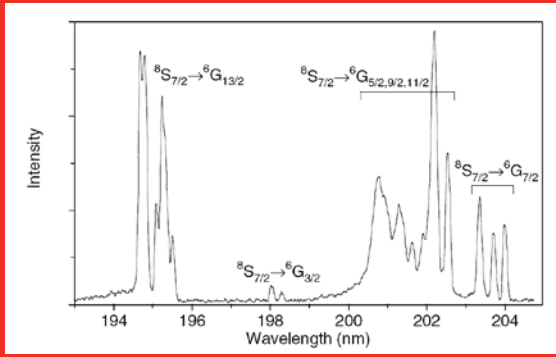
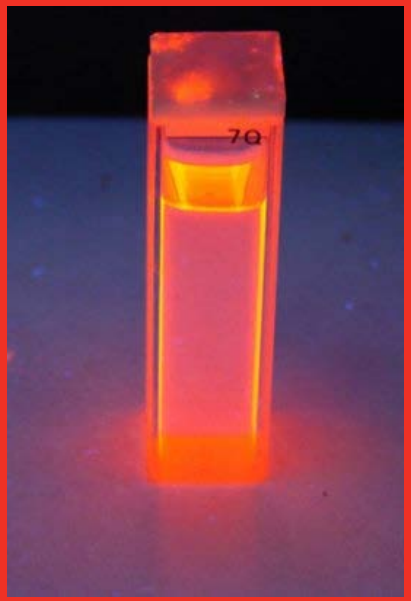
Electronic Structure and Transition Intensities in Rare-Earth Materials





Michael F Reid

School of Physical and Chemical Sciences
Te Kura Matū
University of Canterbury
Christchurch, New Zealand

http://www.phys.canterbury.ac.nz

The Dodd-Walls Centre
for Photonic and Quantum Technologies

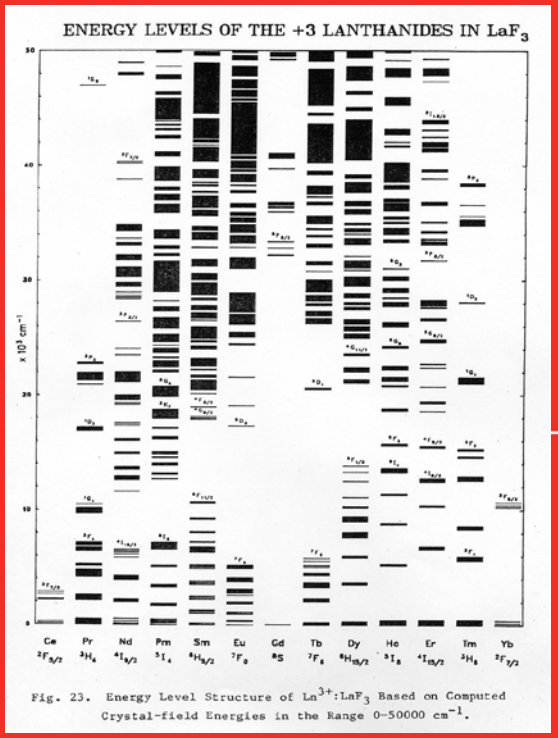
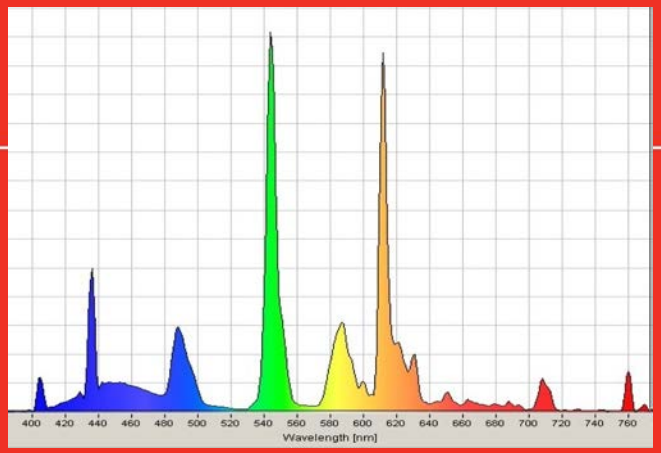


Fig. 23. Energy Level Structure of $Ln^{3+}:LaF_3$ Based on Computed Crystal-field Energies in the Range 0–50000 cm^{-1}.



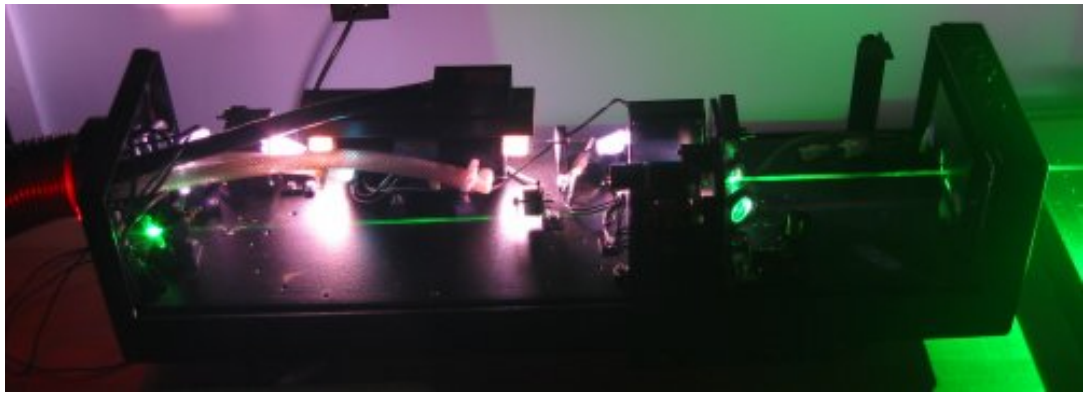
January 2018 v01

UC
UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

Outline

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

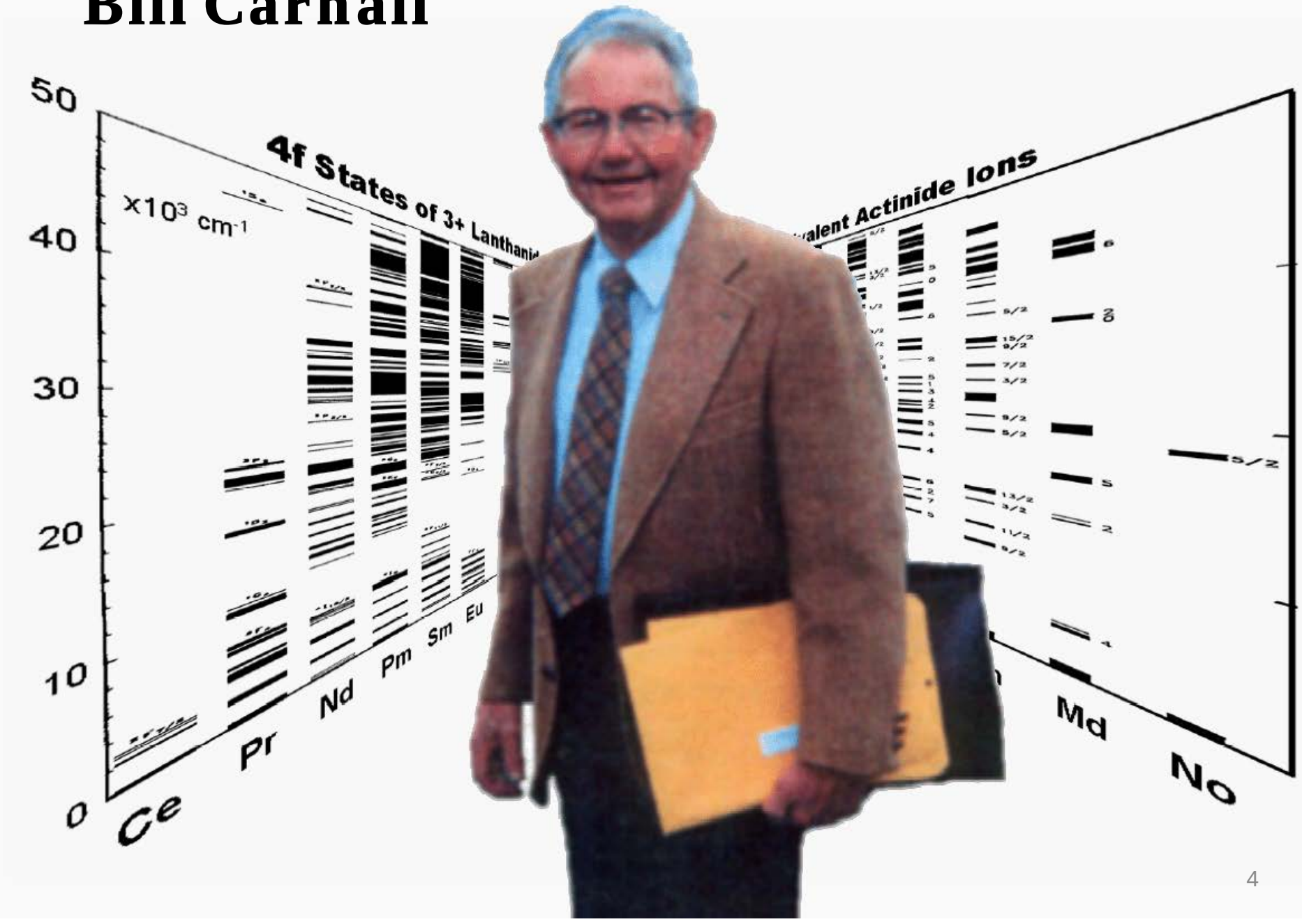
- Background on rare-earth (lanthanide) ions.
- States and transitions
- Effective Hamiltonian for $4f^N$
- Some simple calculations of energy levels
- Transition intensities
- $4f^{N-1}5d$
- Ab-initio calculations



Gerhard Dieke

Johns Hopkins 1950-1965

Bill Carnall



1960's Theory: Judd, Ofelt, Wybourne

Filling of orbitals

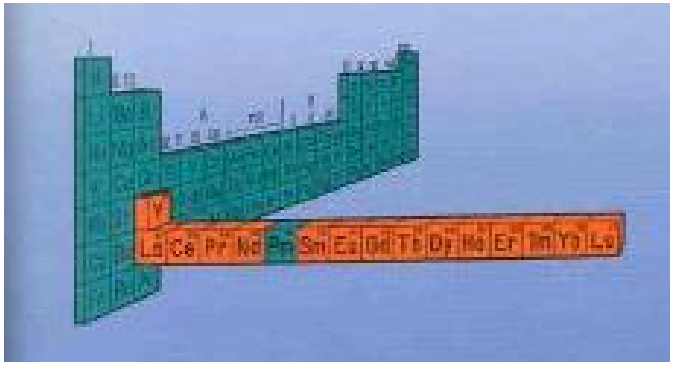
s

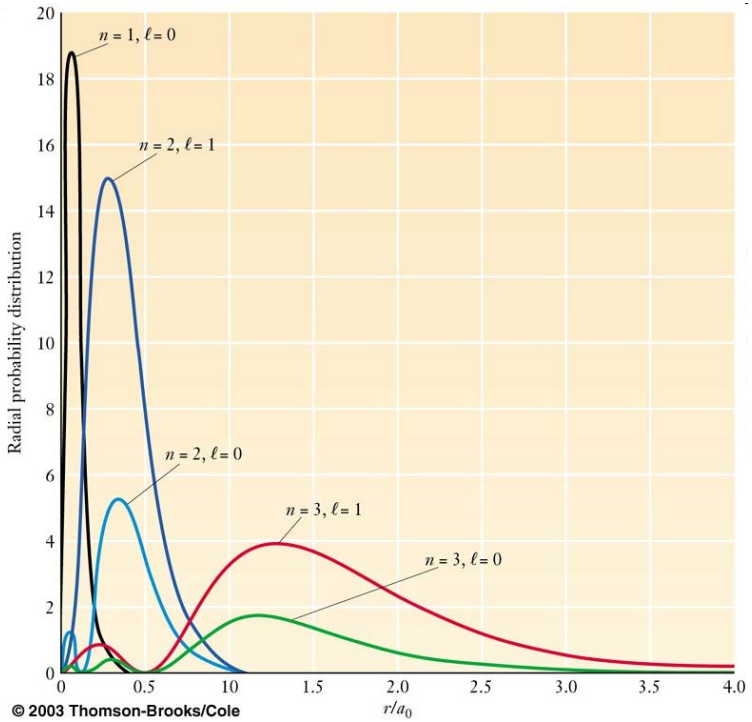
p

d

f

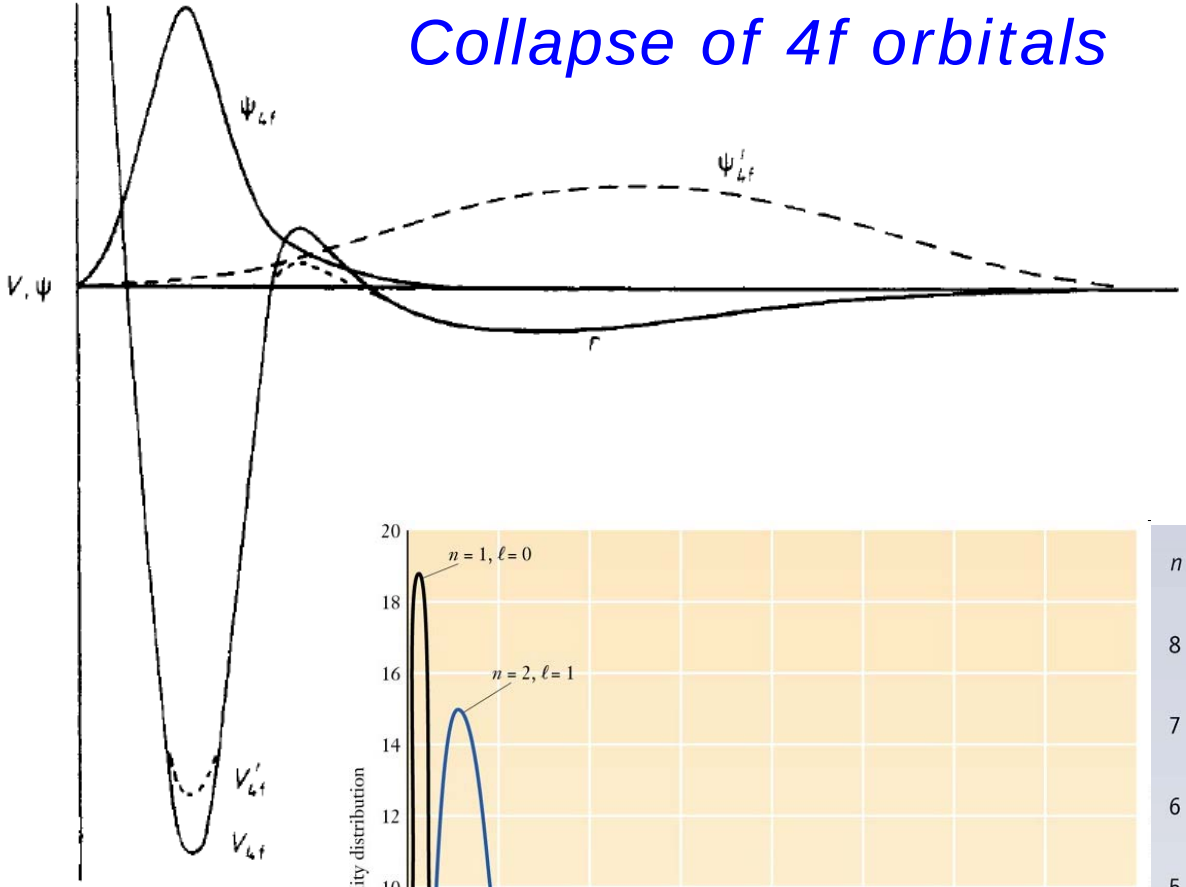
s

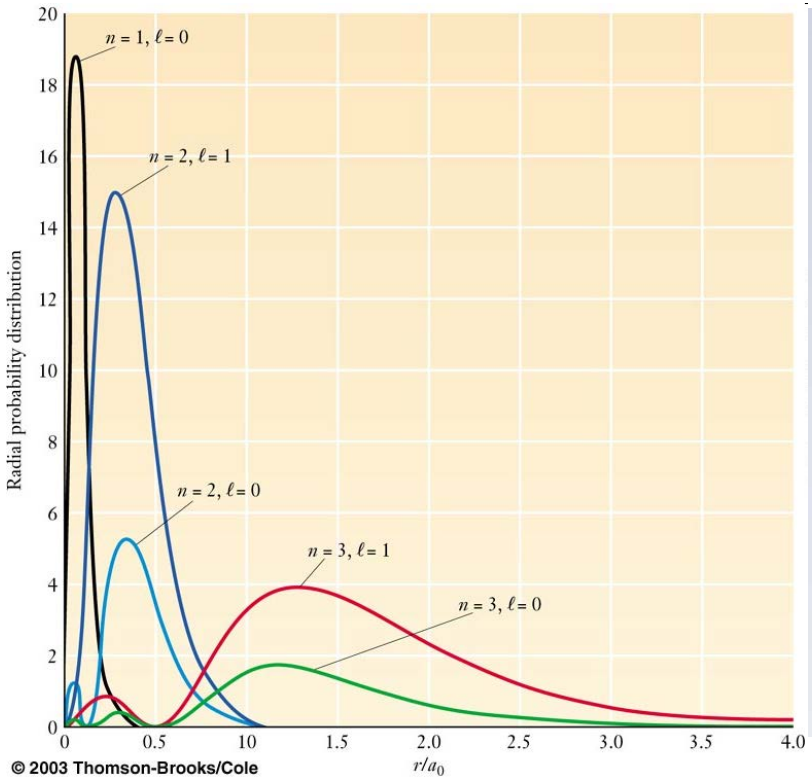


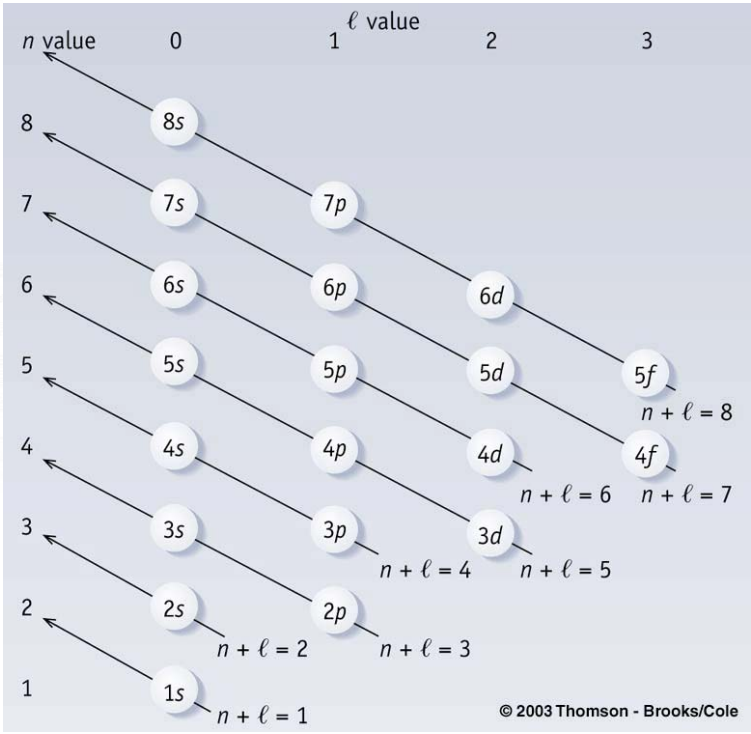


Collapse of 4f orbitals

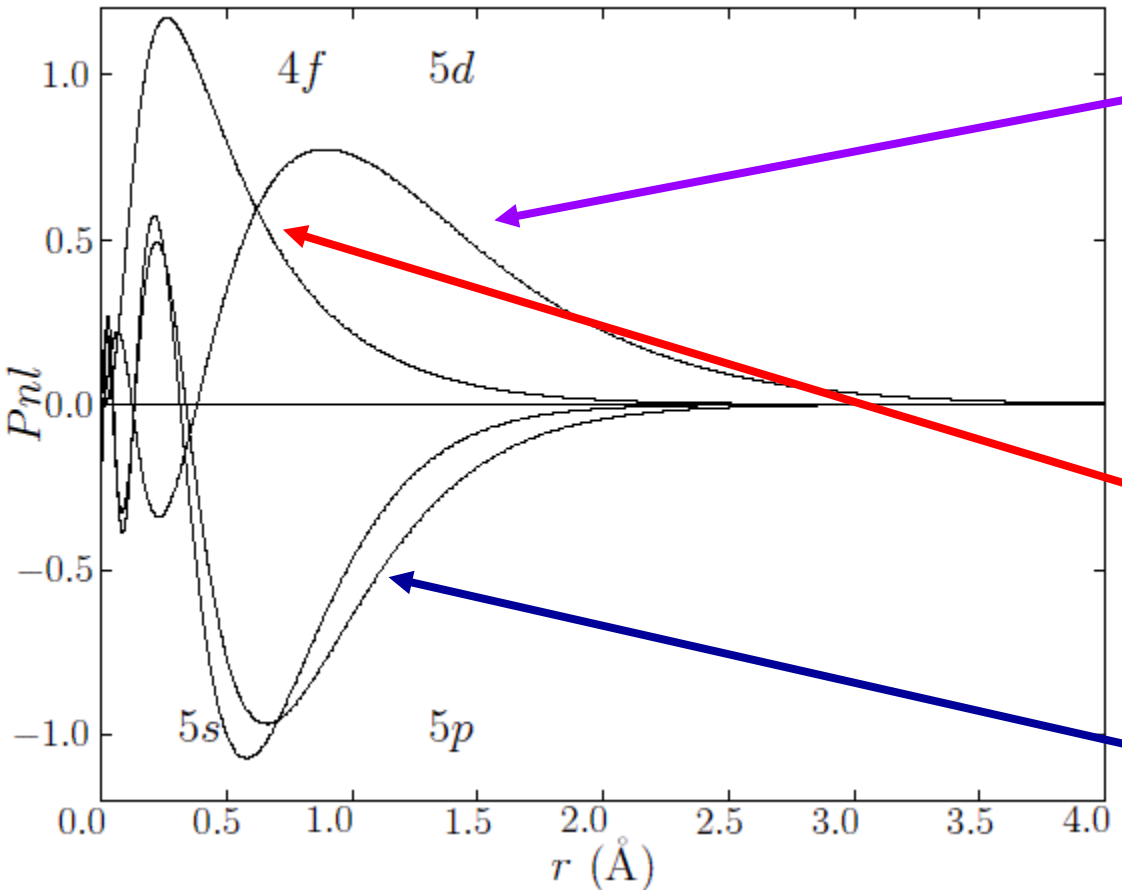
JP Connerade, 1982

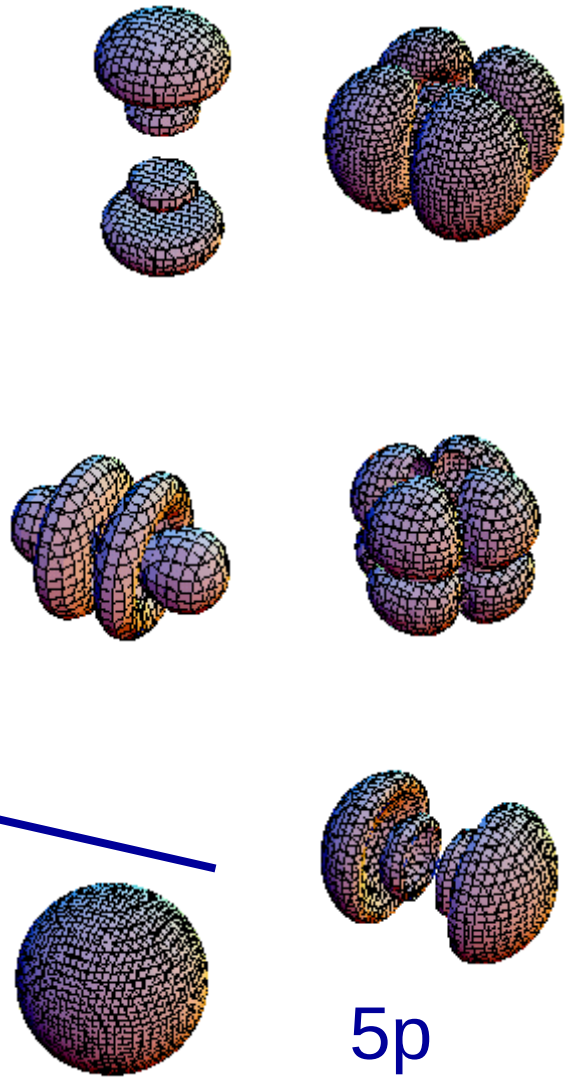






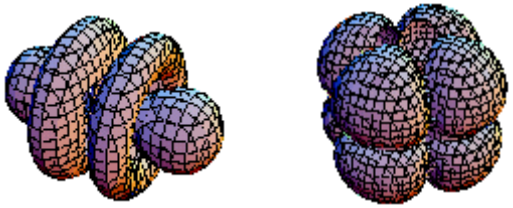
Lanthanide 3+ ground state: $5s^2\ 5p^6\ 4f^N\ 5d^0$



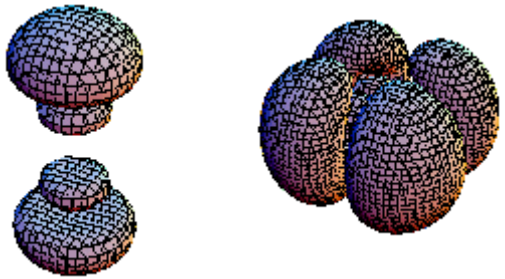


Lanthanides: $4f^N$, $4f^{N-1}5d$, Excitons

- **$4f^N$**
  - Sharp lines
  - Long lifetimes
  - So ideal for laser and phosphor applications

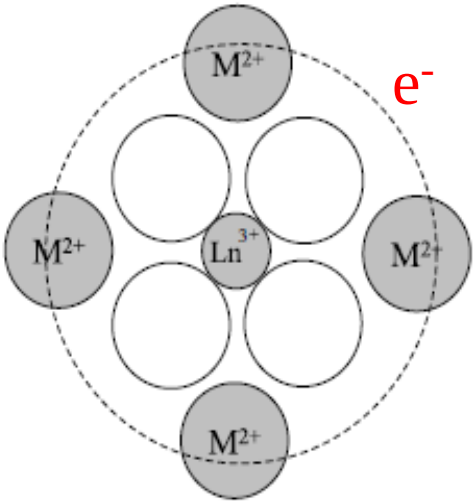


- **$4f^{N-1}5d$**
  - Broad absorption bands from $4f^N$
  - Useful for absorbing energy
  - Short lifetimes useful in some applications, such as scintillators



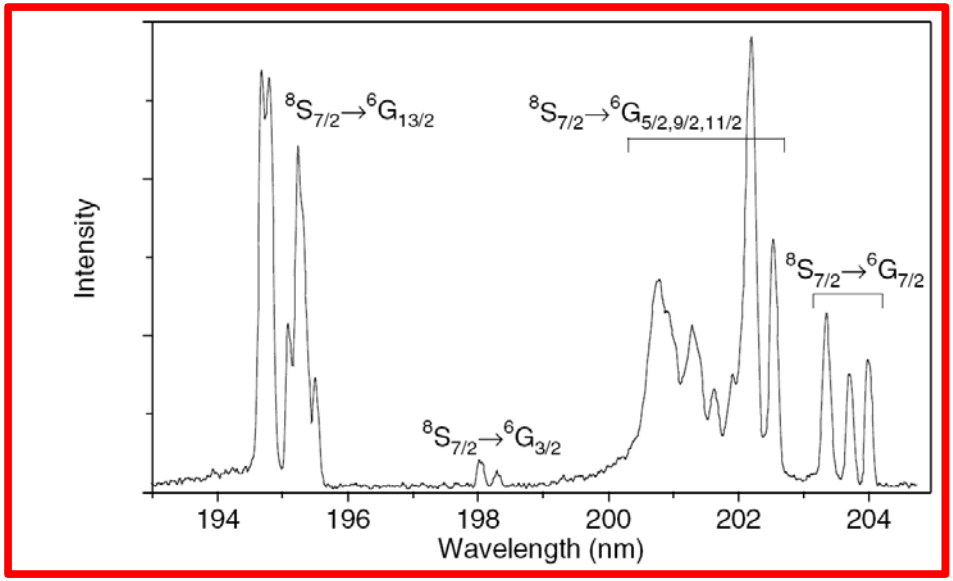
- **Excitons**
  - Excited electron can become delocalized, giving an excitonic state.

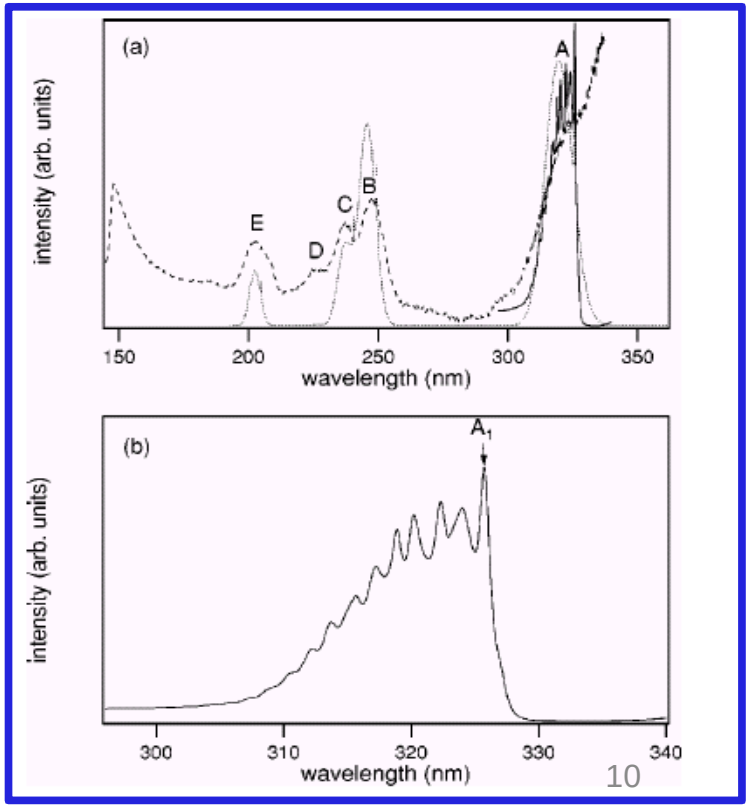
- **Charge Transfer Transitions**
  - Ligand to lanthanide electron transfer

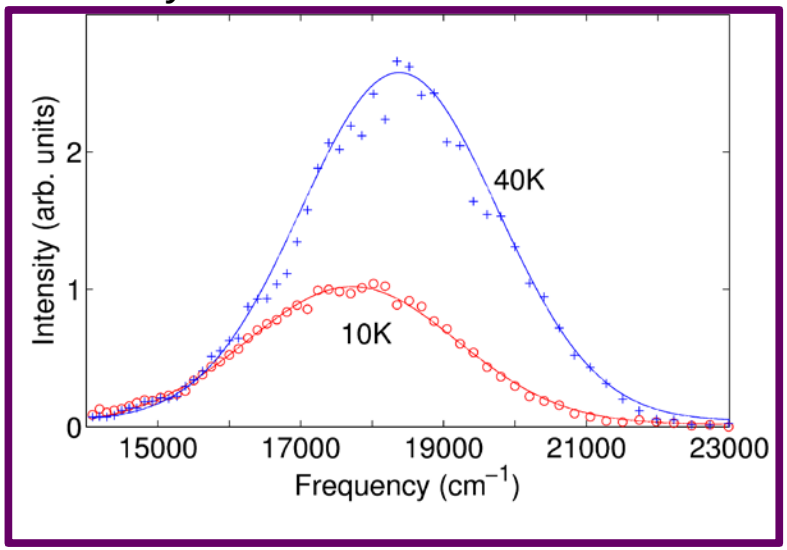


Transitions

- $4f^N - 4f^N$
  - No configuration shift
  - Sharp lines
- $4f^N - 4f^N5d$
  - Configuration shift
  - Broad bands
- Excitonic states $\rightarrow 4f^N$
  - Large configuration shift
  - Very broad bands







How do we proceed?

- Ab-initio (first principles) calculations
  - Well established in atoms
  - Hartree-Fock + perturbations
  - Now viable for lanthanide complexes but slow
- Effective Hamiltonians (“crystal field”)
  - Requires parameter fitting
  - Relatively quick and easy, allowing rapid interpretation of spectra.
  - Can be related to ab-initio calculations.

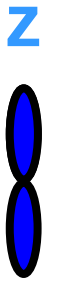
Effective Hamiltonian Calculations

- $H \quad |\Psi_i\rangle = E_i \, |\Psi_i\rangle$ (H is Hamiltonian)
- $H_{eff} \, |\phi_i\rangle = E_i \, |\phi_i\rangle$ (H_{eff} is Effective Hamiltonian)

$E_{Theory} \quad E_{Expt}$

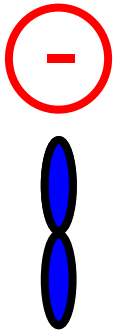
$(H) \rightarrow (H_{eff})$

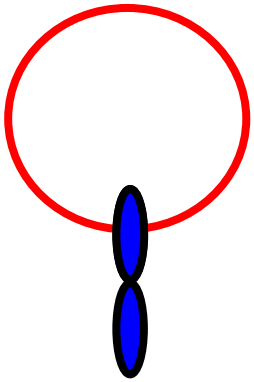
$(H_{eff}) \rightarrow \sum_\alpha P_\alpha (M_\alpha)$

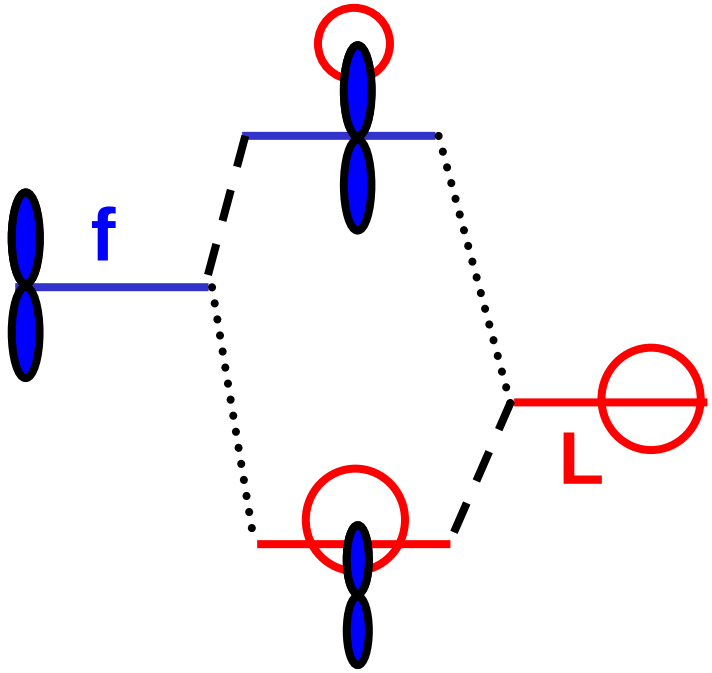


“Crystal Field”

$$\left(\sum_{k,q} B_q^k C_q^{(k)} \right)$$





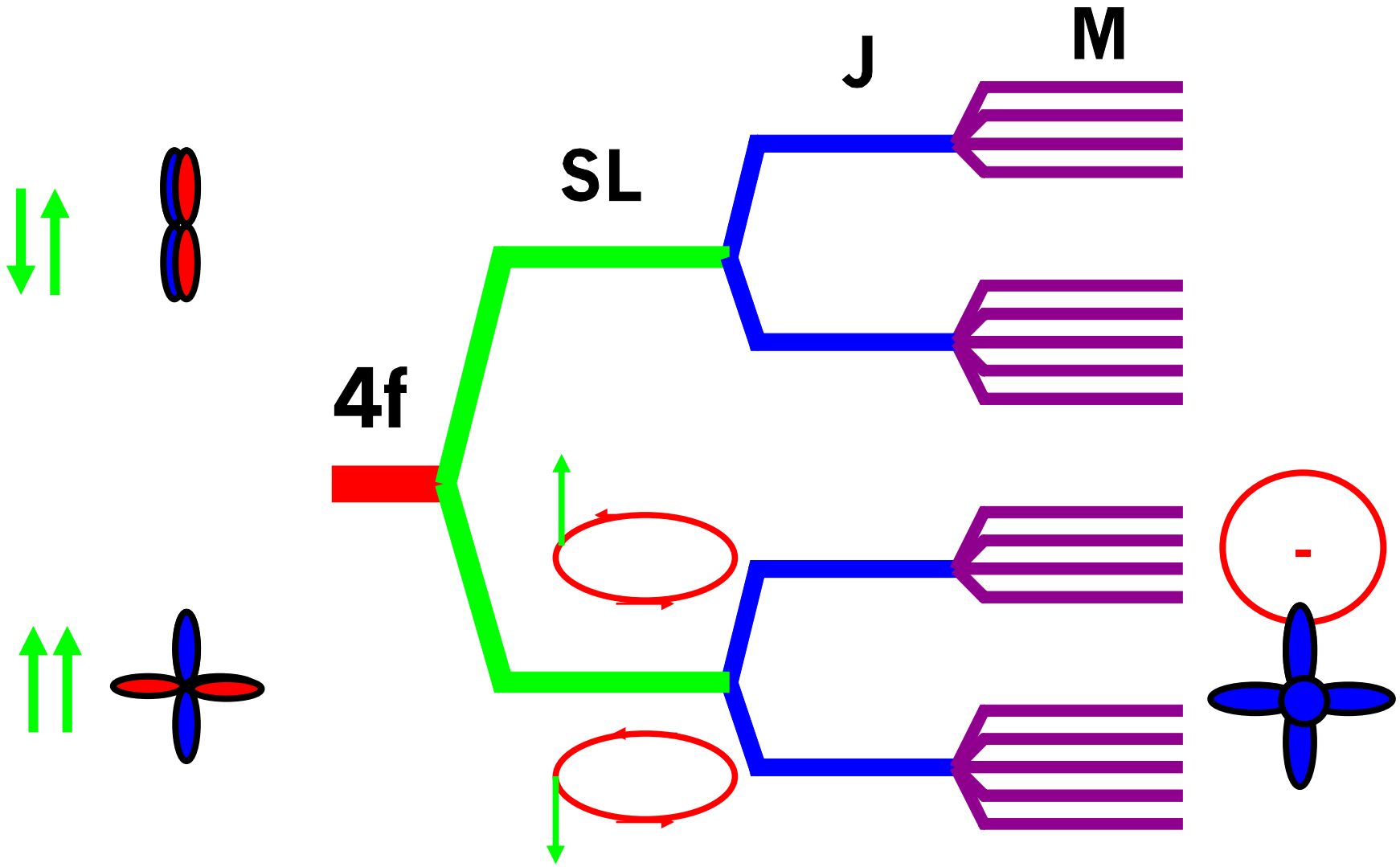


Electrostatic **Overlap** **Covalency**

All increase energy of z orbital more than x,y

Orbital energies ↔ crystal-field parameters

Understanding the energy levels: $4f^N$



Effective Hamiltonian for $4f^N$

$$H = E_{avg} + \sum_{k=2,4,6} F^k f_k + \zeta_f A_{so} + \sum_{k,q} B_q^k C_q^{(k)}$$

Coulomb **Spin-Orbit** **Crystal Field**

Correlation and other corrections

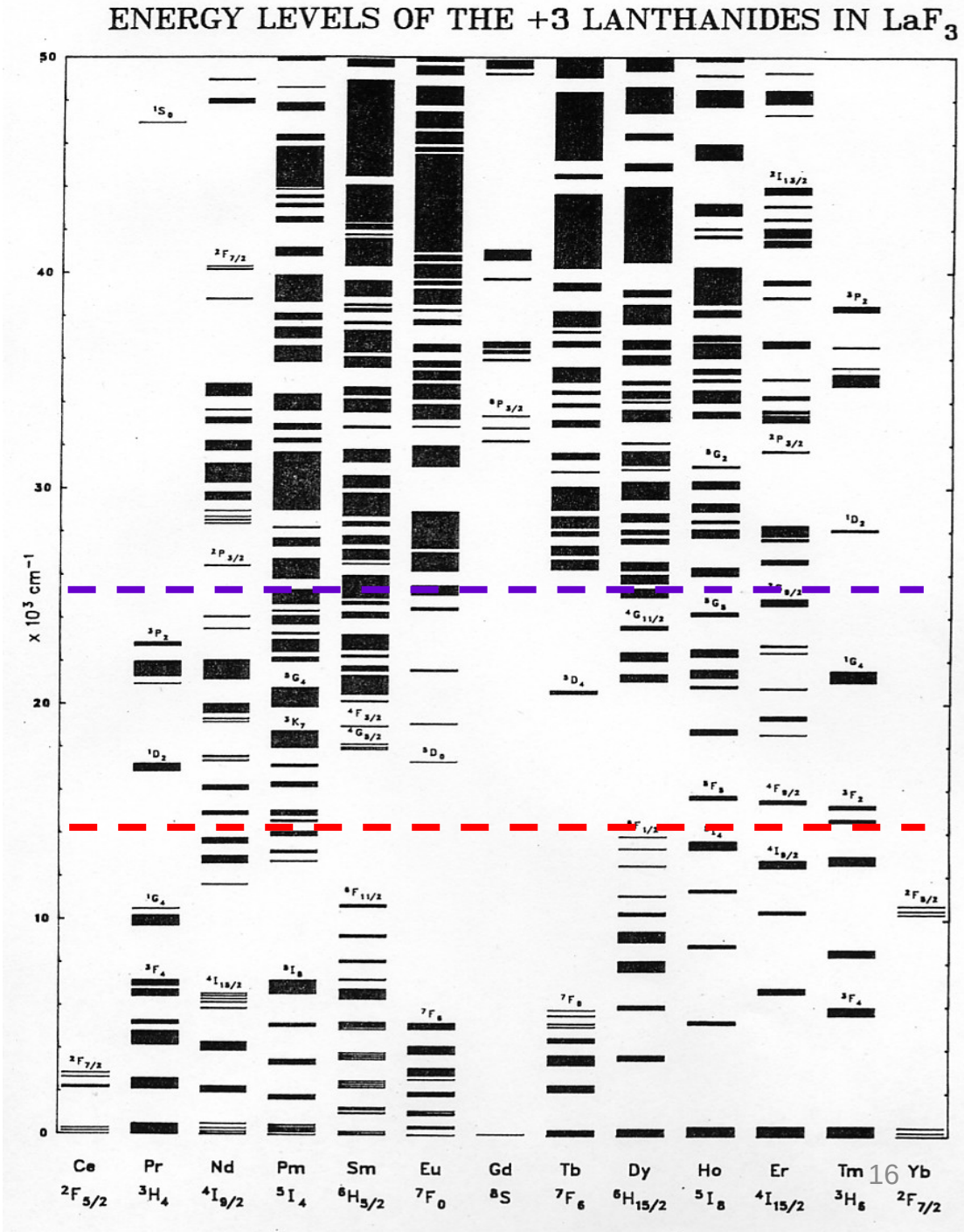
$$+\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{i=2,3,4,6,7,8} T^i t_i$$

$$+ \sum_{h=0,2,4} M^h m_h + \sum_{k=2,4,6} P^k p_k$$

“Dieke Diagram” 1960s

Carnall, Goodman, Rajnak, Rana, **1988**

20,000 cm^{-1}
500 nm
2.5 eV



Calulating Matrix elements

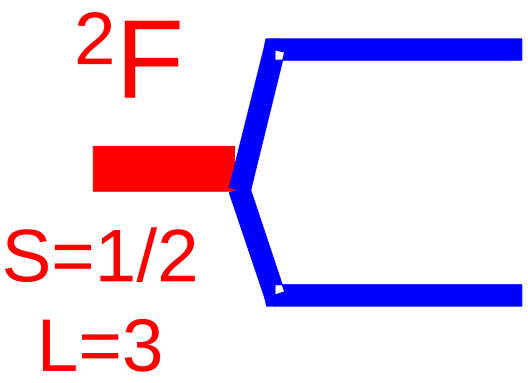
- Wigner-Eckart Theorem

$$\langle \alpha J M | T_q^{(k)} | \alpha' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \alpha J || T^{(k)} || \alpha' J' \rangle$$

matrix element "geometrical" factors "reduced" matrix element

- Selection Rules
  - M'+q = M
  - J k J' form a triangle: $|J-J'| \leq k \leq J+J'$
- |SLJM> states
  - More complex versions of WET.
  - Triangle rules for S S' L L' J J' and operator labels.

Ce^{3+}: $4f^1\ 5d^1$



J=7/2 $E_{avg} + 1.5\ \zeta = 2253\ cm^{-1}$

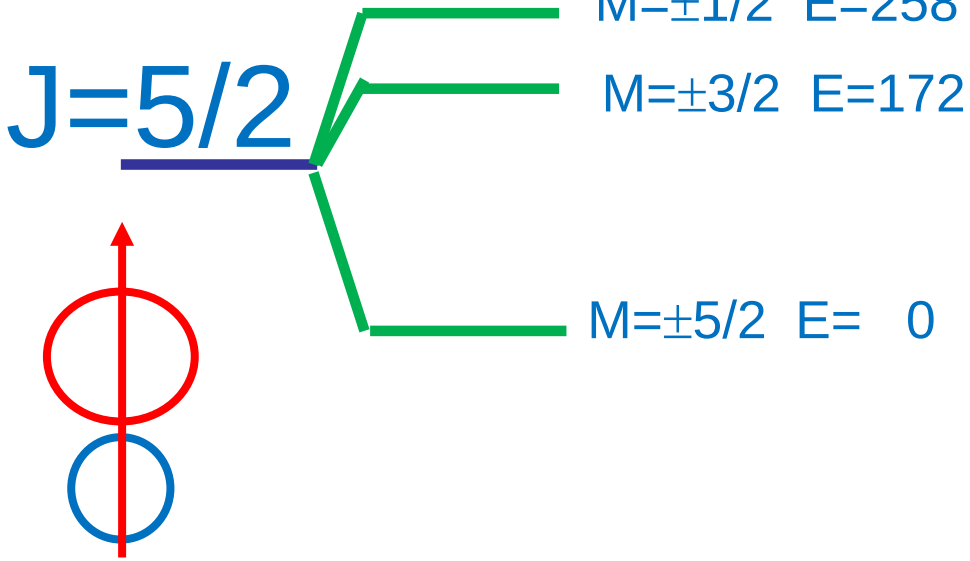
J=5/2 $E_{avg} - 2.0\ \zeta = 0\ cm^{-1}$

Free-ion splitting is 2253 cm^{-1} so $\zeta = 644\ cm^{-1}$

Similarly for $5d^1$

Splitting of J=5/2 multiplet

- Magnetic field
  - Even spacing:
    - 0.4 cm^{-1} for 1T field

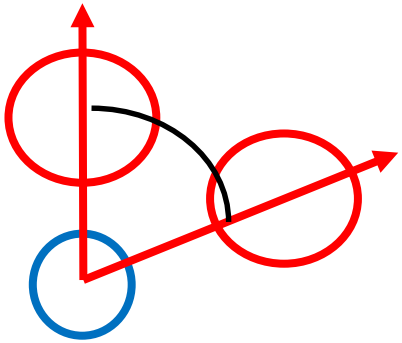


- Crystal Field

$$H_{\mathrm{cf}} = \sum_{k,q} B_q^k C_q^{(k)}$$

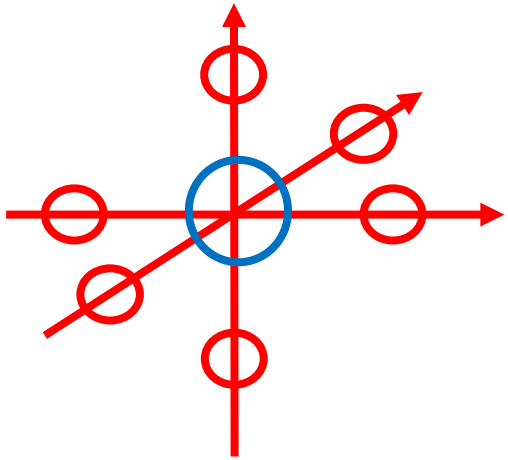
  - Uneven spacing
  - Example:
    - $B^2_0 = 500\ cm^{-1}$
  - More complex cases mix up M labels.

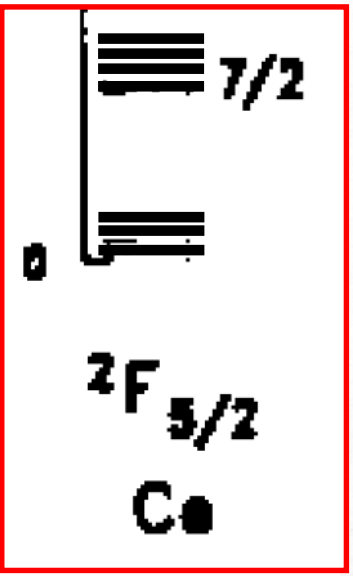
Superposition Model

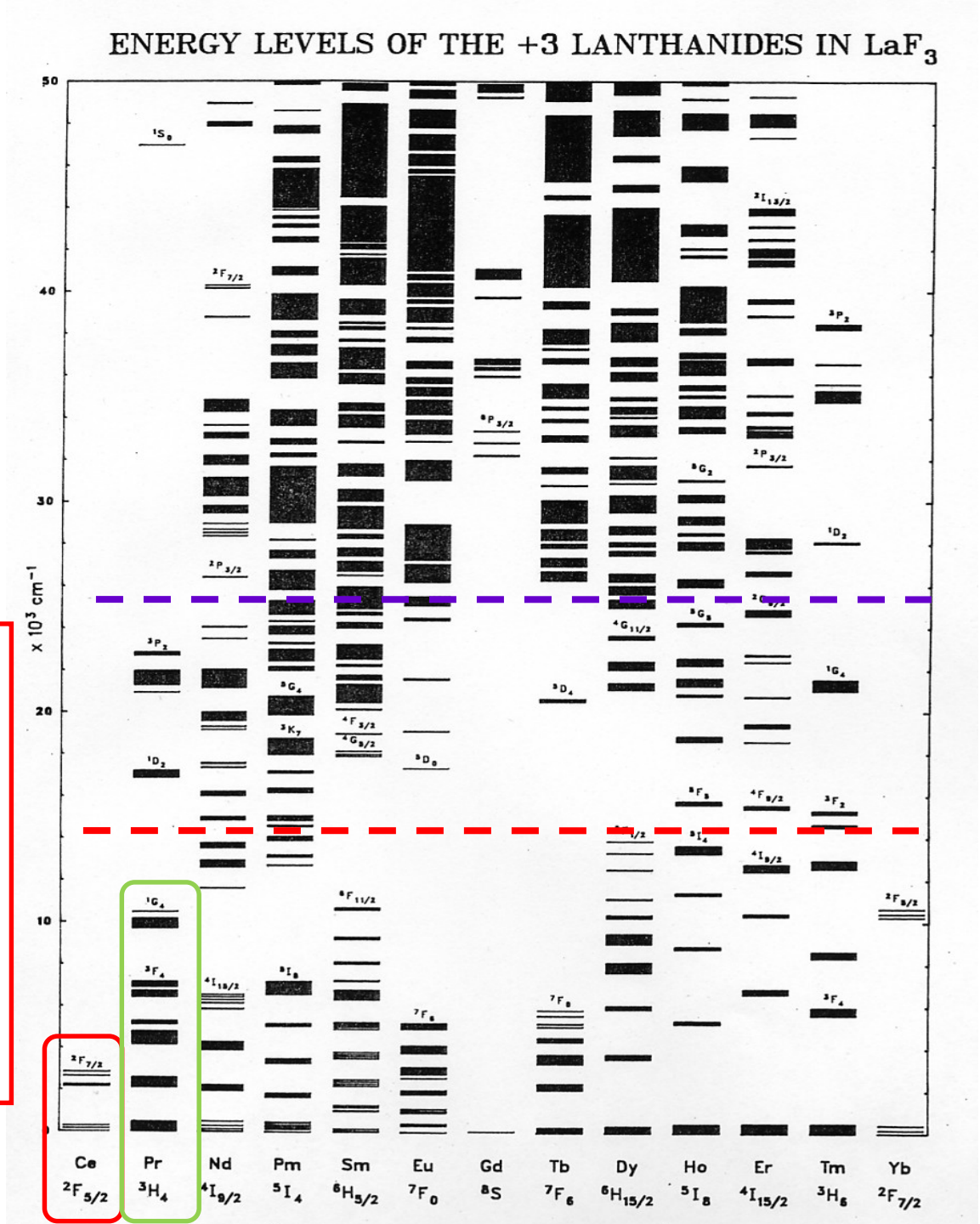


$$B_q^k = \sum_L \bar{B}_k(R_0)(-1)^q C_{-q}^{(k)}(\theta_L, \phi_L) \left(\frac{R_0}{R_L}\right)^{t_k}$$

$$C_0^{(2)}(x, y, z) = \frac{1}{r^2}\sqrt{\frac{1}{4}}(3z^2 - r^2)$$

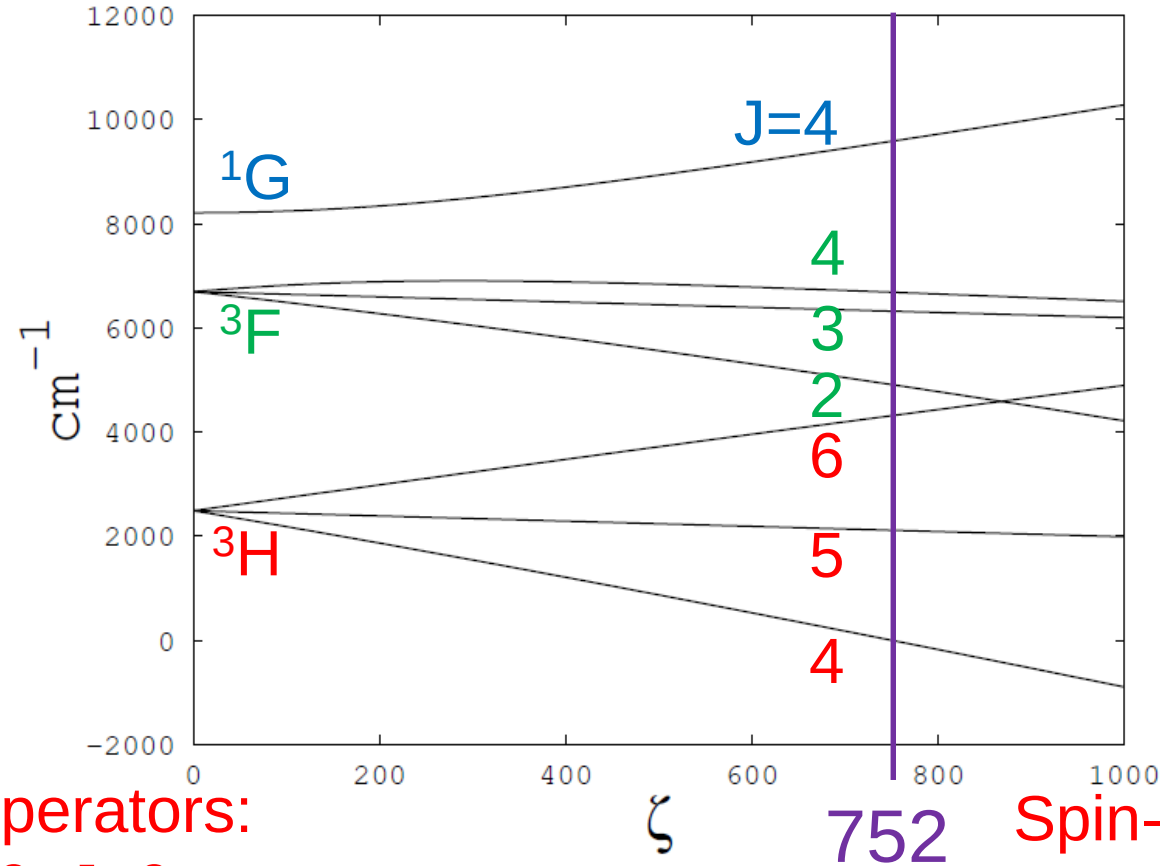



7/2
0
$^2F_{5/2}$
Ce


ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF_3
x 10^3 cm^{-1}
50
40
30
20
10
0
Ce $^2F_{5/2}$
Pr $^3H_4$
Nd $^4I_{9/2}$
Pm $^5I_4$
Sm $^6H_{5/2}$
Eu $^7F_0$
Gd ^8S
Tb $^7F_6$
Dy $^6H_{15/2}$
Ho $^5I_8$
Er $^4I_{15/2}$
Tm $^3H_6$
Yb $^2F_{7/2}$

Pr^{3+} : $4f^2$ Coulomb + Spin-orbit

$$
\begin{aligned}
E(^3H_J) &= -0.0906F^2 - 0.0328F^4 + 0.0162F^6 = -7359\ \mathrm{cm}^{-1},\\
E(^3F_J) &= -0.0239F^2 - 0.0163F^4 - 0.0209F^6 = -3155\ \mathrm{cm}^{-1},\\
E(^1G_4) &= -0.1128F^2 + 0.1031F^4 + 0.0285F^6 = -1641\ \mathrm{cm}^{-1}.
\end{aligned}
$$

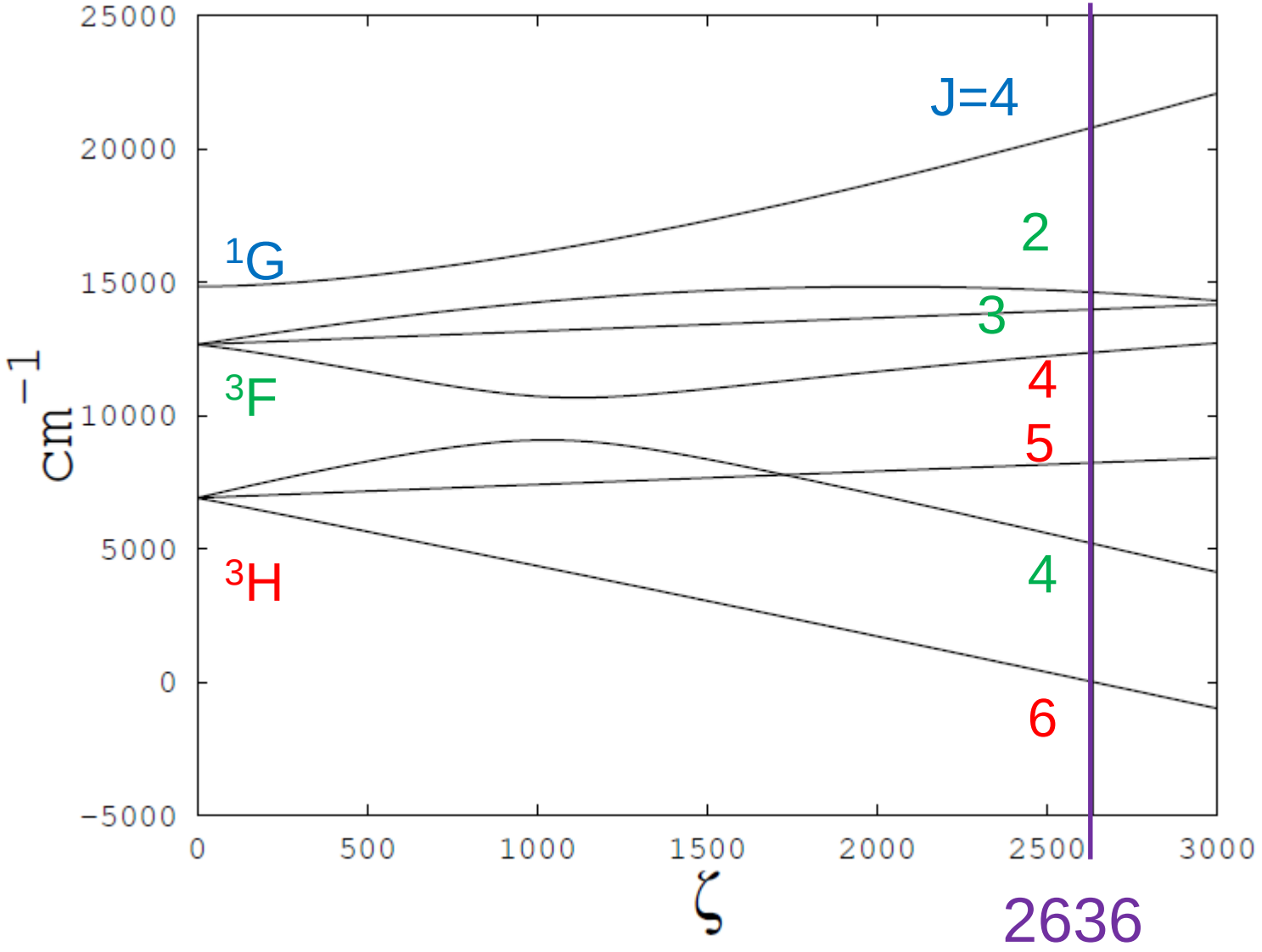


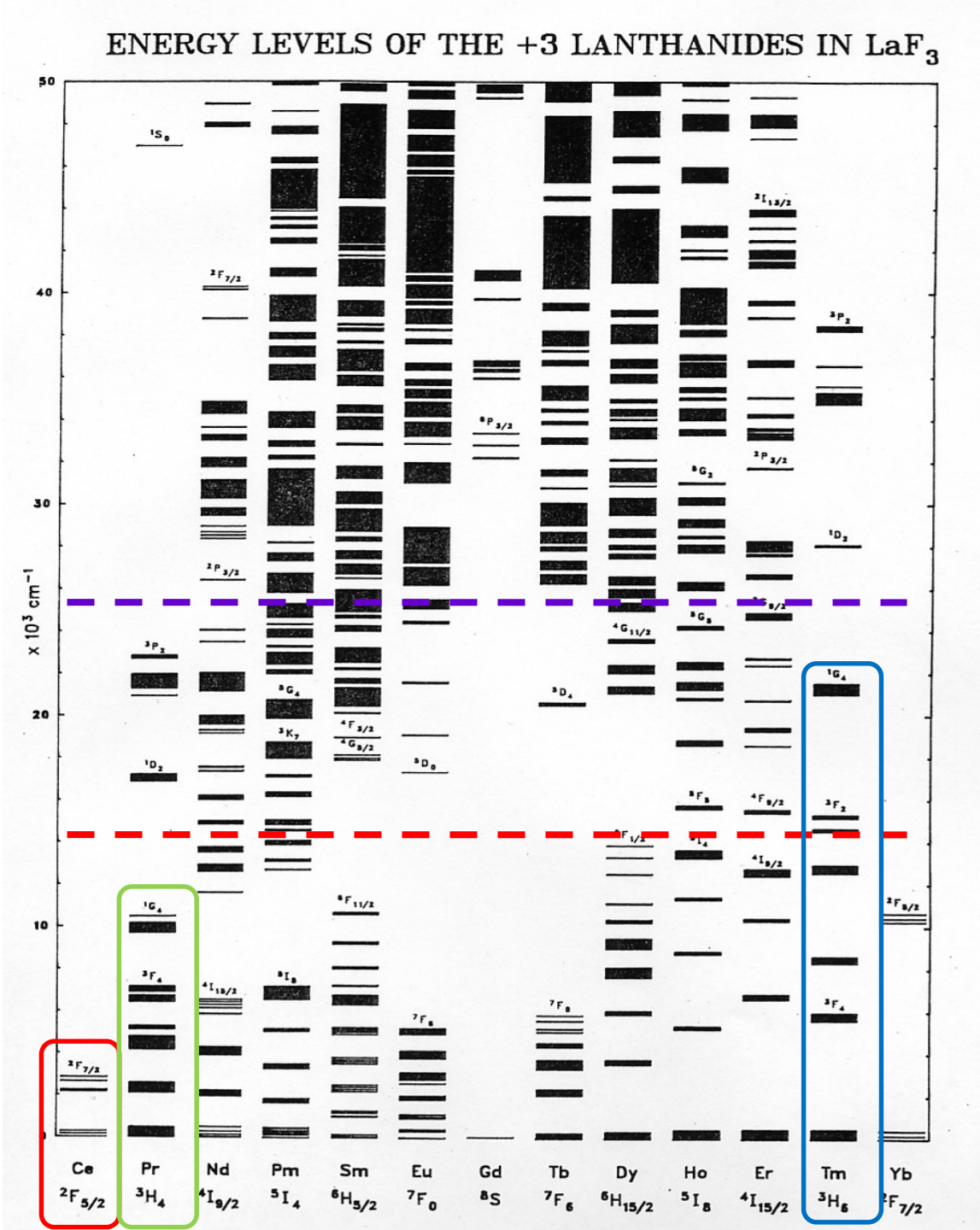
Coulomb operators:
S=0, L=0, J=0

Spin-orbit operator:
S=1, L=1, J=0

Tm^{3+}: $4f^{12}$

Spin-orbit much larger and matrix elements change sign.




ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF3
x 10^3 cm^-1
50
40
30
20
10
Ce 2F5/2
Pr 3H4
Nd 4I9/2
Pm 5I4
Sm 6H5/2
Eu 7F0
Gd 8S
Tb 7F6
Dy 6H15/2
Ho 5I8
Er 4I15/2
Tm 3H6
Yb 2F7/2

Transition Intensities

- Electric Dipole, Magnetic Dipole, …
- ED between $4f^N$ and $4f^{N-1}5d$ can be calculated directly
  - But require modelling of vibronic bands.
- ED within $4f^N$ are parity forbidden.
  - Construct Effective ED operator that accounts for mixing of configurations of opposite parity on ion or ligand.
  - First detailed treatment: Judd, Ofelt, 1962.

Effective Electric Dipole Operator

$$D_{\mathrm{eff},q} = D_q^{(1)} + D_q^{(1)} \sum_{\beta \notin \mathrm{M}} \frac{|\beta\rangle\langle\beta|V}{E_0 - E_\beta^{(0)}} + \sum_{\beta \notin \mathrm{M}} \frac{V|\beta\rangle\langle\beta|}{E_0 - E_\beta^{(0)}} D_q^{(1)} + \ldots$$

Can derive a parametrization. λ=2,4,6, t=$\lambda\pm$1, λ

$$D_{\mathrm{eff},q} = \sum_{\lambda,t,p} A_{tp}^{\lambda} U_{p+q}^{(\lambda)} (-1)^q \langle \lambda(p+q), 1-q | tp \rangle$$

Dipole strength

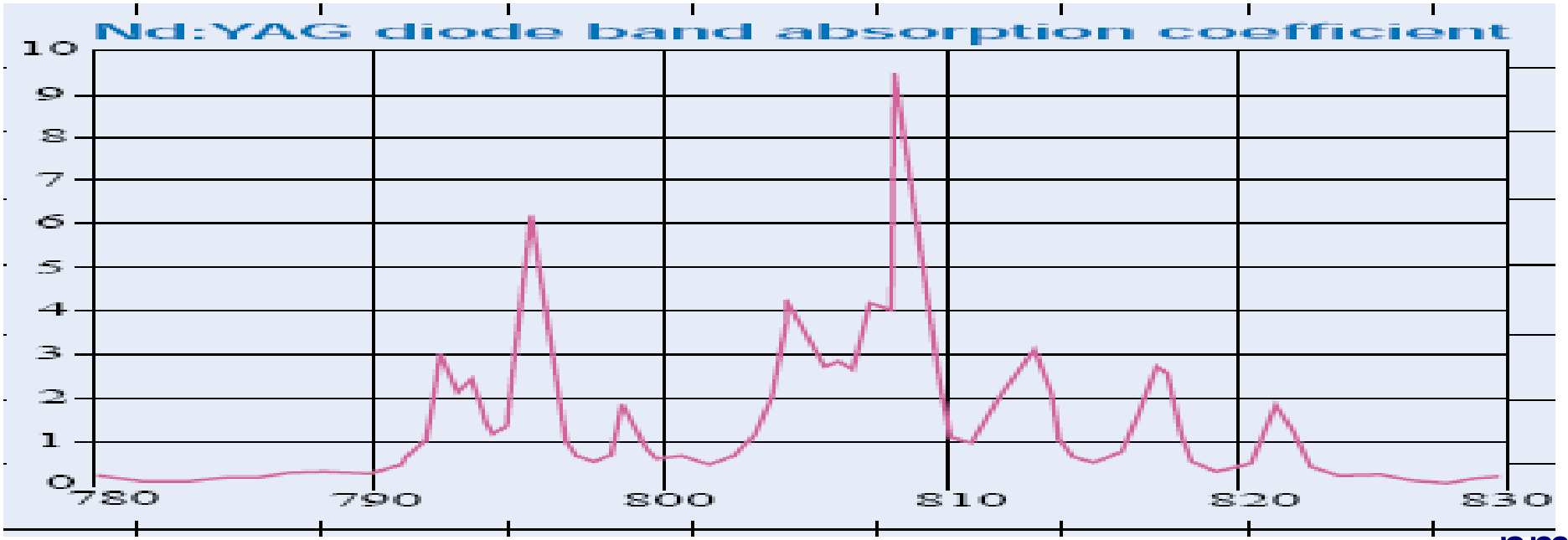
$$S_{FI,q}^{\mathrm{ED}} = \sum_i \sum_f e^2 \left| \langle F f | D_q^{(1)} | I i \rangle \right|^2$$

Oscillator strength

$$f_{FI,q}^{\mathrm{ED}} = \frac{2m\omega}{\hbar e^2} \frac{\chi_{\mathrm{L}}}{n} \frac{1}{g_I} S_{FI,q}^{\mathrm{ED}}$$

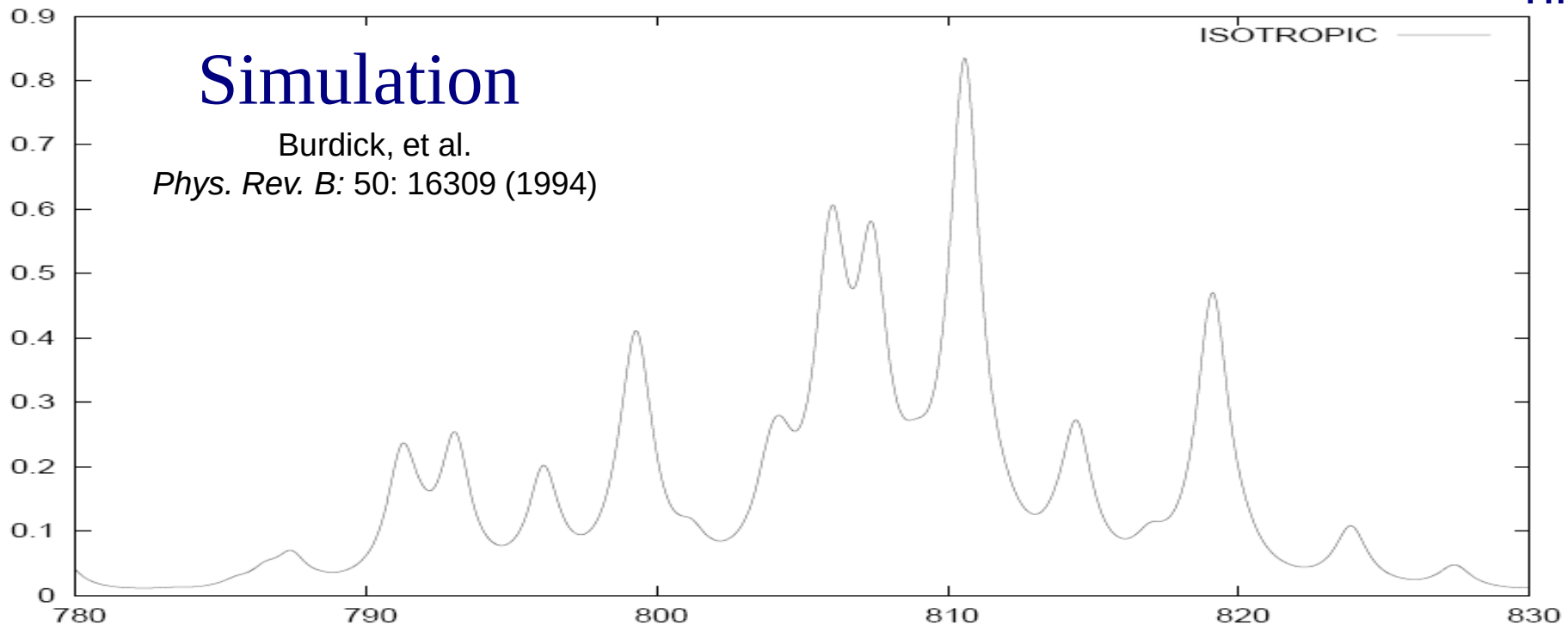
Einstein A coefficients ($1/\tau$)

$$A_{FI,q}^{\mathrm{ED}} = \frac{1}{4\pi\epsilon_0} \frac{4\omega^3}{\hbar c^3} n \chi_{\mathrm{L}} \frac{1}{g_I} S_{FI,q}^{\mathrm{ED}}$$



Simulation

Burdick, et al.
Phys. Rev. B: 50: 16309 (1994)

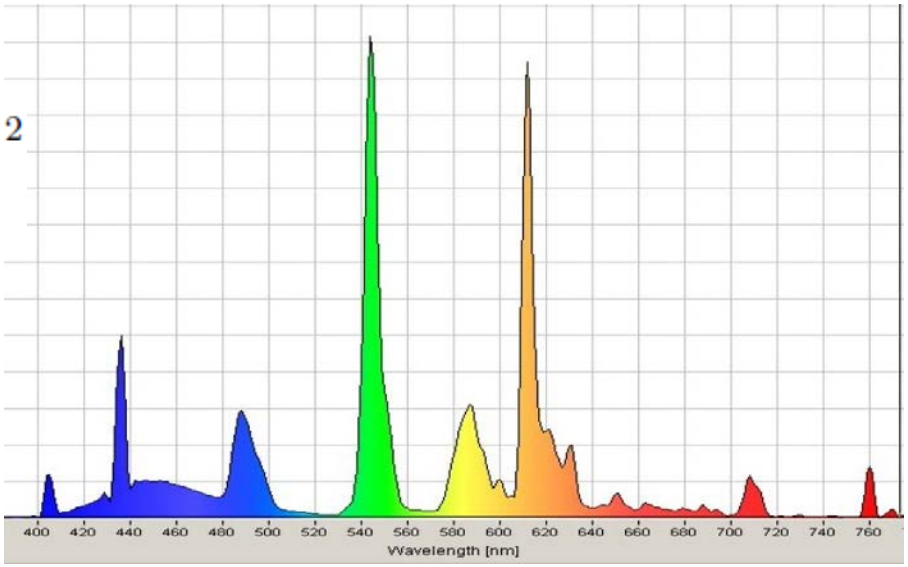


Multiplet-Multiplet transitions

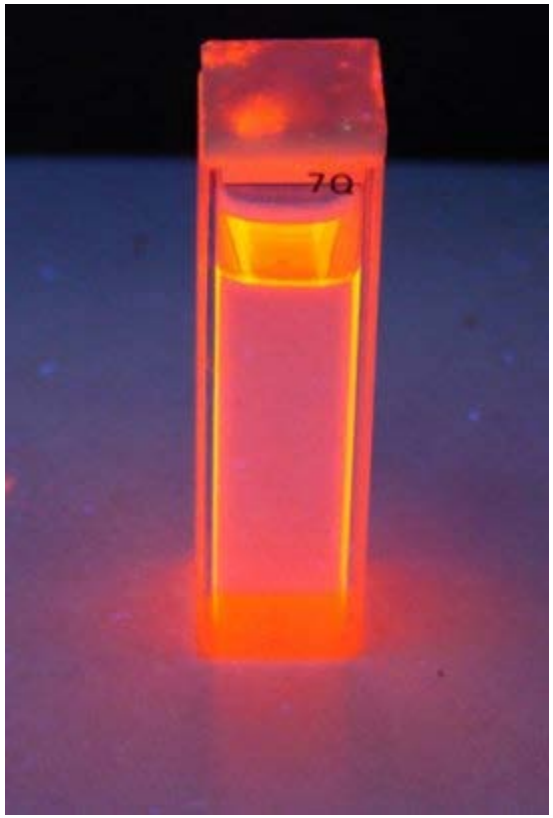
- Judd 1962
  - For solutions and glasses at room temperature.
  - Sum over all states in a multiplet and all polarizations.
  - Reduces to three-parameter *linear* fit.
  - Ω_λ parameters with λ=2,4,6
  - Over 3000 citations!

$$\bar{S}^{\mathrm{ED}}_{\alpha_F J_F, \alpha_I J_I} = \frac{1}{3} e^2 \sum_\lambda \Omega_\lambda \langle \alpha_F J_F \| \mathbf{U}^{(\lambda)} \| \alpha_I J_I \rangle^2$$

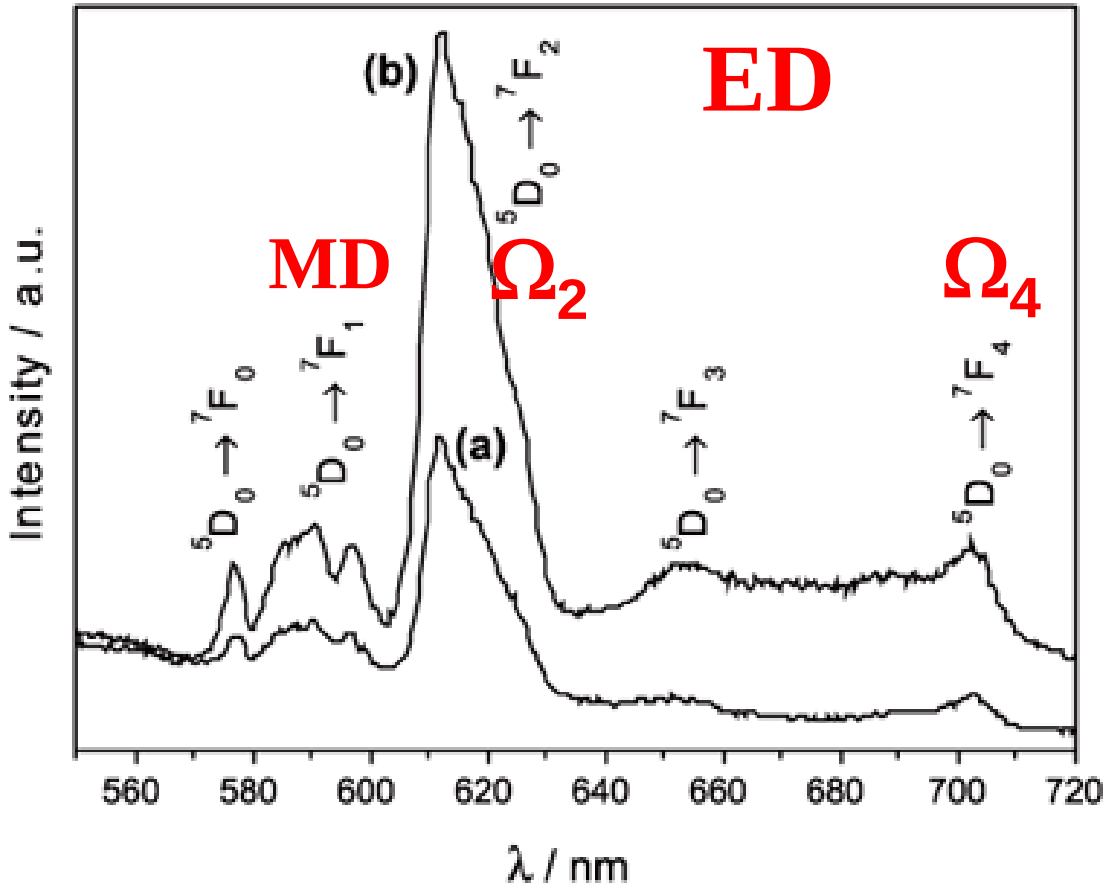
$$\Omega_\lambda = \sum_{t,p} \frac{1}{2\lambda + 1} \left| A^\lambda_{tp} \right|^2$$



Eu^{3+}: $^5D_0 \rightarrow {}^7F_J$ Emission

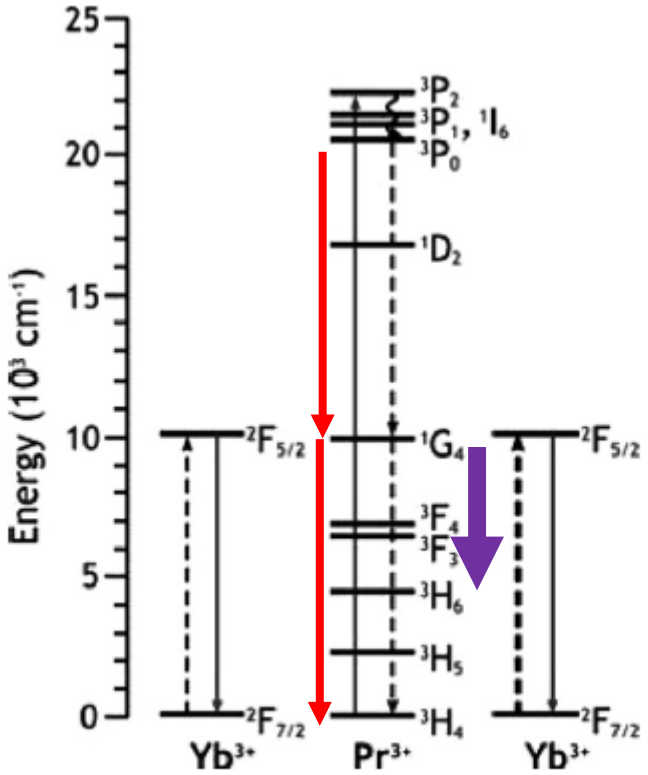


$$\frac{1}{3}e^2 \sum_{\lambda} \Omega_\lambda \langle \alpha_F J_F \| \mathbf{U}^{(\lambda)} \| \alpha_I J_I \rangle^2$$



Eliminate options: Pr-Yb downconversion

Linda Aarts ,
Spectroscopy Letters, 43:373–381, 2010



$$\frac{1}{3}e^2\sum_{\lambda}\Omega_\lambda\langle\alpha_F J_F\|\mathbf{U}^{(\lambda)}\|\alpha_I J_I\rangle^2$$

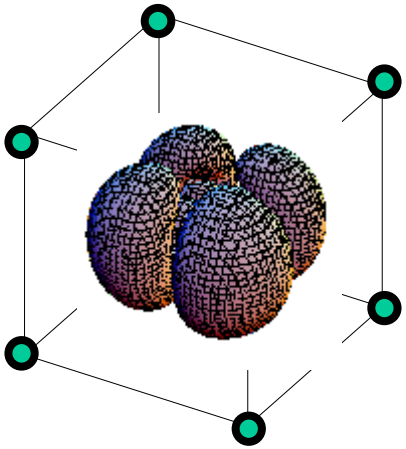
TABLE 1 Reduced Matrix Elements $(U^{(t)})^2$ for Transition Starting from the Pr^{3+} $^1G_4$ Level

Transition	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$
$^1G_4 \rightarrow {}^3H_4$	0.00141	0.00635	0.02206
$^1G_4 \rightarrow {}^3H_5$	0.03739	0.09615	0.41314
$^1G_4 \rightarrow {}^3H_6$	0.25226	0.25337	0.23683
$^1G_4 \rightarrow {}^3F_2$	0.00004	0.01580	0.00587
$^1G_4 \rightarrow {}^3F_3$	0.00381	0.00531	0.05173
$^1G_4 \rightarrow {}^3F_4$	0.07819	0.14271	0.34419
Sum	0.37310	0.51968	1.07382
Percentage ($^1G_4 \rightarrow {}^3H_4$)	0.38	1.2	2.1

The percentages in the bottom row give the $(U^{(t)})^2$ strength for the $^1G_4 \rightarrow {}^3H_4$ transitions relative to the sum of all $(U^{(t)})^2$ values for a given value of t.

$^1G_4 \rightarrow {}^3H_4$ can never be strong…

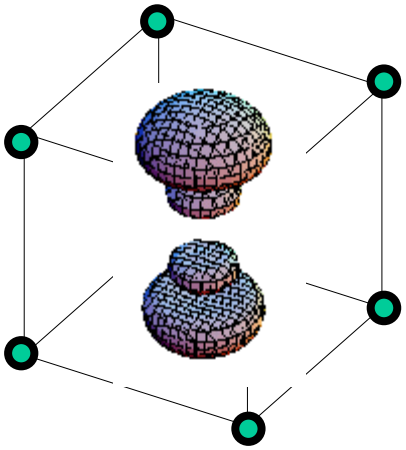
Understanding the energy levels: $4f^{N-1}5d$



T_2

Cubic:

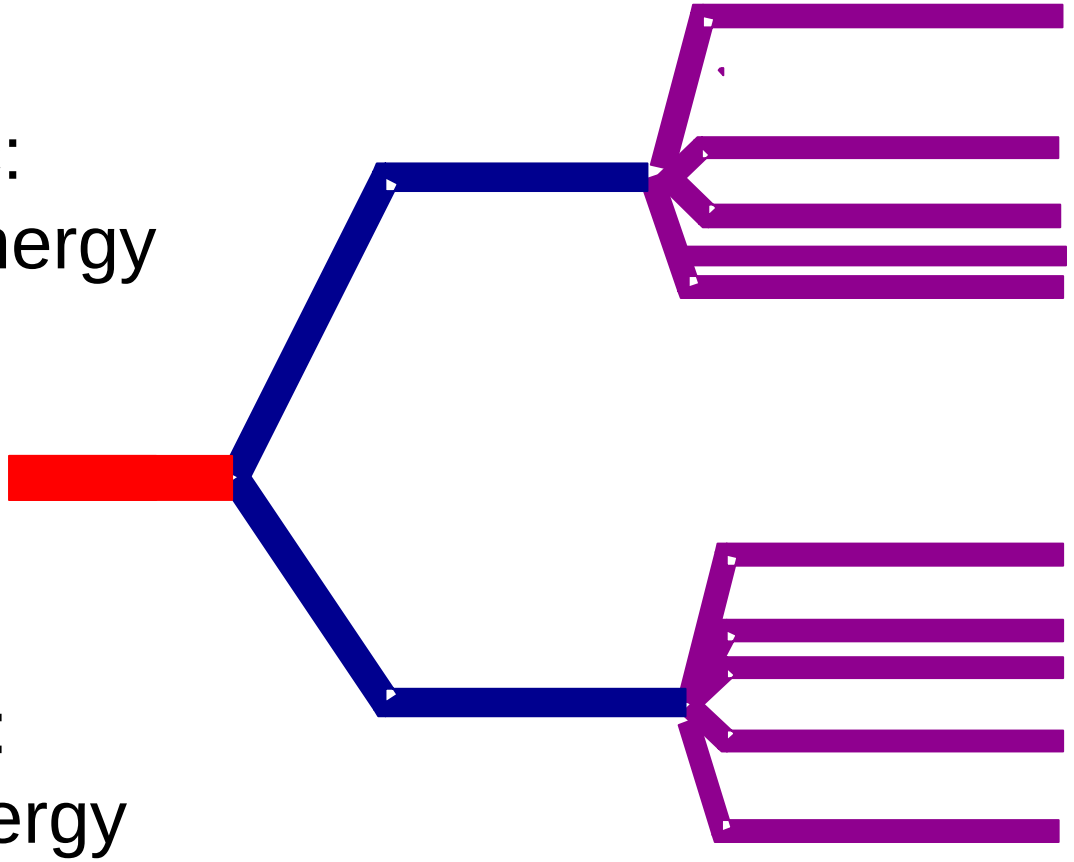
higher energy



E

Cubic:

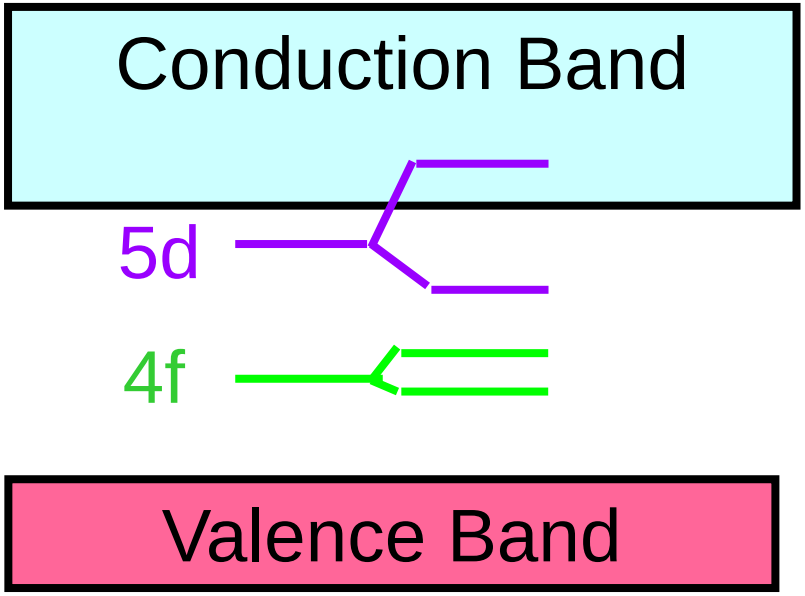
lower energy



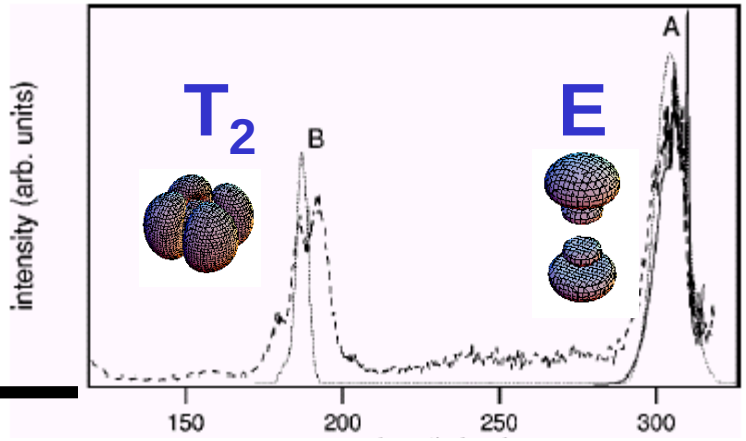
Crystal field Coulomb, etc

40 x 4f (20,000 vs 500)

Conduction Band, Free Electrons, Excitons

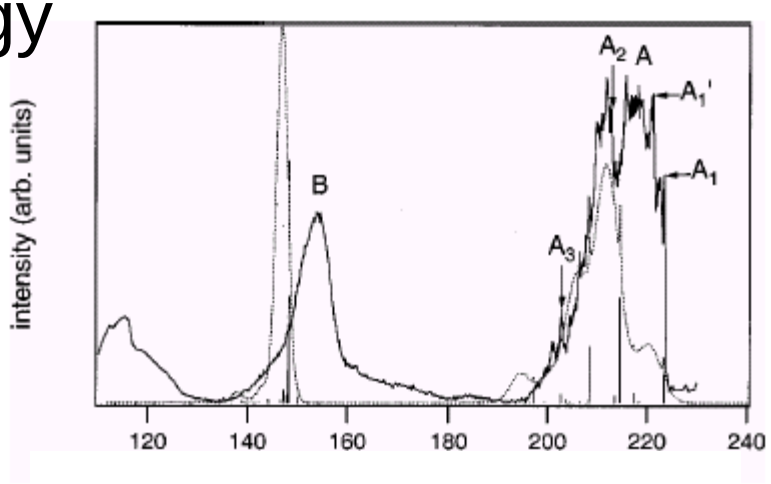


CaF_2 (cubic sites)

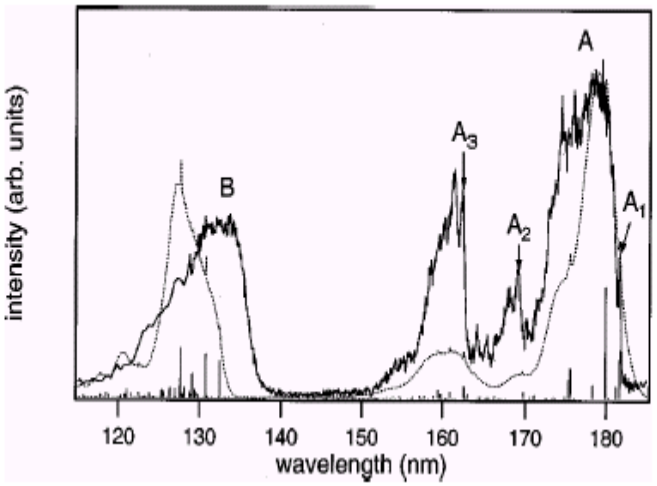


Energy

$Ce^{3+} : 4f^1 \rightarrow 5d^1$



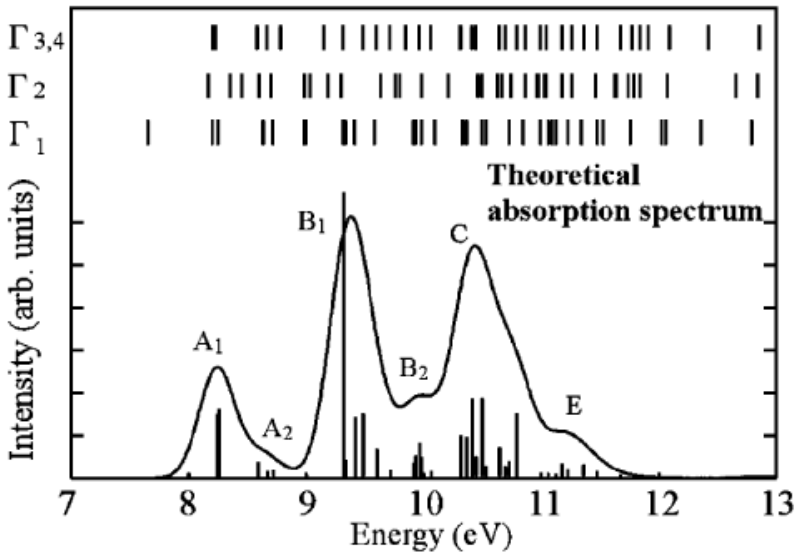
$Pr^{3+} : 4f^2 \rightarrow 4f^15d^1$

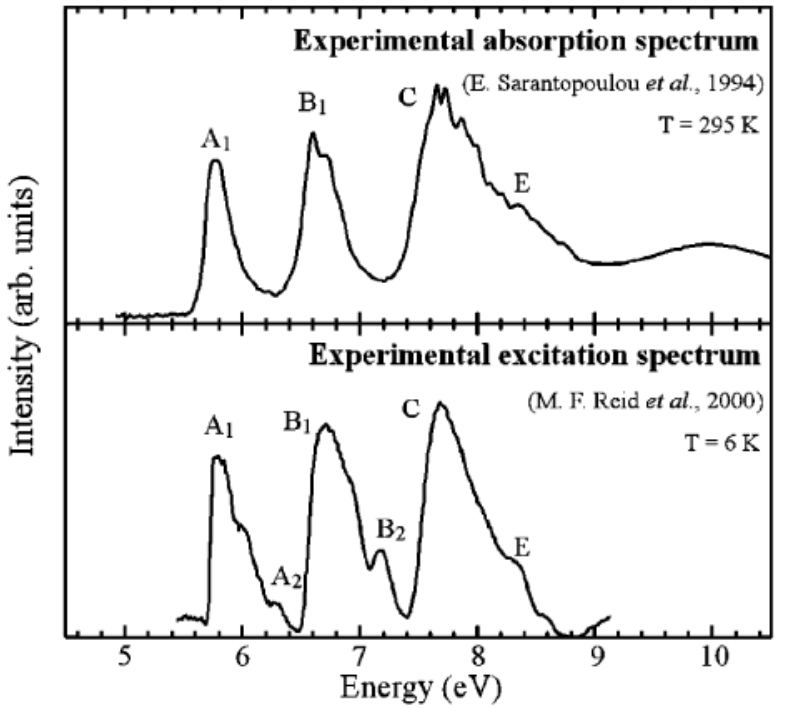


$Nd^{3+} : 4f^3 \rightarrow 4f^25d^1$

First-Principles Calculations

- Relativistic ab-initio calculations are now possible for these systems.
- Ogasawara et al.
  J. Solid State Chem. 178, 412 (2005).
  - Calculations for entire series. Some inaccuracies.
- Seijo et al.
  J. Chem. Phys. 125, 074511 (2006)
  - Very accurate and detailed calculations for particular ions, including potential surfaces.

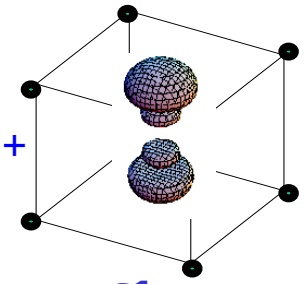




$Pr^{3+}:LiYF_4$

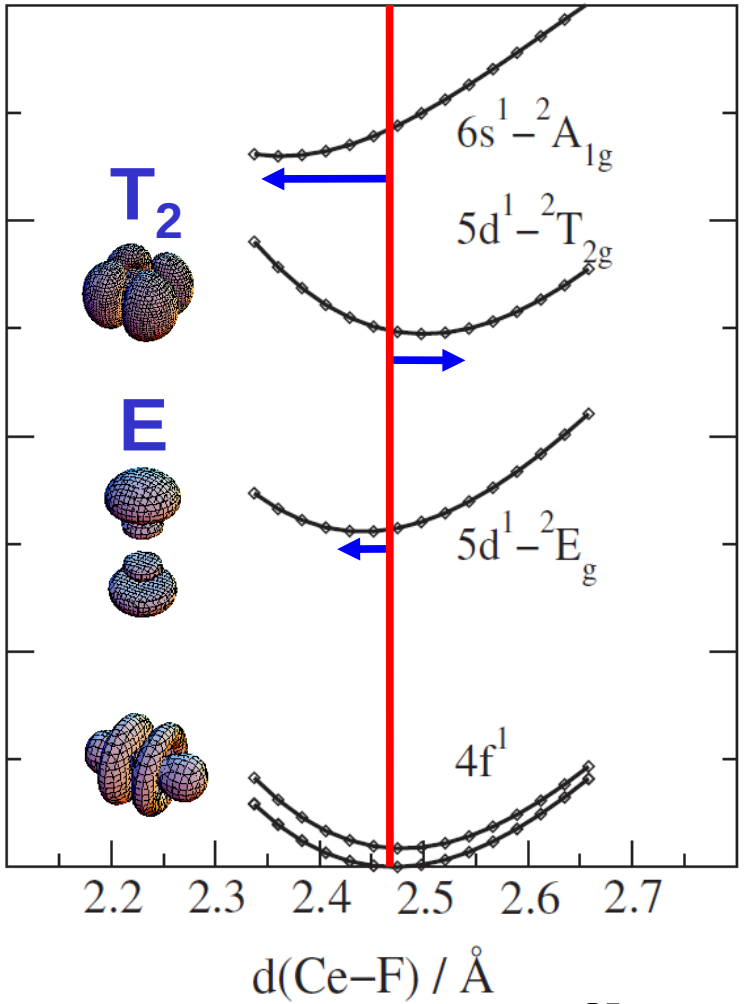
34

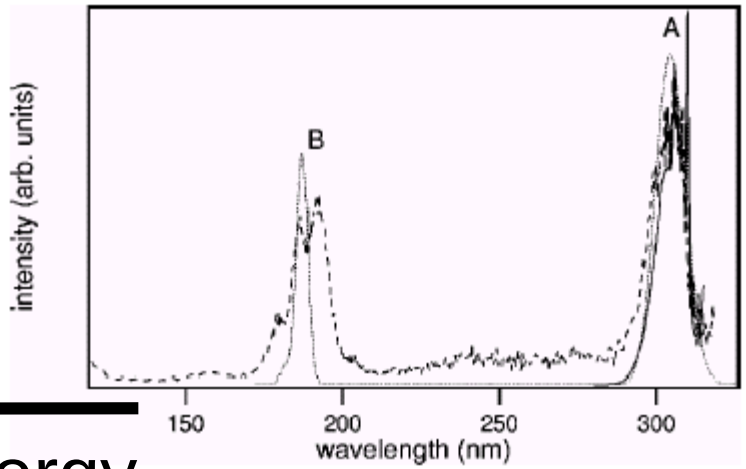
Excited-state geometry: $CaF_2:Ce^{3+}$



- Pascual, Schamps, Barandiaran, Seijo, PRB 74, 104105 (2006) $BaF_2:Ce^{3+}$ cubic sites.
- Potential surfaces:
  - 5d E is contracted
  - 5d T_2 is expanded
  - As bond length contracts 6s orbital becomes delocalized.

Ce^{3+} : $4f^1 \rightarrow 5d^1$



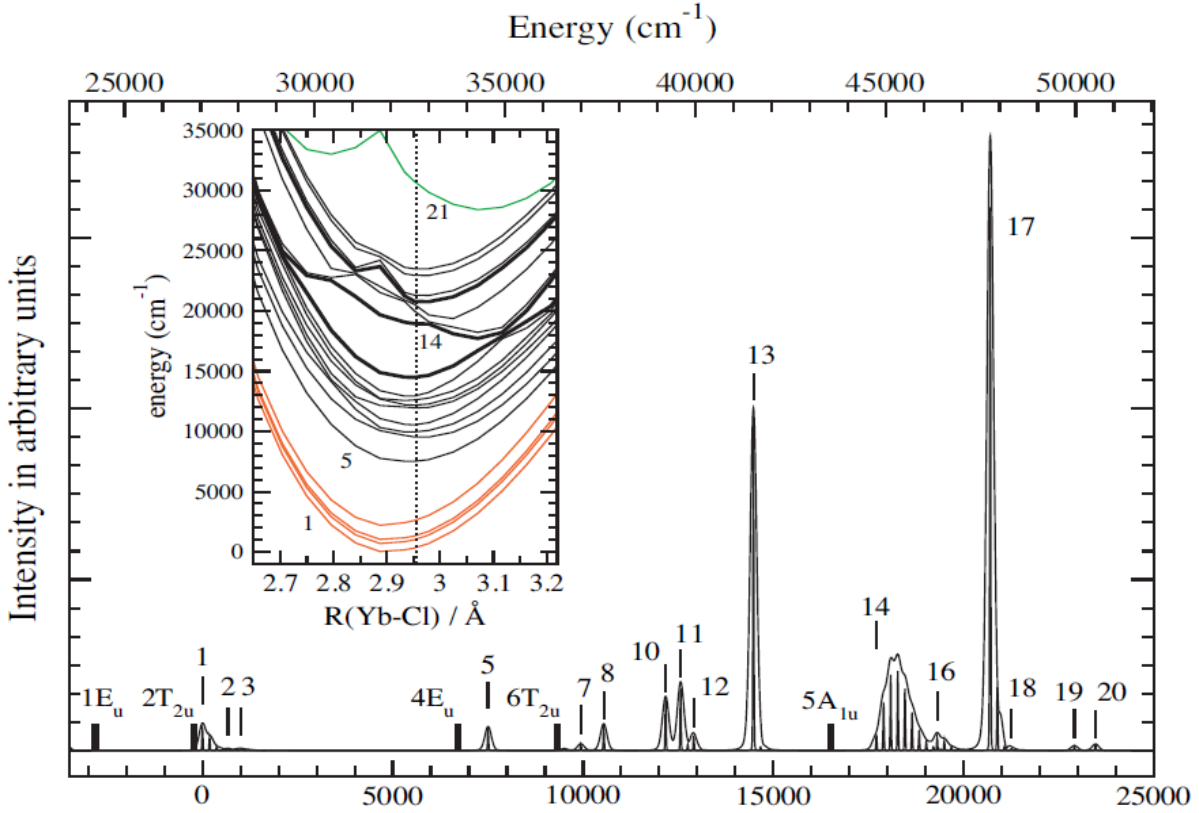


Energy

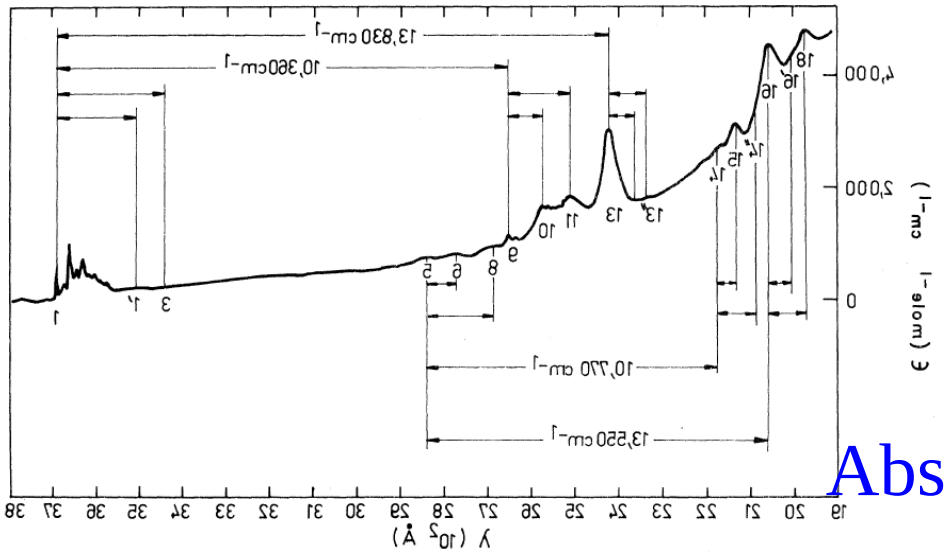
$Ce^{3+}:CaF_2$ $4f^1 \rightarrow 5d^1$

$SrCl_2:Yb^{2+}$

Sánchez-Sanz et al.
J. Chem. Phys.
133, 114509 2010



Some of our recent work is on extracting parameters from these calculations.

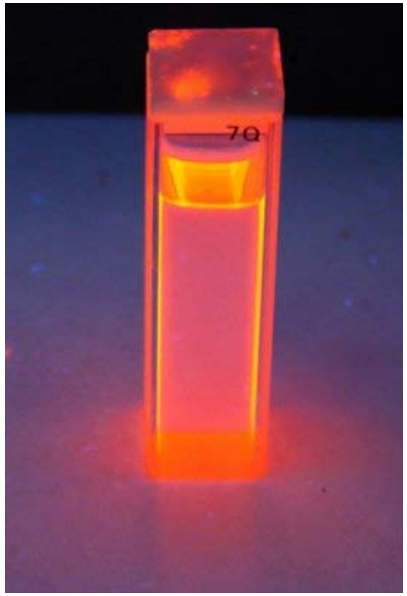


Absorption

Conclusion

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

- Effective Hamiltonian for $4f^N$
- Examples of energy level calculations
- Transition intensities
- $4f^{N-1}5d$
- Ab-initio calculations



- Further information and *exercises*:

  http://www2.phys.canterbury.ac.nz/~mfr24/

  http://www.phys.canterbury.ac.nz/people/reid.shtml

  Email: mike.reid@canterbury.ac.nz

The Dodd-Walls Centre
for Photonic and Quantum Technologies