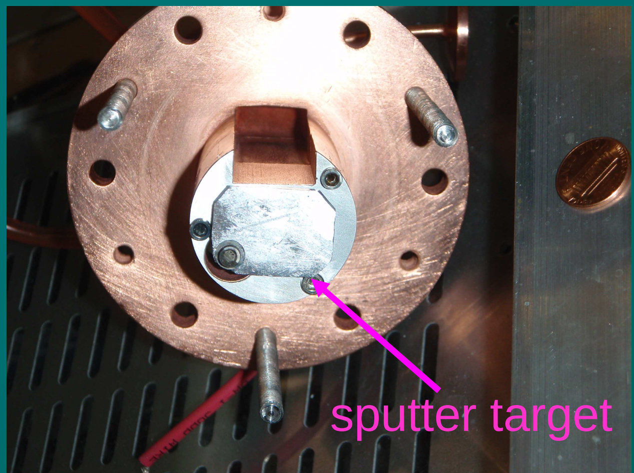
Resonant Excitation Stark Ionization Spectroscopy



(1) Beams of highly charged ions are created by the ECR and accelerated by +25 kV
(2) Beam of 100 keV Th^{4+} is selected using a 20º analyzing magnet
(3) $(Th^{3+})^*$ beam is formed by charge capture from a Rydberg target
(4) $(Th^{3+})^*$ beam is separated from remaining Th^{4+} beam using a 15º analyzing magnet
(5) CO_2 laser excites transitions between specific high-L Rydberg states
(6) States excited by the CO_2 laser are ionized and detected

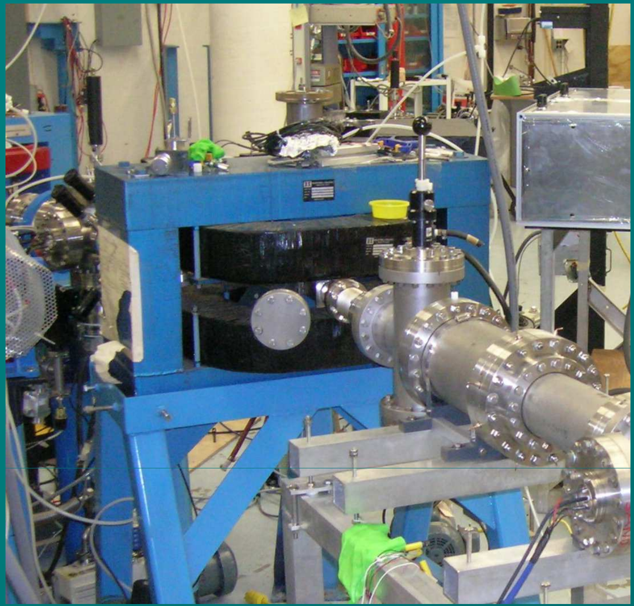
ECR Ion Source



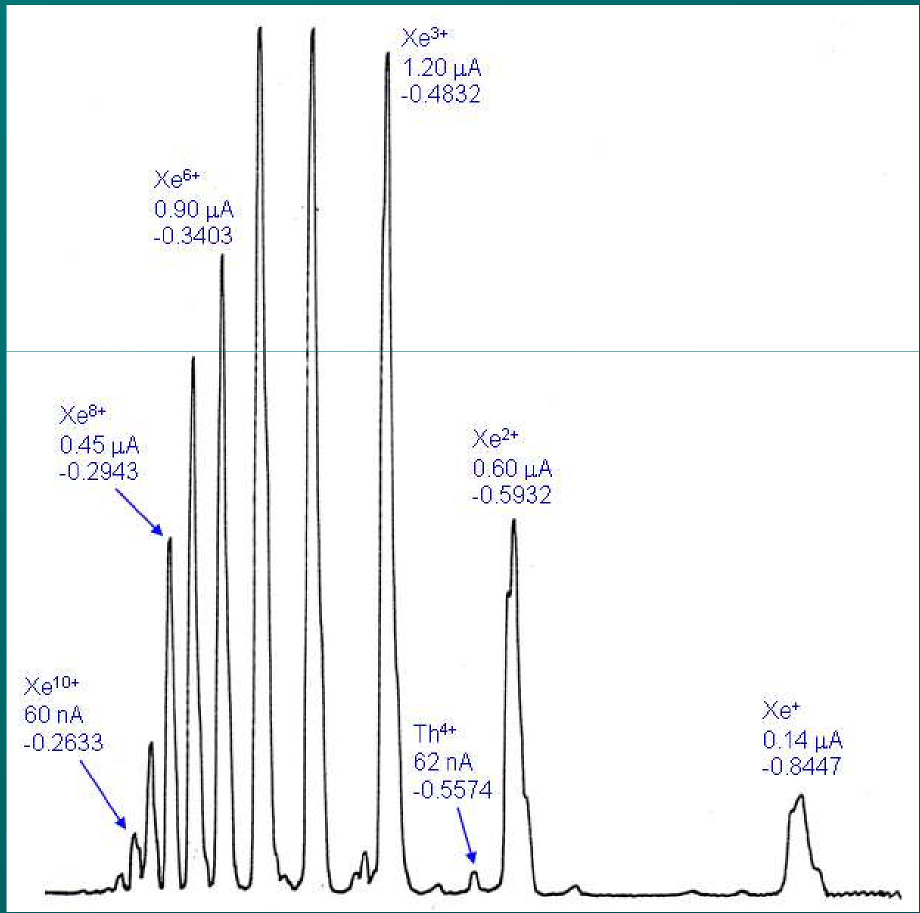


- 14 GHz Permanent magnet ECR ion source
- Solid samples of Th are sputtered in a Xe atmosphere
- Microwave power typically between 6 to14 W

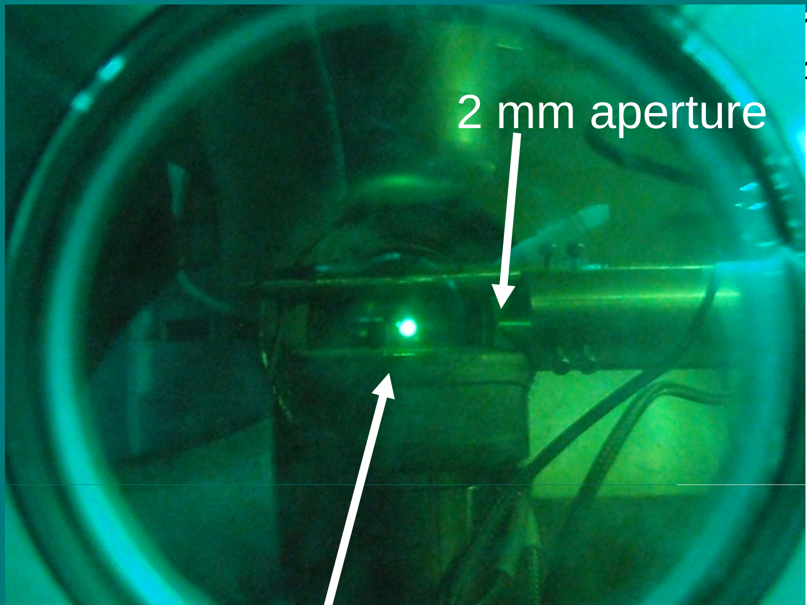
Primary Beam Selection



- 20º Magnet in conjunction with a 2 mm aperture analyzes beams by charge and mass
- Mass resolution: $\frac{\Delta M}{M} \approx 3\%$
- Velocity spread: $\frac{\Delta v}{v} \leq 0.02\%$

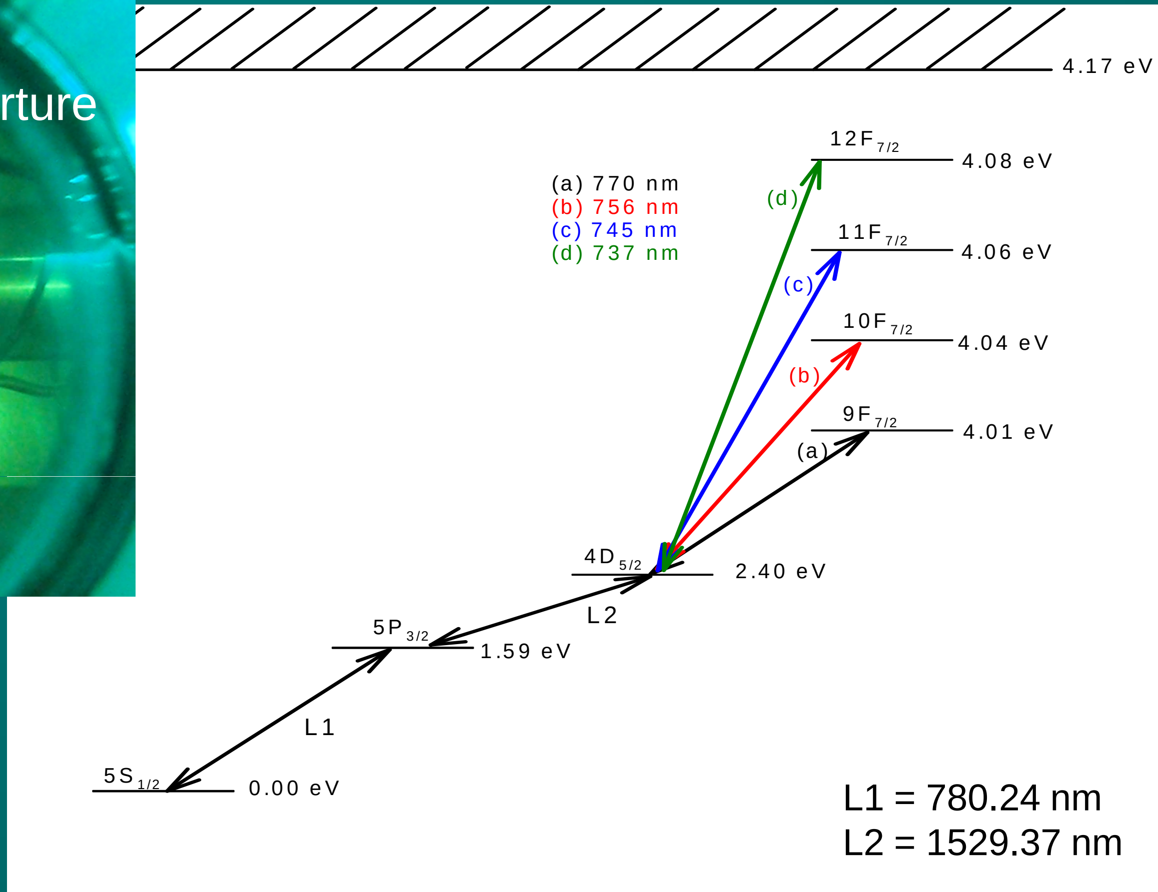


Rydberg Target



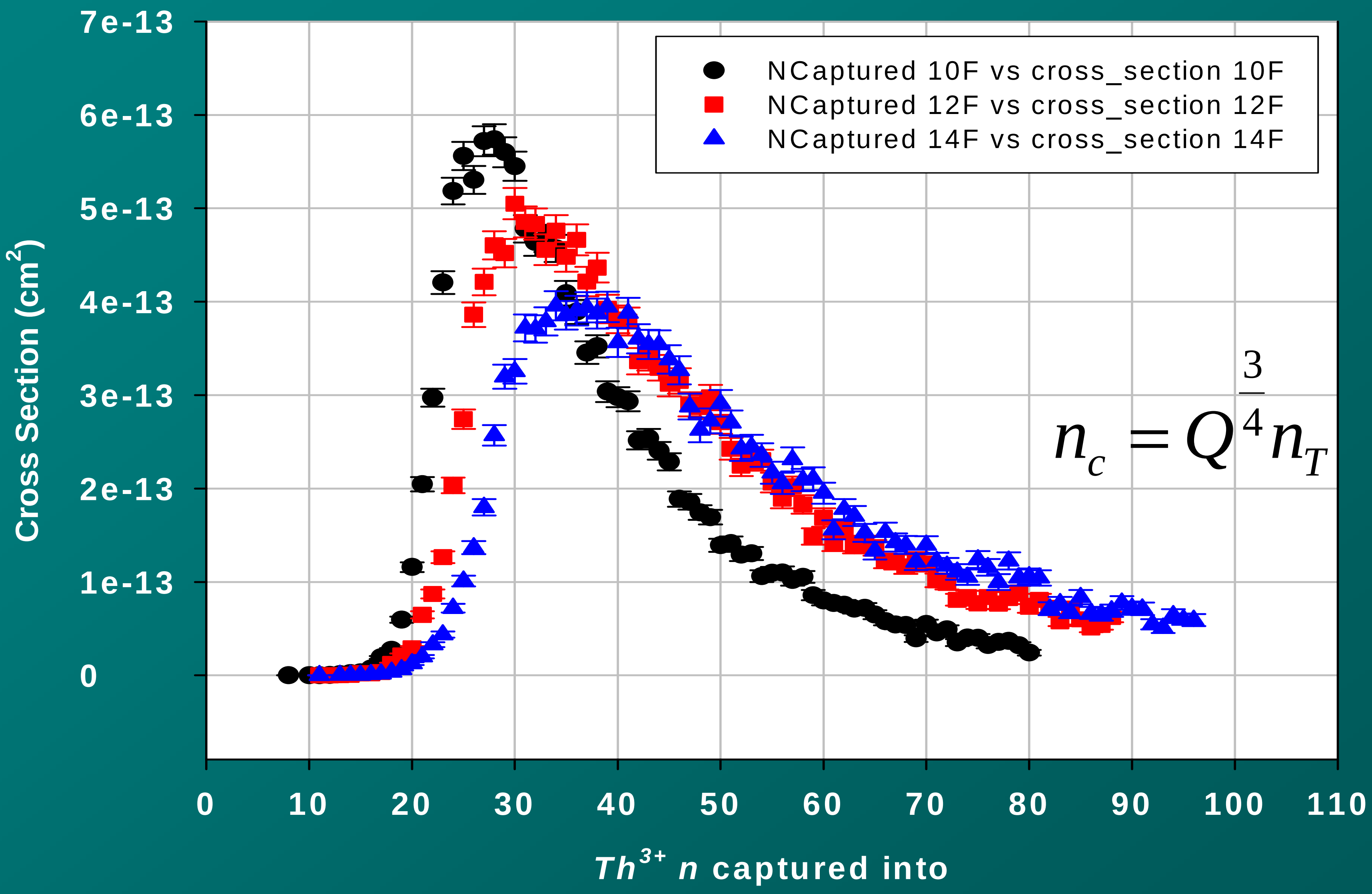
Rydberg target

Characteristic “blue fluorescence” is the result of transition from (n+1)$D_{5/2}$ state to $5P_{3/2}$ state



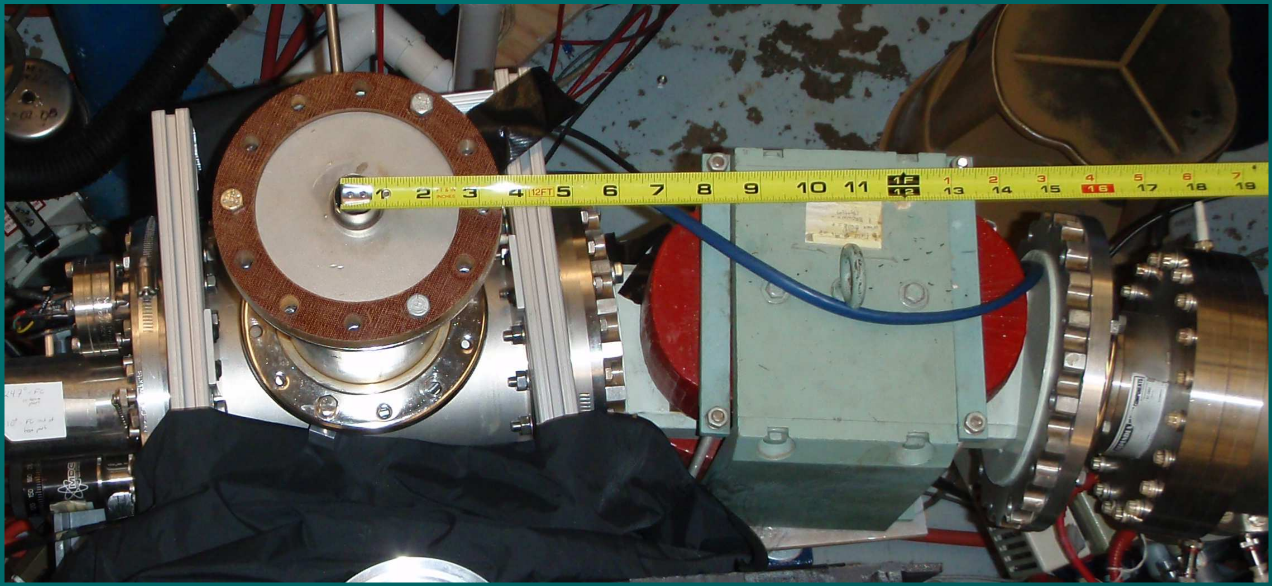
- Thermal plume of Rb is excited to a high *n*F state using 3 CW lasers.
- Typically only 2% of the ion beam captures a Rydberg electron

Rydberg Target

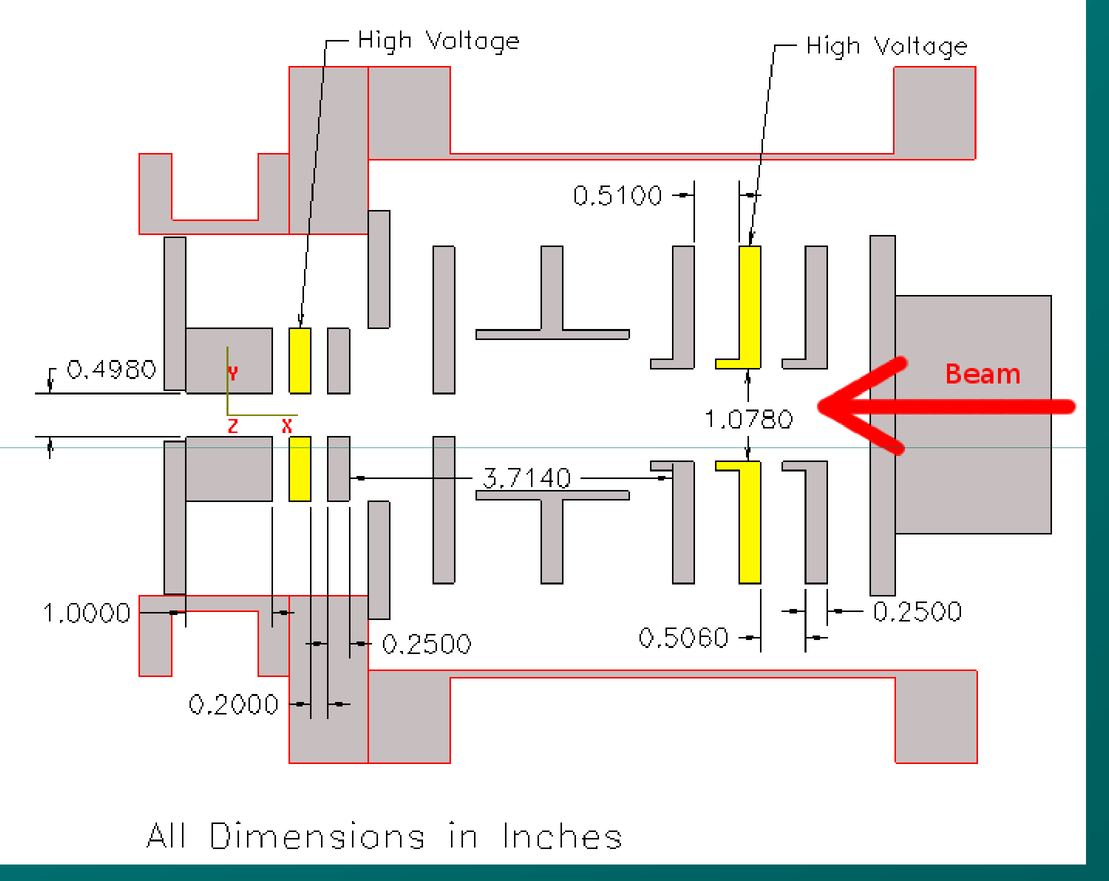


Charge Transfer beam selection

- Following the Rydberg target is a 15º mass and charge analyzing magnet.
- This magnet is used to separate the ion beam that captured a Rydberg electron from the remaining primary beam, significantly reducing the background in our detector.

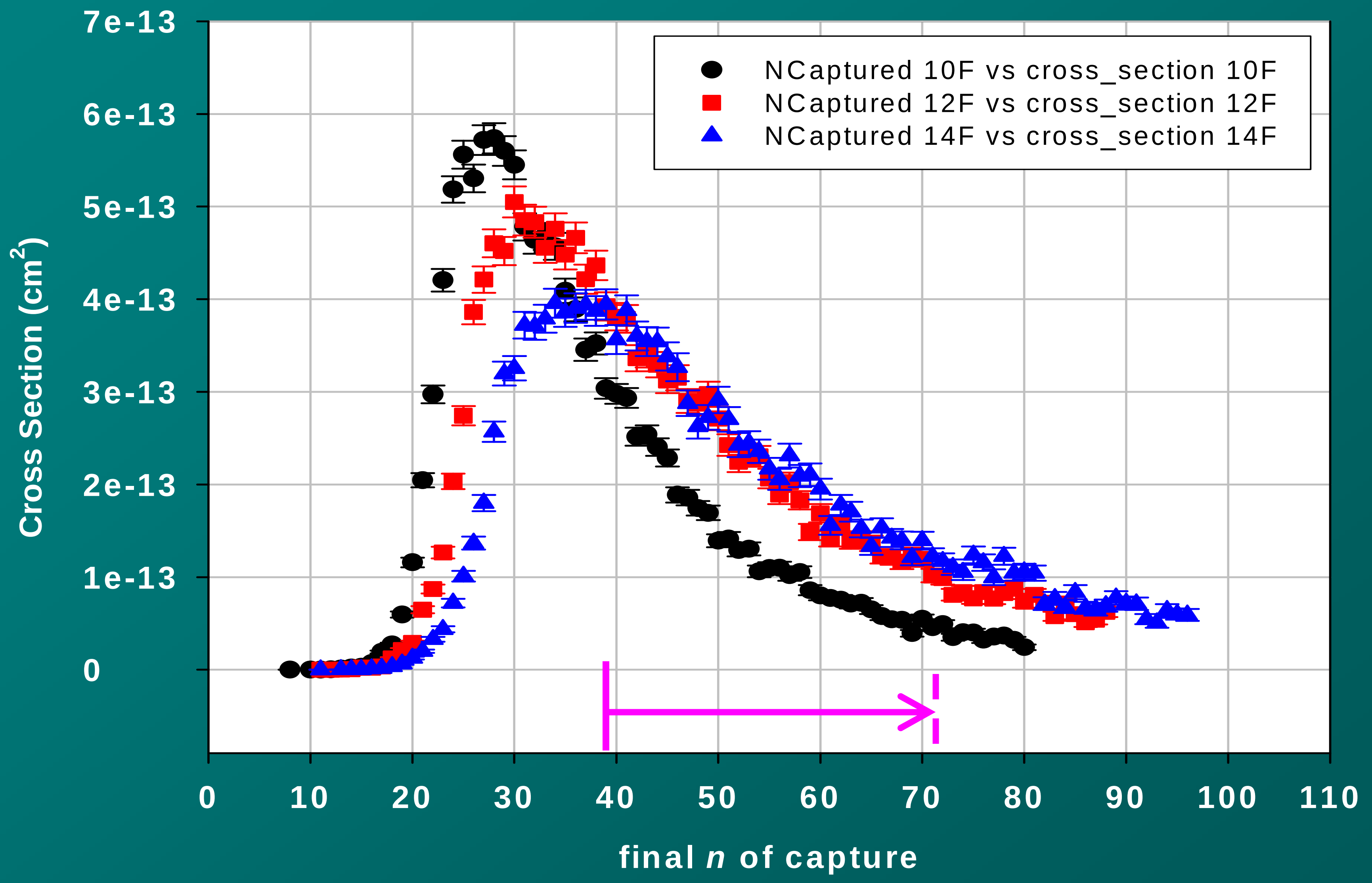


Pre-ionization

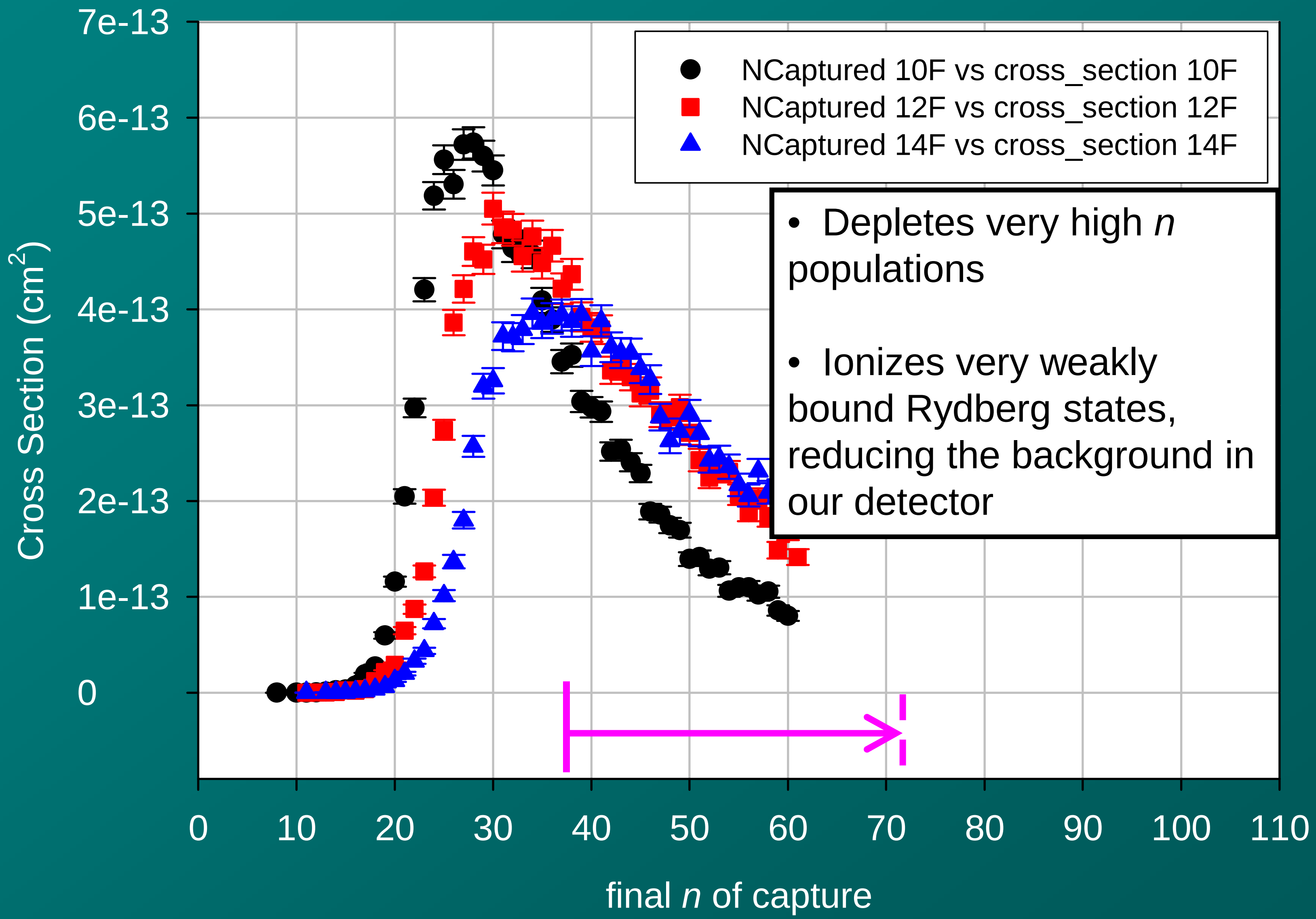


- Typical fields:
  - Pre-ionizing lens 1: ~4500 V/cm @ 10.5 kV
  - Pre-ionizing lens 2: ~3800 V/cm @ 4.0 kV

Background removal and signal enhancement by Pre-Ionization



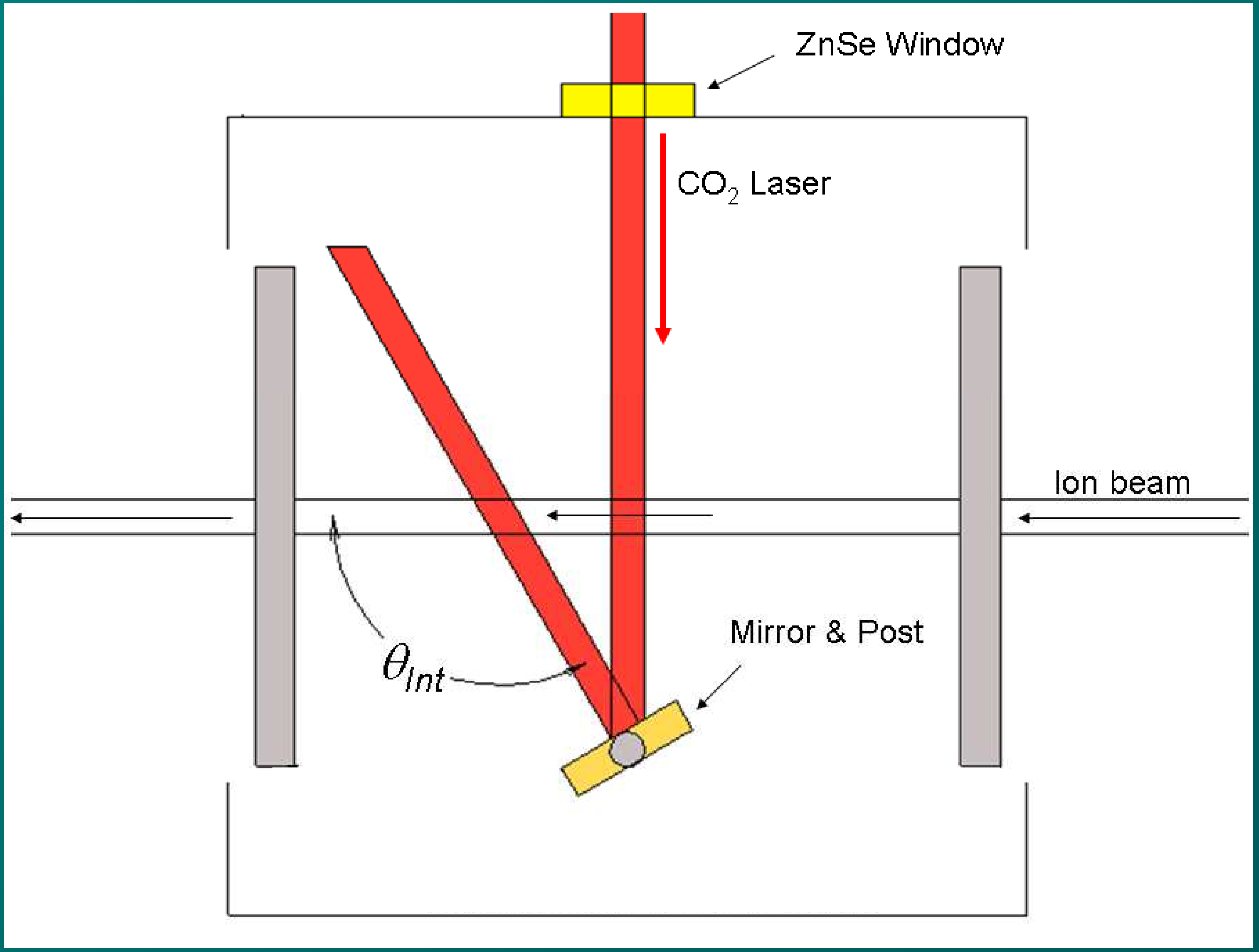
Background removal and signal enhancement by Pre-ionization



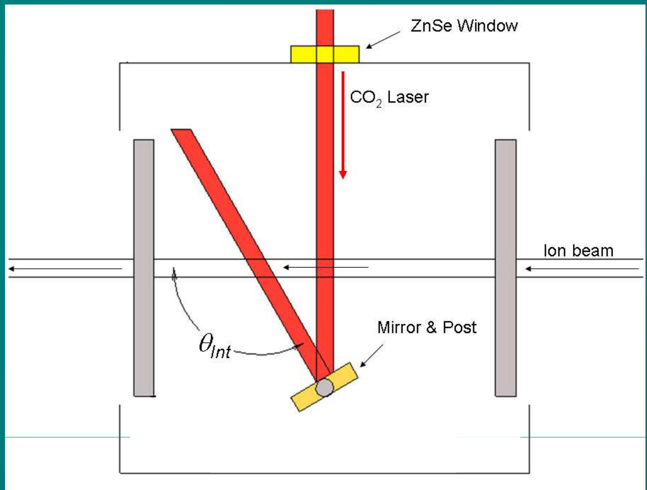
- Depletes very high *n* populations

- Ionizes very weakly bound Rydberg states, reducing the background in our detector

Resonant Excitation

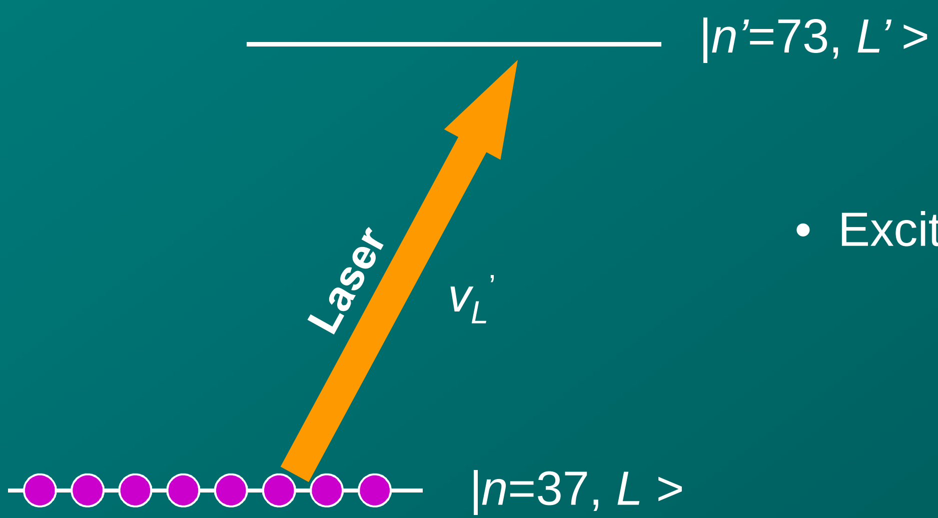


Resonant Excitation



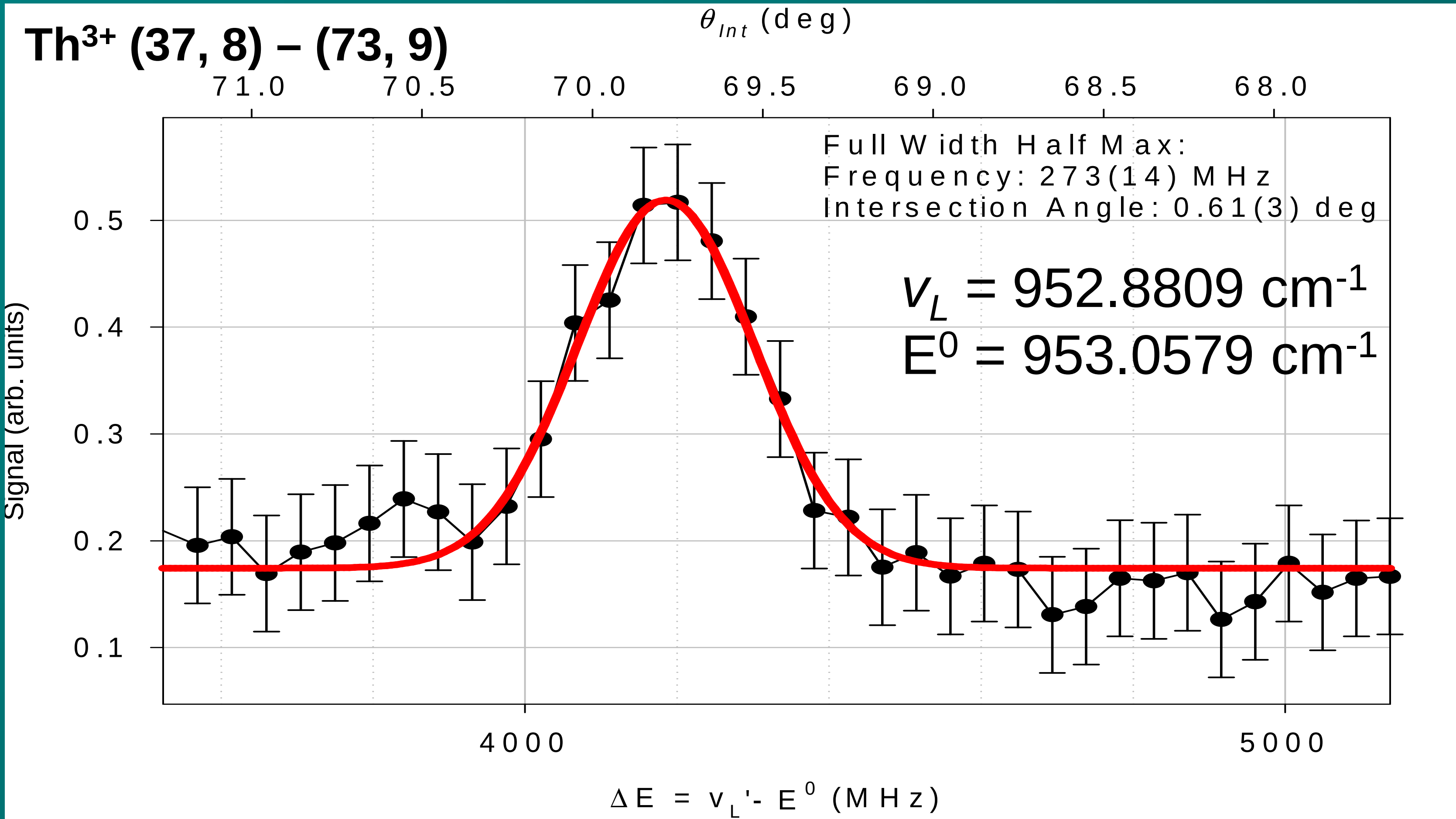
$$\nu'_L = \frac{\nu_L}{\sqrt{1-\beta^2}}\left[1+\beta\cos\left(\theta_{Int}\right)\right]$$

By smoothly varying θ_{Int} the Doppler tuned frequency is varied through the resonant transition frequency between high-*L* Rydberg states, allowing for partial resolution of the Rydberg fine structure.



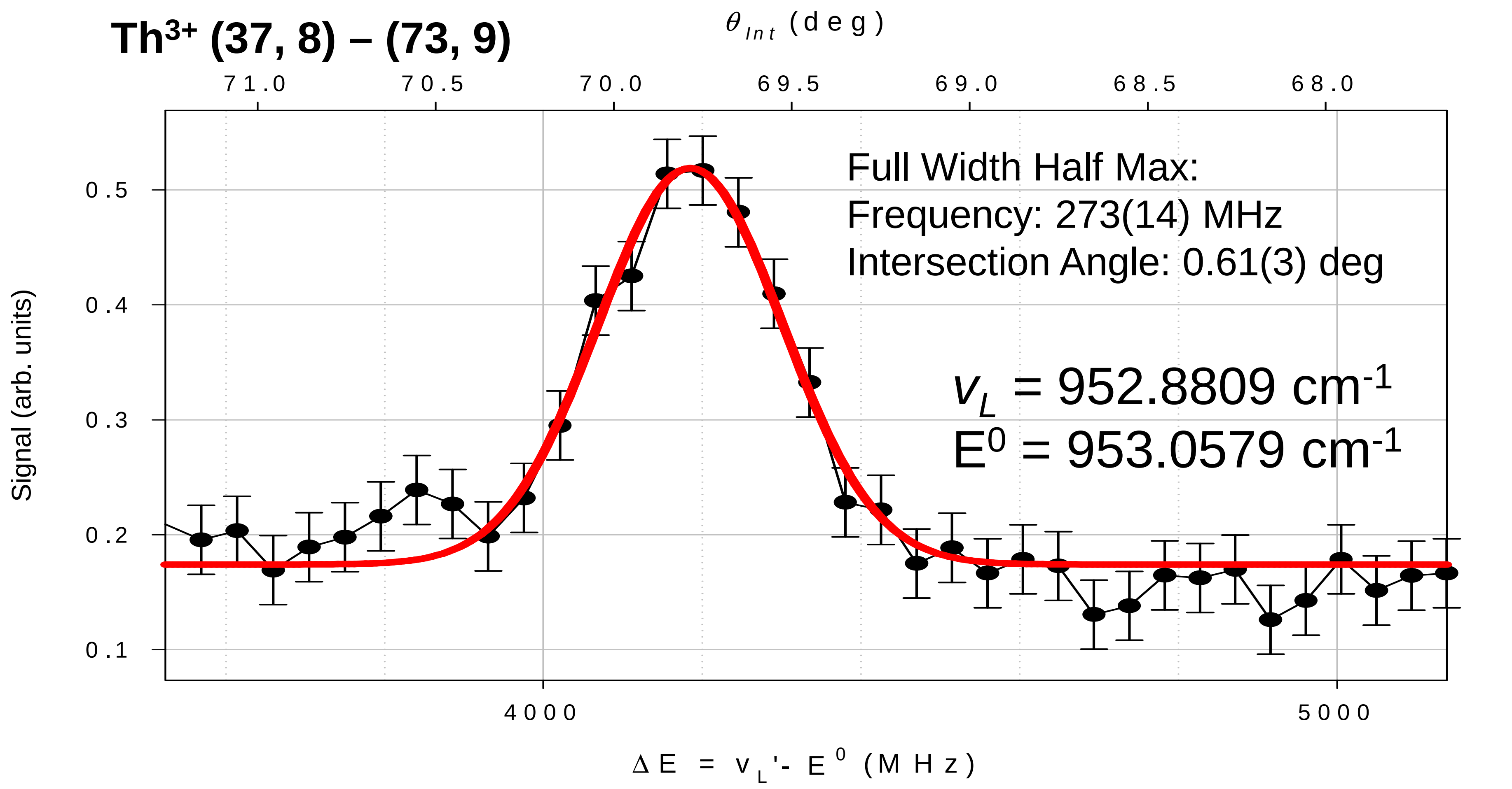
- Excitation is upwards so $L'=L \pm 1$ is allowed

Resonant Excitation (an example)



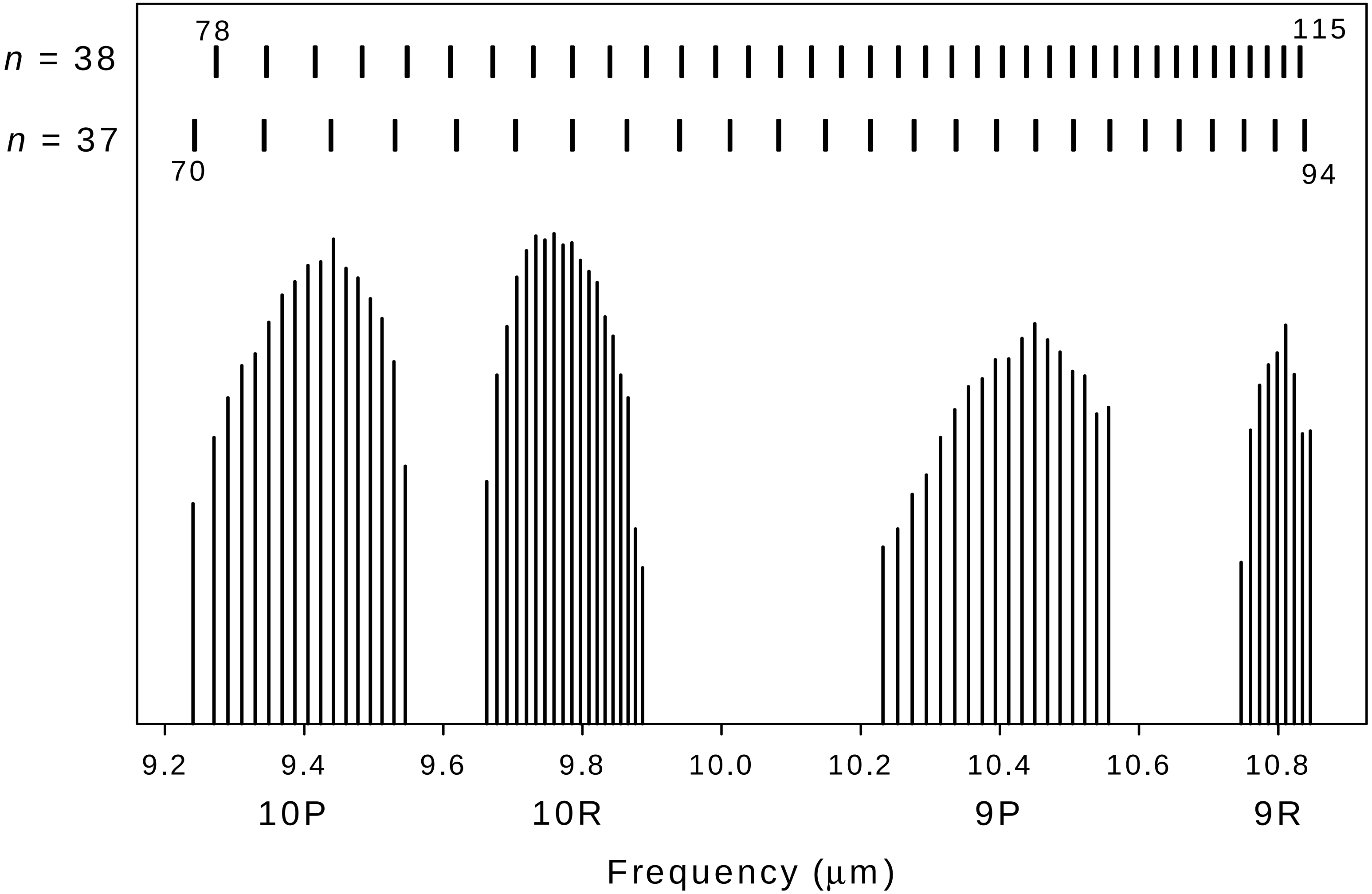
The x-axis is the difference between the CO_2 laser's Doppler-tuned frequency and the hydrogenic transition frequency between the n = 37 and n' = 73 Rydberg levels in Th^{3+}.

Resonant Excitation (an example)

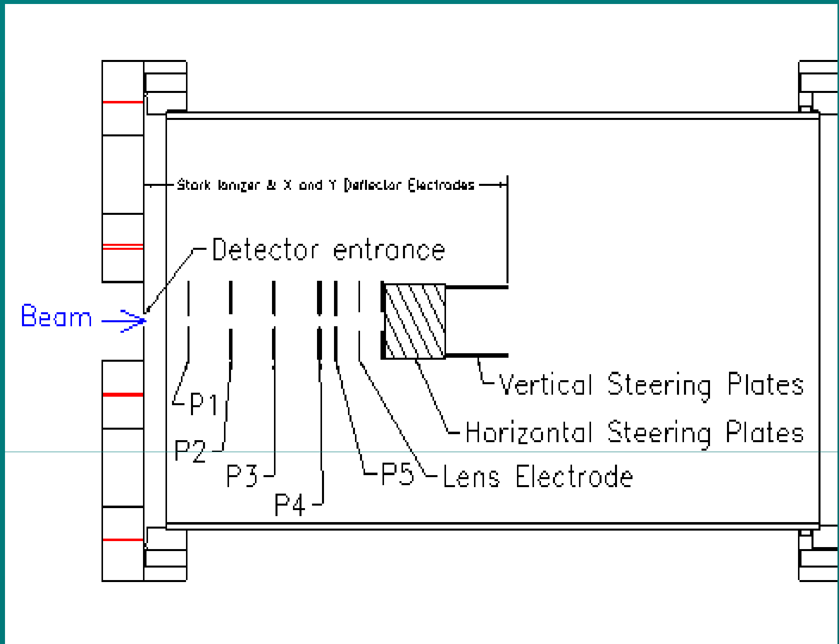


The x-axis is the difference between the CO_2 laser's Doppler-tuned frequency and the hydrogenic transition frequency between the n = 37 and n' = 73 Rydberg levels in Th^{3+}.

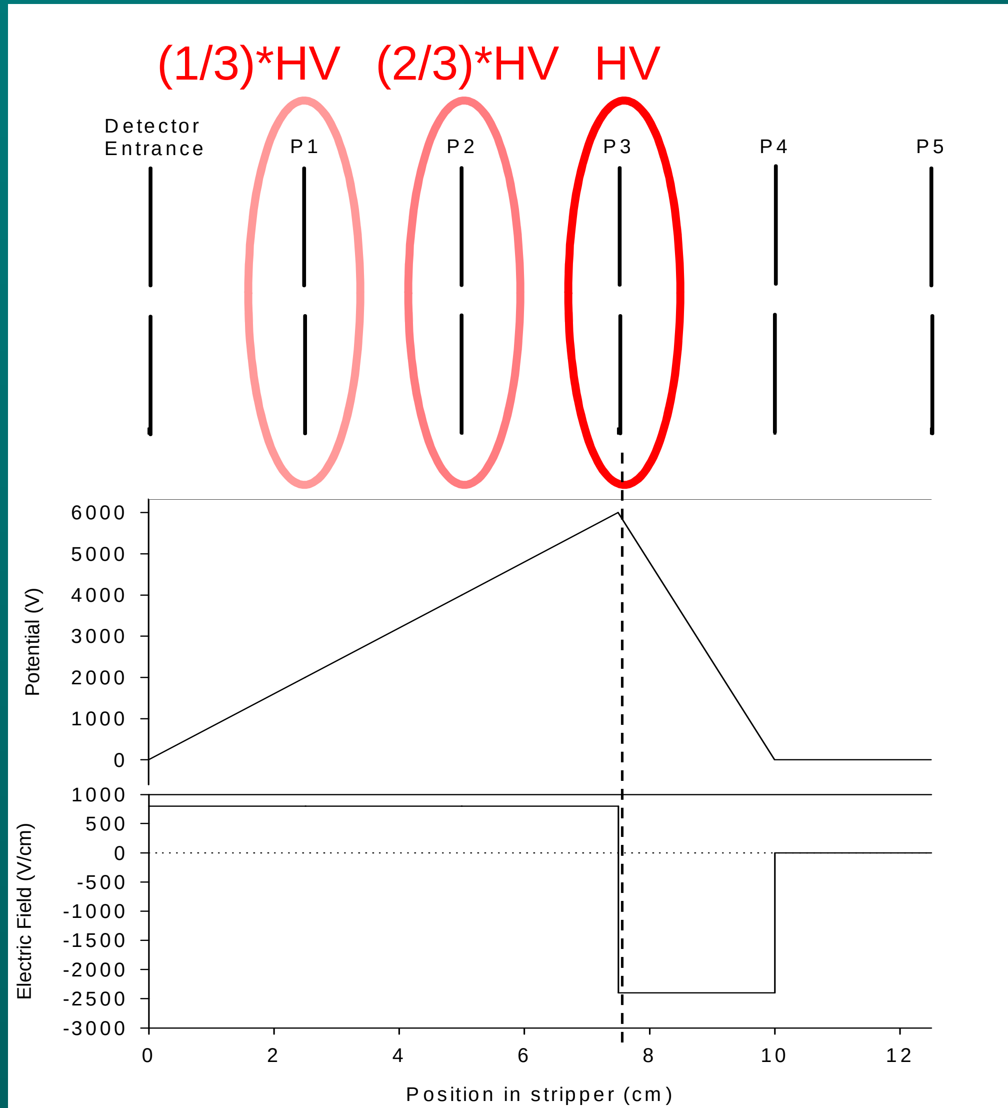
Resonant Excitation: Why use a CO_2 laser?



Stark Ionization & Detection



Electric field is tuned such that only specific upper-states are ionized.



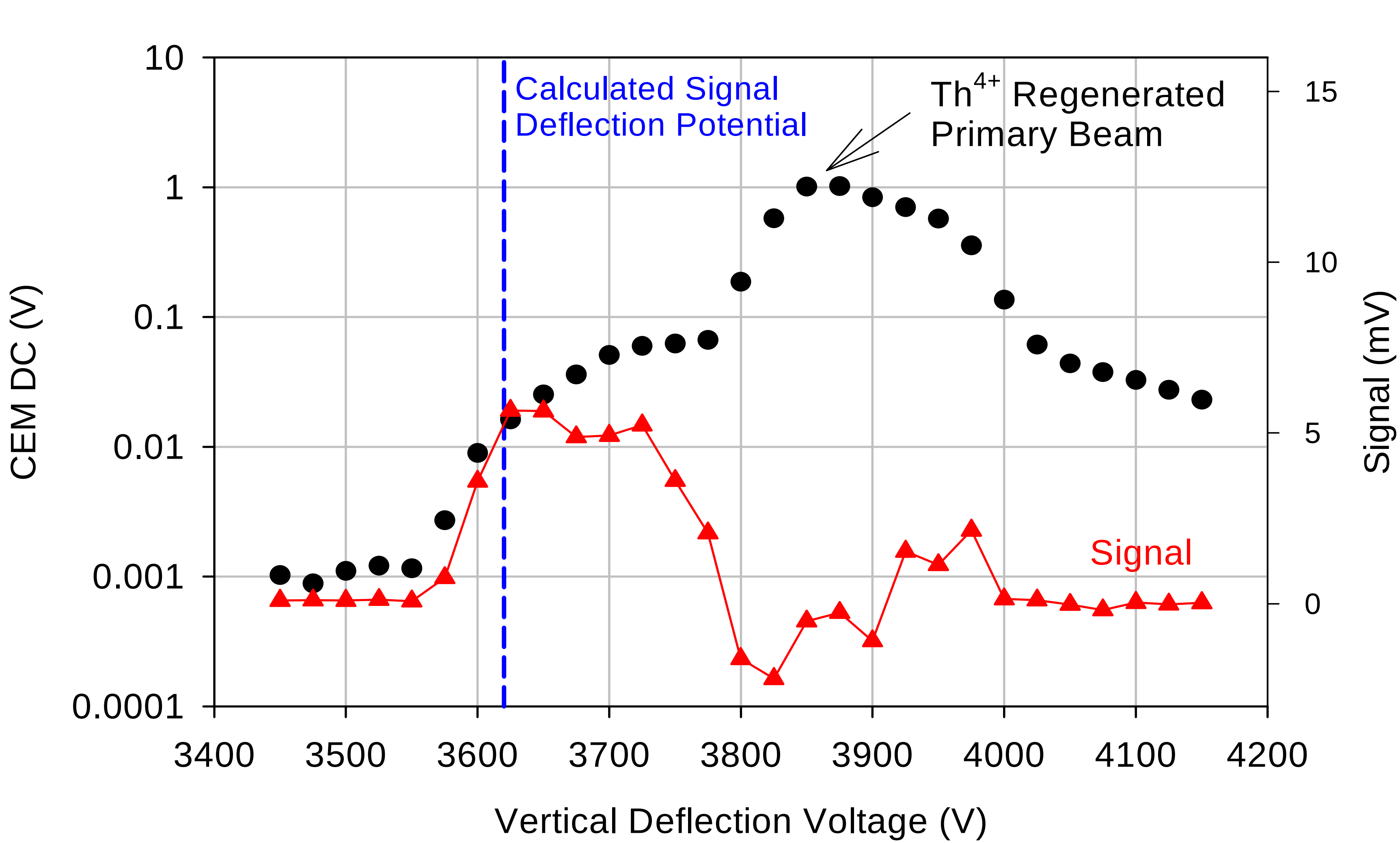
Stark Ionization and Detection

- When ionization occurs in the Stark Ionizer the kinetic energy of the ions is changed by:

$$\Delta KE = e \cdot V_{Stripper}$$

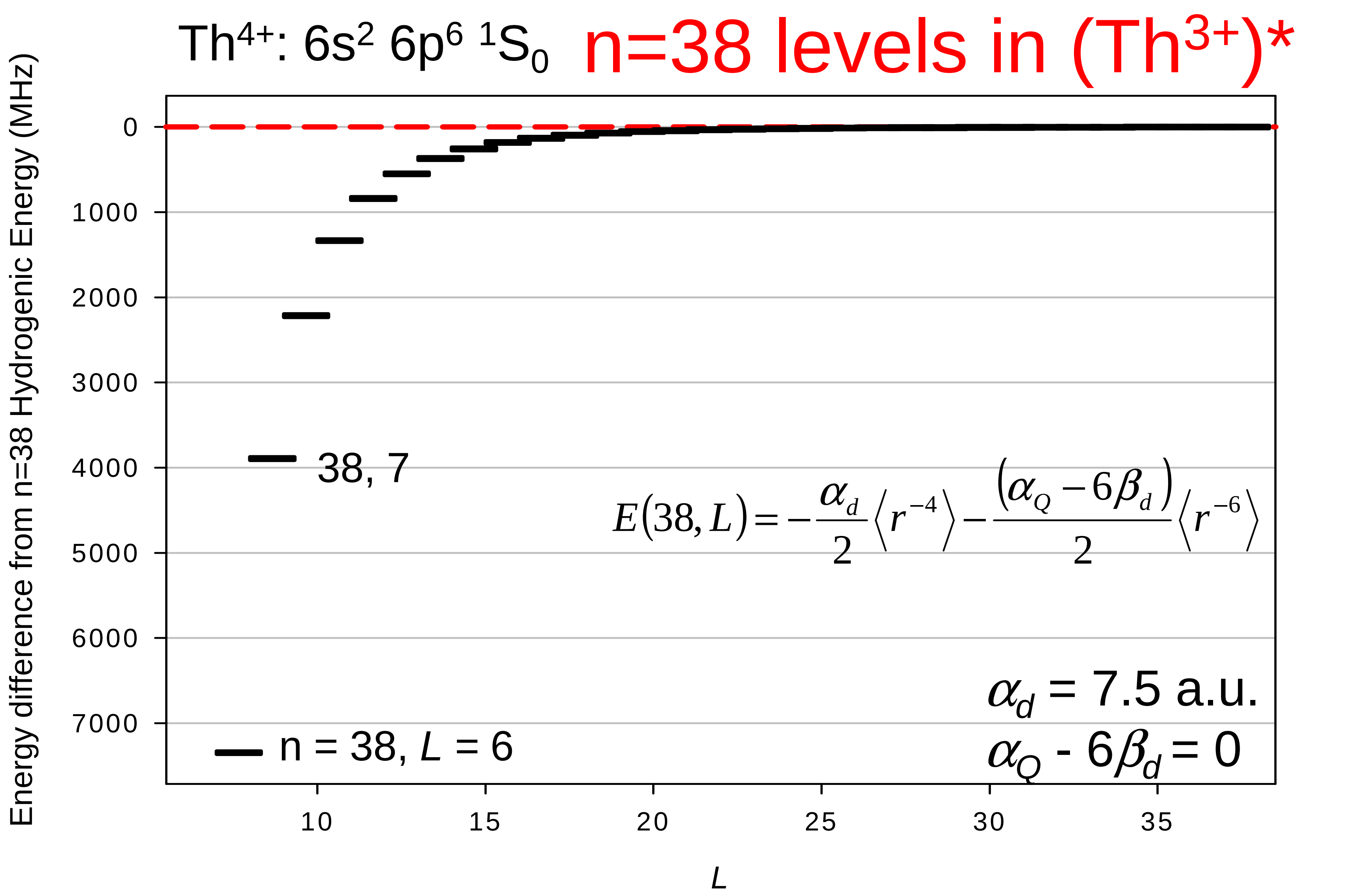
- This "energy tags" the ions formed in the Stark ionizer. Differentiating these ions from ions that are of similar charge formed by other processes.

Energy Tagging in the detector

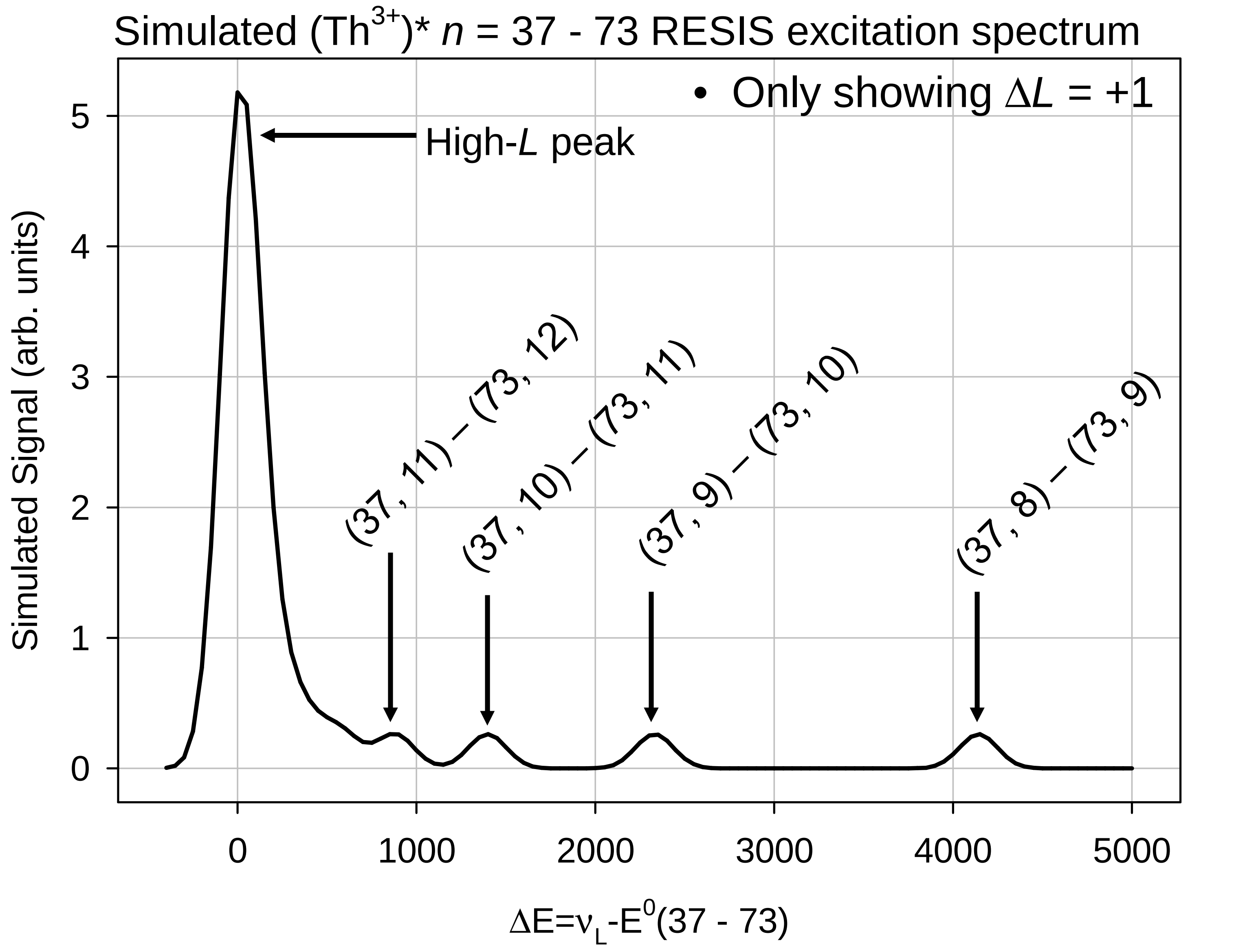


Terminal Potential: +25.0 kV P4 Potential: -6.0 kV

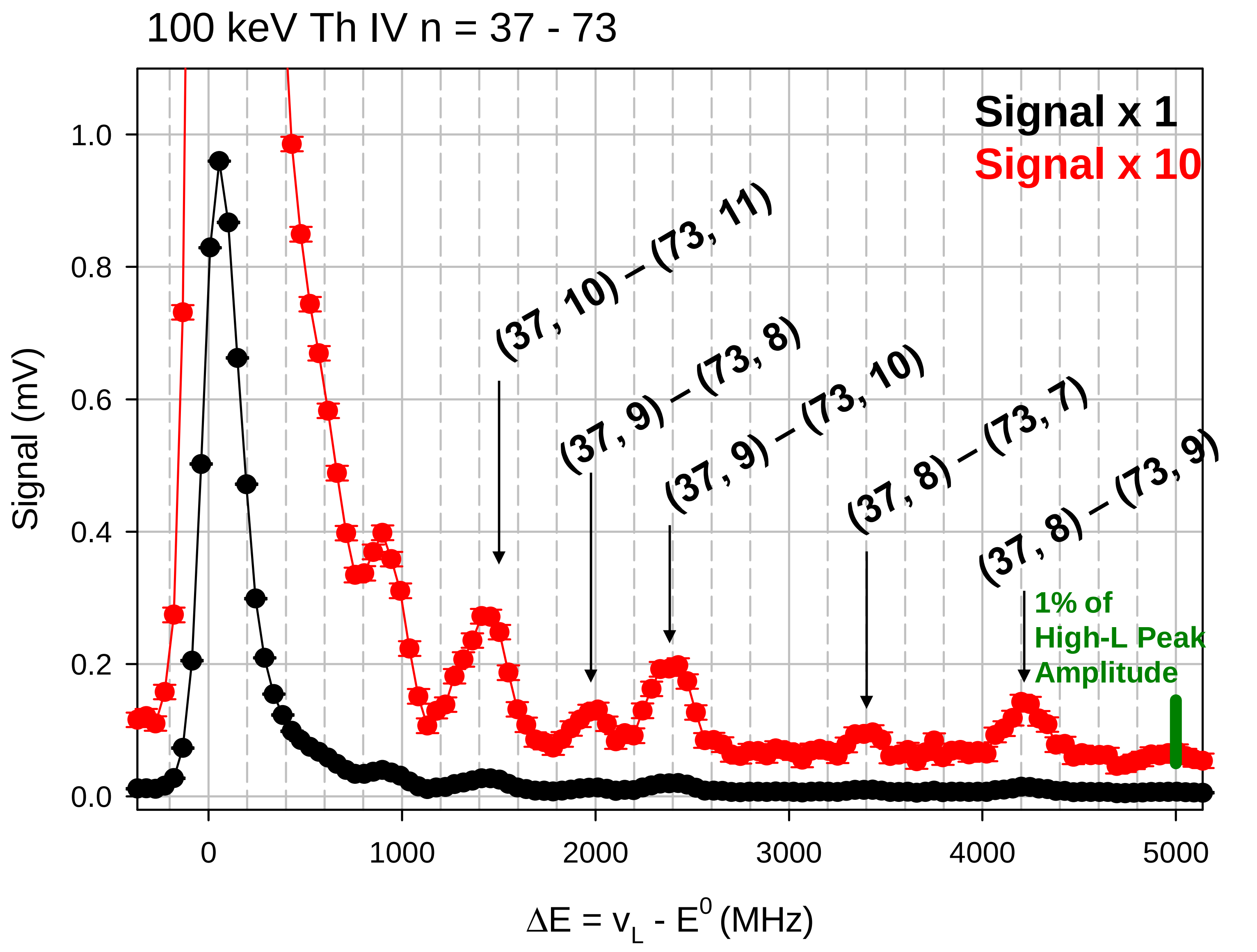
What's a Typical Pattern?



What do we expect to see?



$(Th^{3+})^*$ Fine Structure Observations



$(Th^{3+})^*$ Fine structure observations

- Observed transition energies

$$\Delta E^{Obs} = \nu'_L - \Delta E^0 - \Delta E^{Stark}(n', L')$$

Transition	θ_{Int}	$\upsilon'_L - \Delta E^0$ **(MHz)**	ΔE^{Stark} **(MHz)**	ΔE^{Obs} **(MHz)**
(37, 7) – (76, 8)	67.926(88)º	8094(39)	-1(1)	8095(39)
(37, 10) – (73, 11)	75.850(24)º	1415(11)	1(1)	1414(11)
(37, 9) – (73, 10)	73.836(26)º	2341(11)	1(1)	2340(11)
(37, 8) – (73, 9)	69.786(18)º	4189(8)	1(1)	4188(8)
(37, 7) – (73, 8)	60.918(58)º	8046(24)	-2(2)	8048(24)
(38, 10) – (79, 11)	106.776(28)º	1335(13)	1(1)	1334(13)
(38, 9) – (79, 10)	104.898(24)º	2186(12)	2(2)	2184(12)
(38, 8) – (79, 9)	101.168(34)º	3892(16)	3(3)	3892(16)

Rydberg Level Energy Deviations: How they are related to the properties of the ion core?

- Energy deviations can be described using the "Long Range Polarization" model
  - The weak interaction of the Rydberg electron with the ion core is treated as a small perturbation to the energy of the Rydberg electron.
  - Two key assumptions:
    1) Rydberg electron is distinguishable from all other electrons
    2) Rydberg electron never penetrates the space of the ion core
- Non-relativistic Hamiltonian for the full system, ignoring spin:

$$
\begin{aligned}
H &= \left[\sum_{i=1}^{N-1}\left(\frac{|\vec{p}_i|}{2m}-\frac{Z}{r_i}\right)+\sum_{i>j}^{N-1}\frac{1}{r_{ij}}\right]+\left[\frac{|\vec{p}_N|^2}{2m}-\frac{Q}{r_N}\right]+\left[\sum_{i=1}^{N-1}\frac{1}{r_{iN}}-\frac{(N-1)}{r_N}\right] \\
&= H_{Core}+H_{Ryd}^{0}+V
\end{aligned}
$$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

$$H = \left[\sum_{i=1}^{N-1}\left(\frac{|\vec{p}_i|}{2m} - \frac{Z}{r_i}\right) + \sum_{i>j}^{N-1}\frac{1}{r_{ij}}\right] + \left[\frac{|\vec{p}_N|^2}{2m} - \frac{Q}{r_N}\right] + \left[\sum_{i=1}^{N-1}\frac{1}{r_{iN}} - \frac{(N-1)}{r_N}\right]$$

$$= \quad H_{Core} + H^0_{Ryd} + \cancel{V}$$

ignore temporarily

Ignoring V, Hamiltonian is a sum of two terms: $H = H_{Core} + H^0_{Ryd}$

Zeroth order wave function for the system: $\Psi^0 = \Psi^0_{Core} \otimes \Psi^0_{Ryd}$

- Zeroth order core wave function is unknown
- Zeroth order Rydberg wave function is hydrogenic

Zeroth order energies: $E^{[0]} = E_{Core}(\lambda, J) - \dfrac{Q^2}{2n^2}$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

- Recall the small perturbation *V*:

$$V=\sum_{i=1}^{N-1}\frac{1}{r_{iN}}-\frac{(N-1)}{r_N}$$

- Re-write using multipole expansion:

$$V=\sum_{\kappa=0}^{\infty}\sum_{i=1}^{N-1}\left(\frac{r_<^{\kappa}}{r_>^{\kappa+1}}\right)C^{[\kappa]}(\Omega_i)\bullet C^{[\kappa]}(\Omega_N)-\frac{(N-1)}{r_N}$$

- Non-penetrating states:

$$V=\sum_{\kappa=1}^{\infty}\sum_{i=1}^{N-1}\left(\frac{r_i^{\kappa}}{r_N^{\kappa+1}}\right)C^{[\kappa]}(\Omega_i)\bullet C^{[\kappa]}(\Omega_N)$$

monopole term vanishes because: $|r_N|\geq|r_i|$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

$$H = H_{Core} + H_{Ryd}^{0} + \sum_{\kappa=1}^{\infty}\sum_{i=1}^{N-1}\left(\frac{r_i^{\kappa}}{r_N^{\kappa+1}}\right)C^{[\kappa]}(\Omega_i)\bullet C^{[\kappa]}(\Omega_N)$$

- Apply time independent perturbation theory:

$$E = E^{[0]} + E^{[1]} + E^{[2]} + \cdots$$

$$E^{[1]} = \left\langle \Psi^0 \middle| V \middle| \Psi^0 \right\rangle = 0$$

$E^{[1]} = 0$ for $^1S_0$ cores

$$E^{[2]} = \sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{E\left(\Psi^0\right) - E\left(\Psi'^0\right)}$$

$$\vdots$$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

$$H = H_{Core} + H^0_{Ryd} + \sum_{\kappa=1}^{\infty} \sum_{i=1}^{N-1} \left(\frac{r_i^{\kappa}}{r_N^{\kappa+1}} \right) C^{[\kappa]}(\Omega_i) \bullet C^{[\kappa]}(\Omega_N)$$

- Use time independent perturbation theory:

$$E = E^{[0]} + E^{[1]} + E^{[2]} + \cdots$$

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$$E^{[2]} = \sum_{\Psi'^0 \neq \Psi^0} \frac{\left| \left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle \right|^2}{E(\Psi^0) - E(\Psi'^0)}$$

$$\vdots$$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

$$E^{[2]} = \sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{E(\Psi) - E(\Psi')} = -\sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core} + \Delta E_{Ryd}}$$

$$\Delta E_{Core} = E(\lambda', J') - E(\lambda, J)$$

$$\Delta E_{Ryd} = E(n', L') - E(n, L)$$

- In the limit that $\Delta E_{Ryd} << \Delta E_{Core}$:

$$\frac{1}{\Delta E_{Core} + \Delta E_{Ryd}} \approx \frac{1}{\Delta E_{Core}} - \frac{\Delta E_{Ryd}}{(\Delta E_{Core})^2} + \frac{(\Delta E_{Ryd})^2}{(\Delta E_{Core})^3} - \cdots$$

Use the "Adiabatic Expansion"

Rydberg Level Energy Deviations: How they are related to the properties of the ion core?

- Apply the adiabatic expansion …

$$E^{[2]} \approx -\sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core}} + \sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{\left(\Delta E_{Core}\right)^2} \Delta E_{Ryd} + \cdots$$

… and skip a lot of algebra:

$$E^{[2]} \approx -\sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| \vec{D} \bullet \frac{C^{[1]}(\Omega_N)}{r_N^2} \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core}} - \sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| \overleftrightarrow{Q} \bullet \frac{C^{[2]}(\Omega_N)}{r_N^3} \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core}} + \sum_{\Psi' \neq \Psi} \frac{\left|\left\langle \Psi \middle| \vec{D} \bullet \frac{C^{[1]}(\Omega_{Ryd})}{r_{Ryd}^2} \middle| \Psi' \right\rangle\right|^2}{\left(\Delta E_{Core}\right)^2} \Delta E_{Ryd}$$

$$\vec{D} = \sum_{i=1}^{N-1} r_i \, C^{[1]}(\Omega_i) \qquad \overleftrightarrow{Q} = \sum_{i=1}^{N-1} r_i^2 C^{[2]}(\Omega_i)$$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

- Skip a lot more algebra:

$$\alpha_d = \frac{2}{3}\sum_{n_c'} \frac{\left|\left\langle n_c S \left| \vec{D} \right| n_c' P \right\rangle\right|^2}{\Delta E_{Core}} \qquad \alpha_Q = \frac{2}{5}\sum_{n_c'} \frac{\left|\left\langle n_c S \left| \overleftrightarrow{Q} \right| n_c' D \right\rangle\right|^2}{\Delta E_{Core}} \qquad \beta_d = \frac{1}{3}\sum_{n_c'} \frac{\left|\left\langle n_c S \left| \vec{D} \right| n_c' P \right\rangle\right|^2}{\left(\Delta E_{Core}\right)^2}$$

$$E^{[2]} \approx -\frac{\alpha_d}{2}\left\langle r^{-4} \right\rangle_{nL} - \frac{\alpha_Q}{2}\left\langle r^{-6} \right\rangle + 3\beta_d \left\langle r^{-6} \right\rangle_{nL}$$

Effects of the interaction of the Rydberg electron with the ion core can be described as a sum of a few parameters and simple radial expectation values!!!

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

- Energy for the full system can be written as:

$$E(\lambda, J, n, L) \approx E(\lambda, J) - \frac{Q^2}{2n^2} - \frac{\alpha_d}{2}\left\langle r^{-4}\right\rangle_{nL} - \frac{(\alpha_Q - 6\beta_d)}{2}\left\langle r^{-6}\right\rangle_{nL} + \cdots$$

$$E(\lambda, J, n, L) \approx E(\lambda, J) - E^0(n) - \left\langle n, L \middle| V_{eff} \middle| n, L\right\rangle$$

$$E(\lambda, J, n, L) \approx E(\lambda, J) - E^0(n) - E^{[1]}_{V_{eff}}(n, L)$$

- Effective Potential:

$$V_{eff} = \frac{\alpha_d}{2r^4} + \frac{(\alpha_Q - 6\beta_d)}{2r^6} + \cdots$$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

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- Energy that I observe can be written as:

$$E(\lambda, J, n, L) \approx -\frac{Q^2}{2n^2} - \frac{\alpha_d}{2}\left\langle r^{-4}\right\rangle_{nL} - \frac{(\alpha_Q - 6\beta_d)}{2}\left\langle r^{-6}\right\rangle_{nL} + \cdots$$

$$E(\lambda, J, n, L) \approx -E^0(n) - \left\langle n, L \middle| V_{eff} \middle| n, L \right\rangle$$

$$E(\lambda, J, n, L) \approx -E^0(n) - E^{[1]}_{V_{eff}}(n, L)$$

- Effective Potential:

$$V_{eff} = \frac{\alpha_d}{2r^4} + \frac{(\alpha_Q - 6\beta_d)}{2r^6} + \cdots$$

Th^{4+} Polarizability

- The observed energy difference between Rydberg levels:

$$\Delta E^{\mathrm{Obs}}(n, L - n', L') = E^{[1]}(n', L') - E^{[1]}(n, L)$$

- Neglects two important contributions:
  - Energy contributions due to the kinetic energy of the electron: $$E^{\mathrm{Rel}}(n, L) = \frac{\alpha^2 Z^4}{2n^4}\left(\frac{3}{4} - \frac{n}{L + \frac{1}{2}}\right)$$
  - Application of V_{eff} in 2nd order:

$E^{[2]}$ is computed using the analytical formula developed by Drake and Swainson.

Th^{4+} Polarizability

$$E^{[1]}_{V_{eff}}(n,L) = \langle n.L | V_{eff} | n,L \rangle = \frac{\alpha_d}{2}\langle r^{-4}\rangle_{n,L} + \frac{(\alpha_Q - 6\beta_d)}{2}\langle r^{-6}\rangle_{n,L} + \cdots$$

$$E^{\mathrm{Rel}}(n,L) = \frac{\alpha^2 Z^4}{2n^4}\left(\frac{3}{4} - \frac{n}{L+\frac{1}{2}}\right)$$

$$E^{[2]}_{V_{eff}}(n,L) = \text{Big formula![1]}$$

- The observed energy difference between Rydberg levels:

$$\begin{aligned}\Delta E^{\mathrm{Obs}}(n,L-n',L') &= \left[E^{[1]}(n',L') + E^{[2]}(n',L') + E^{\mathrm{Rel}}(n',L')\right] \\ &\quad - \left[E^{[1]}(n,L) + E^{[2]}(n,L) + E^{\mathrm{Rel}}(n,L)\right] \\ &= \Delta E^{[1]} + \Delta E^{[2]} + \Delta E^{\mathrm{Rel}}\end{aligned}$$

[1] G. W. F. Drake and R. A. Swainson, Phys. Rev. A **44,** 5448 (1991).

Th^{4+} Polarizability

- Isolate $\Delta E^{[1]}$: $\Delta E^{[1]}_{V_{eff}} = \Delta E^{\mathrm{Obs}} - \Delta E^{[2]}_{V_{eff}} - \Delta E^{\mathrm{Rel}}$

Transition (n, L) – (n', L')	ΔE^{obs} (MHz)	$\Delta E^{[2]}$ (MHz)	ΔE^{rel} (MHz)	$\Delta E^{[1]}$ (MHz)
(37, 7) – (76, 8)	8095(39)	38.626(365)	89.1	7968(39)
(37, 10) – (73, 11)	1414(11)	0.876(14)	57.5	1356(11)
(37, 9) – (73, 10)	2340(11)	2.695(43)	65.5	2277(12)
(37, 8) – (73, 9)	4188(8)	9.403(149)	75.3	4103(8)
(37, 7) – (73, 8)	8048(24)	38.479(610)	87.7	7922(24)
(38, 10) – (79, 11)	1334(13)	0.816(13)	54.7	1279(13)
(38, 9) – (79, 10)	2184(12)	2.508(40)	62.1	2117(11)
(38, 8) – (79, 9)	3892(16)	8.739(139)	71.3	3809(16)

Th^{4+} Polarizability

- Isolating $\Delta E^{[1]}$ amounts to isolating contributions due to V_{eff}:

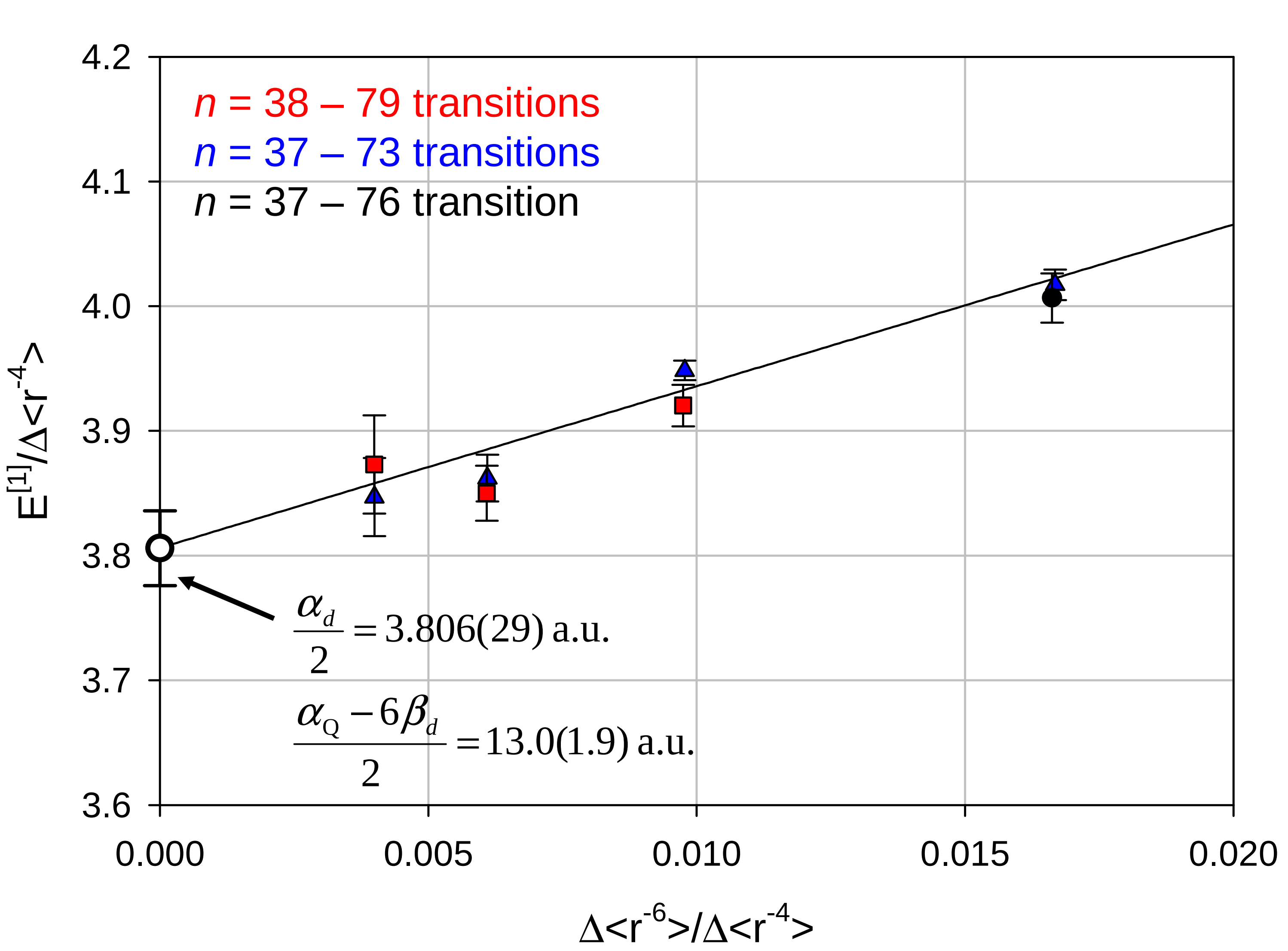
$$\Delta E^{[1]}_{V_{eff}} = \frac{\alpha_d}{2}\Delta\left\langle r^{-4}\right\rangle + \frac{\left(\alpha_Q - 6\beta_d\right)}{2}\Delta\left\langle r^{-6}\right\rangle + \cdots$$

- Scale by $\Delta\langle r^{-4}\rangle$:

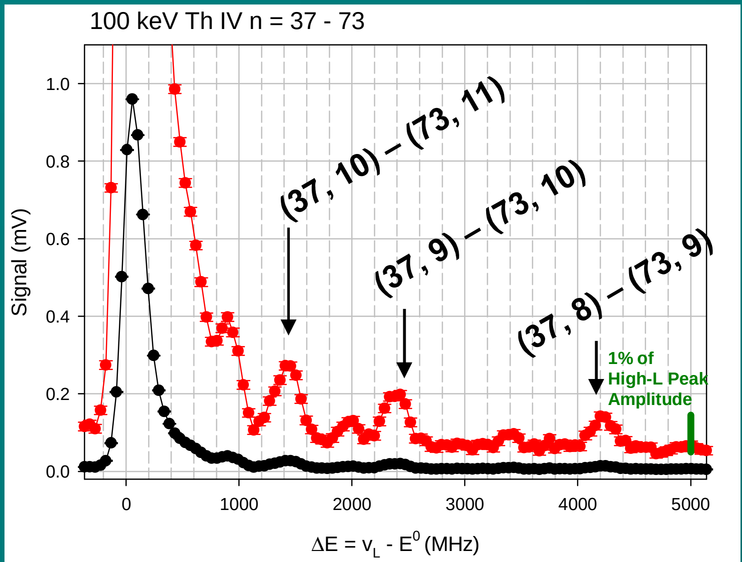
$$\frac{\Delta E^{[1]}_{V_{eff}}}{\Delta\left\langle r^{-4}\right\rangle} = \frac{\alpha_d}{2} + \frac{\alpha_Q - 6\beta_d}{2}\frac{\Delta\left\langle r^{-6}\right\rangle}{\Delta\left\langle r^{-4}\right\rangle} + \cdots \approx A_4 + A_6\frac{\Delta\left\langle r^{-6}\right\rangle}{\Delta\left\langle r^{-4}\right\rangle}$$

Looks like a line if we ignore higher order terms!
Intercept = $\alpha_d/2$

Th^{4+} Polarizability



(Th^{3+})* Fine Structure Observations



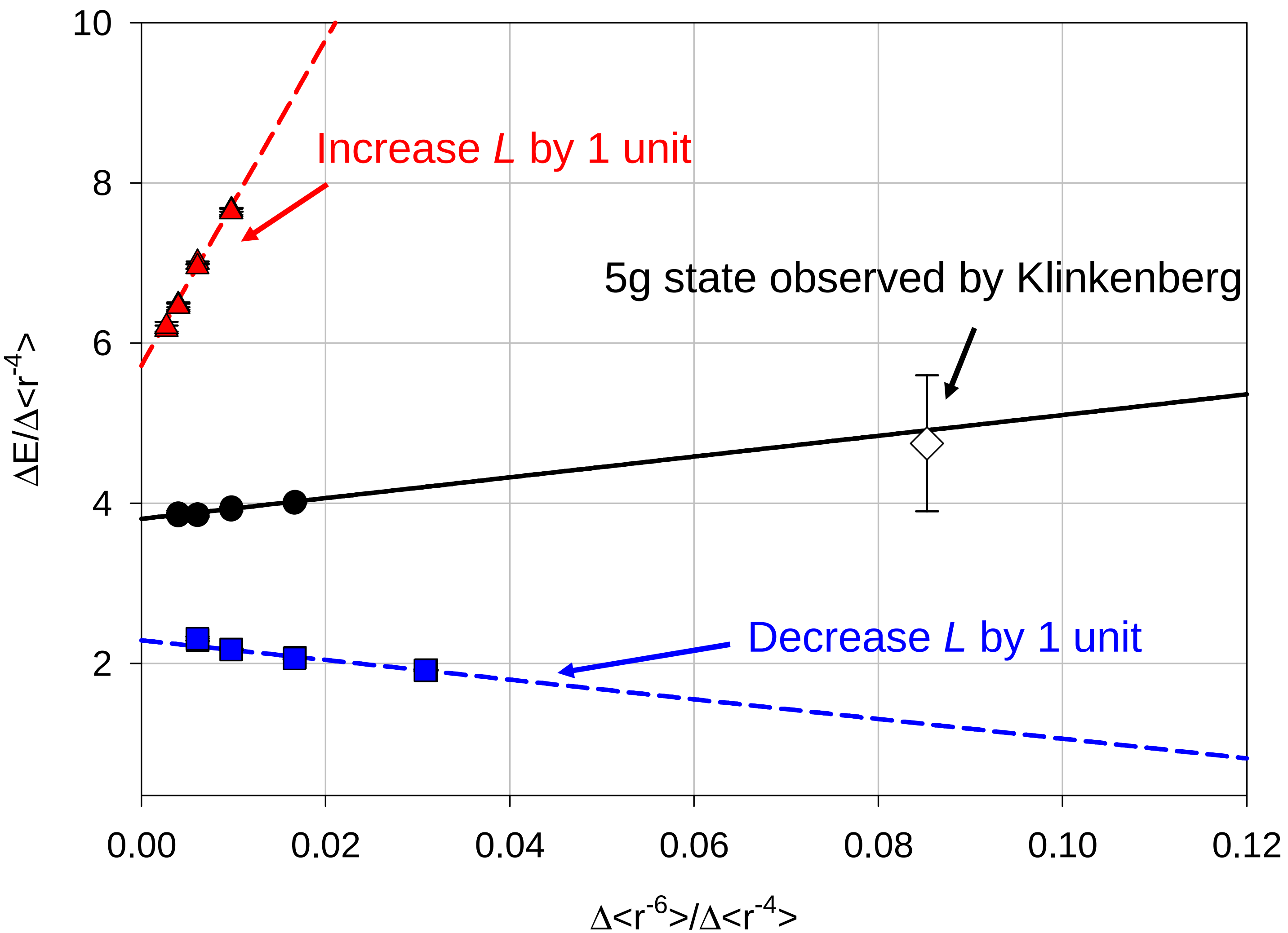
- Clear pattern of resolved transitions is not enough to identify the transitions.

- Rely on theoretical estimates or prior optical spectroscopy observations of lower lying states
- U. I. Safronova theoretical estimate
  - α_d = 7.75 a.u.
  - accurate within a factor of 2.
- P.F. Klinkenberg (sparse) optical spectroscopy [1]
  - Highest *n*, *L* state observed in Th^{3+}: 5g

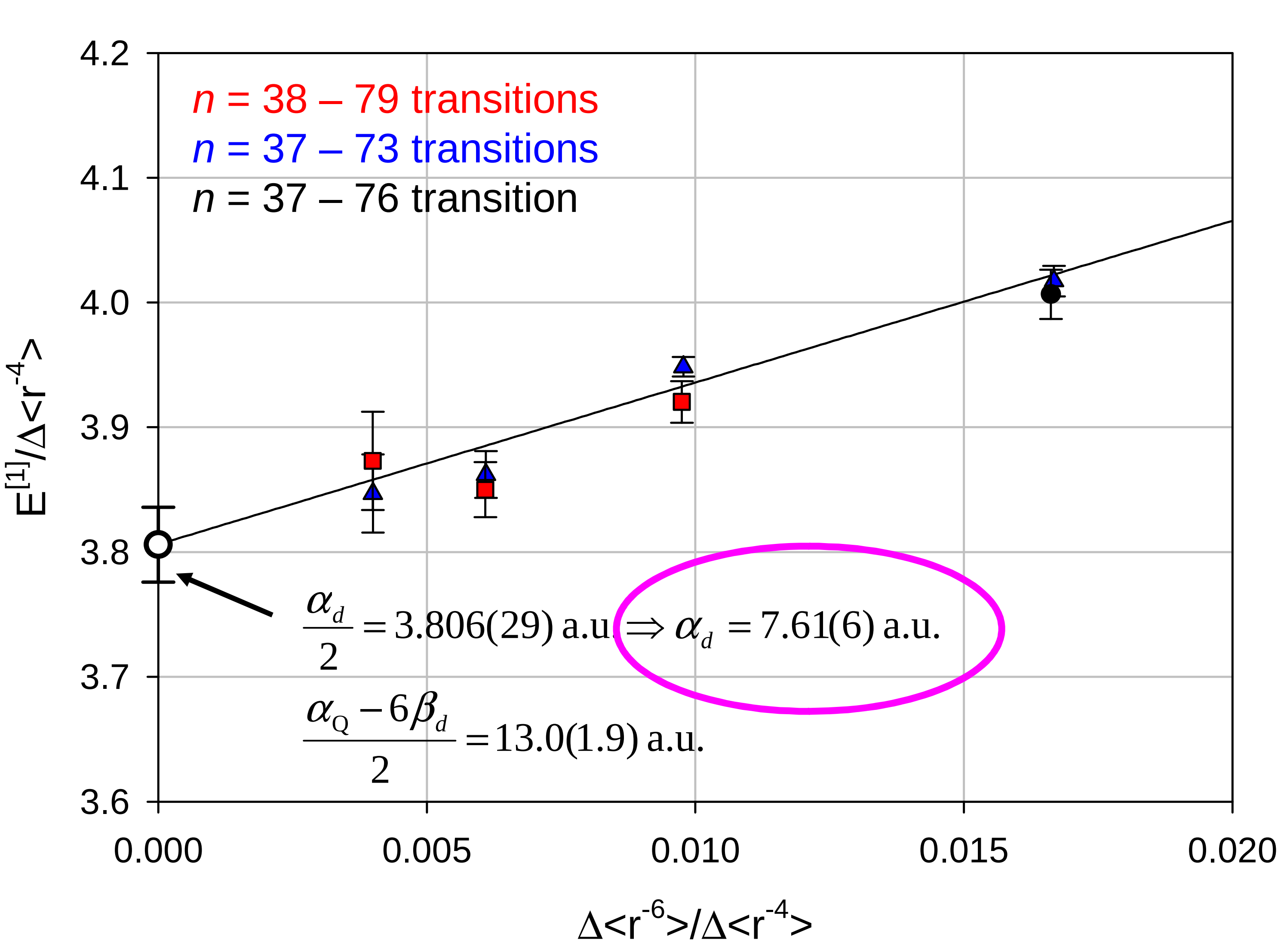
[1] P. F. A. Klinkenberg, Physica B+C (Utrecht) **151**, 552 (1988).

Th^{4+} Polarizability

All 3 choices of *L* values can be fit using polarization model.



Th^{4+} Polarizability



Th^{4+} Conclusions

Th^{4+} Core Property	Experimentally determined value (a.u.)	Theoretically Determined value (a.u.)	Comparison of Theory to Experiment
α_d	7.61(6)	10.26 [1] 8.96 [2] 7.75 [3] 7.699 [4]	1.348(11) 1.177(9) 1.018(8) 1.012(8)
$\alpha_Q - 6\beta_d$	26(4)	--	--
β_d	--	3.1(2) [5]	
α_Q	45(4)	29 [5]	1.55(14)

[1] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier Scientific Pub., Amsterdam, 1976).

[2] A. Derevianko, *private communication,* (2010).

[3] U. I. Safronova, W. R. Johnson, and M. S. Safronova, Phys. Rev. A **76,** 042504 (2007).

[4] A. Borschevsky and P. Schwerdtfeger, *private communication,* (2010).

[5] M. Safronova, *private communication*, (2010).

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Relativistic methods seem to be very close to my observations!

[1] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier Scientific Pub., Amsterdam, 1976).

[2] A. Derevianko, *private communication,* (2010).

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β_d	--	3.1(2) [5]	
α_Q	45(4)	29 [5]	1.55(14)

Not sure why the discrepancy here. Terms proportional to $\langle r^{-8} \rangle$, that were neglected in the linear fit to the data, could be important.

[5] M. Safronova, *private communication*, (2010).

Th^{4+} Conclusions

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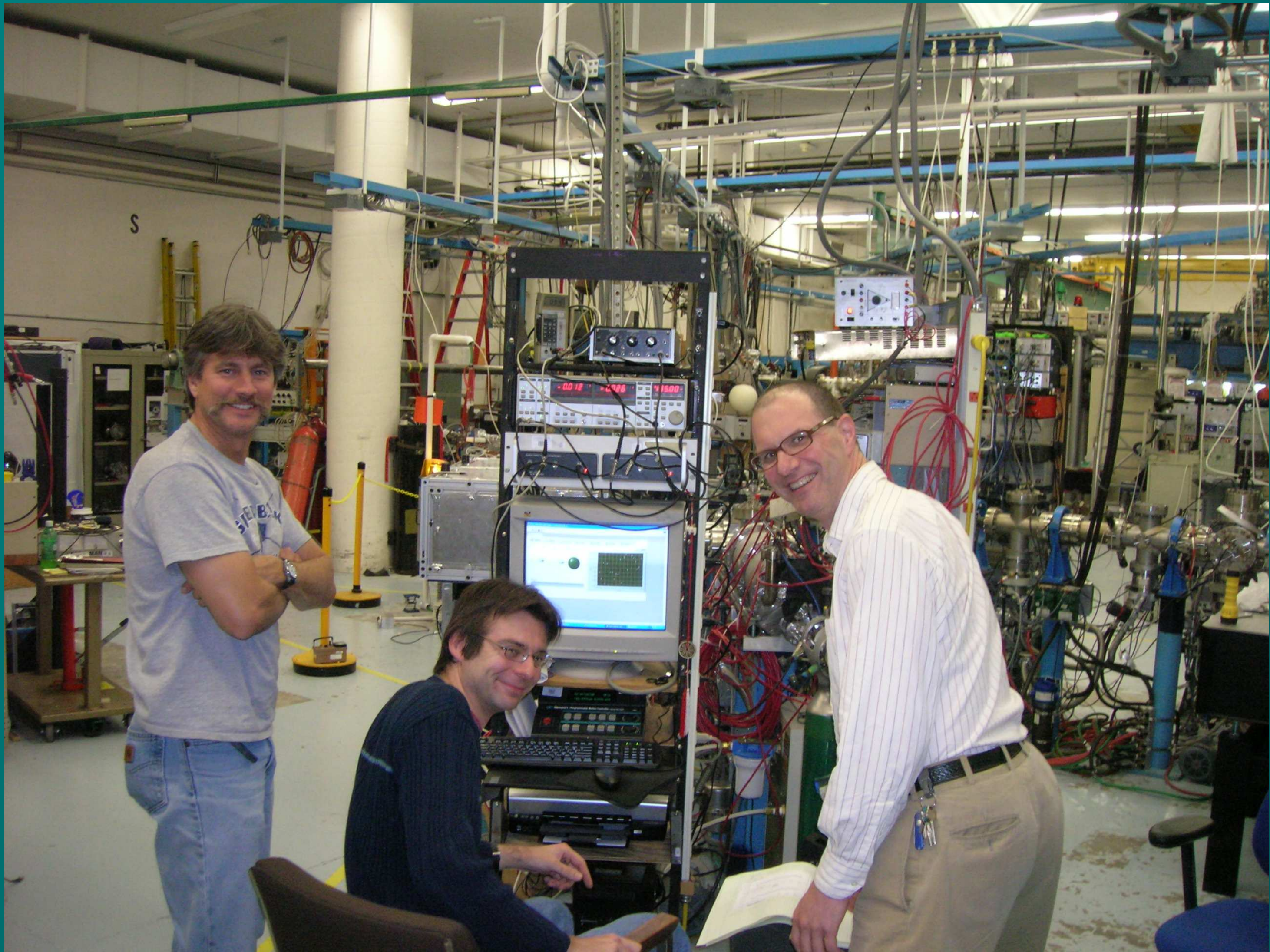
Colorado State University



Rydberg Level Energy Deviations: How they are related to the properties of the ion core?

$$E^{[2]} \approx -\sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core}} + \sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| V \middle| \Psi'^0 \right\rangle\right|^2}{\left(\Delta E_{Core}\right)^2} \Delta E_{Ryd} + \cdots$$

$$\approx E^{[2]}_{Ad} + E^{[2]}_{NAd} + \cdots$$

- Use the multipole expansion:

$$E^{[2]}_{Ad} \approx -\sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| \vec{D} \bullet \frac{C^{[1]}(\Omega_N)}{r_N^2} \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core}} - \sum_{\Psi'^0 \neq \Psi^0} \frac{\left|\left\langle \Psi^0 \middle| \overleftrightarrow{Q} \bullet \frac{C^{[2]}(\Omega_N)}{r_N^3} \middle| \Psi'^0 \right\rangle\right|^2}{\Delta E_{Core}}$$

$$E^{[2]}_{NAd} \approx \sum_{\Psi' \neq \Psi} \frac{\left|\left\langle \Psi \middle| \vec{D} \bullet \frac{C^{[1]}(\Omega_{Ryd})}{r_{Ryd}^2} \middle| \Psi' \right\rangle\right|^2}{\left(\Delta E_{Core}\right)^2} \Delta E_{Ryd}$$

$$\vec{D} = \sum_{i=1}^{N-1} r_i \, C^{[1]}(\Omega_i)$$

$$\overleftrightarrow{Q} = \sum_{i=1}^{N-1} r_i^2 C^{[2]}(\Omega_i)$$

Rydberg Level Energy Deviations:
How they are related to the properties of the ion core?

- Define properties of the ion core in terms of the dipole and quadrupole operators:

$$\alpha_d = \frac{2}{3}\sum_{n_c'} \frac{\left|\langle n_c S|\vec{D}|n_c' P\rangle\right|^2}{\Delta E_{Core}}$$

Dipole polarizability

$$\alpha_Q = \frac{2}{5}\sum_{n_c'} \frac{\left|\langle n_c S|\overleftrightarrow{Q}|n_c' D\rangle\right|^2}{\Delta E_{Core}}$$

Quadrupole polarizability

$$\beta_d = \frac{1}{3}\sum_{n_c'} \frac{\left|\langle n_c S|\vec{D}|n_c' P\rangle\right|^2}{\left(\Delta E_{Core}\right)^2}$$

First non-adiabatic correction to the Dipole polarizability