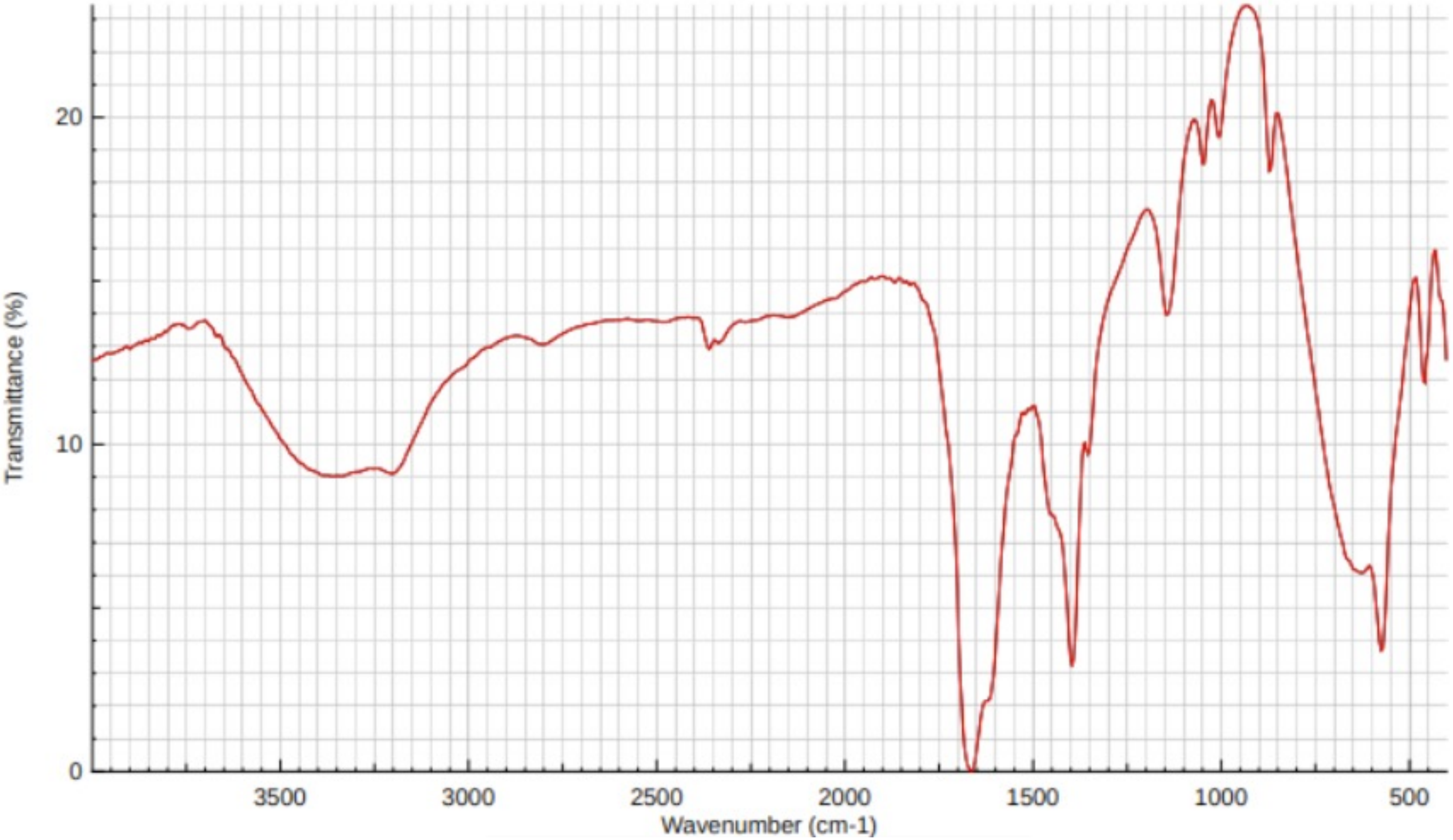
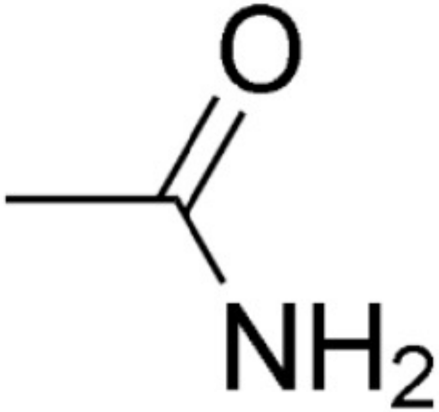
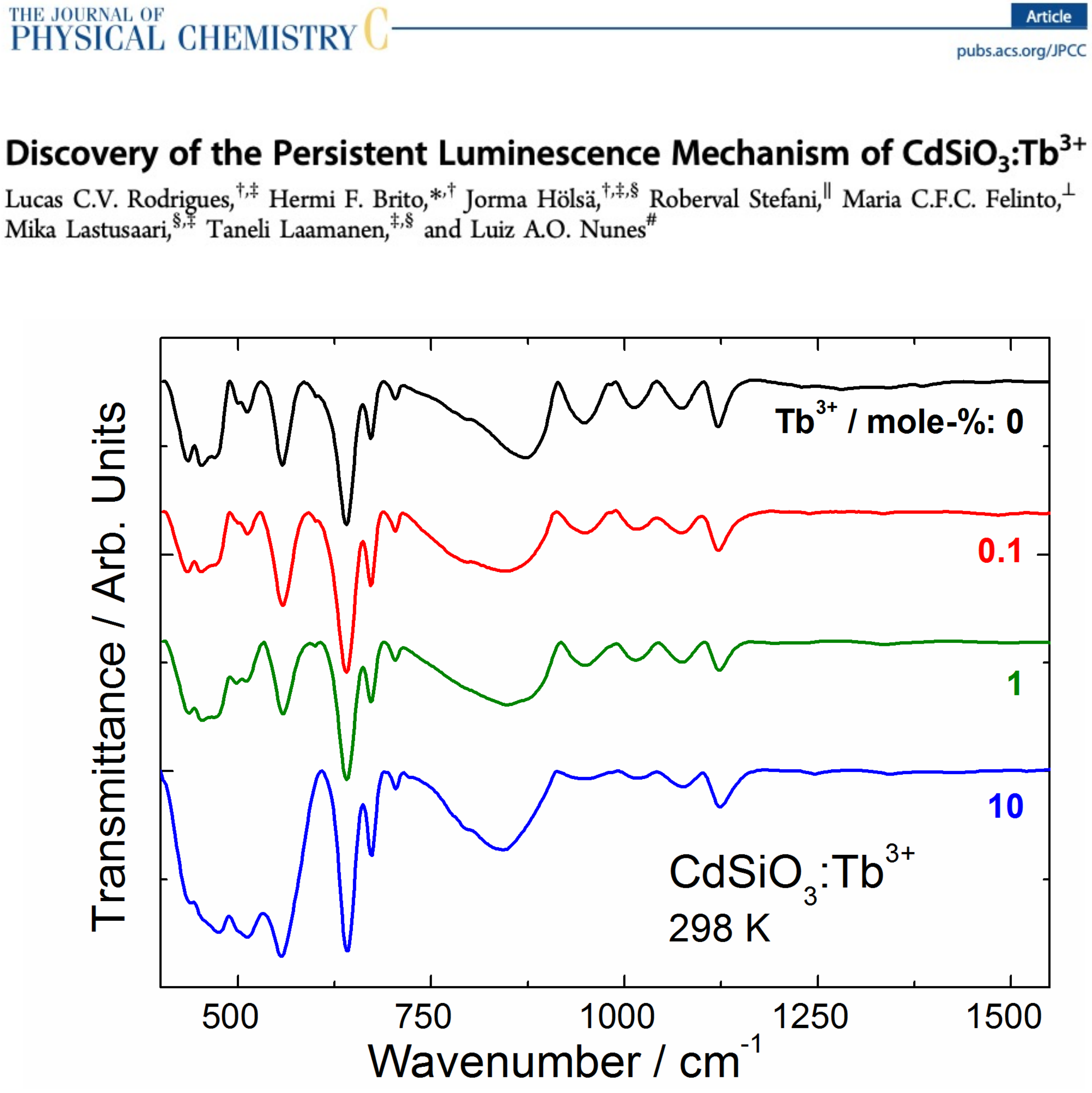
Métodos Espectroscópicos

- Eletrônicos
- Absorção e espalhamento de raios X

Espectroscopia Vibracional







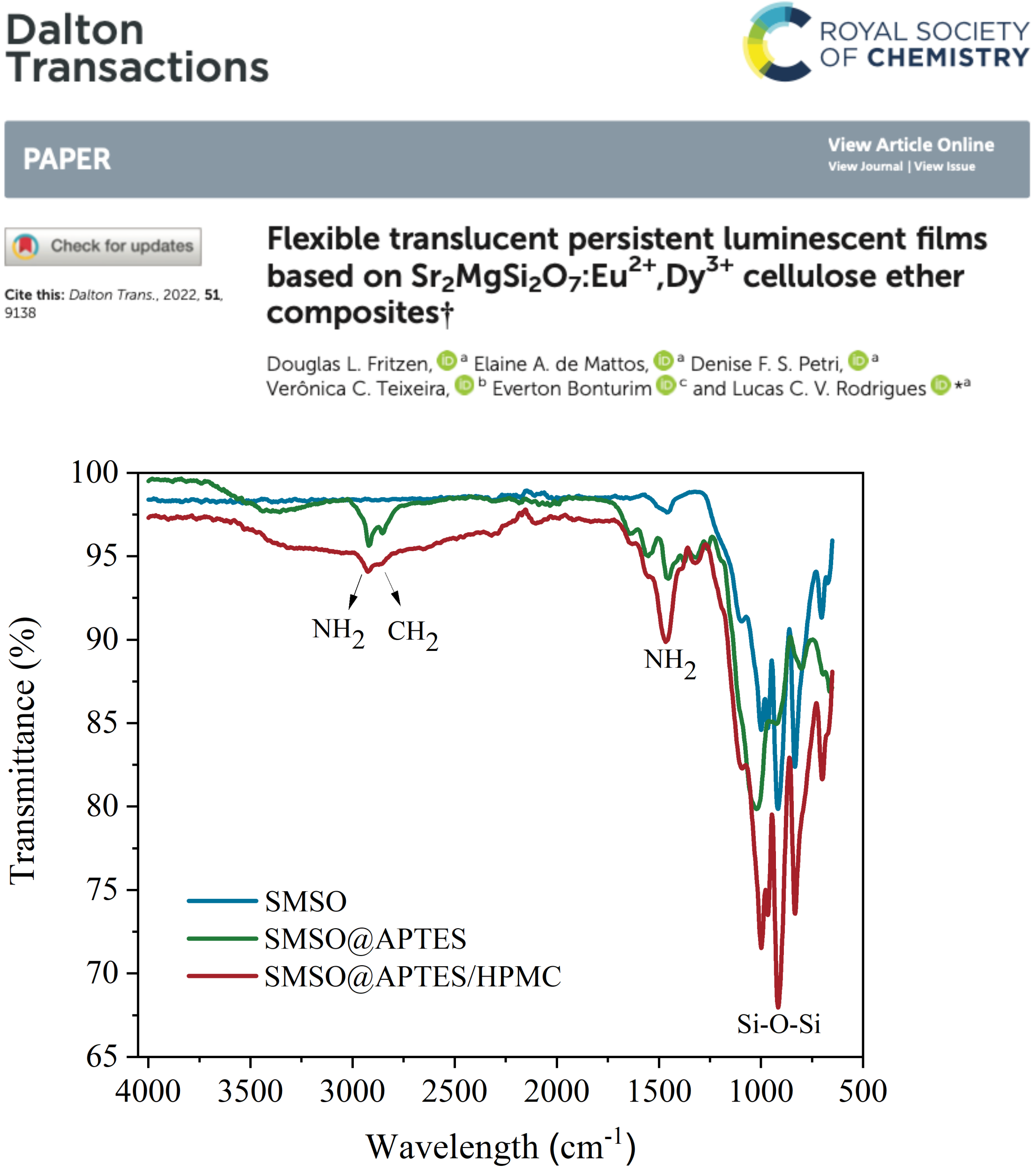
THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Discovery of the Persistent Luminescence Mechanism of $CdSiO_3$:Tb^{3+}

Lucas C.V. Rodrigues,[†,‡] Hermi F. Brito,[*,†] Jorma Hölsä,[†,‡,§] Roberval Stefani,[∥] Maria C.F.C. Felinto,[⊥] Mika Lastusaari,[§,‡] Taneli Laamanen,[‡,§] and Luiz A.O. Nunes[#]



Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: *Dalton Trans.*, 2022, **51**, 9138

Flexible translucent persistent luminescent films based on $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} cellulose ether composites†

Douglas L. Fritzen,[a] Elaine A. de Mattos,[a] Denise F. S. Petri,[a] Verônica C. Teixeira,[b] Everton Bonturim[c] and Lucas C. V. Rodrigues[*a]

Estados Eletrônicos

Qual equação descreve um estado eletrônico?

Born–Oppenheimer approximation

Repulsão núcleo-núcleo

Operador de interação eletrostática núcleo-elétrons (i: elétrons, A núcleos)

$$H = \boxed{-\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)} - \boxed{\sum_{i,A}\frac{Z_A e^2}{4\pi\varepsilon_0 R_{iA}}} + \boxed{\sum_i\sum_{j\neq i}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}} + \boxed{\sum_A\sum_{B\neq A}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}}}$$

Operador de energia cinética total dos elétrons

Repulsão elétron-elétron

SE NÃO HOUVESSE REPULSÃO INTERELETRÔNICA:

$$\psi = \phi_1(1)\phi_2(2)\ldots\phi_N(N)$$

A função de onda poderia ser descrita como o produto da função de onda de cada elétron.

ϕ_1 é a função de onda do elétron 1 e $\phi_1{}^2$ é a probabilidade de encontrar o elétron no espaço. Logo ϕ_1 é a descrição do orbital

Tratar espectroscopia usando orbital não é a melhor aproximação...

- Números quânticos…
- O que é um bom número quântico?

Aproximação de Russel-Saunders para estados de energia atômicos

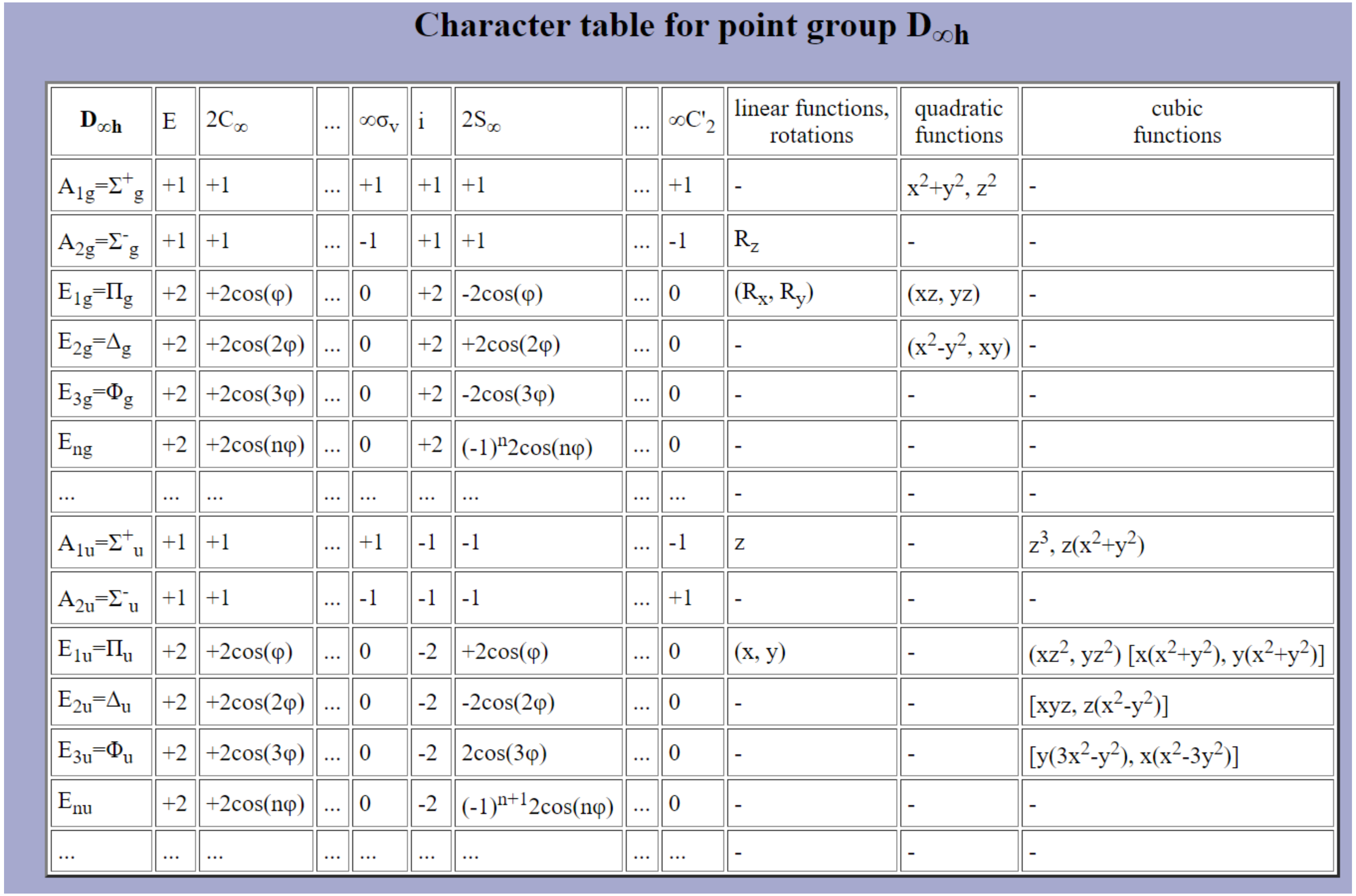
Lembram do

$$^{2S+1}L_J$$

Para os estados excitados:

- Miessler Cap 11
- Links das aulas de graduação de espectroscopia

Para moléculas



Character table for point group $D_{\infty h}$

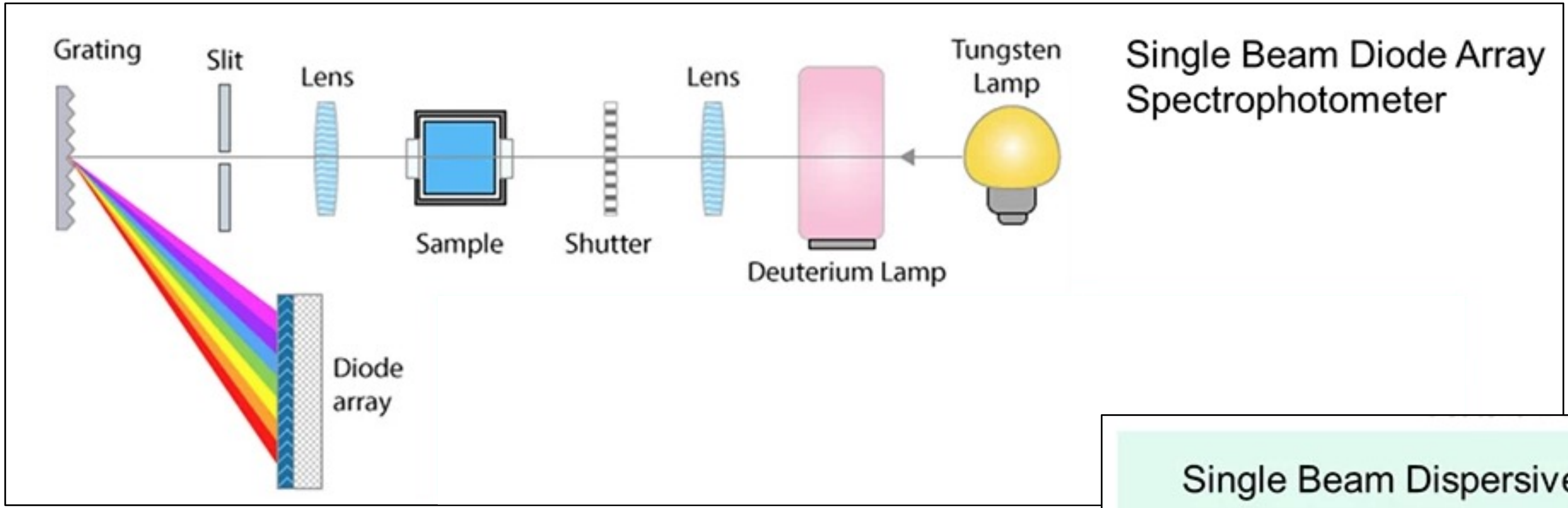
$D_{\infty h}$	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C'_2$	linear functions, rotations	quadratic functions	cubic functions
$A_{1g}=\Sigma^+_g$	+1	+1	...	+1	+1	+1	...	+1	-	x^2+y^2, z^2	-
$A_{2g}=\Sigma^-_g$	+1	+1	...	-1	+1	+1	...	-1	R_z	-	-
$E_{1g}=\Pi_g$	+2	+2cos(φ)	...	0	+2	-2cos(φ)	...	0	(R_x, R_y)	(xz, yz)	-
$E_{2g}=\Delta_g$	+2	+2cos(2φ)	...	0	+2	+2cos(2φ)	...	0	-	(x^2-y^2, xy)	-
$E_{3g}=\Phi_g$	+2	+2cos(3φ)	...	0	+2	-2cos(3φ)	...	0	-	-	-
E_{ng}	+2	+2cos(nφ)	...	0	+2	$(-1)^n$2cos(nφ)	...	0	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-
$A_{1u}=\Sigma^+_u$	+1	+1	...	+1	-1	-1	...	-1	z	-	z^3, $z(x^2+y^2)$
$A_{2u}=\Sigma^-_u$	+1	+1	...	-1	-1	-1	...	+1	-	-	-
$E_{1u}=\Pi_u$	+2	+2cos(φ)	...	0	-2	+2cos(φ)	...	0	(x, y)	-	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
$E_{2u}=\Delta_u$	+2	+2cos(2φ)	...	0	-2	-2cos(2φ)	...	0	-	-	$[xyz, z(x^2-y^2)]$
$E_{3u}=\Phi_u$	+2	+2cos(3φ)	...	0	-2	2cos(3φ)	...	0	-	-	$[y(3x^2-y^2), x(x^2-3y^2)]$
E_{nu}	+2	+2cos(nφ)	...	0	-2	$(-1)^{n+1}$2cos(nφ)	...	0	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-

Para mais detalhes:

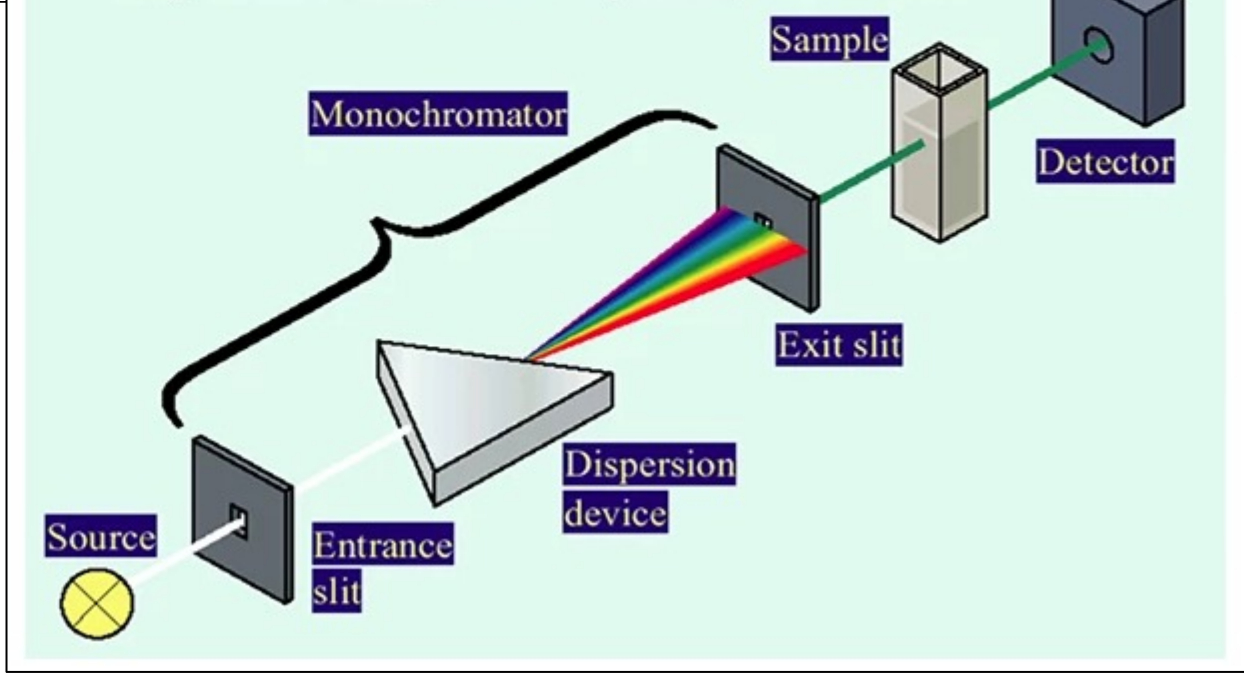
- McQuarrie, Physical Chemistry, a Molecular approach, item 9-14

Transições eletrônicas

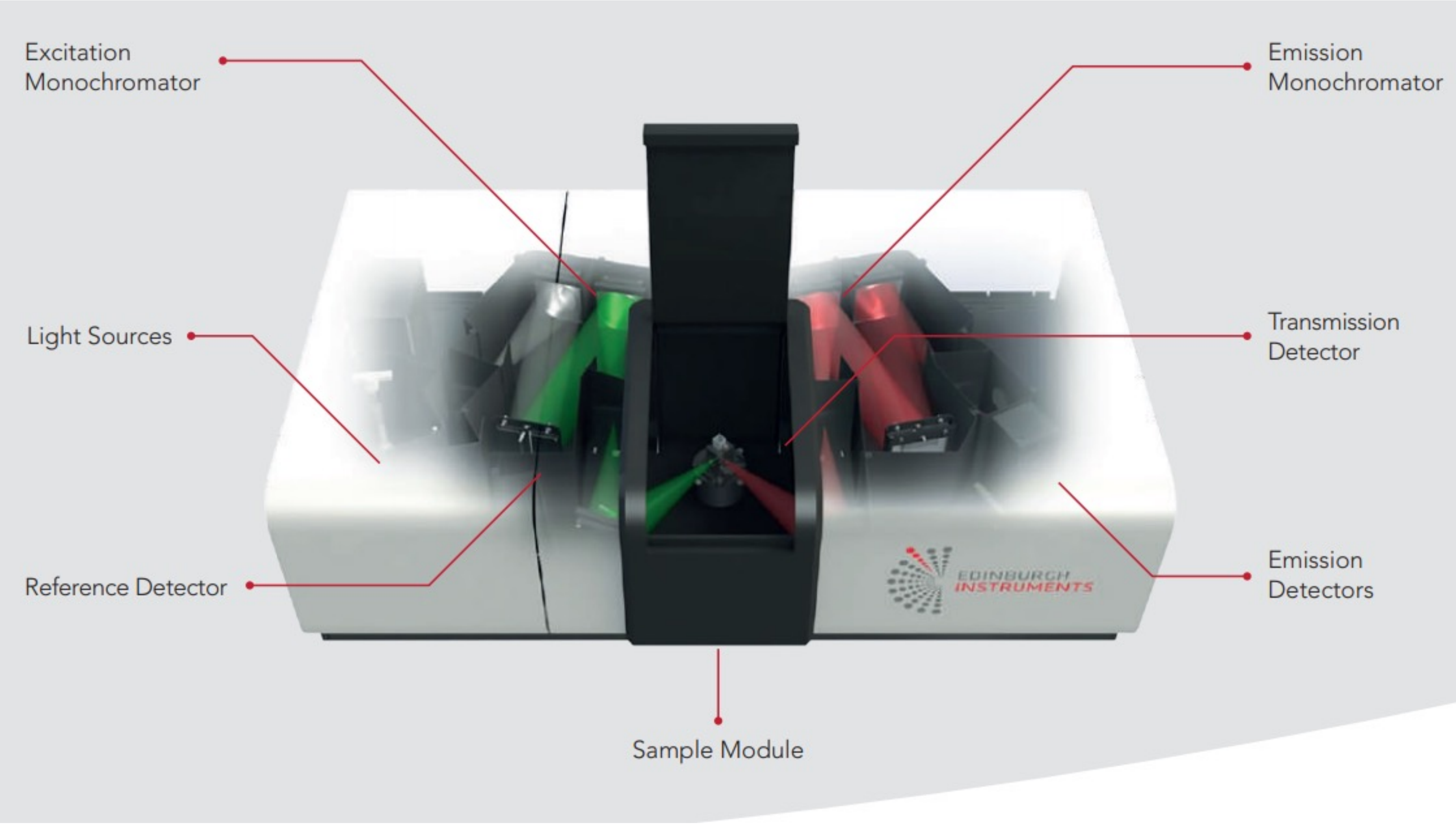
Fotos by @ton_bonturim


Single Beam Diode Array Spectrophotometer

Single Beam Dispersive Spectrophotometer

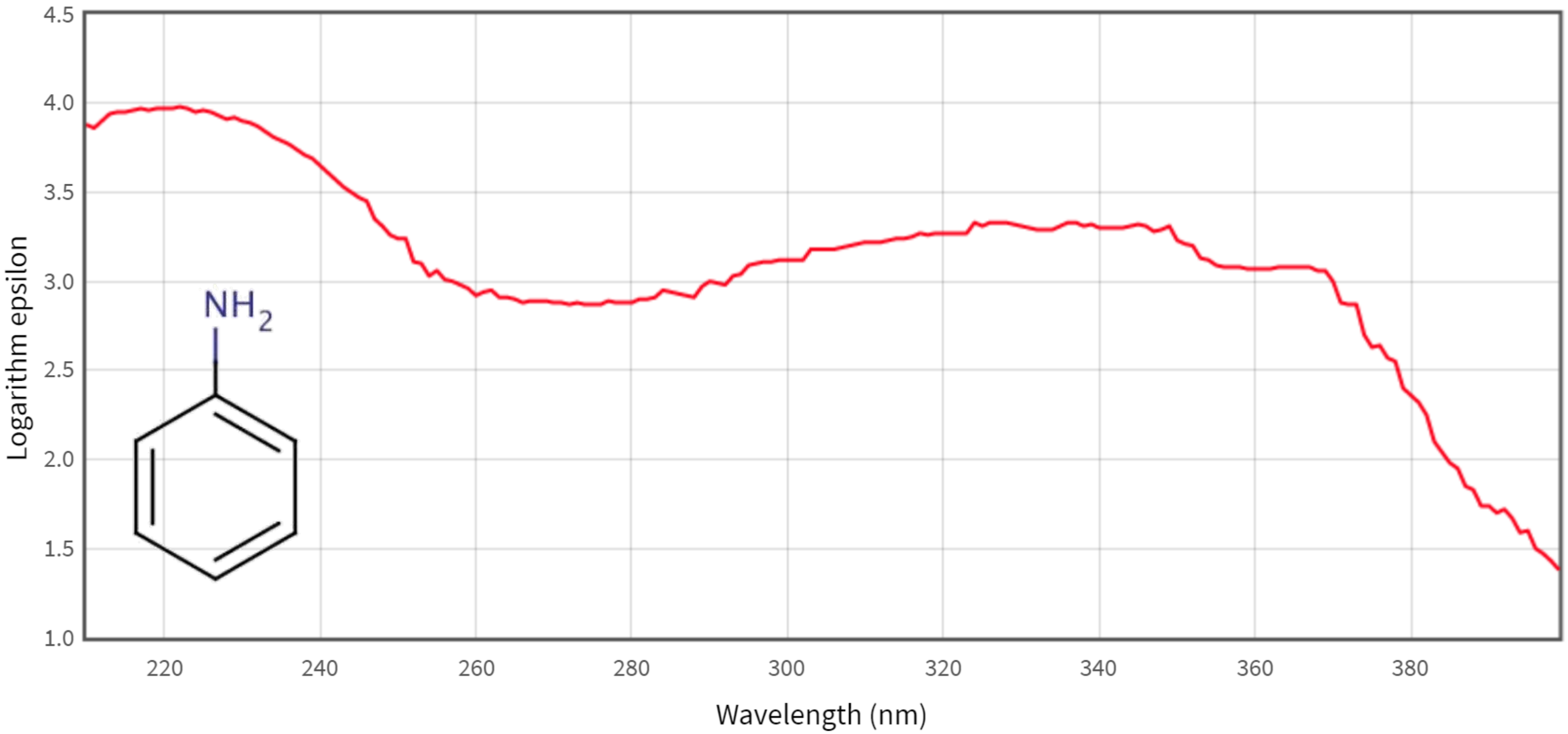


https://www.ssi.shimadzu.com/products/uv-vis-spectrophotometers/faqs/instrument-design.html



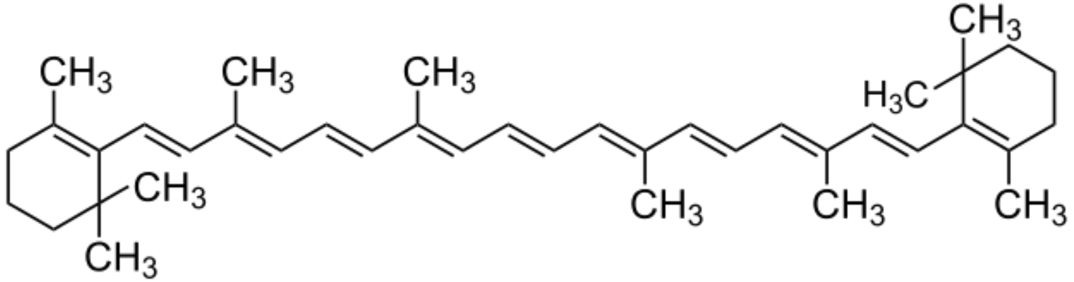
https://www.edinst.com/wp-content/uploads/2020/04/EI_FS5-Brochure_16pp_FINAL_WEB-compressed-1.pdf

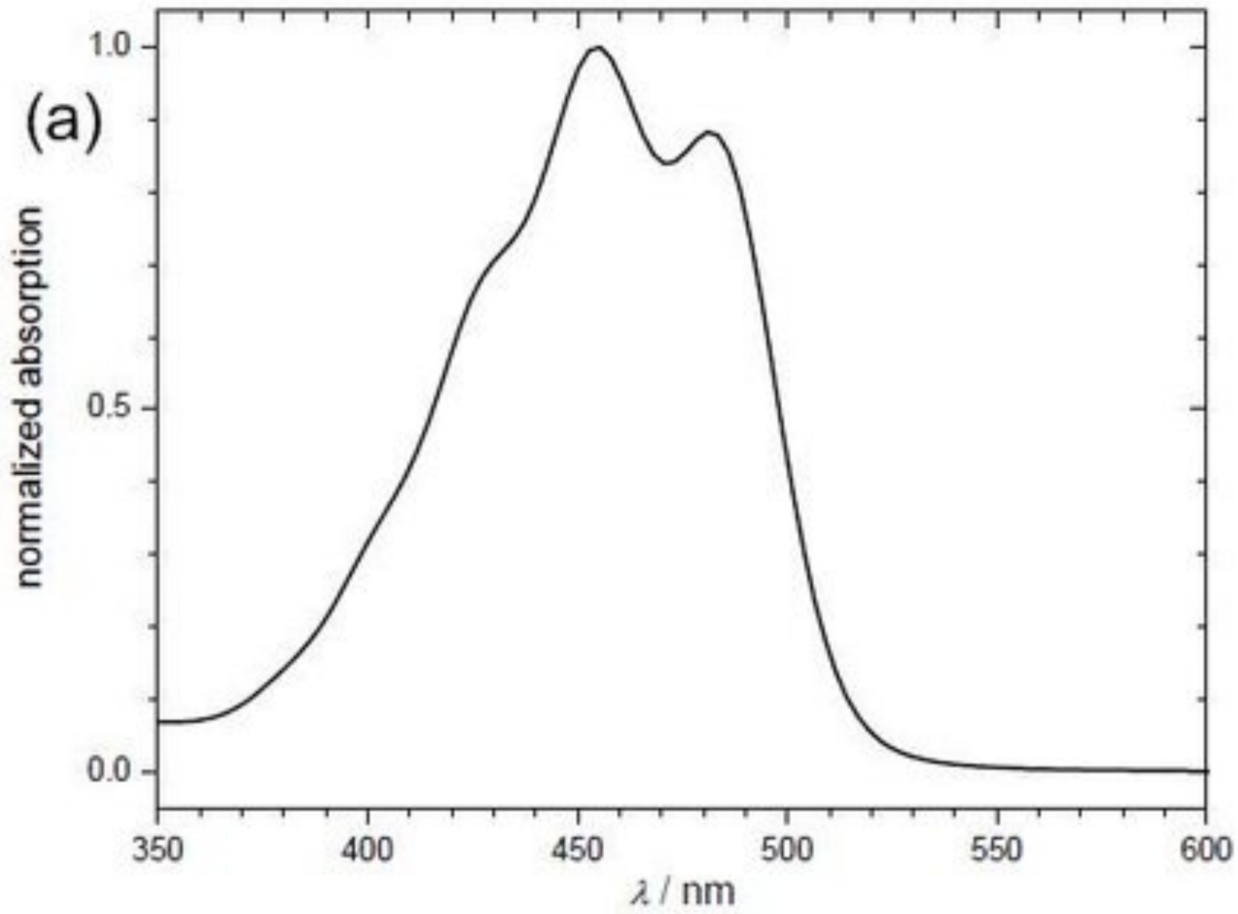
Exemplos de espectro

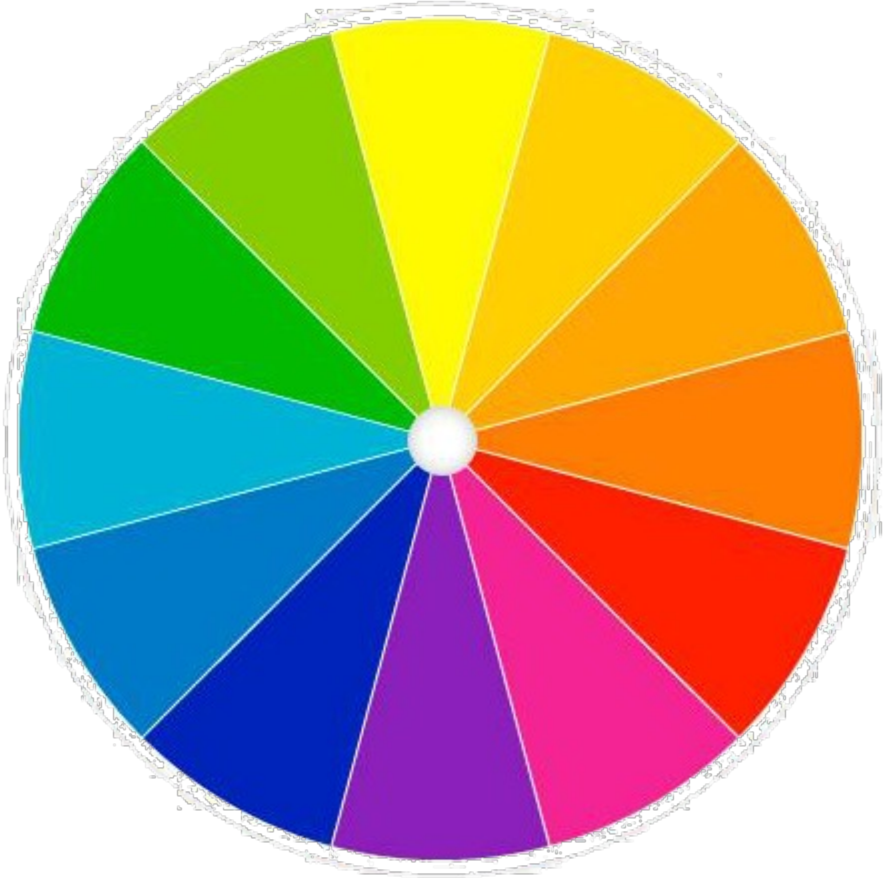


https://webbook.nist.gov/cgi/cbook.cgi?ID=C62533&Units=SI

Cores dos compostos

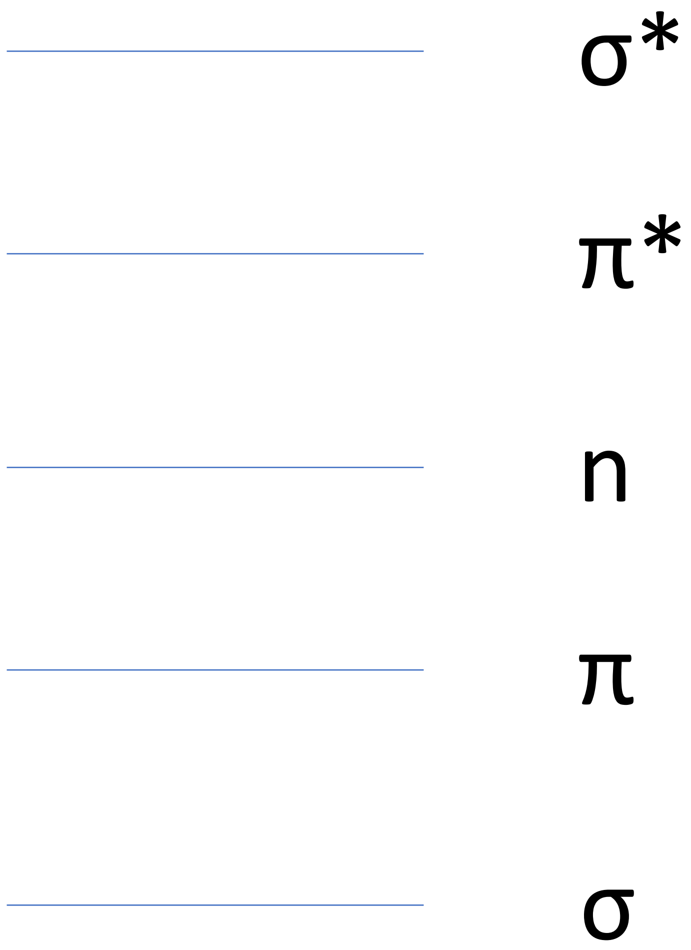






Rees, Thomas. (2017). Bis-homoleptic, Terdentate, Cyclometalates of Group 8 and 9.

Ordem das transições em compostos orgânicos



σ*

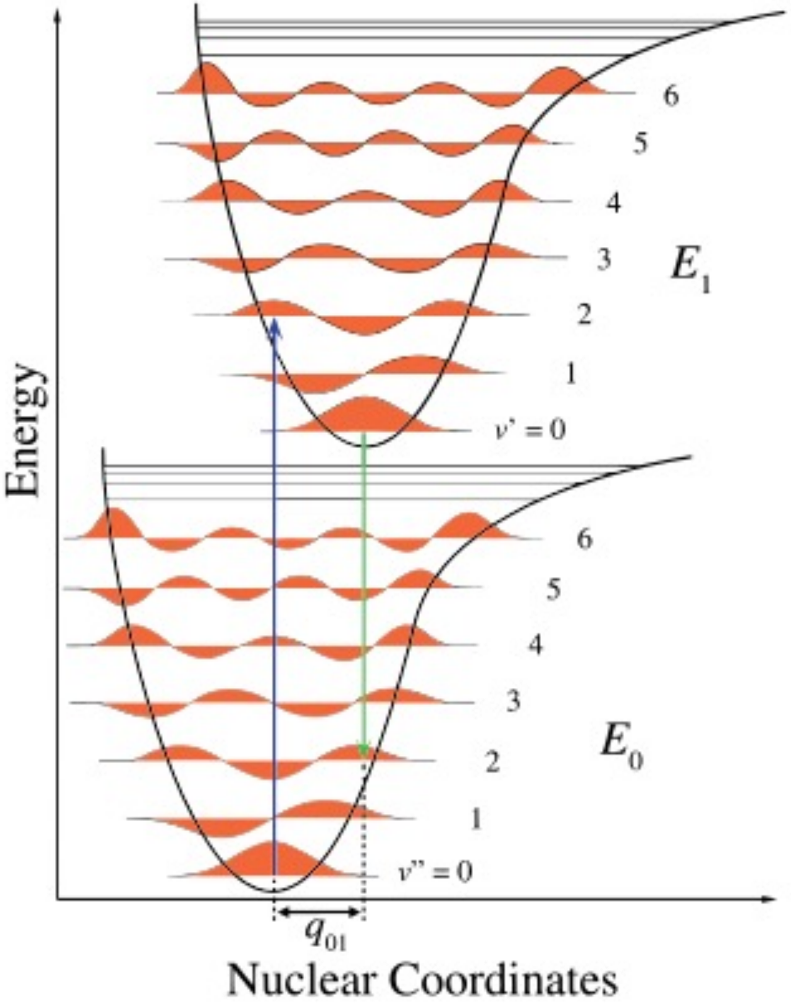
π*

n

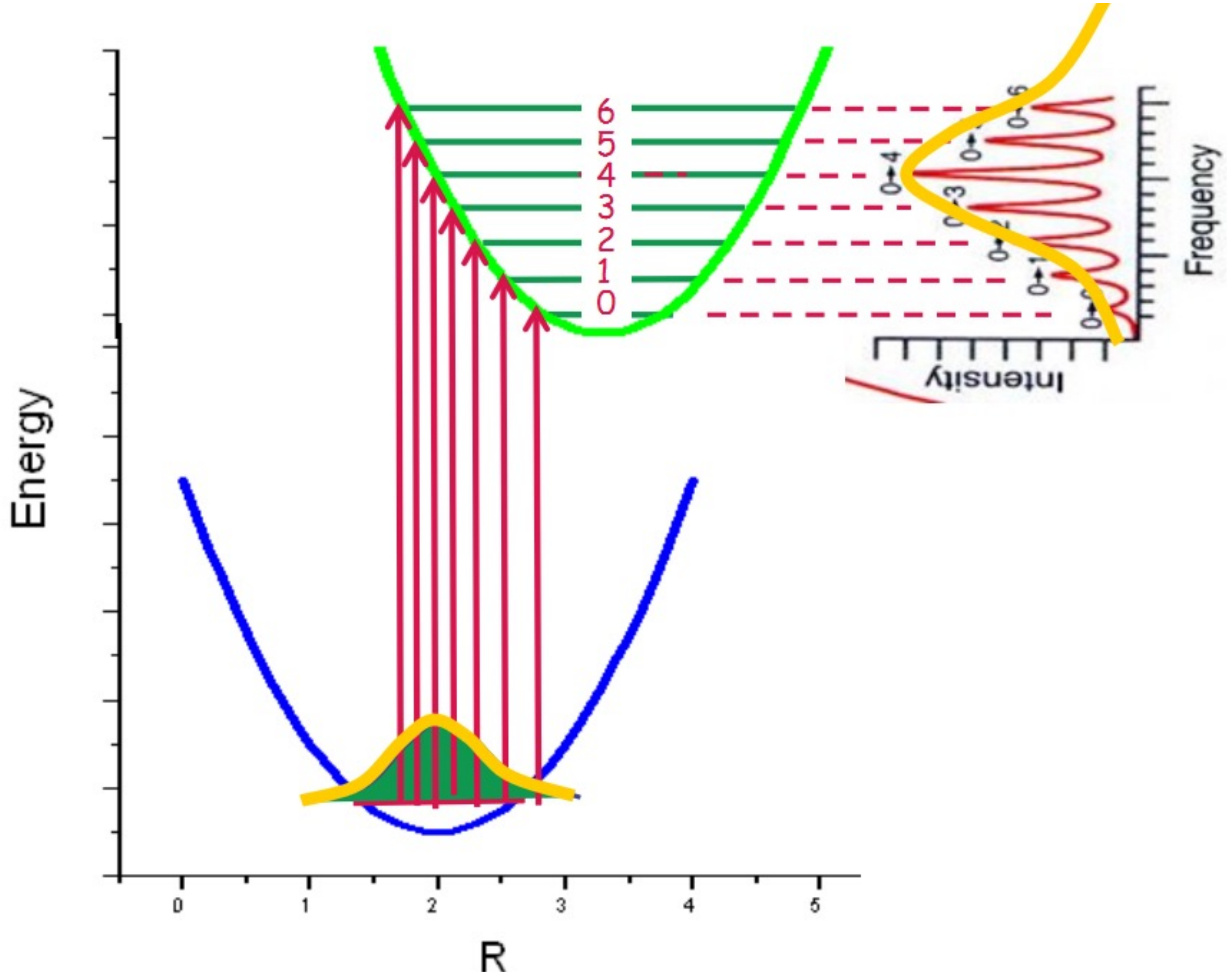
π

σ

Porque vemos o espectro em bandas?



Princípio de Franck-Condon



Probabilidades de transição

Regras de Seleção - Spin

$$P_{\mathrm{spin}}(i \rightarrow j) = |\langle \phi_i, \phi_j \rangle|^2$$

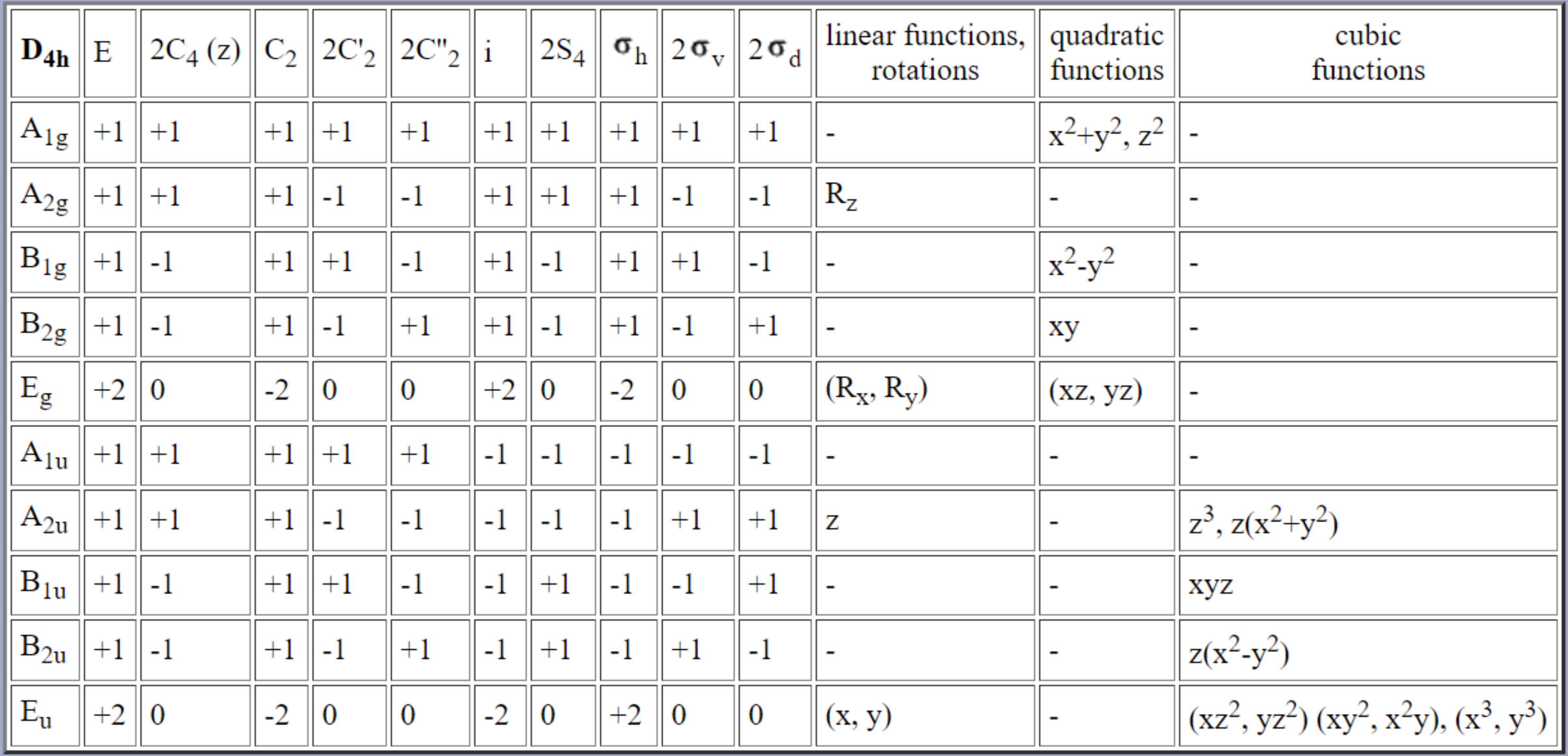
Regra de seleção de orbital

$$\boldsymbol{M}_{21} = \int \Psi_2 \boldsymbol{\mu} \Psi_1 \, \mathrm{d}\tau$$

$\boldsymbol{M}_{21}$ = vetor momento de dipolo da transição de 1 para 2
$|M_{21}|^2$ = probabilidade intrínseca da transição

Character table for point group D_{4h}

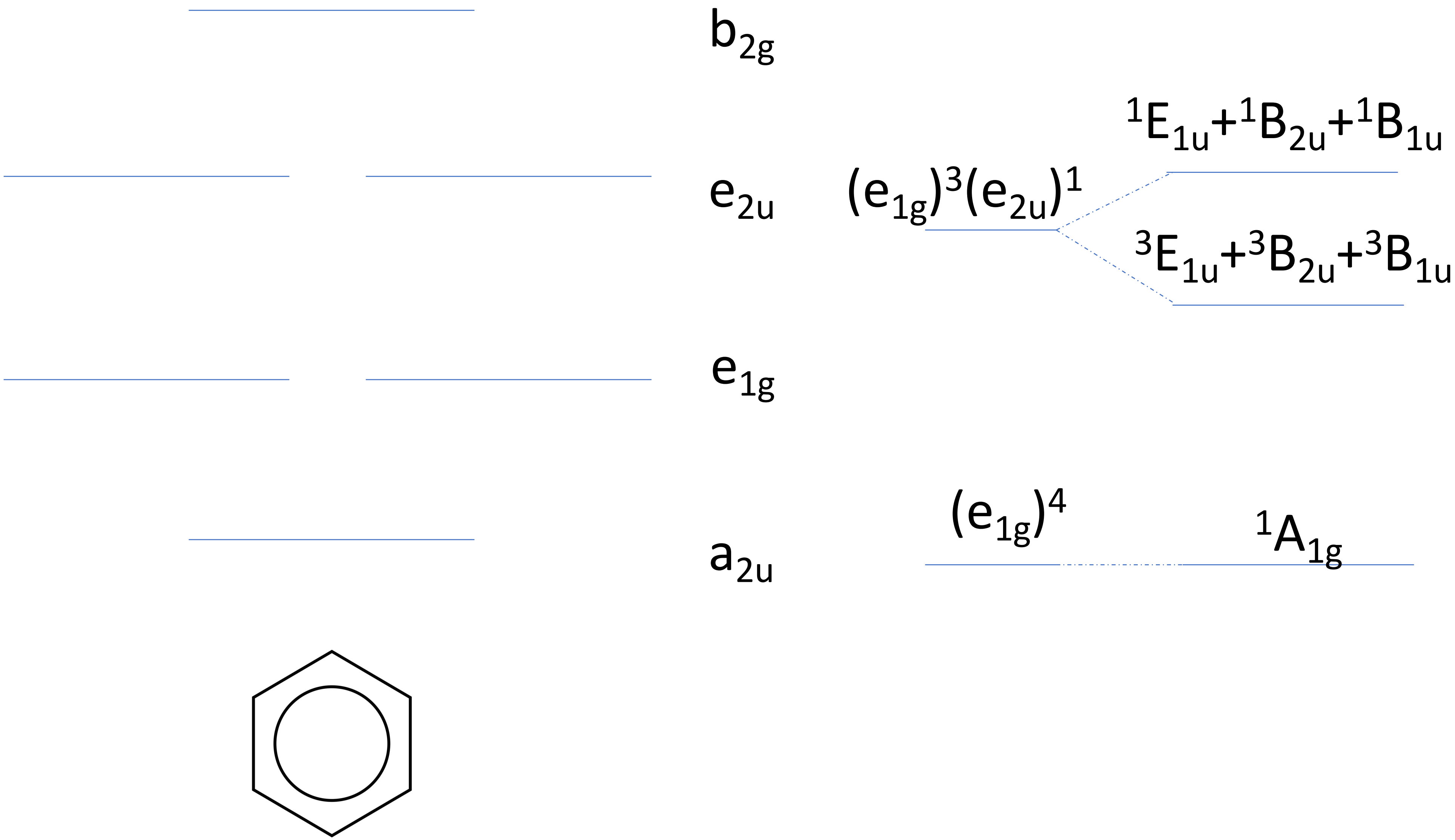
(x axis coincident with C'_2 axis)



$\mathbf{D_{4h}}$	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-	z^3, $z(x^2+y^2)$
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-	xyz
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	$z(x^2-y^2)$
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-	(xz^2, yz^2) (xy^2, x^2y), (x^3, y^3)

Precisamos olhar a simetria

- O produto das representações irredutíveis com o operador dipolo elétrico deve possuir a representação totalmente simetrica



b_{2g}

$^1E_{1u}+^1B_{2u}+^1B_{1u}$

e_{2u}

$(e_{1g})^3(e_{2u})^1$

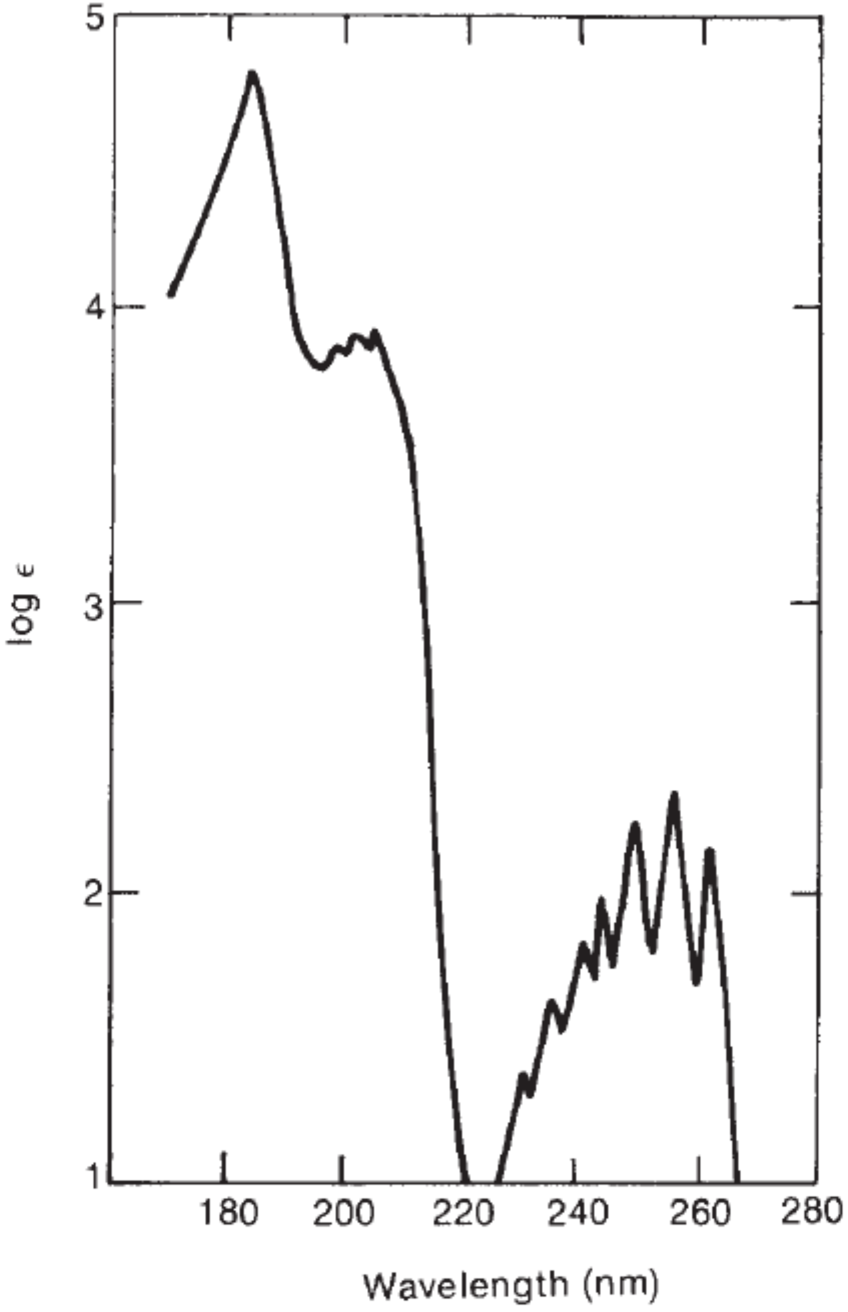
$^3E_{1u}+^3B_{2u}+^3B_{1u}$

e_{1g}

$(e_{1g})^4$

$^1A_{1g}$

a_{2u}



$^1A_{1g} \rightarrow {}^1E_{1u}$, permitida ε = 47000

$^1A_{1g} \rightarrow {}^1B_{1u}$, proibida ε = 7400

$^1A_{1g} \rightarrow {}^1B_{2u}$, proibida ε = 230

Regra de Laporte

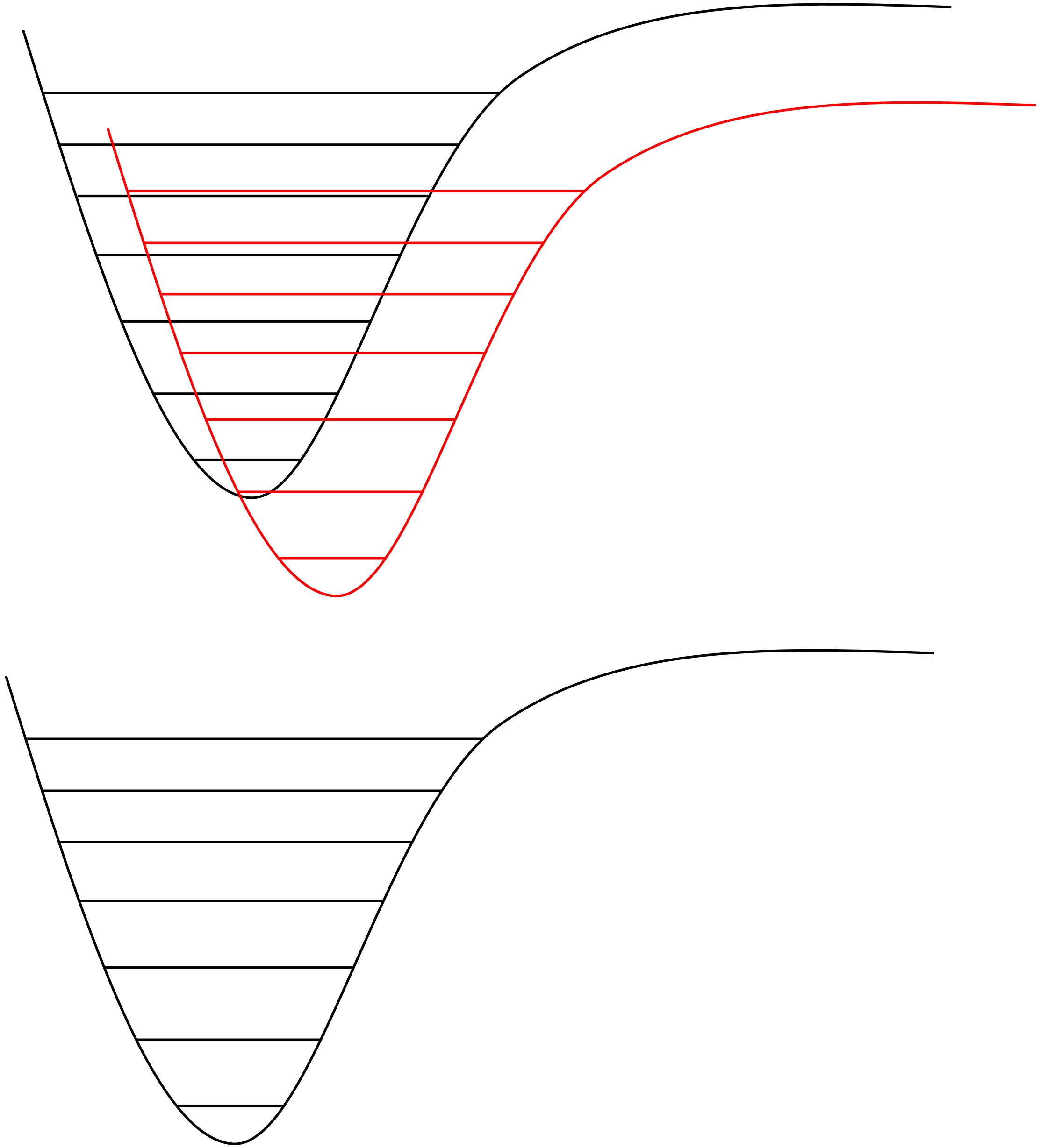
Para moléculas com centro de inversão: transições com $\Delta l \neq \pm 1$ são proibidas

Diagrama de OM de um complexo

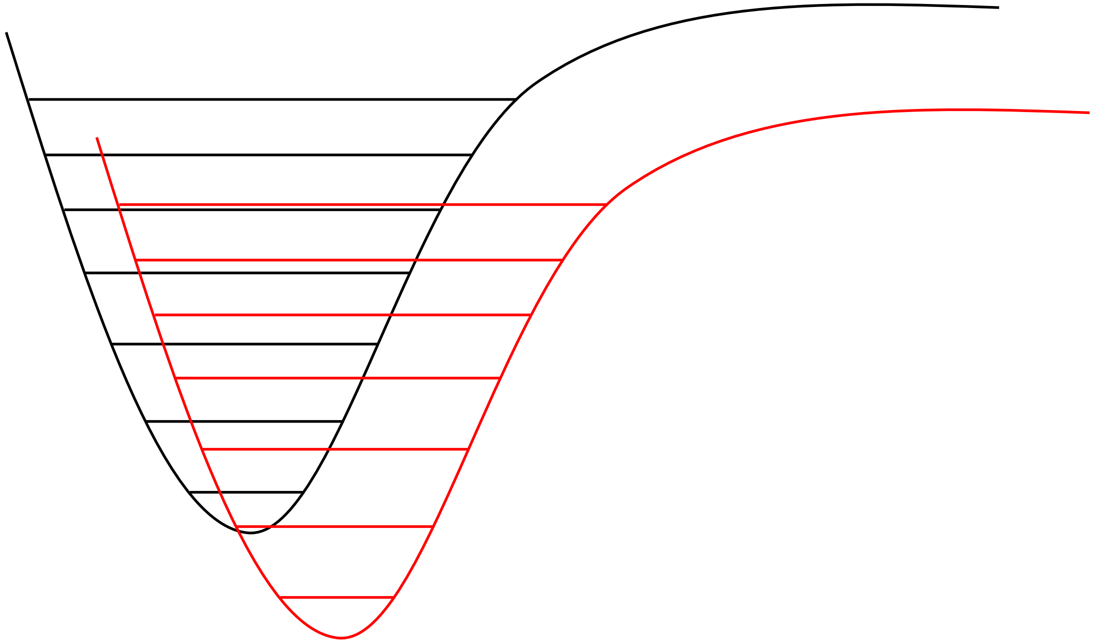
Ordem de Grandeza das absortividades molares

Transição	Regra de spin	Regra de dipolo	Laporte	E / L mol^{-1} cm^{-1}
LMCT / MLCT	Permitida por spin	Permitida por orbital	Permitida	3000 – 50000
d-d (T_d)	Permitida por spin	Proibida por orbital	Não relevante	250 – 1000
d-d (O_h)	Permitida por spin	Proibida por orbital	Proibida por Laporte	5 – 100
d-d (O_h)	Proibida por spin	Proibida por orbital	Proibida por Laporte	<1

Fenômenos de emissão



Fenômenos de emissão



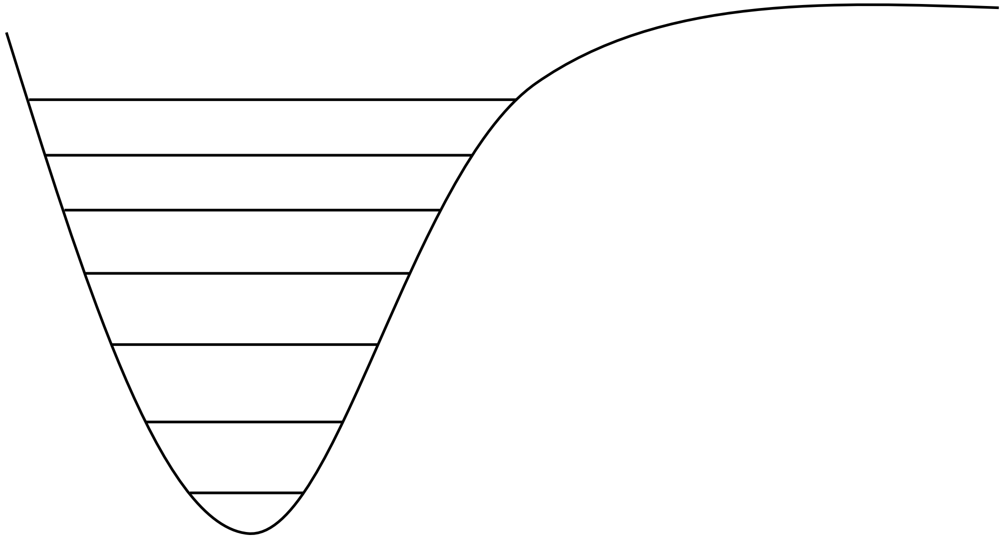
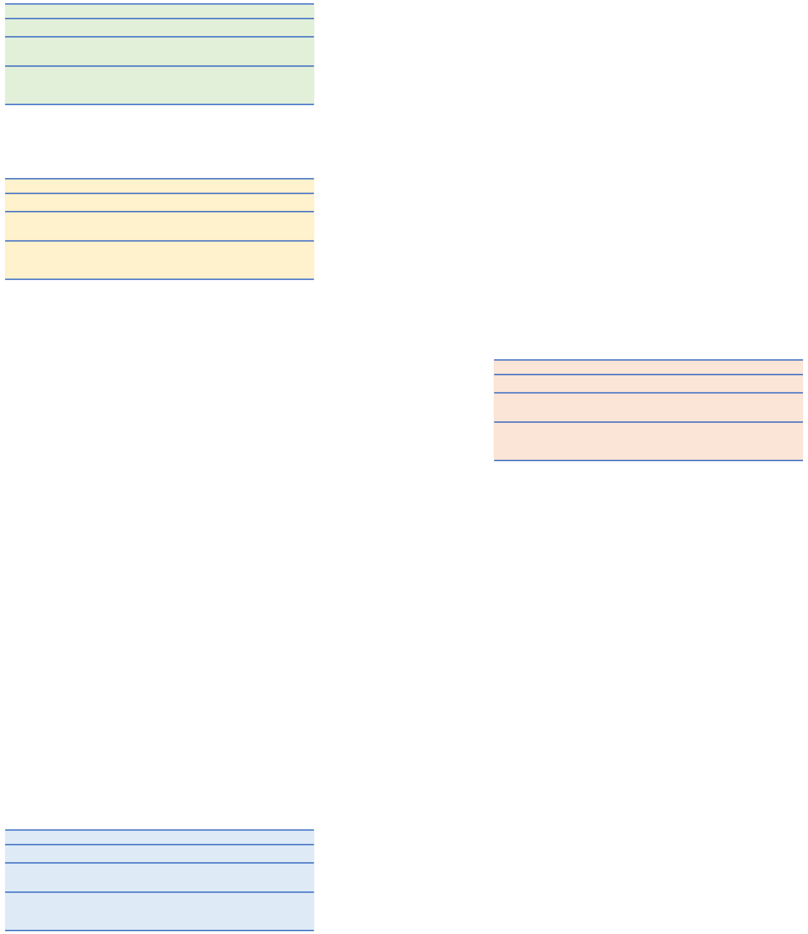


Diagrama de Jablonski



Excitação / Absorção: 10^{-15} s

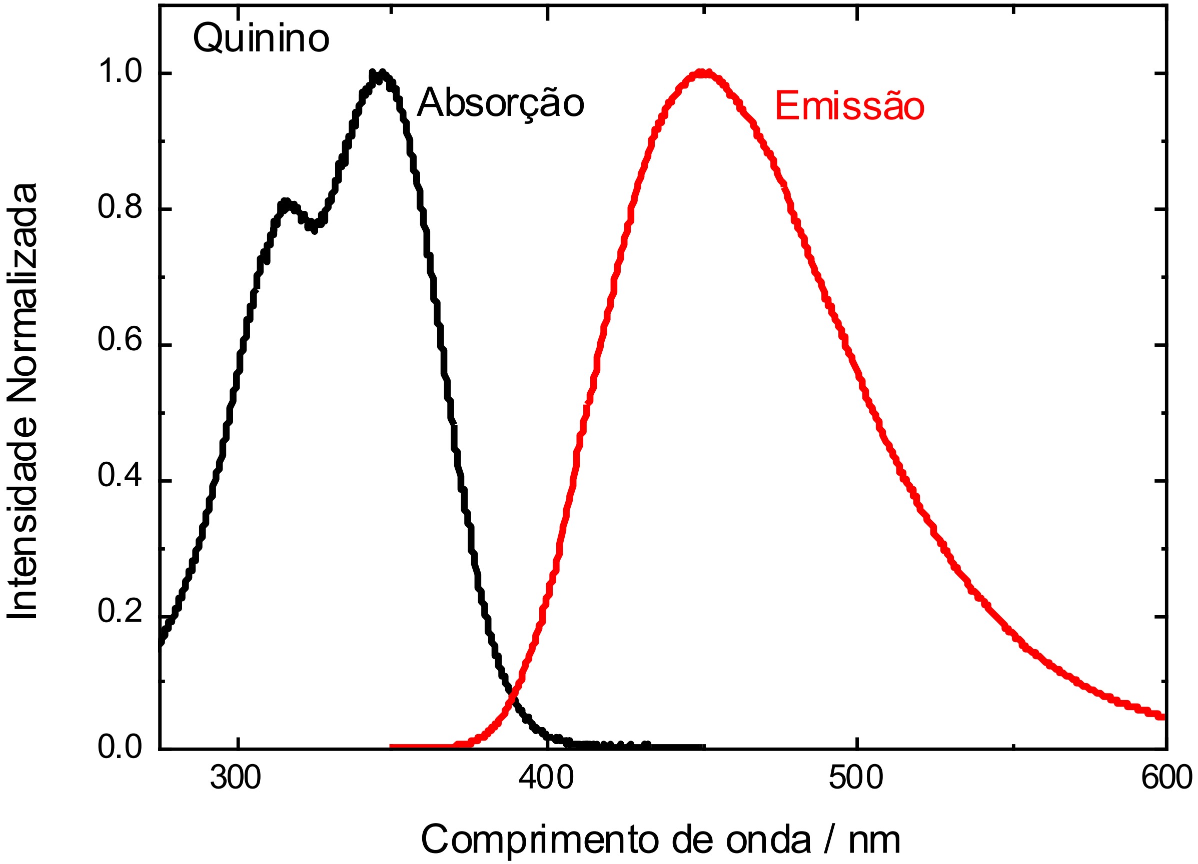
C.I. (Conversão Interna) e Relaxamento Vibracional: $10^{-14} – 10^{-11}$ s

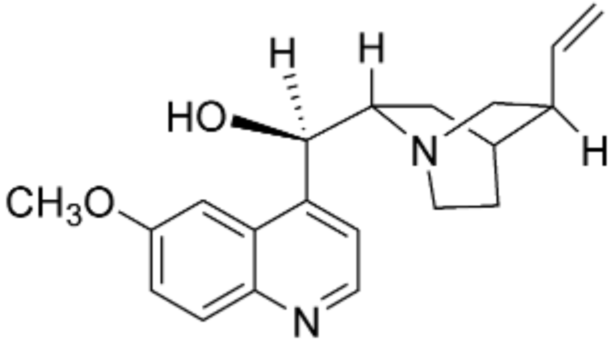
Fluorescência: $10^{-9} – 10^{-7}$ s

C.I.S. (Cruzamento Intersistema) : $10^{-8} – 10^{-3}$ s

Fosforescência: $10^{-3} – 10^{2}$ s

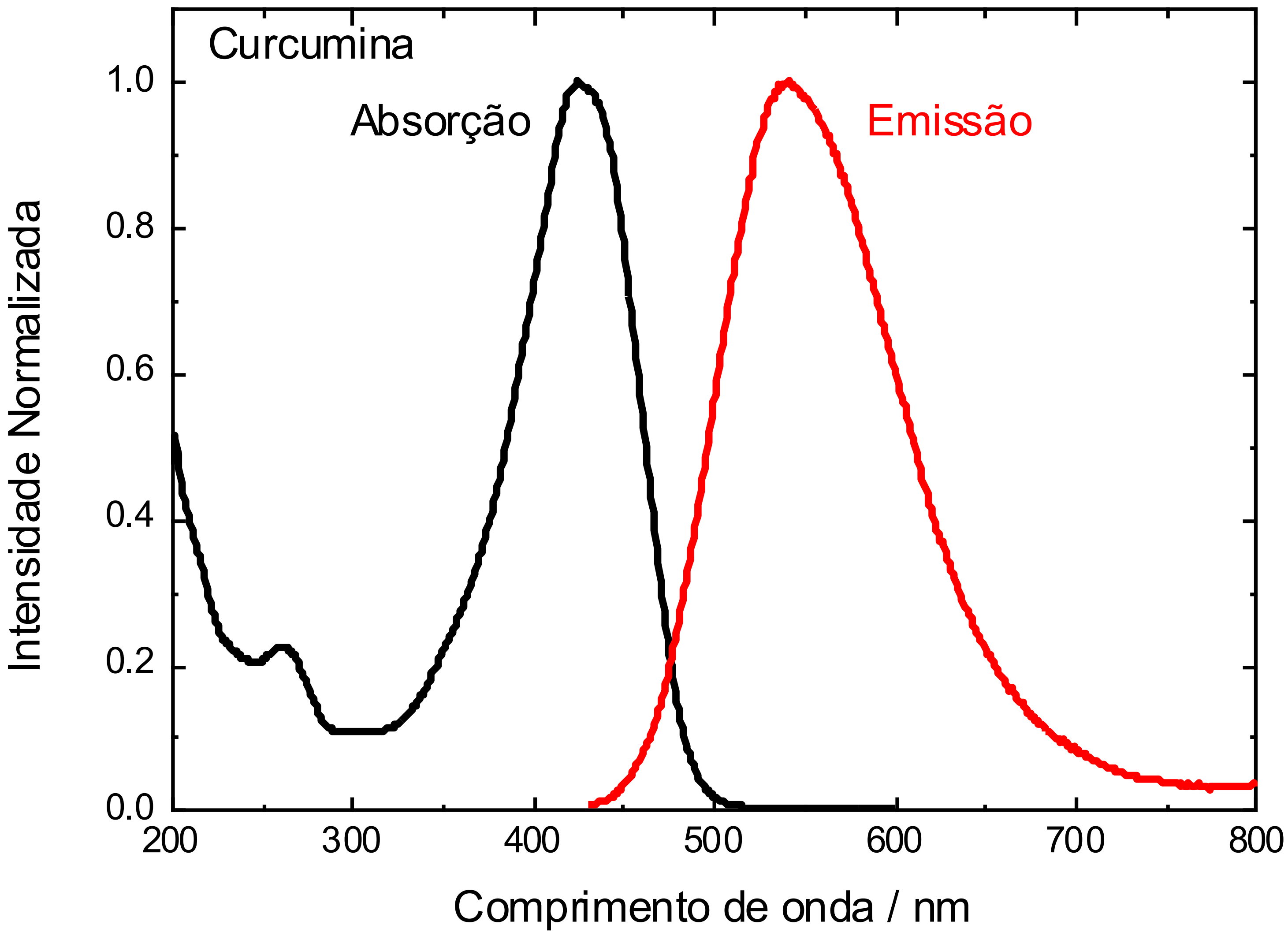
Exemplos de espectro

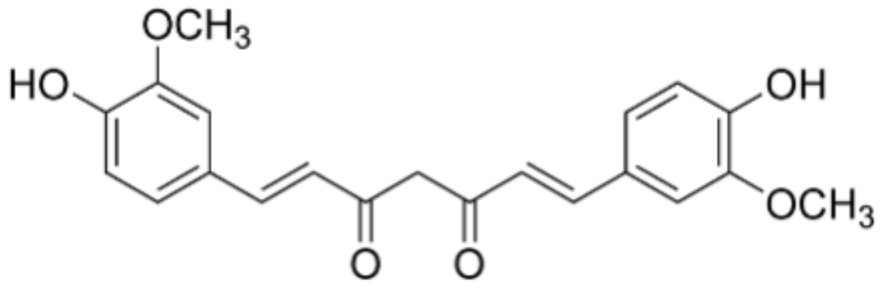




Quinino

“PhotochemCAD 3: Diverse Modules for Photophysical Calculations with Access to Multiple Spectral Databases,” Taniguchi, M.; Du, H.; Lindsey, J. S. Photochem. Photobiol. **2018**, 94, 277–289.
“Database of Absorption and Fluorescence Spectra of >300 Common Compounds for Use in PhotochemCAD,” Taniguchi, M.; Lindsey, J. S. Photochem. Photobiol. **2018**, 94, 290–327.





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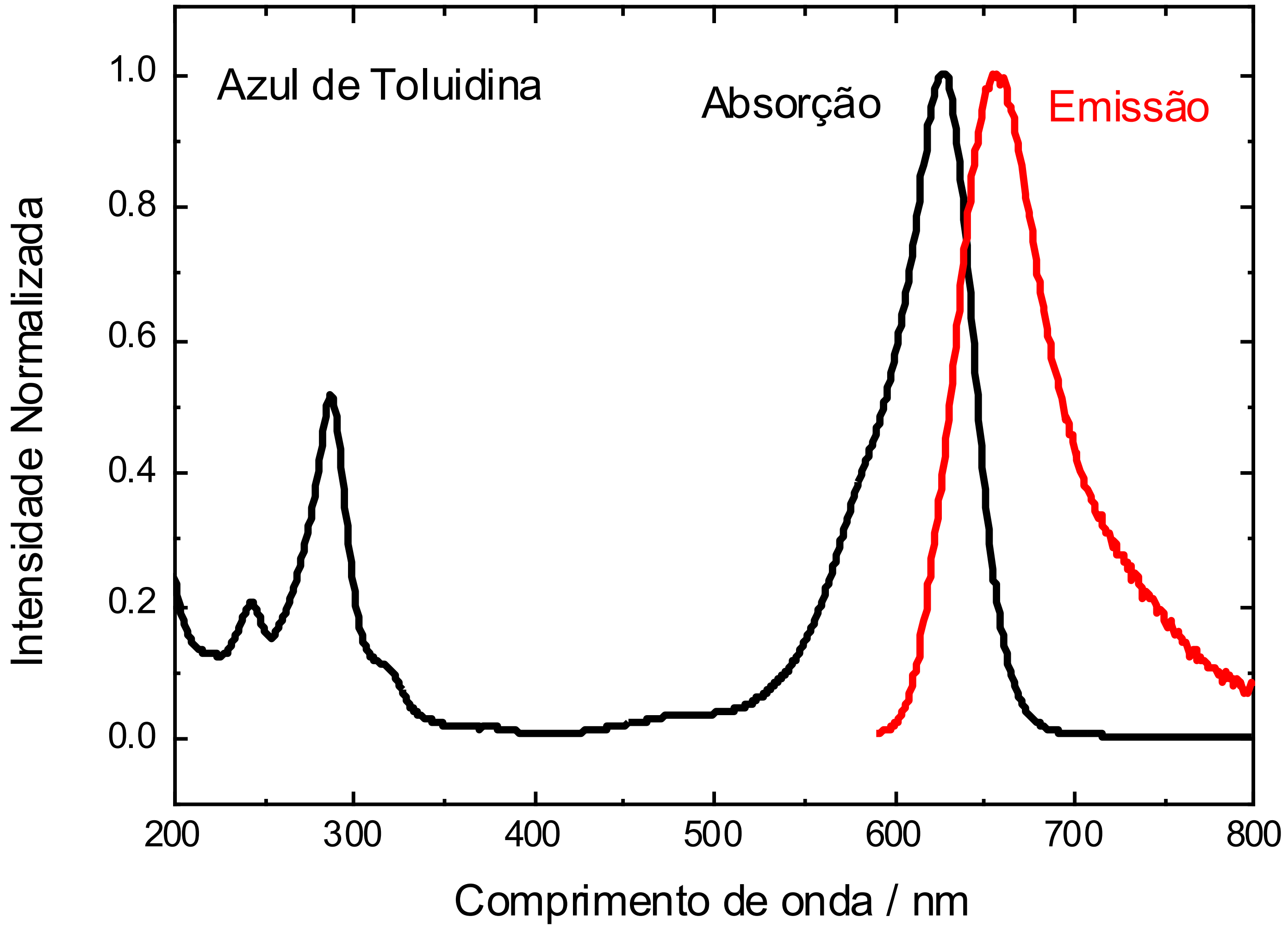
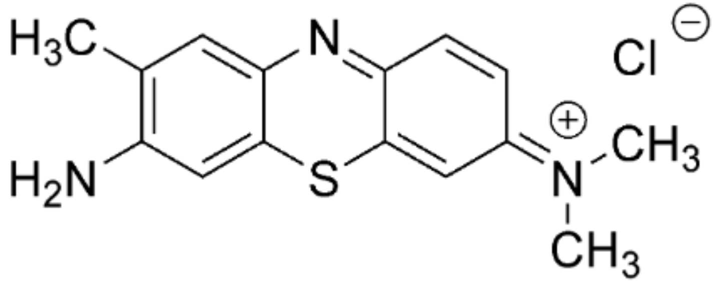




Azul de toluidina

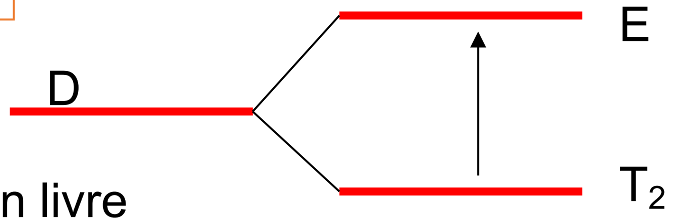
“PhotochemCAD 3: Diverse Modules for Photophysical Calculations with Access to Multiple Spectral Databases,”Taniguchi, M.; Du, H.; Lindsey, J. S. Photochem. Photobiol. **2018**, 94, 277–289.
“Database of Absorption and Fluorescence Spectra of >300 Common Compounds for Use in PhotochemCAD,” Taniguchi, M.; Lindsey, J. S. Photochem. Photobiol. **2018**, 94, 290–327.

E em um sólido?

ESPECTROSCOPIA DE CAMPO LIGANTE

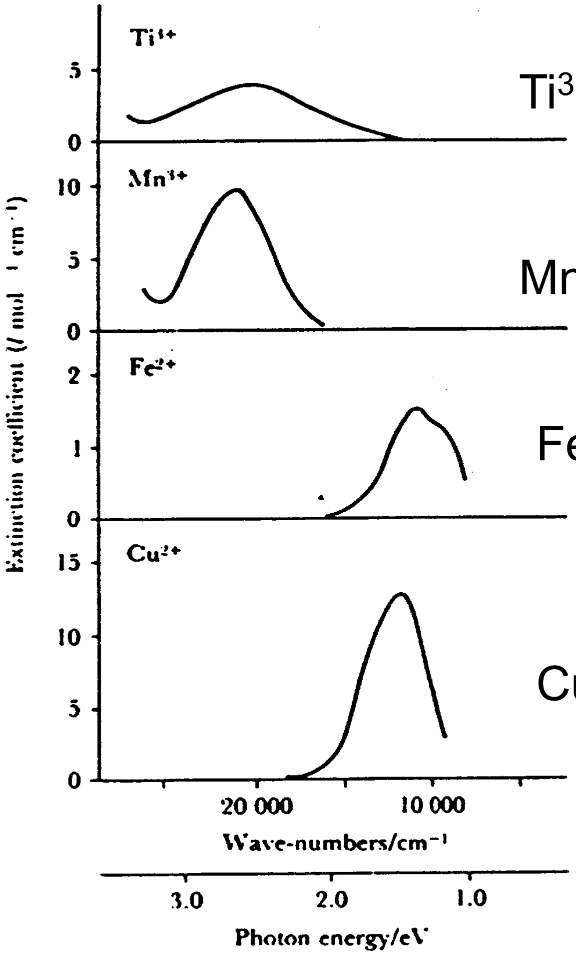
O campo ligante, atuando sobre os elétrons do metal, provoca a quebra da degenerescência orbital, bem como o desdobramento dos estados de energia:

Termos Espectroscópicos do Íon Livre	Representação de Simetria dos Estados desdobrados (O_h)
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{2g} + T_{1g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$



íon livre
d^1, d^9
d^4 e $d^6_{\text{spin-alto}}$

complexo octaédrico correspondente



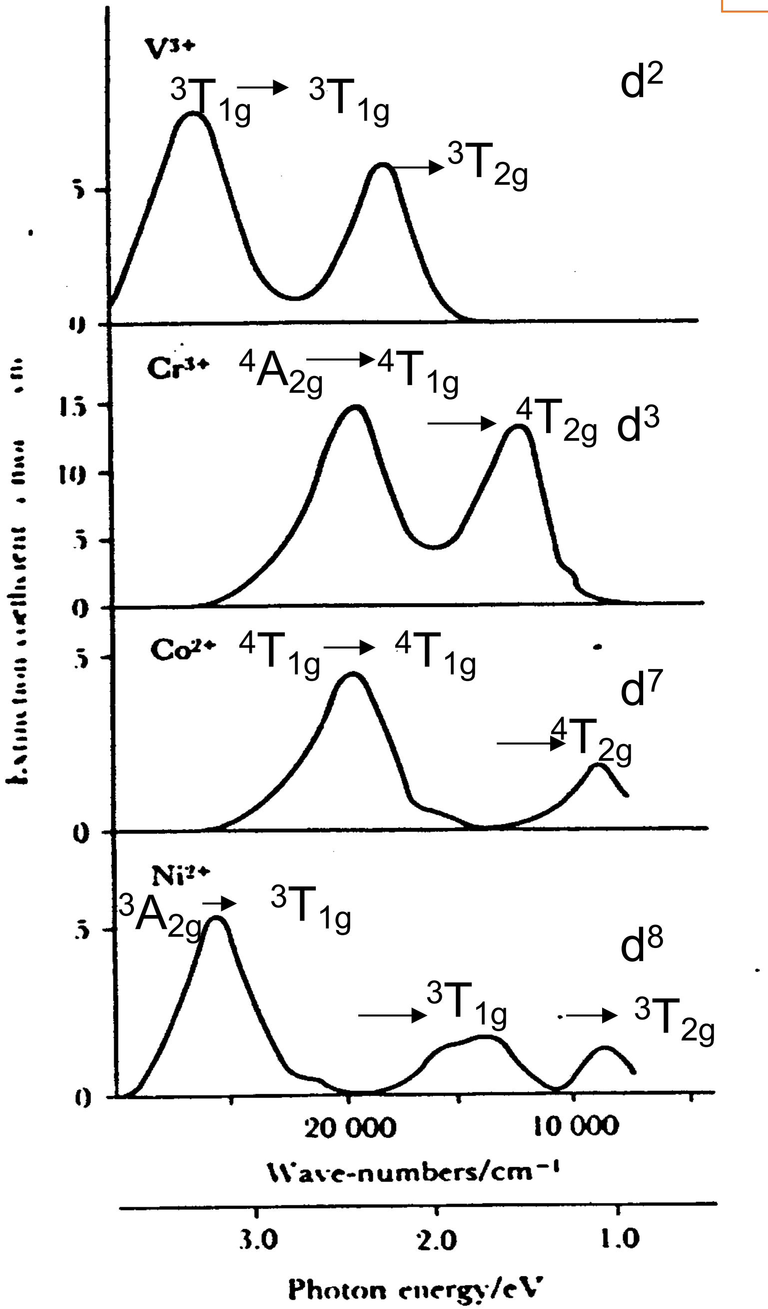
$Ti^{3+}_{(aq)}$ d^1

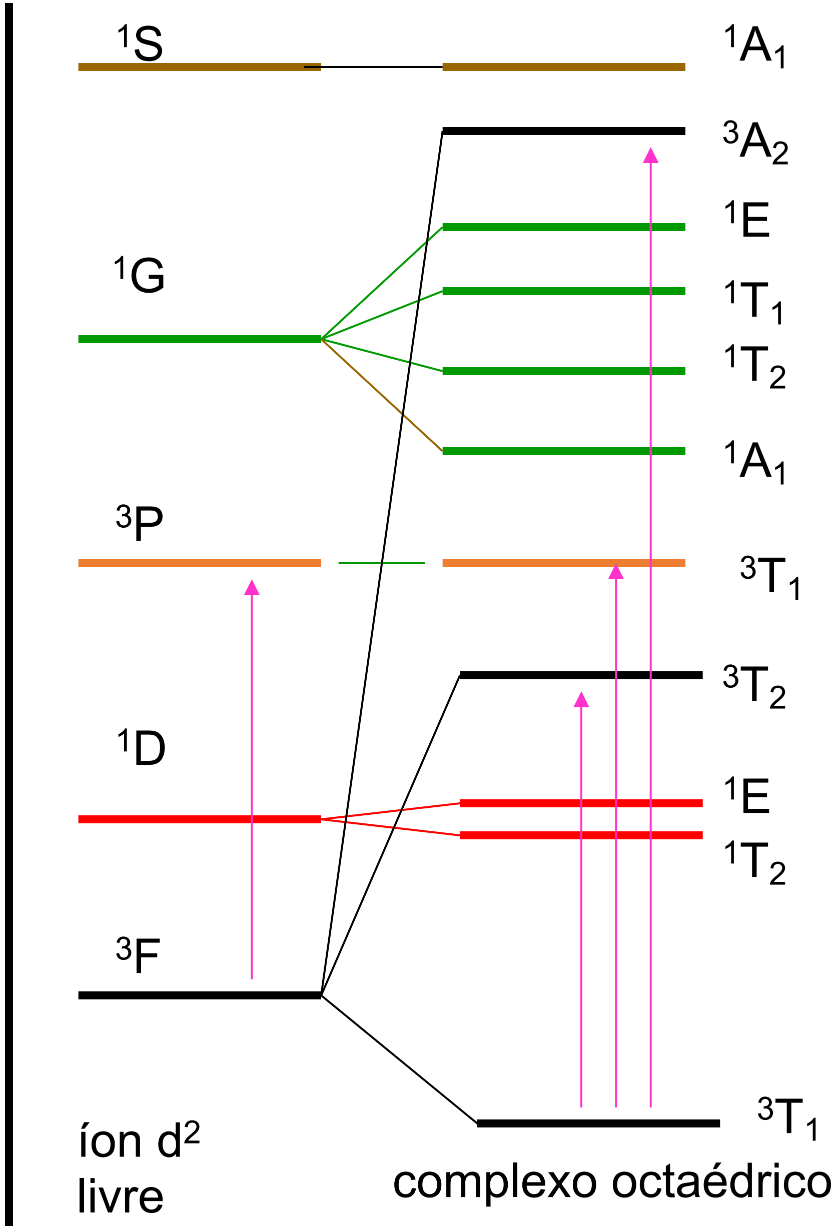
$Mn^{3+}_{(aq)}$ d^4

$Fe^{2+}_{(aq)}$ d^6

$Cu^{2+}_{(aq)}$ d^9

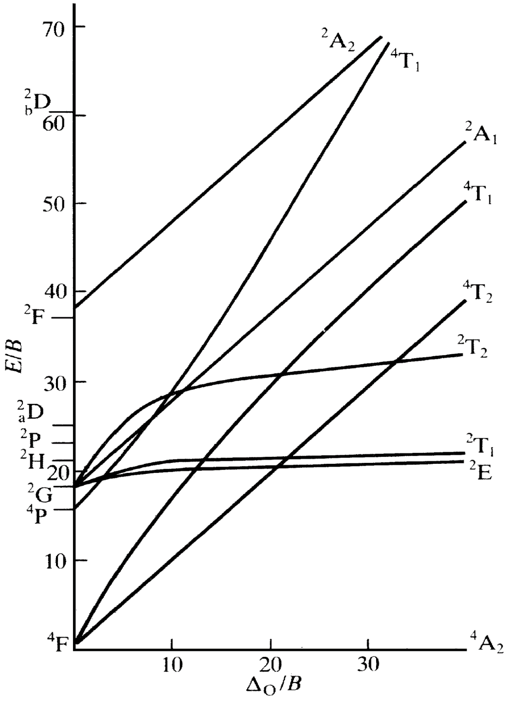
ESPECTROSCOPIA DE CAMPO LIGANTE



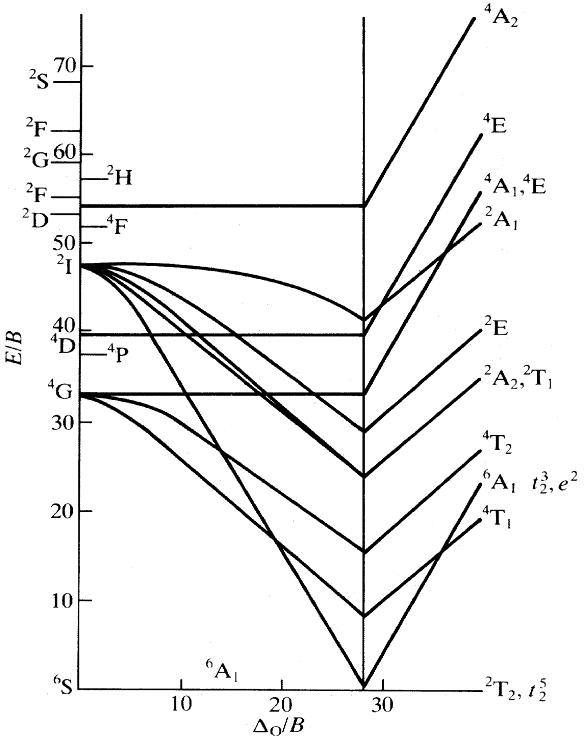


Diagramas de Orgel / Tanabe-Sugano

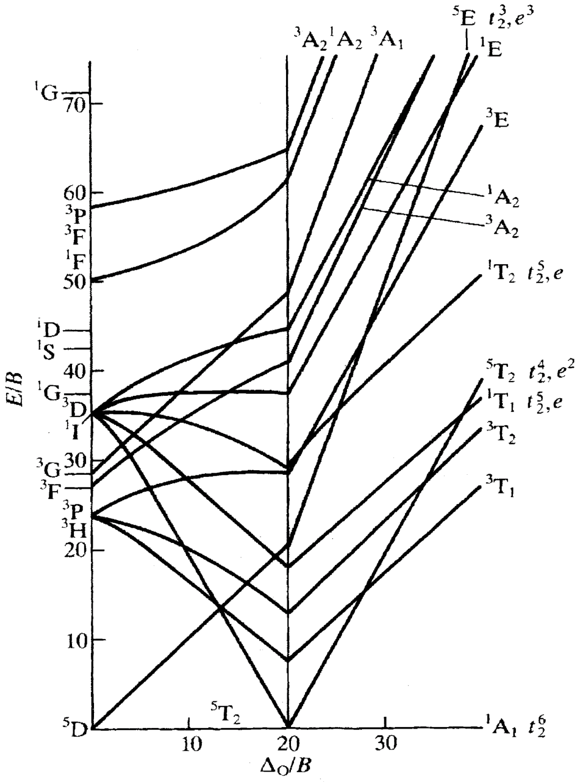
Diagramas de Tanabe-Sugano



Íon d³



íon d5



íon d6

Shedding Light on the Color of Gems and Minerals: The selective absorption of light according to wavelength—the result of various electronic processes whose energies correspond to certain wavelengths of visible light—gives minerals their distinctive hues

Author(s): Bruce M. Loeffler and Roger G. Burns

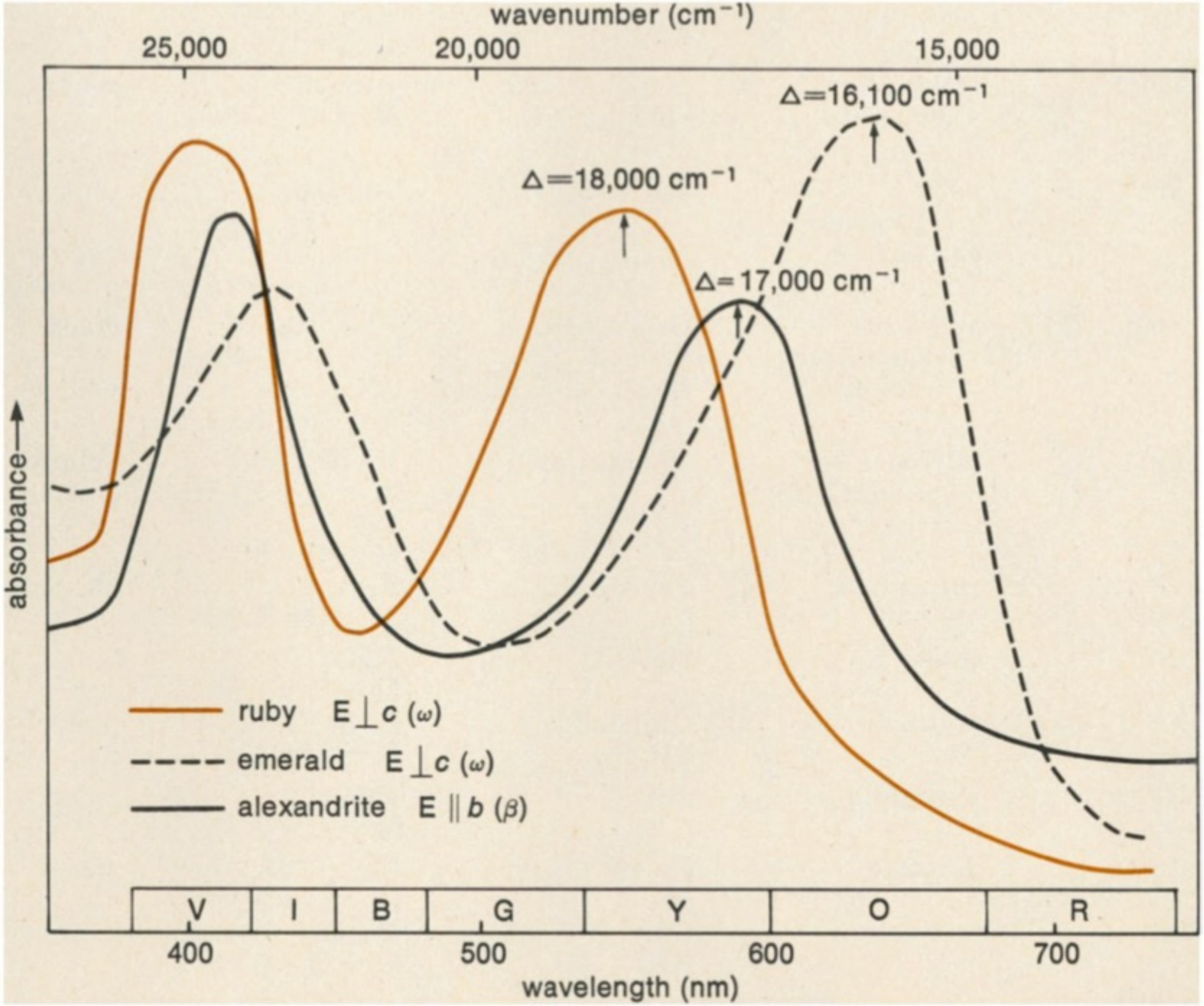
Source: American Scientist , November-December 1976, Vol. 64, No. 6 (November- December 1976), pp. 636-647

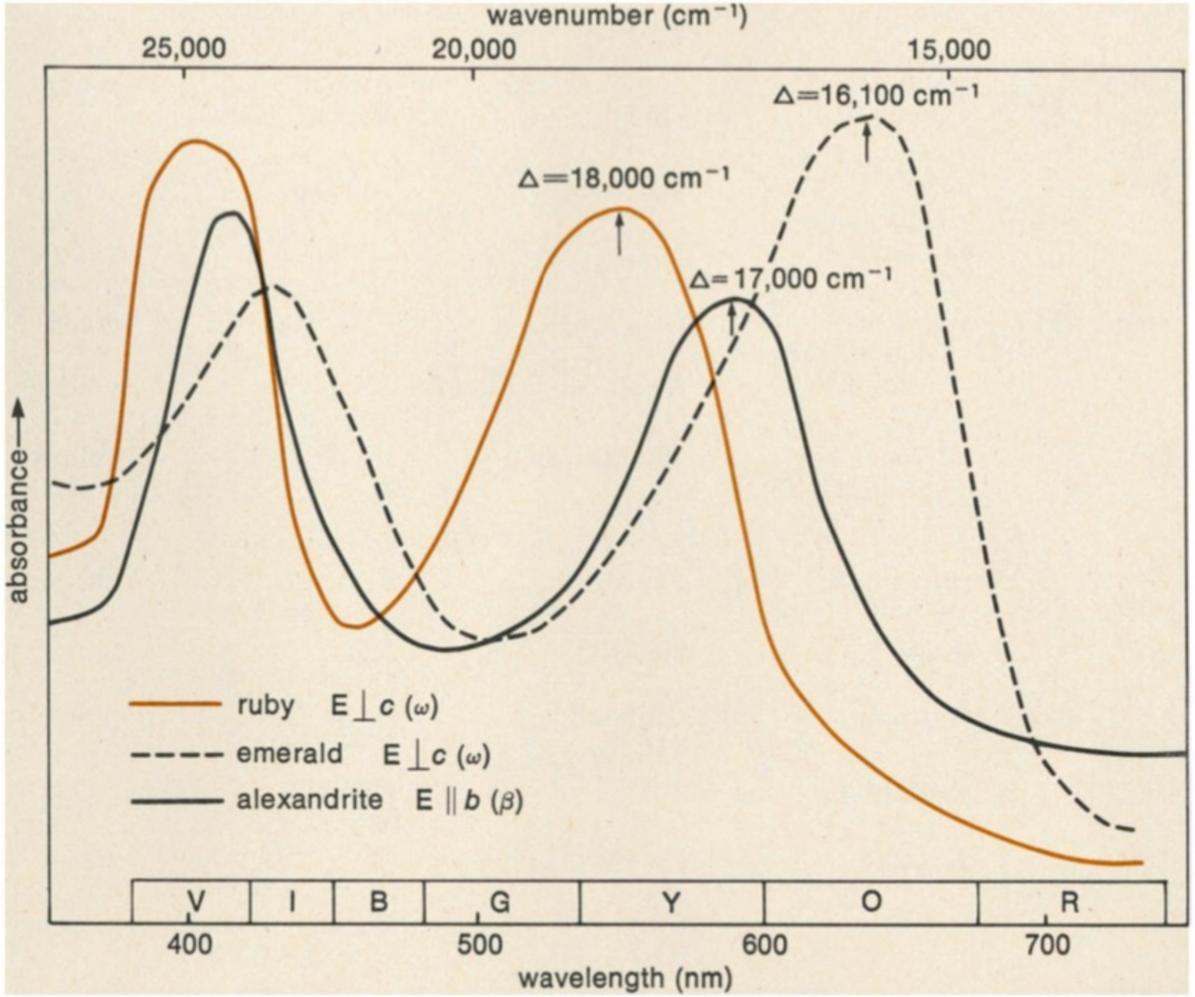
https://www.jstor.org/stable/27847555

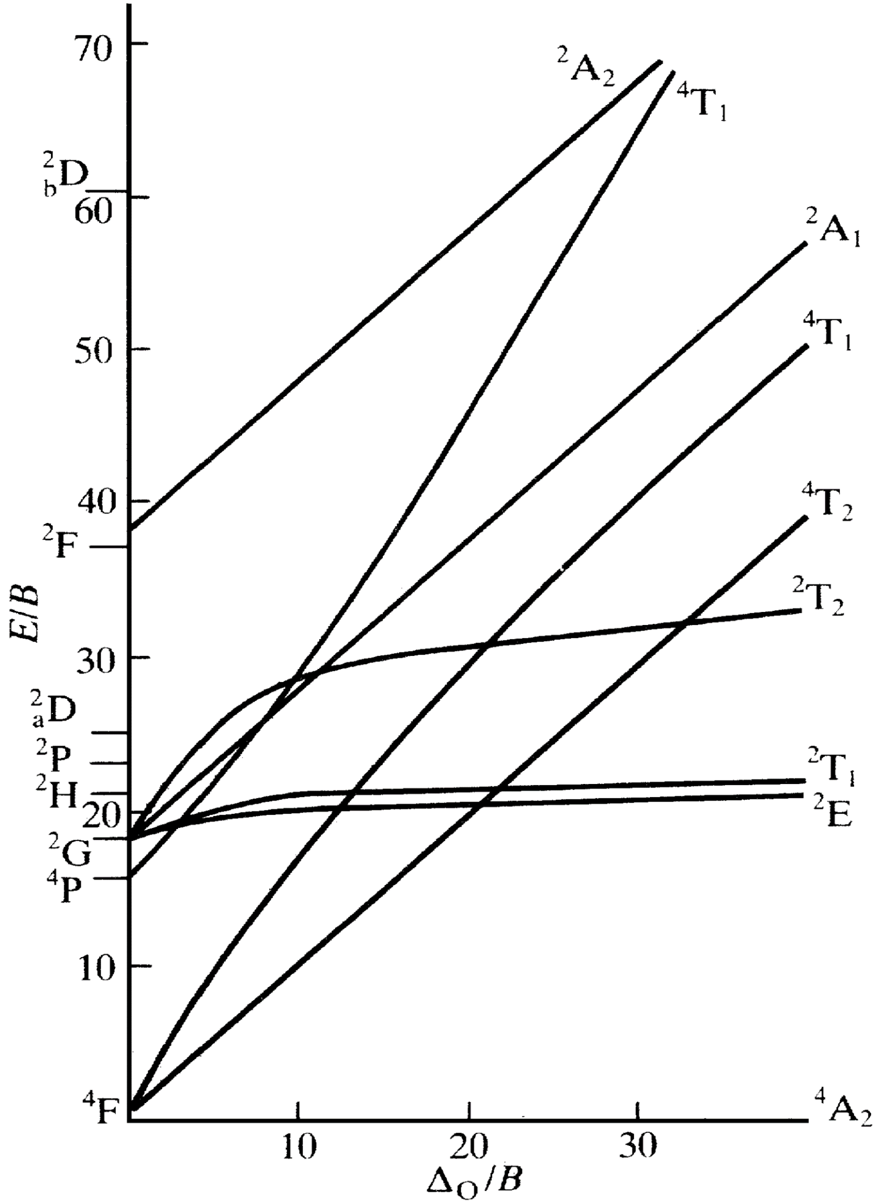
$Al_2O_3:Cr^{3+}$

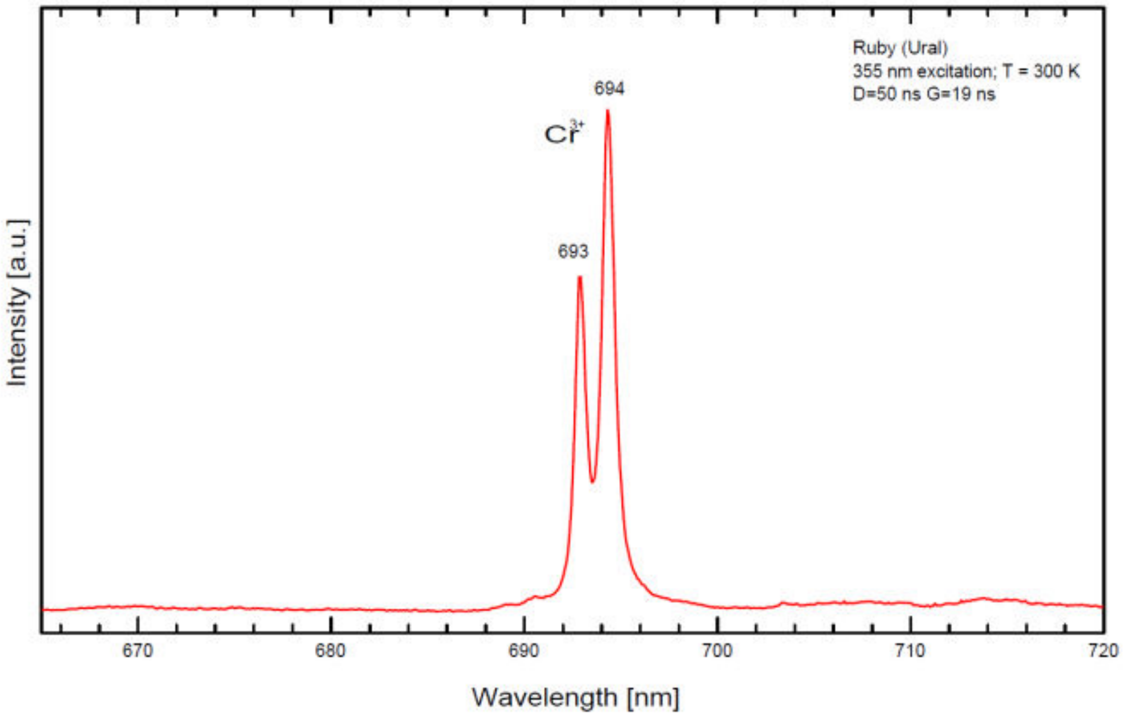
$Be_3Al_2Si_6O_{18}:Cr^{3+}$

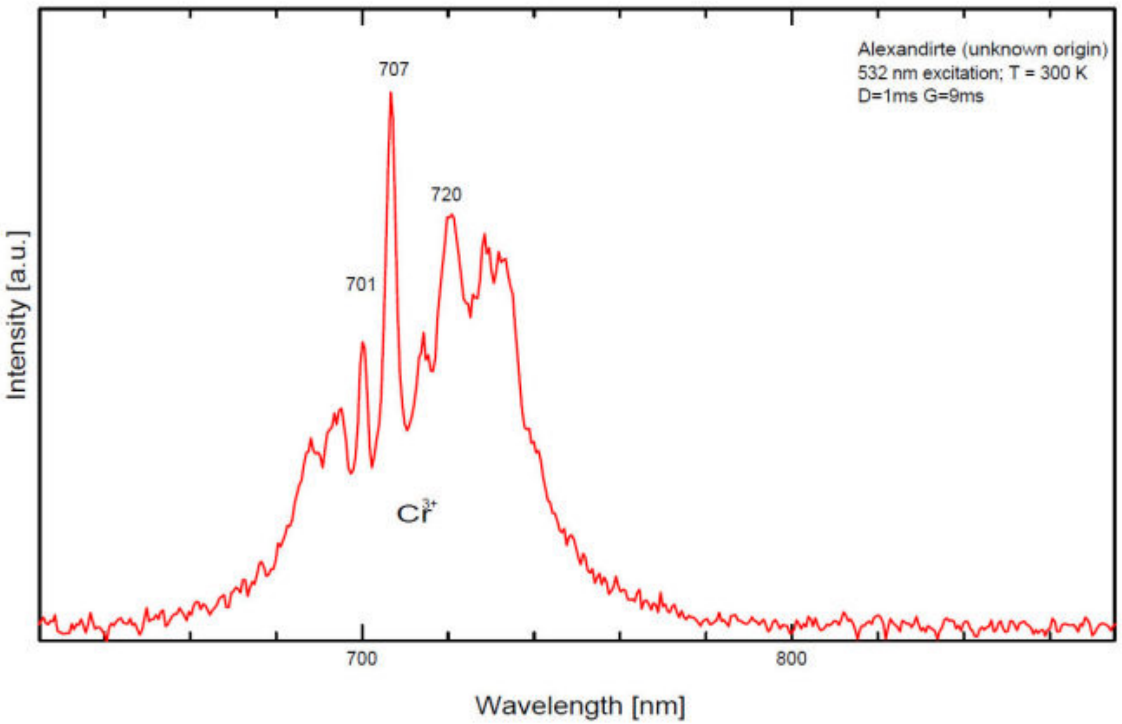
$BeAl_2O_4:Cr^{3+}$




wavenumber (cm⁻¹)
25,000
20,000
15,000
Δ=16,100 cm⁻¹
Δ=18,000 cm⁻¹
Δ=17,000 cm⁻¹
absorbance
ruby E ⊥ c (ω)
emerald E ⊥ c (ω)
alexandrite E ∥ b (β)
V
I
B
G
Y
O
R
400
500
600
700
wavelength (nm)

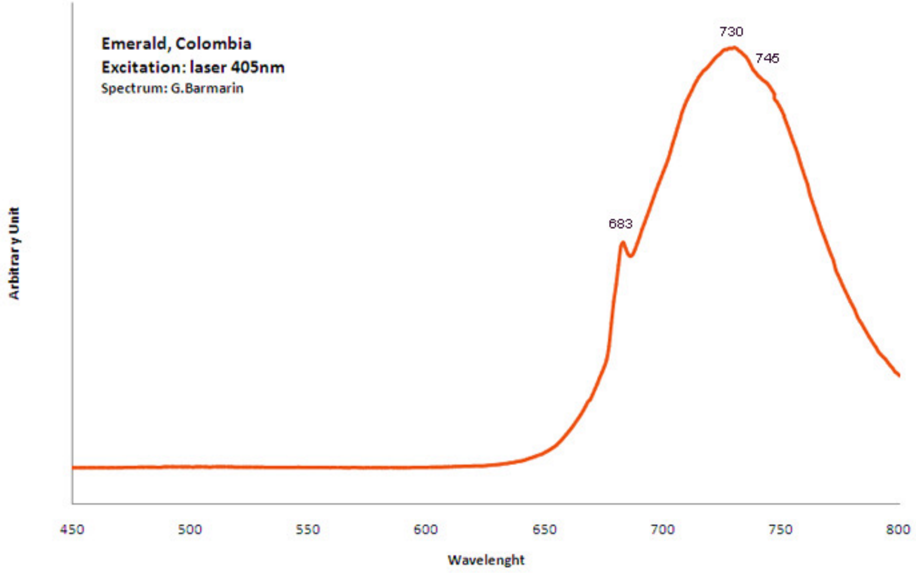

E/B
70
60
50
40
30
20
10
10
20
30
Δ_O/B
²A₂
⁴T₁
²A₁
⁴T₁
⁴T₂
²T₂
²T₁
²E
⁴A₂
²bD
²F
²aD
²P
²H
²G
⁴P
⁴F





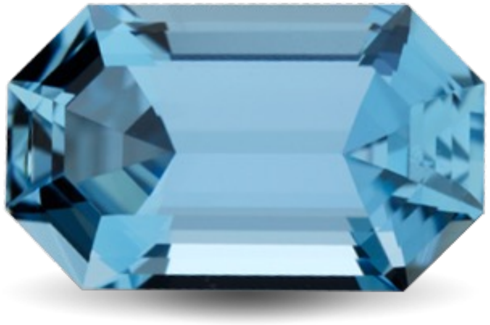
Reference: Gaft, Reisfeld & Panczer (2005): Luminescence spectroscopy of Minerals and Materials, Springer, Berlin Heidelberg, 356 p.

Refere

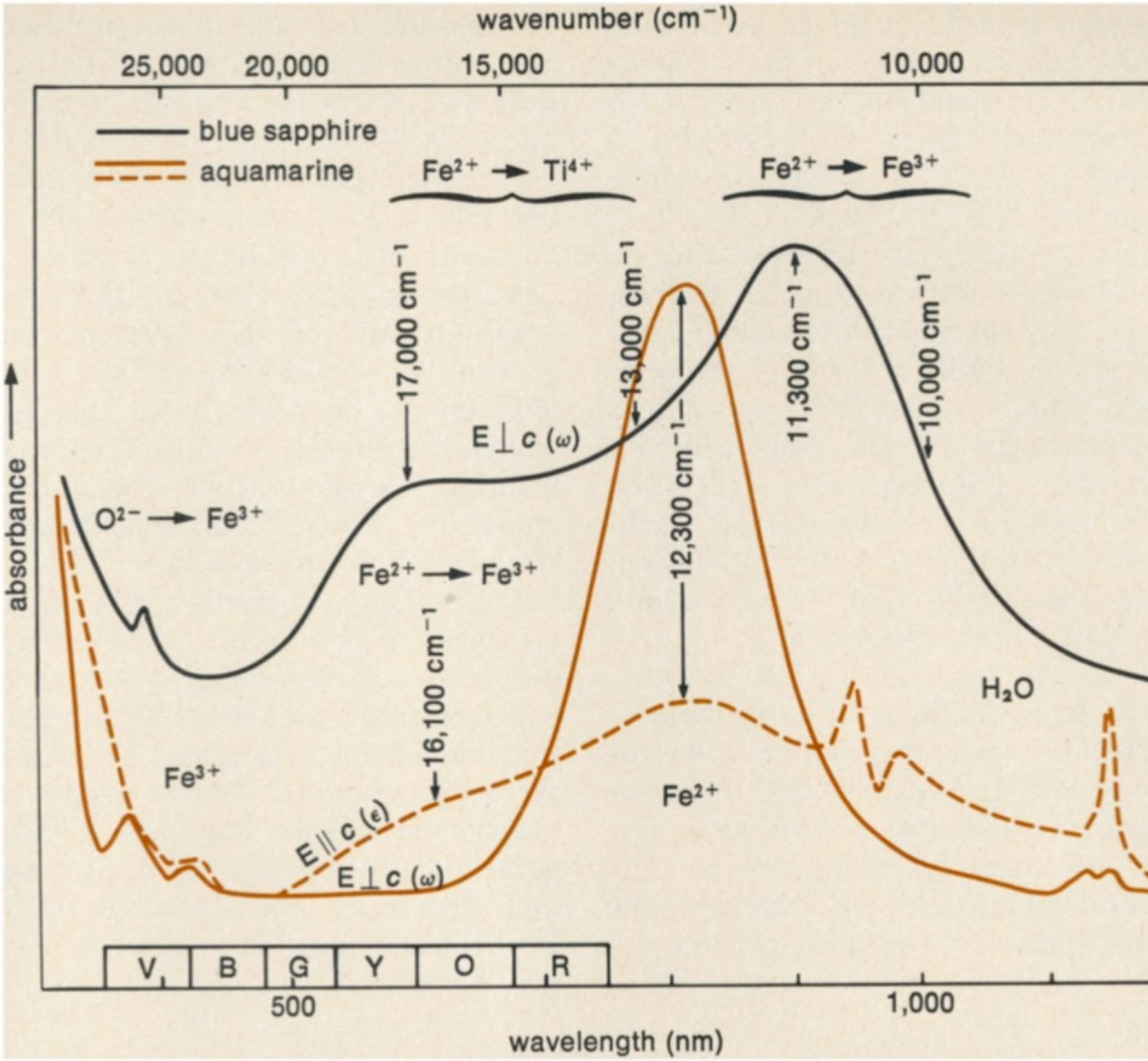


https://www.fluomin.org/uk/

Al_2O_3:Fe^{2+},Ti^{4+}



$Be_3Al_2Si_6O_{18}$: Fe^{2+},Fe^{3+}



$Al_2O_3:Cr^{3+}$

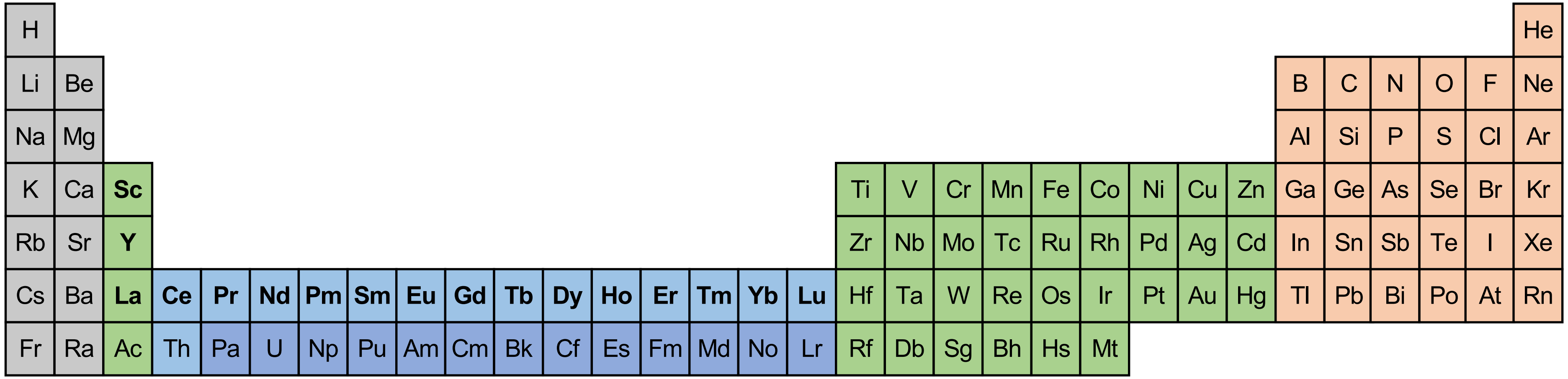
$Al_2O_3:Fe^{2+},Ti^{4+}$

$Be_3Al_2Si_6O_{18}:Cr^{3+}$

$Be_3Al_2Si_6O_{18}: Fe^{2+},Fe^{3+}$

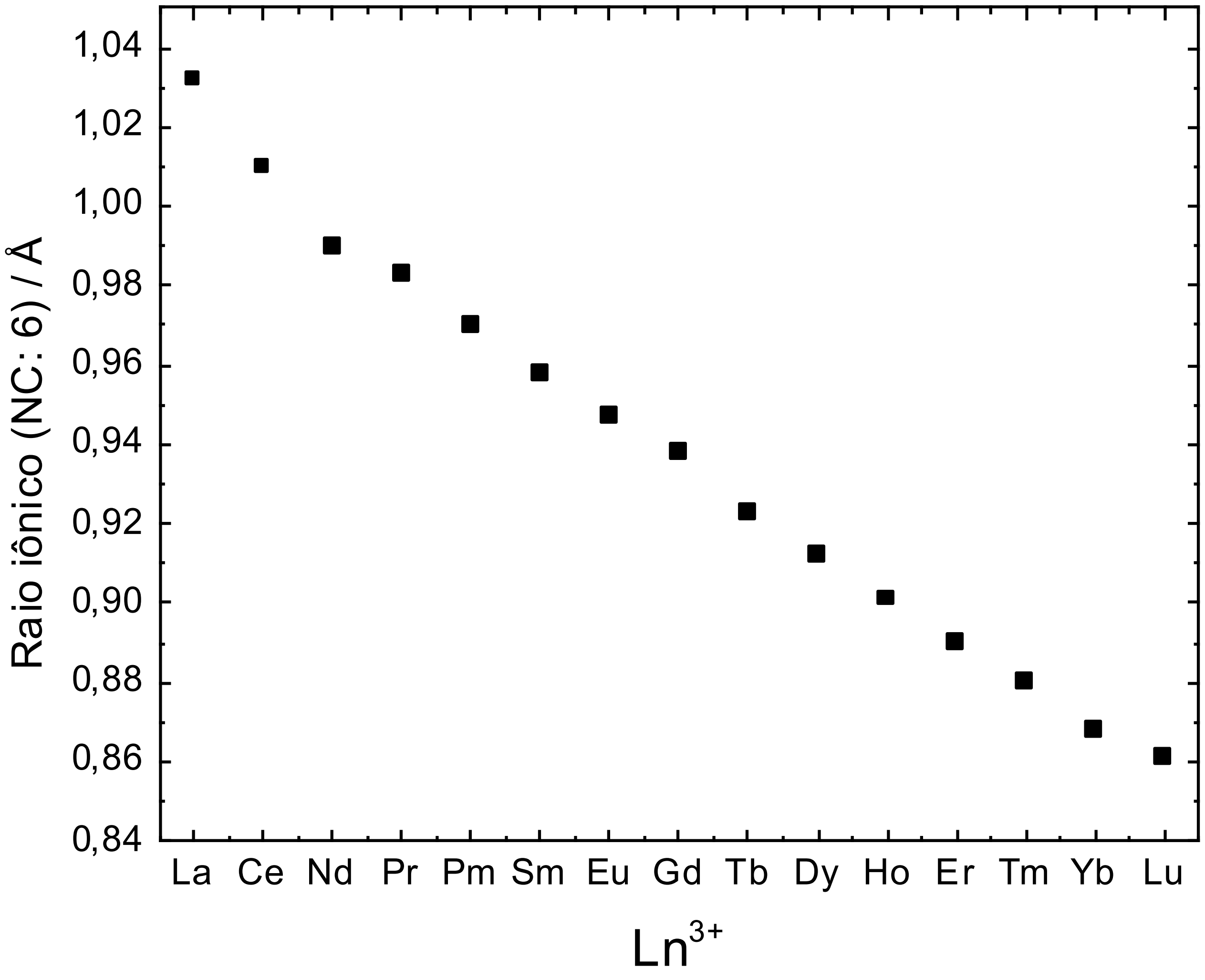
Lantanídeos

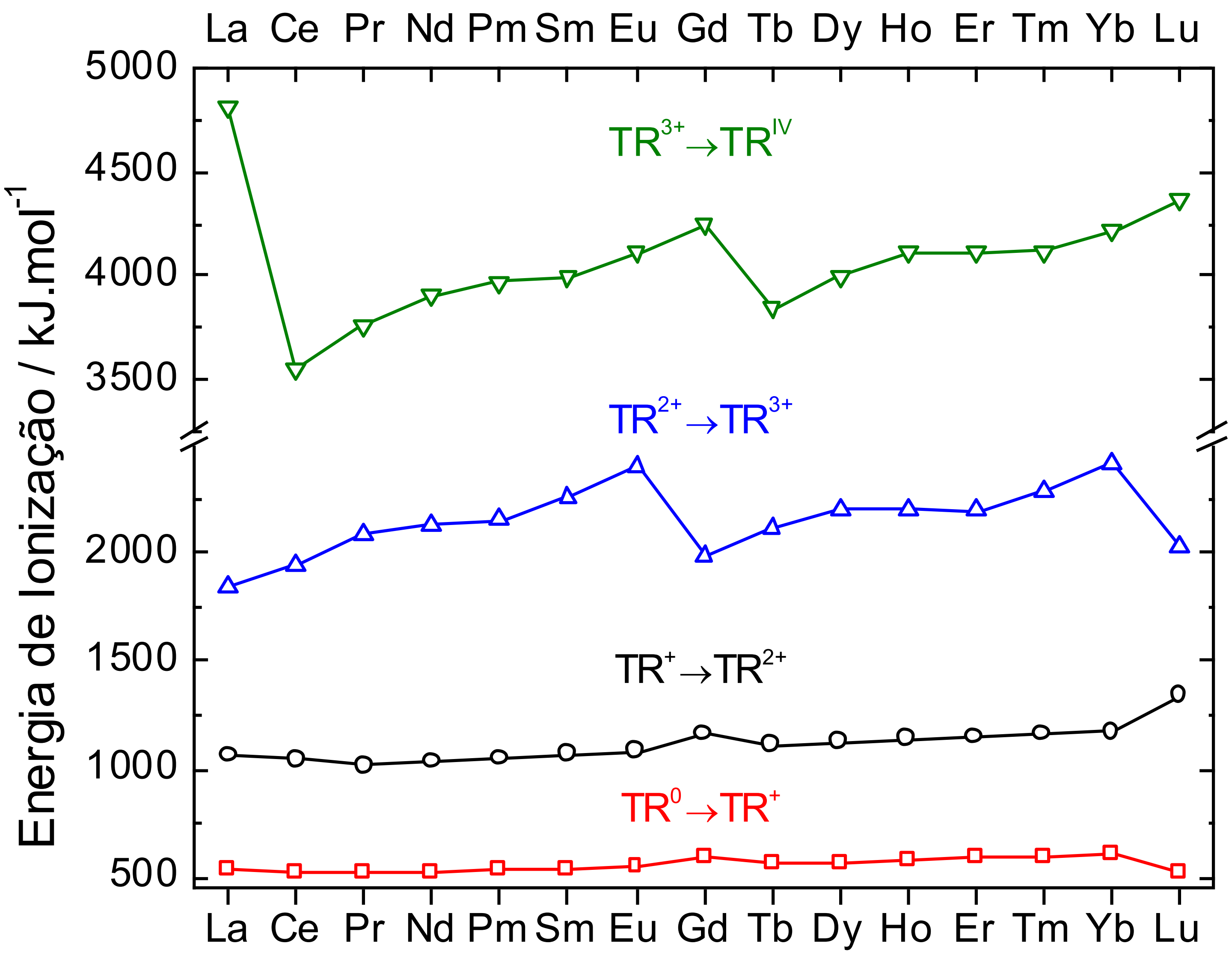
Tabela Periódica com os Lantanídeos e Actinídeos no seu lugar de direito!



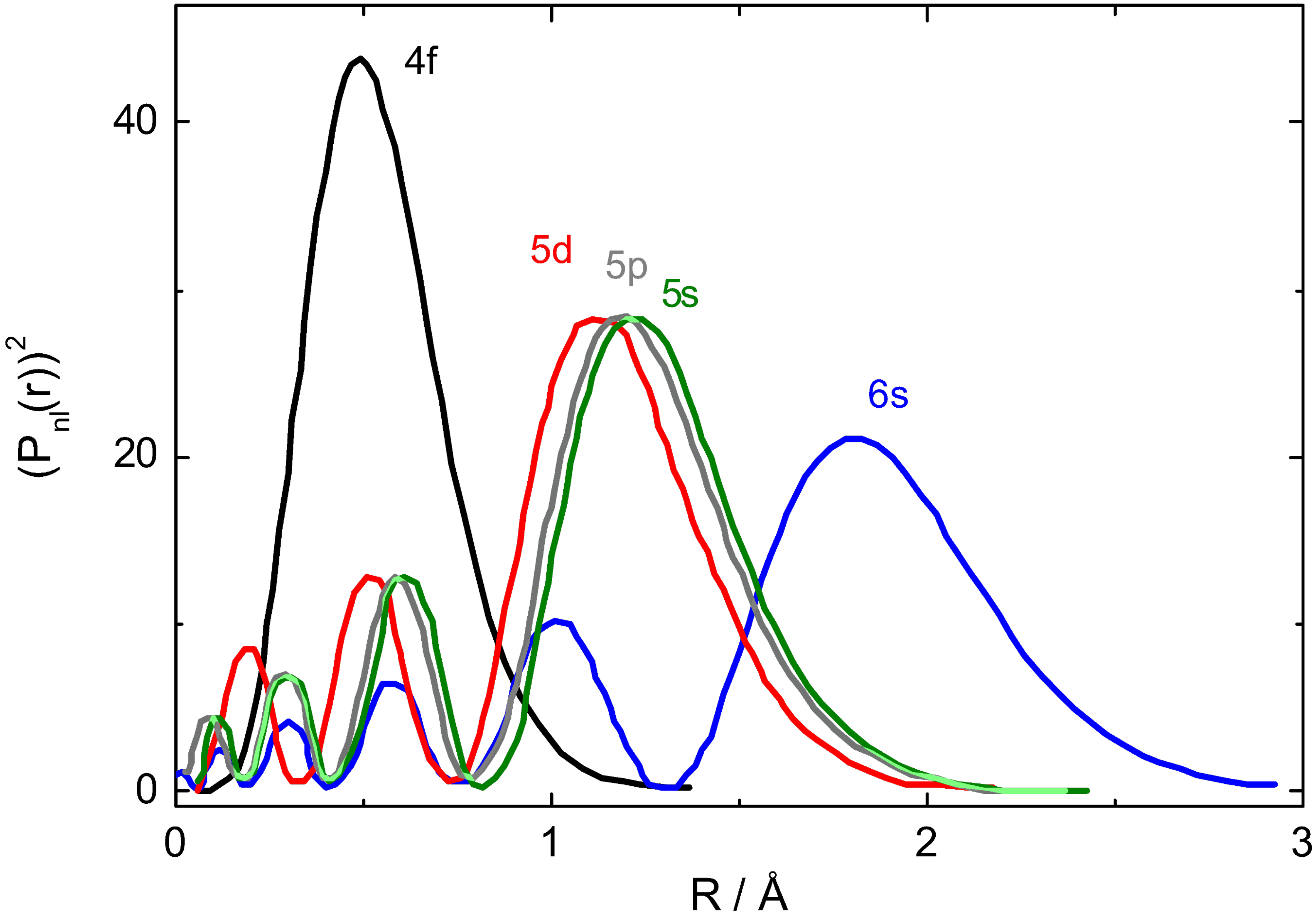
H																															He
Li	Be																									B	C	N	O	F	Ne
Na	Mg																									Al	Si	P	S	Cl	Ar
K	Ca	**Sc**															Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	**Y**															Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	**La**	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt									

Propriedades químicas

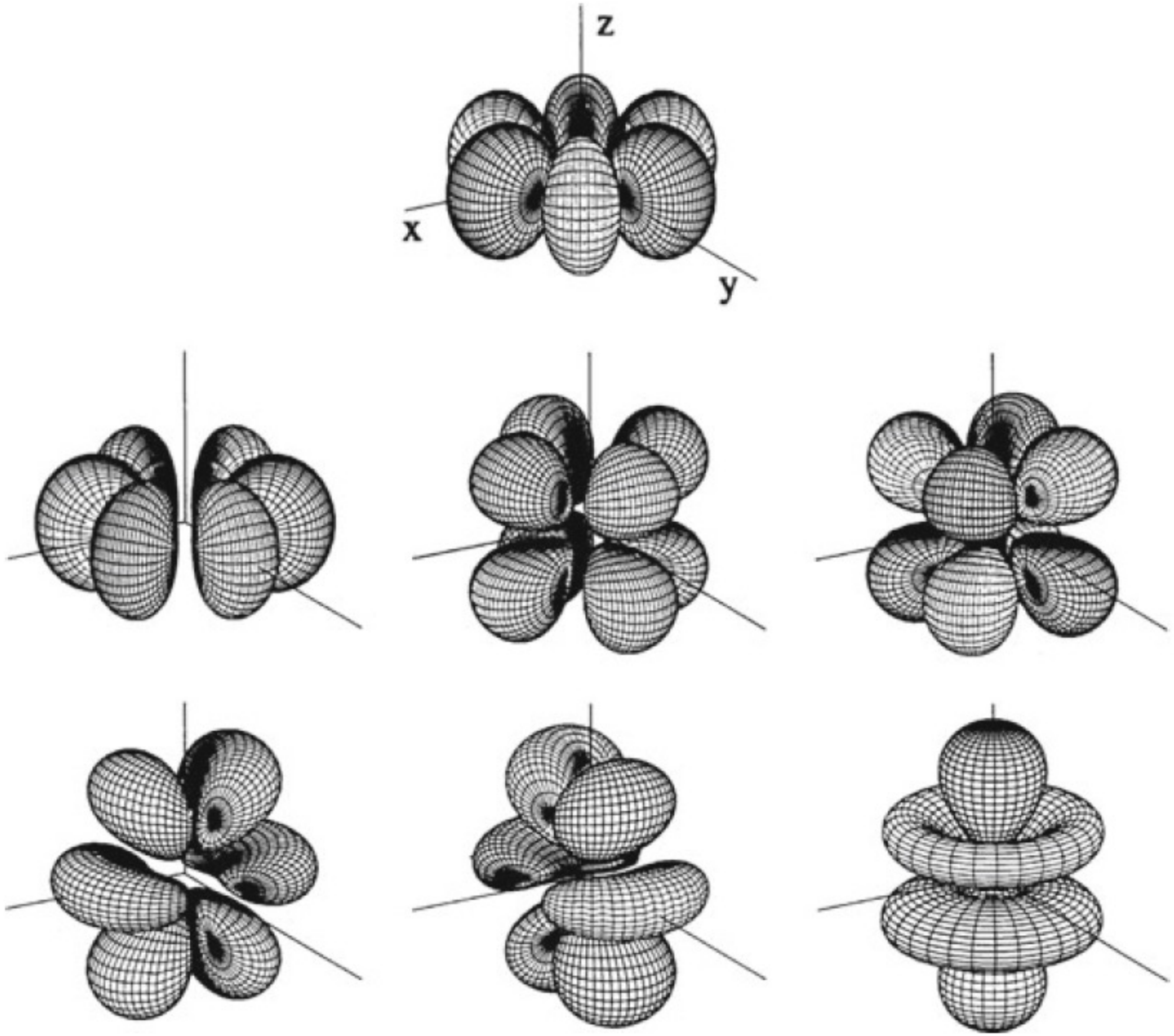




Qual os NOX mais estáveis dos íons Ln^{x+}??


4f
5d
5p
5s
6s
$(P_{nl}(r))^2$
0
20
40
0
1
2
3
R / Å

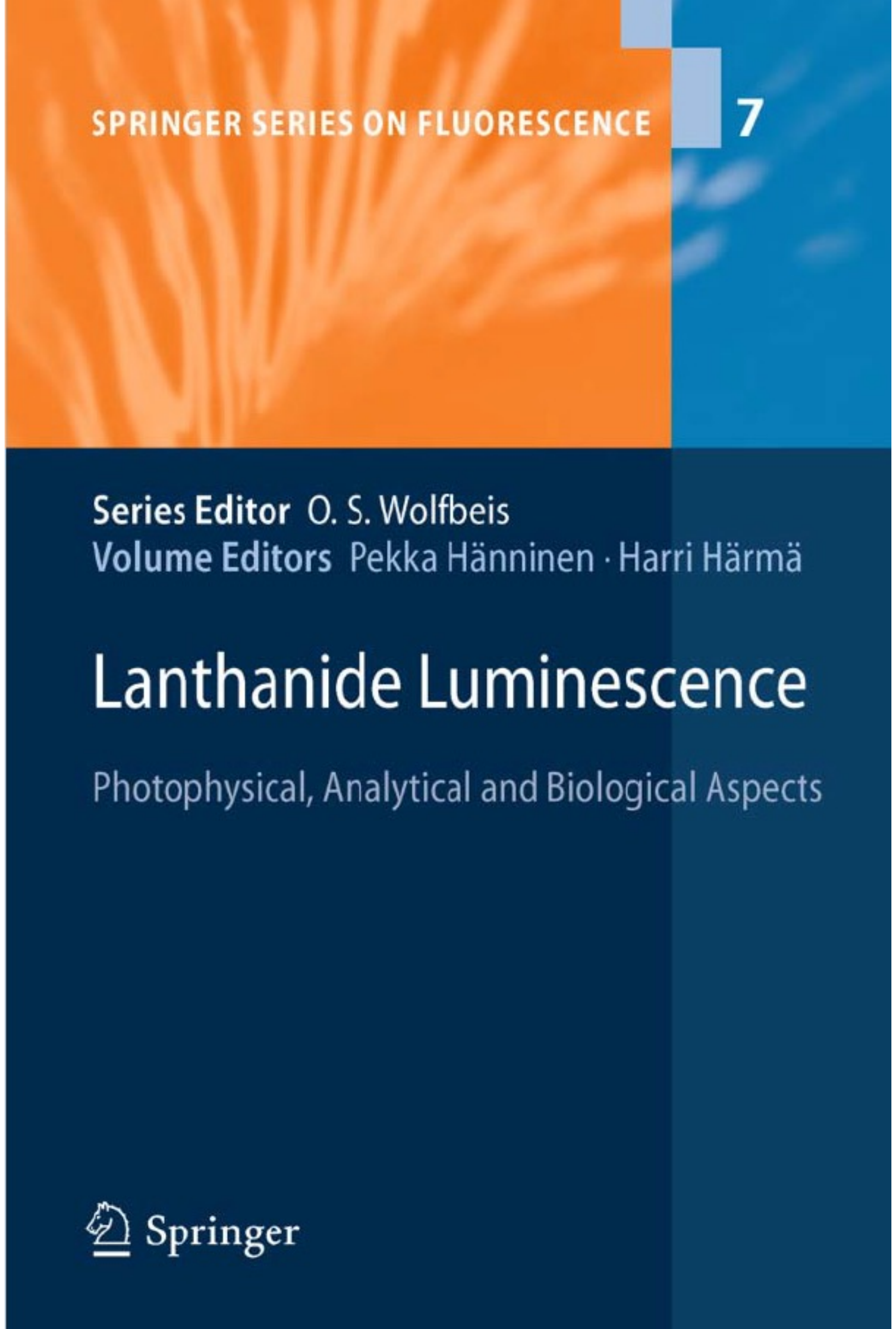
Como seriam os OMs de um complexo LnL_3?



Compostos iônicos

Ácidos duros

Pequena covalência (ex)



SPRINGER SERIES ON FLUORESCENCE 7

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Lanthanide Luminescence

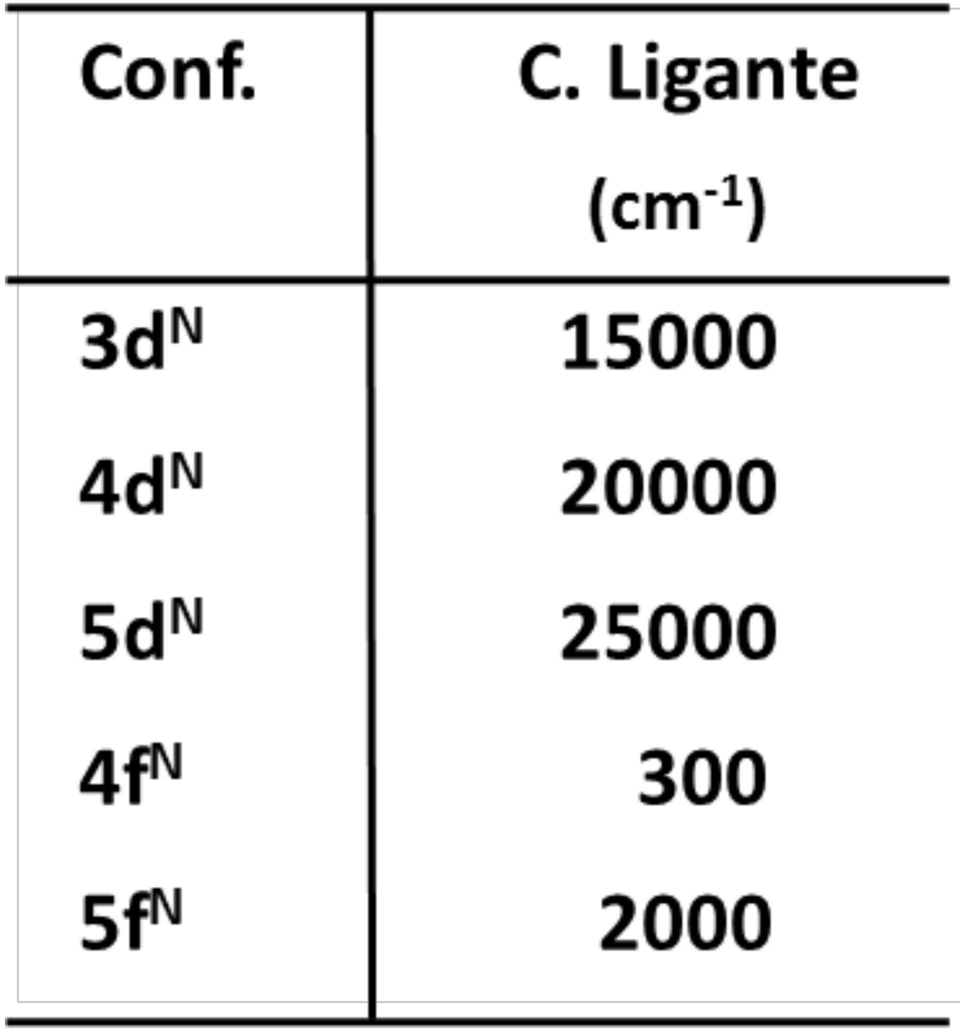
Photophysical, Analytical and Biological Aspects

Springer

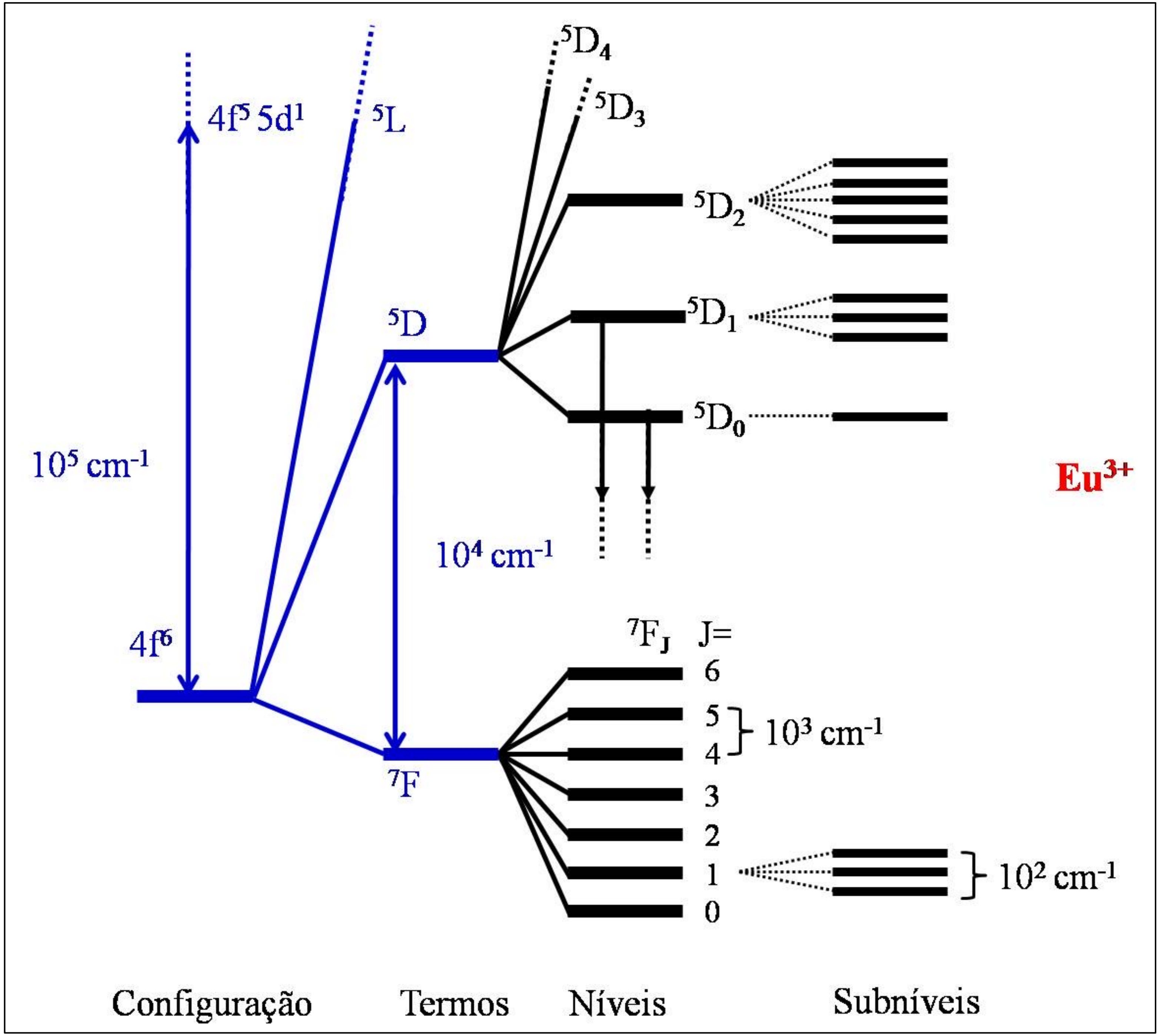
Basics of Lanthanide Photophysics

Jean-Claude G. Bünzli and Svetlana V. Eliseeva

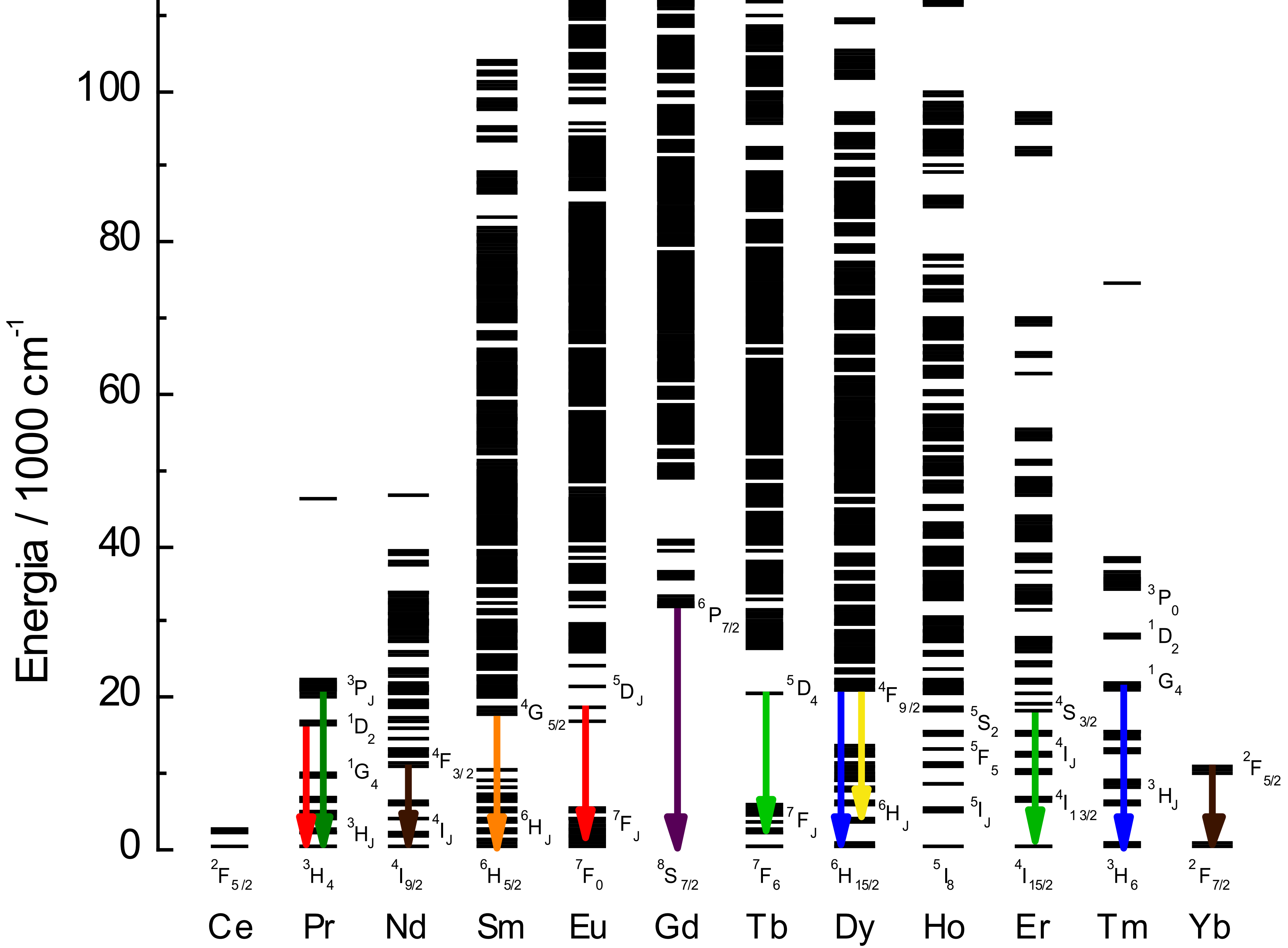
Efeito do Campo Ligante

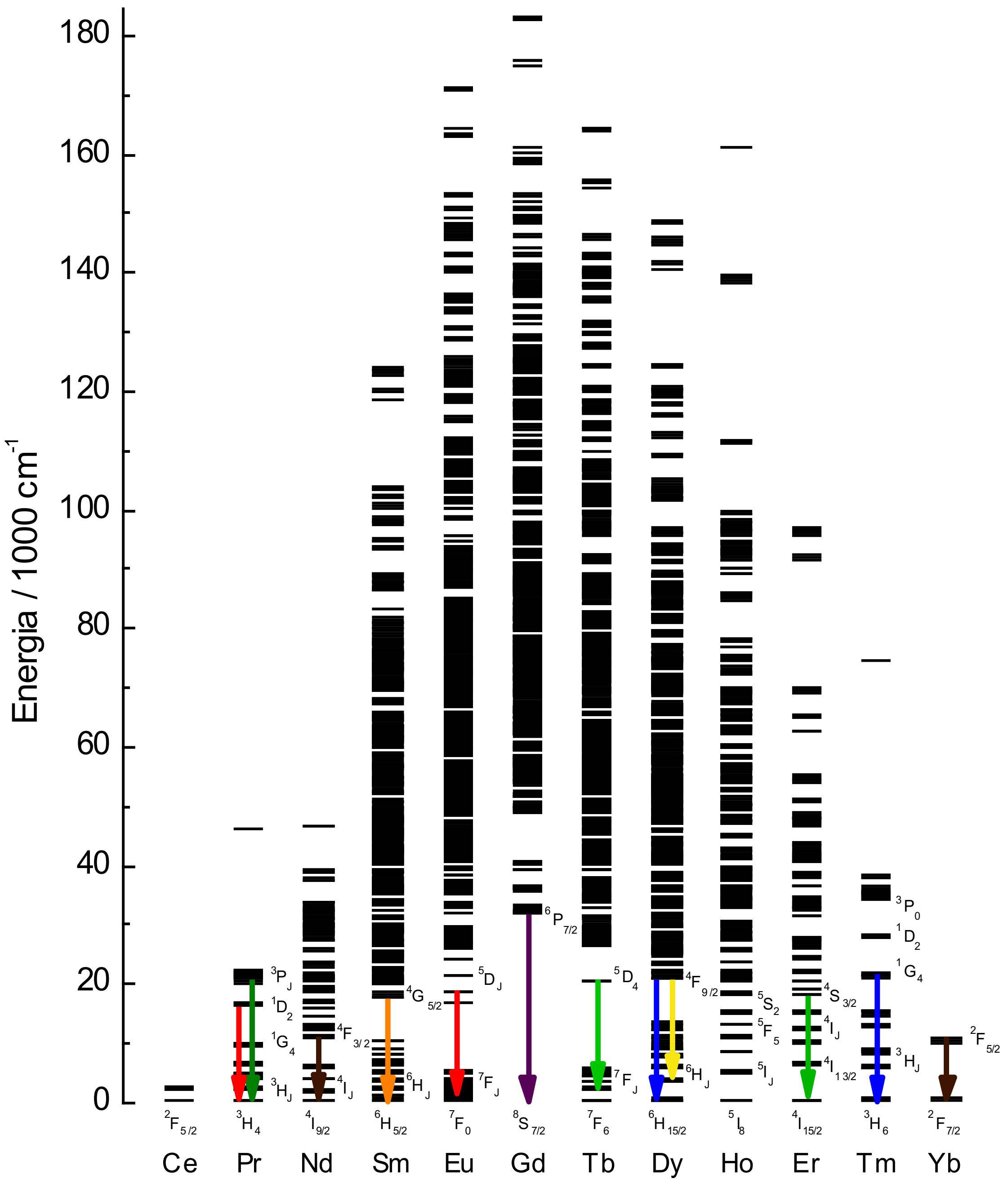


Conf.	**C. Ligante (cm^{-1})**
$3d^N$	**15000**
$4d^N$	**20000**
$5d^N$	**25000**
$4f^N$	**300**
$5f^N$	**2000**


$4f^5\,5d^1$
^5L
$^5D_4$
$^5D_3$
$^5D_2$
$^5D_1$
$^5D_0$
^5D
10^5 cm^{-1}
10^4 cm^{-1}
Eu^{3+}
$4f^6$
^7F_J J=
6
5
4
10^3 cm^{-1}
3
2
1
0
10^2 cm^{-1}
^7F
Configuração
Termos
Níveis
Subníveis

Configurations	Terms ^{2S+1}L				Number of J levels $^{2S+1}L_J$	Maximum number of crystal-field levels
f^1 and f^{13}	^{2}F				2	14
f^2 and f^{12}	^{1}SDGI	^{3}PFH			13	91
f^3 and f^{11}	^{2}PDFGHIKL 2 2 22	^{4}SDFGI			41	364/2
f^4 and f^{10}	^{1}SDFGHIKLN 24 4232	^{3}PDFGHIKLM 32 4 3 4 22	^{5}SDFGI		107	1001
f^5 and f^9	^{2}PDFGHIKLMNO 4 57675532	^{4}SPDFGHIKLM 23 4 4 3 32	^{6}PFH		193	2002/2
f^6 and f^8	^{1}SPDFGHIKLMNQ 464 8473422	^{3}PDFGHIKLMNO 6 97 96633	^{5}SPDFGHIKL 3 2 3 2 2	^{7}F	295	3003
f^7	^{2}SPDF G HIKLMNOQ 257 10109 97 5 4 2	^{4}SPDFGHIKLMN 2 2 6 5 7 55 3	^{6}PDFGHI	^{8}S	327	3432/2


Energia / 1000 cm^{-1}
100
80
60
40
20
0
^3P_J
$^1D_2$
$^1G_4$
^3H_J
$^4F_{3/2}$
^4I_J
$^4G_{5/2}$
^6H_J
^5D_J
^7F_J
$^6P_{7/2}$
$^5D_4$
^7F_J
$^4F_{9/2}$
^6H_J
$^5S_2$
$^5F_5$
^5I_J
$^4S_{3/2}$
^4I_J
$^4I_{13/2}$
$^3P_0$
$^1D_2$
$^1G_4$
^3H_J
$^2F_{5/2}$
$^2F_{5/2}$
$^3H_4$
$^4I_{9/2}$
$^6H_{5/2}$
$^7F_0$
$^8S_{7/2}$
$^7F_6$
$^6H_{15/2}$
$^5I_8$
$^4I_{15/2}$
$^3H_6$
$^2F_{7/2}$
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb


Energia / 1000 cm^{-1}
0
20
40
60
80
100
120
140
160
180
$^2F_{5/2}$
Ce
^3P_J
$^1D_2$
$^1G_4$
^3H_J
$^3H_4$
Pr
$^4F_{3/2}$
^4I_J
$^4I_{9/2}$
Nd
$^4G_{5/2}$
^6H_J
$^6H_{5/2}$
Sm
^5D_J
^7F_J
$^7F_0$
Eu
$^6P_{7/2}$
$^8S_{7/2}$
Gd
$^5D_4$
^7F_J
$^7F_6$
Tb
$^4F_{9/2}$
^6H_J
$^6H_{15/2}$
Dy
$^5S_2$
$^5F_5$
^5I_J
$^5I_8$
Ho
$^4S_{3/2}$
^4I_J
$^4I_{13/2}$
$^4I_{15/2}$
Er
$^3P_0$
$^1D_2$
$^1G_4$
^3H_J
$^3H_6$
Tm
$^2F_{5/2}$
$^2F_{7/2}$
Yb

Propriedades Eletrônicas

$$\Delta S = 0$$

$$\Delta l = \pm 1$$

$$D_{\mathrm{ED}} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle \Psi \| U^\lambda \| \Psi' \rangle \right|^2,$$

Operator	Parity	ΔS	ΔL	ΔJ[a]
ED	Opposite	0	≤ 6	≤ 6 (2,4,6 if J or $J' = 0$)
MD	Same	0	0	0, ±1
EQ	Same	0	0, ±1, ±2	0, ±1, ±2

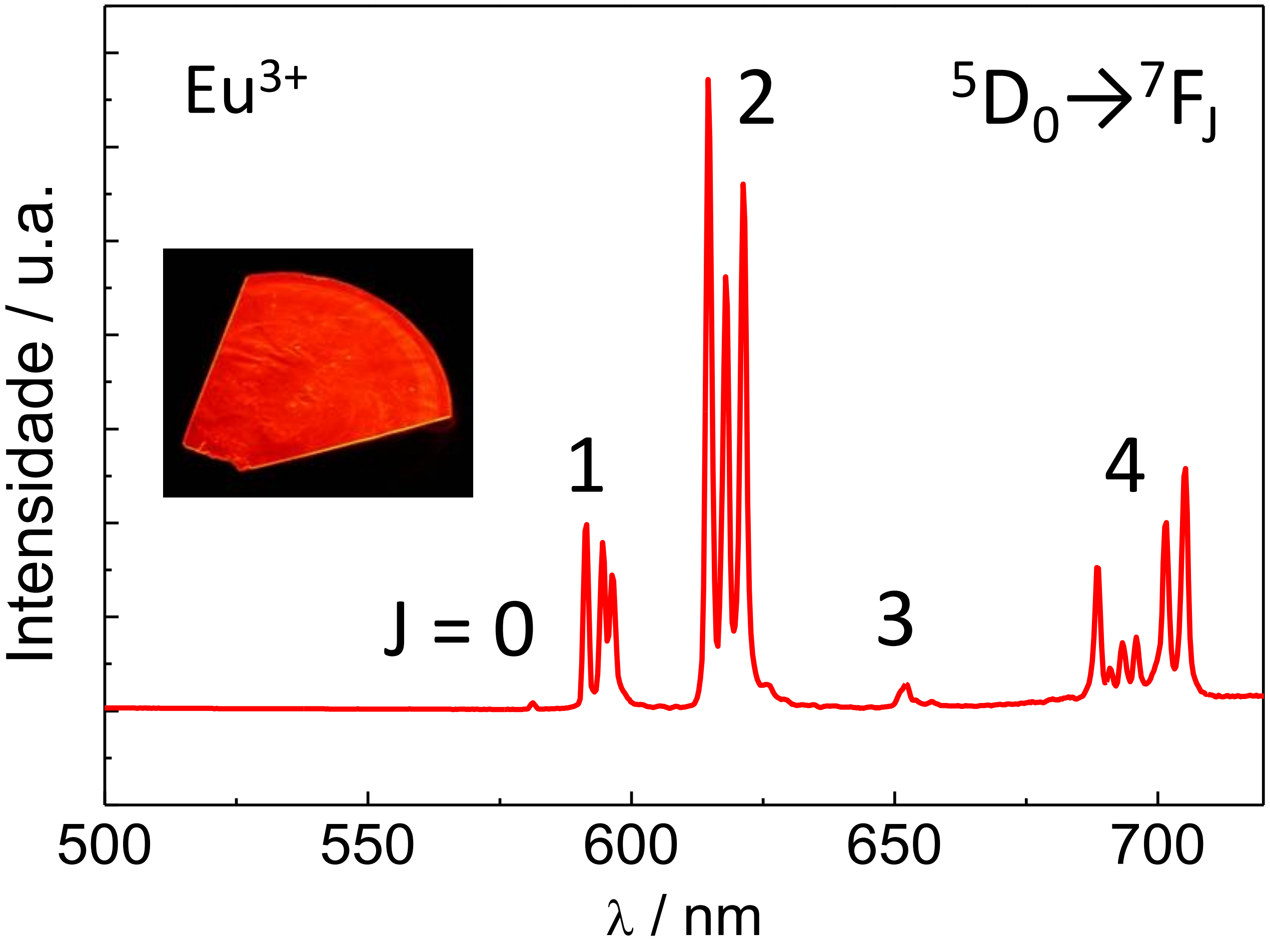
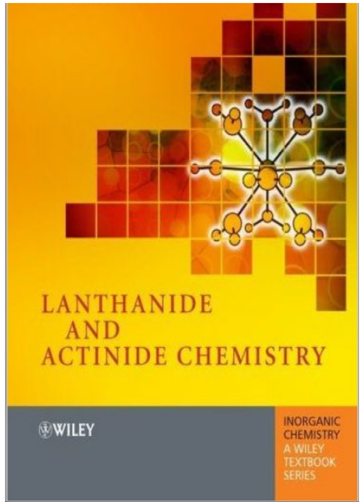

Eu3+
5D0→7FJ
J = 0
1
2
3
4
Intensidade / u.a.
500
550
600
650
700
λ / nm

Table 5.3 Number and degeneracy of $^5D_0$–^7F_J transitions of Eu^{3+} ions in some common symmetries

	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$
Symmetry	ED	MD	ED	ED	ED
I_h	none	T_{1g}	none	none	none
O_h	none	T_{1g}	none	T_{1g}	none
T_d	none	T_1	T_2	T_1	T_2
D_{4h}	none	$A_{2g} + E_g$	E_g	$A_{2g} + E_g$	none
D_{4d}	none	$A_2 + E_3$	E_1	$A_2 + E_3$	$B_2 + E_1$
D_{2d}	none	$A_2 + E$	$B_2 + E$	$B_2 + 2\,E$	$B_2 + 2E$
D_{3h}	none	$A'_2 + E''$	E'	$A'_2 + E''$	$A''_2 + 2E'$
D_{3d}	none	$A_{2g} + E_g$	$A_{1g} + E_g$	none	none
D_3	none	$A_2 + E$	$2E$	$2A_2 + 2E$	$A_2 + 3E$
C_{3v}	A_1	$A_2 + E$	$A_1 + 2E$	$A_1 + 2E$	$2A_1 + 3E$
C_3	A	$A + E$	$A + 2E$	$3A + 2E$	$3A + 3E$
C_{2v}	A_1	$A_2 + B_1 + B_2$	$2A_1 + B_1 + B_2$	$A_1 + 2B_1 + 2B_2$	$3A_1 + 2B_1 + 2B_2$
C_2	A	$A + 2B$	$3A + 2B$	$3A + 4B$	$5A + 4B$
C_i	A	$3A$	$5A$	$7A$	$9A$
C_s	A'	$A' + 2A''$	$3A' + 2A''$	$3A' + 4A''$	$5A' + 4A''$



Coordination Chemistry Reviews 295 (2015) 1–45

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Review

Interpretation of europium(III) spectra

Koen Binnemans*

KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium

Table 5
Overview of the transitions observed in luminescence spectra of europium(III) compounds.

Transition[a]	Dipole character[b]	Wavelength range (nm)	Relative intensity[c]	Remarks
$^5D_0 \rightarrow {}^7F_0$	ED	570–585	vw to s	Only observed in C_n, C_{nv} and C_s symmetry
$^5D_0 \rightarrow {}^7F_1$	MD	585–600	s	Intensity largely independent of environment
$^5D_0 \rightarrow {}^7F_2$	ED	610–630	s to vs	Hypersensitive transition; intensity very strongly dependent on environment
$^5D_0 \rightarrow {}^7F_3$	ED	640–660	vw to w	Forbidden transition
$^5D_0 \rightarrow {}^7F_4$	ED	680–710	m to s	Intensity dependent on environment, but no hypersensitivity
$^5D_0 \rightarrow {}^7F_5$	ED	740–770	vw	Forbidden transition
$^5D_0 \rightarrow {}^7F_6$	ED	810–840	vw to m	Rarely measured and observed

[a] Only transitions starting from the $^5D_0$ level are shown.
[b] ED = induced magnetic dipole transition, MD = magnetic dipole transition.
[c] vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

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Some misconceptions concerning the electronic spectra of tri-positive europium and cerium

Cite this: *Chem. Soc. Rev.*, 2013, **42**, 5090

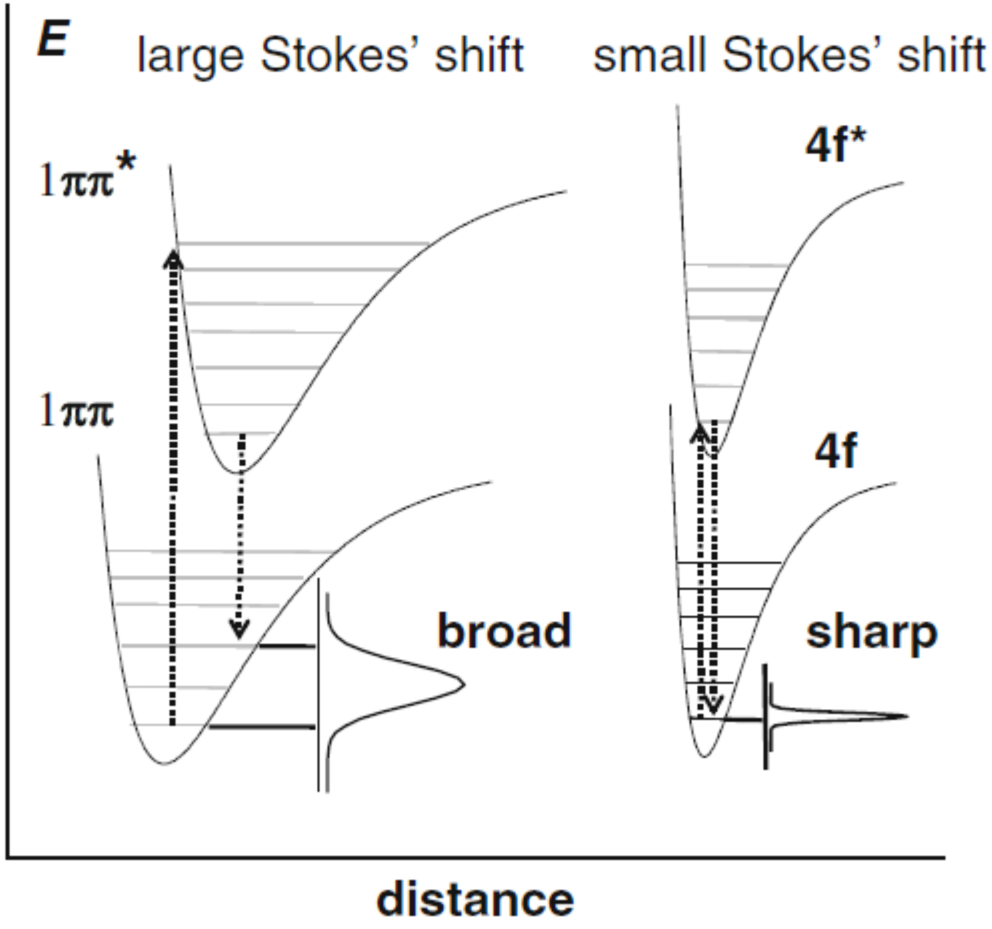
Peter A. Tanner*

Table 2 *SLJ* selection rules for electronic transitions of lanthanide ions[a]

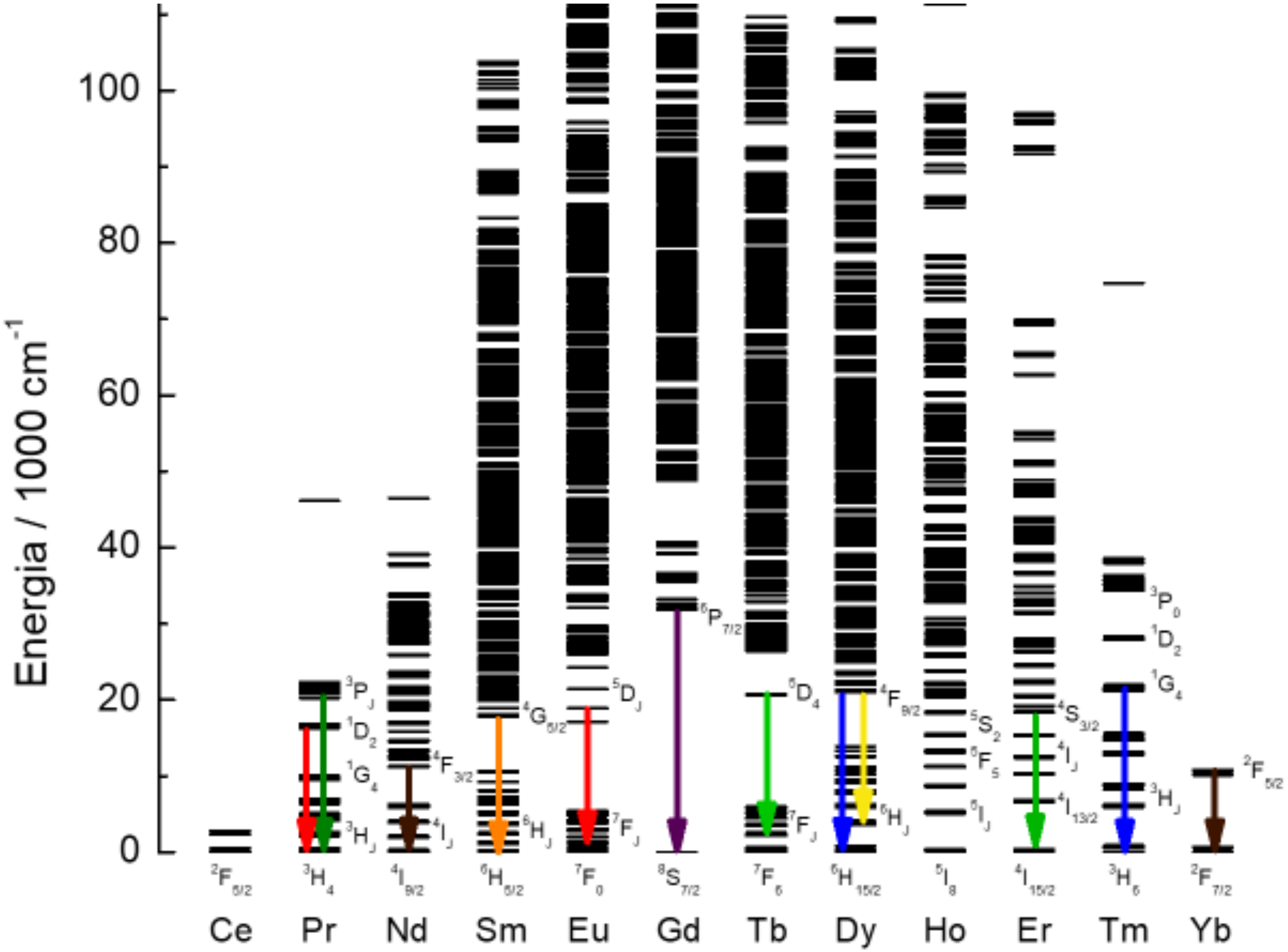
	Type of transition	*SLJ* selection rules	Approximate order of magnitude of oscillator strength
1.	Electric dipole (ED) $4f^N$–$4f^{N-1}5d$ (parity change)	$\Delta S = 0$; $\lvert\Delta L\rvert \leq 1$; $\lvert\Delta J\rvert \leq 1$; $J = 0 \leftrightarrow J' = 0$ and $L = 0 \leftrightarrow L' = 0$ are forbidden.	~ 0.01–1
2.	Judd forced (induced) ED $4f^N$–$4f^N$ (no change in parity)	$\Delta S = 0$; $\lvert\Delta L\rvert \leq 6$; if $L = 0$ or $L' = 0$, $\lvert\Delta L\rvert = 2, 4, 6$; $\lvert\Delta J\rvert \leq 6$; if $J = 0$ or $J' = 0$, $\lvert\Delta J\rvert = 2, 4, 6$. This implies that $J = 0 \leftrightarrow J' = 0$ and $L = 0 \leftrightarrow L' = 0$ are forbidden.	$\sim 10^{-4}$ of ED
3.	Magnetic dipole (MD) $4f^N$–$4f^N$	$\Delta S = 0$; $\Delta L = 0$; $\lvert\Delta J\rvert \leq 1$; $J = 0 \leftrightarrow J' = 0$ is forbidden.	$\sim 10^{-6}$ of ED
4.	Electric quadrupole (EQ) $4f^N$–$4f^N$	$\Delta S = 0$; $\lvert\Delta L\rvert \leq 2$; $\lvert\Delta J\rvert \leq 2$; $J = 0 \leftrightarrow J' = 0, 1$ and $L = 0 \leftrightarrow L' = 0, 1$ are forbidden.	$\sim 10^{-10}$ of ED
5.	One phonon ED vibronic $4f^N$–$4f^N$	The same as forced (induced) ED.	$\sim 10^{-7}$–10^{-10} of ED

[a] The site point group selection rules are equally important in determining whether a transition is allowed or forbidden. Writing the irreducible representations of the initial and final crystal field states as Γ_i and Γ_f, and that of the electric and magnetic dipole moment operators as Γ_{ED} and Γ_{MD}: $\Gamma_i \times \Gamma_{ED} \times \Gamma_f$ contains Γ_1; $\Gamma_i \times \Gamma_{MD} \times \Gamma_f$ contains Γ_1, for electric dipole allowed and magnetic dipole allowed transitions, respectively. The irreps Γ_{ED} and Γ_{MD} transform as cartesian vectors (x,y,z) and rotations (R_x,R_y,R_z) in the relevant point group and Γ_1 is the totally-symmetric irrep (*i.e.* the first listed irrep in the character table).

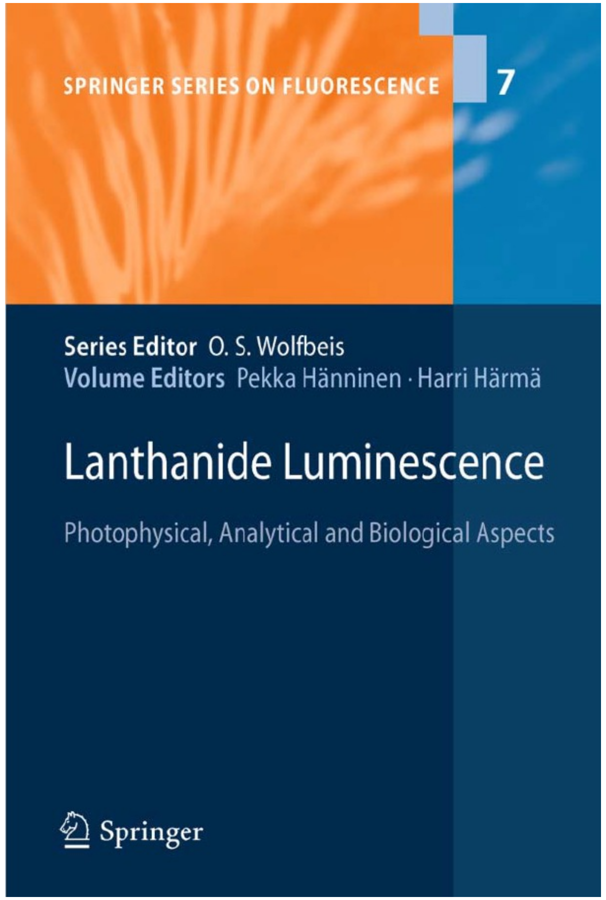
Por que as bandas são finas?



Quais são as transições mais prováveis?



Ln	G	I	F	λ/μm or nm[a]	Gap/cm^{-1}[a]	τ^{rad}/ms[a]
Ce	$^2F_{5/2}$	5d	$^2F_{5/2}$	Tunable, 300–450	–	–
Pr	$^3H_4$	$^1D_2$	$^3F_4$, $^1G_4$, $^3H_4$, $^3H_5$	1.0, 1.44, 600, 690	6,940	(0.05[b]–0.35)
		$^3P_0$	^3H_J (J = 4–6)	490, 545, 615, 640, 700, 725	3,910	(0.003[b]–0.02)
		$^3P_0$	^3F_J (J = 2–4)			
Nd	$^4I_{9/2}$	$^4F_{3/2}$	^4I_J (J = 9/2–13/2)	900, 1.06, 1.35	5,400	0.42 (0.2–0.5)
Sm	$^6H_{5/2}$	$^4G_{5/2}$	^6H_J (J = 5/2–13/2)	560, 595, 640, 700, 775	7,400	6.26 (4.3–6.3)
		$^4G_{5/2}$	^6F_J (J = 1/2–9/2)	870, 887, 926, 1.01, 1.15		
		$^4G_{5/2}$	$^6H_{13/2}$	877		
Eu[c]	$^7F_0$	$^5D_0$	^7F_J (J = 0–6)	580, 590, 615, 650, 720, 750, 820	12,300	9.7 (1–11)
Gd	$^8S_{7/2}$	$^6P_{7/2}$	$^8S_{7/2}$	315	32,100	10.9
Tb	$^7F_6$	$^5D_4$	^7F_J (J = 6–0)	490, 540, 580, 620, 650, 660, 675	14,800	9.0 (1–9)
Dy	$^6H_{15/2}$	$^4F_{9/2}$	^6H_J (J = 15/2–9/2)	475, 570, 660, 750	7,850	1.85 (0.15–1.9)
		$^4I_{15/2}$	^6H_J (J = 15/2–9/2)	455, 540, 615, 695	1,000	3.22[b]
Ho[d]	$^5I_8$	$^5S_2$	^5I_J (J = 8,7)	545, 750	3,000	0.37 (0.51[b])
		$^5F_5$	$^5I_8$	650	2,200	0.8[b]
		$^5F_5$	$^5I_7$	965		
Er[e]	$^4I_{15/2}$	$^4S_{3/2}$	^4I_J (J = 15/2, 13/2)	545, 850	3,100	0.7[b]
		$^4F_{9/2}$	$^4I_{15/2}$	660	2,850	0.6[b]
		$^4I_{9/2}$	$^4I_{15/2}$	810	2,150	4.5[b]
		$^4I_{13/2}$	$^4I_{15/2}$	1.54	6,500	0.66 (0.7–12)
Tm	$^3H_6$	$^1D_2$	$^3F_4$, $^3H_4$, $^3F_3$, $^3F_2$	450, 650, 740, 775	6,650	0.09
		$^1G_4$	$^3H_6$, $^3F_4$, $^3H_5$	470, 650, 770	6,250	1.29
		$^3H_4$	$^3H_6$	800	4,300	3.6[b]
Yb	$^2F_{7/2}$	$^2F_{5/2}$	$^2F_{7/2}$	980	10,250	1.3 or 2.0[f]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Lanthanide Luminescence

Photophysical, Analytical and Biological Aspects

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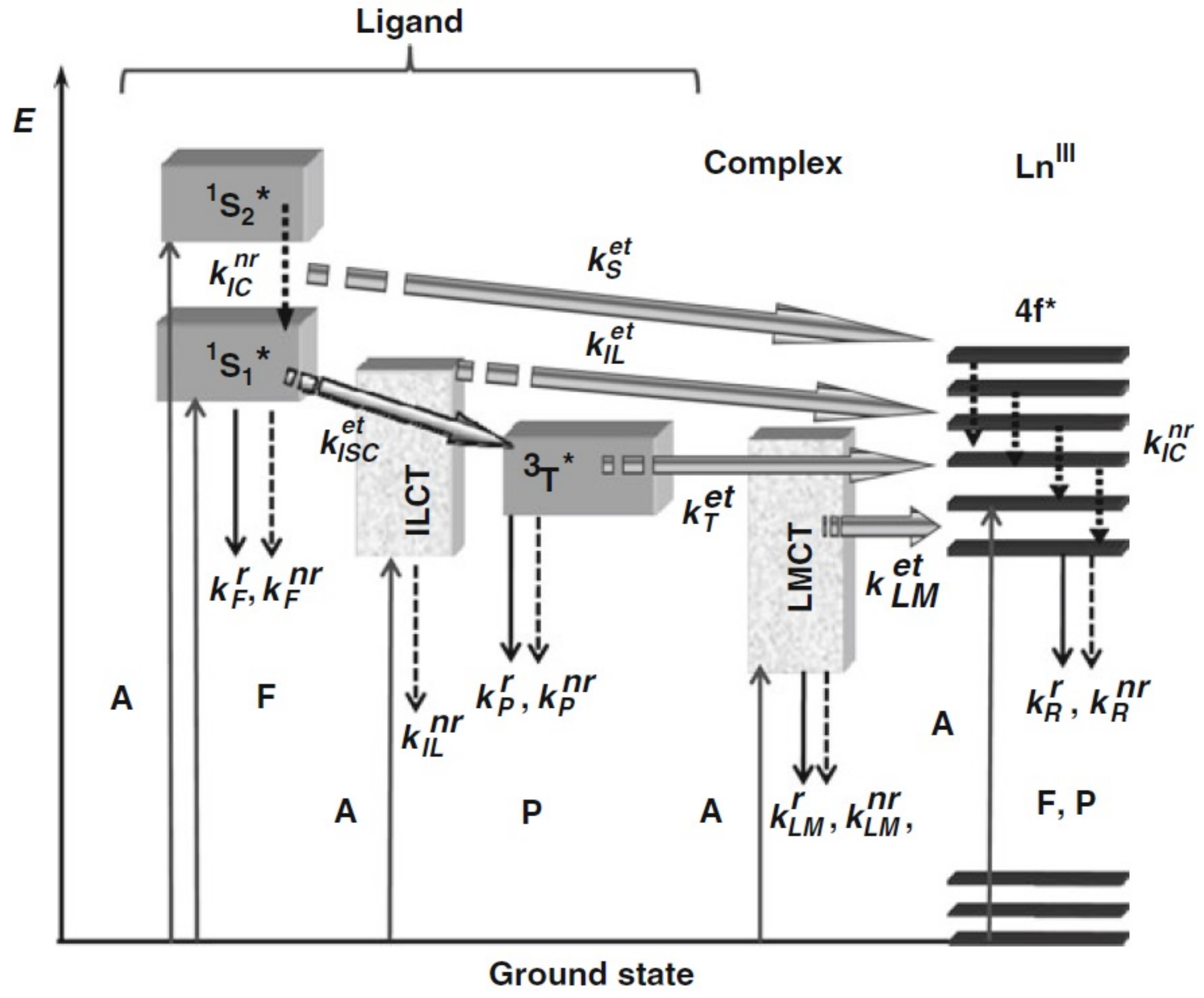
Ln	$\Delta E/\mathrm{cm}^{-1}$	No. of phonons		Lifetime/μs	
		OH	OD	H_2O	D_2O
Gd	32,100	9	15	2,300	n.a.
Tb	14,800	4	7	467	3,800
Eu	12,300	3–4	5–6	108	4,100
Yb	10,250	3	4.5	0.17[a]	3.95
Dy	7,850	2–3	3–4	2.6	42
Sm	7,400	2	3	2.7	60
Er	6,600	2	3	n.a.	0.37
Nd	5,400	1–2	2–3	0.031	0.14

[a] Estimated from quantum yields in water and deuterated water and from $\tau(D_2O)$

Como compensar a baixa absortividade?

Transferência de energia intramolecular



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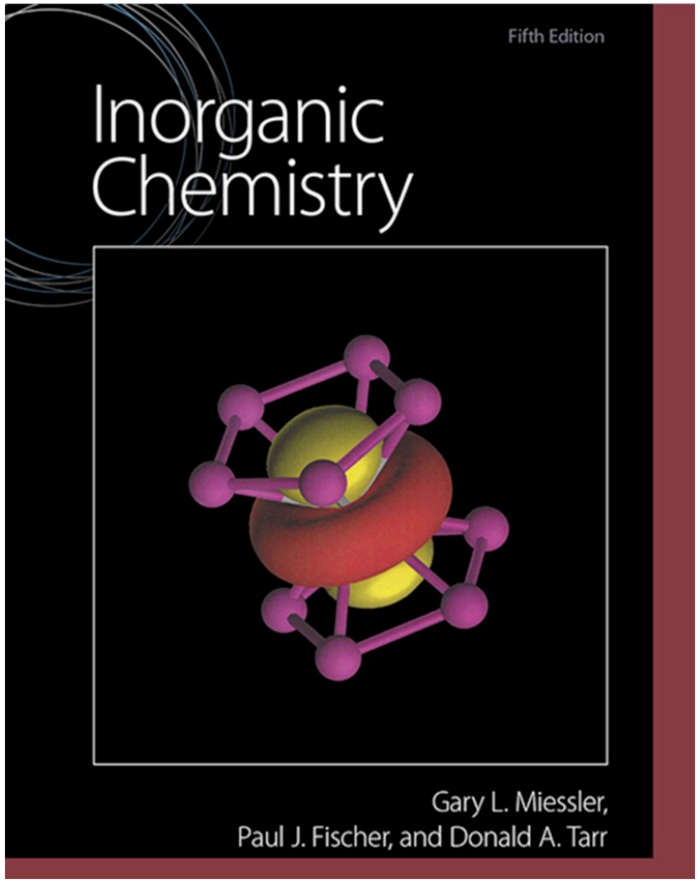

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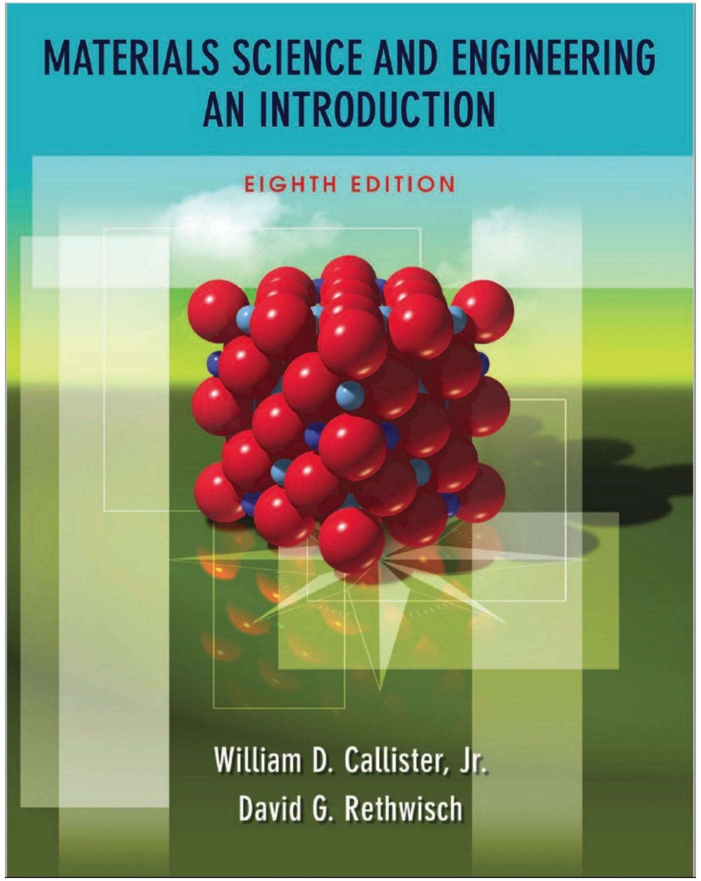

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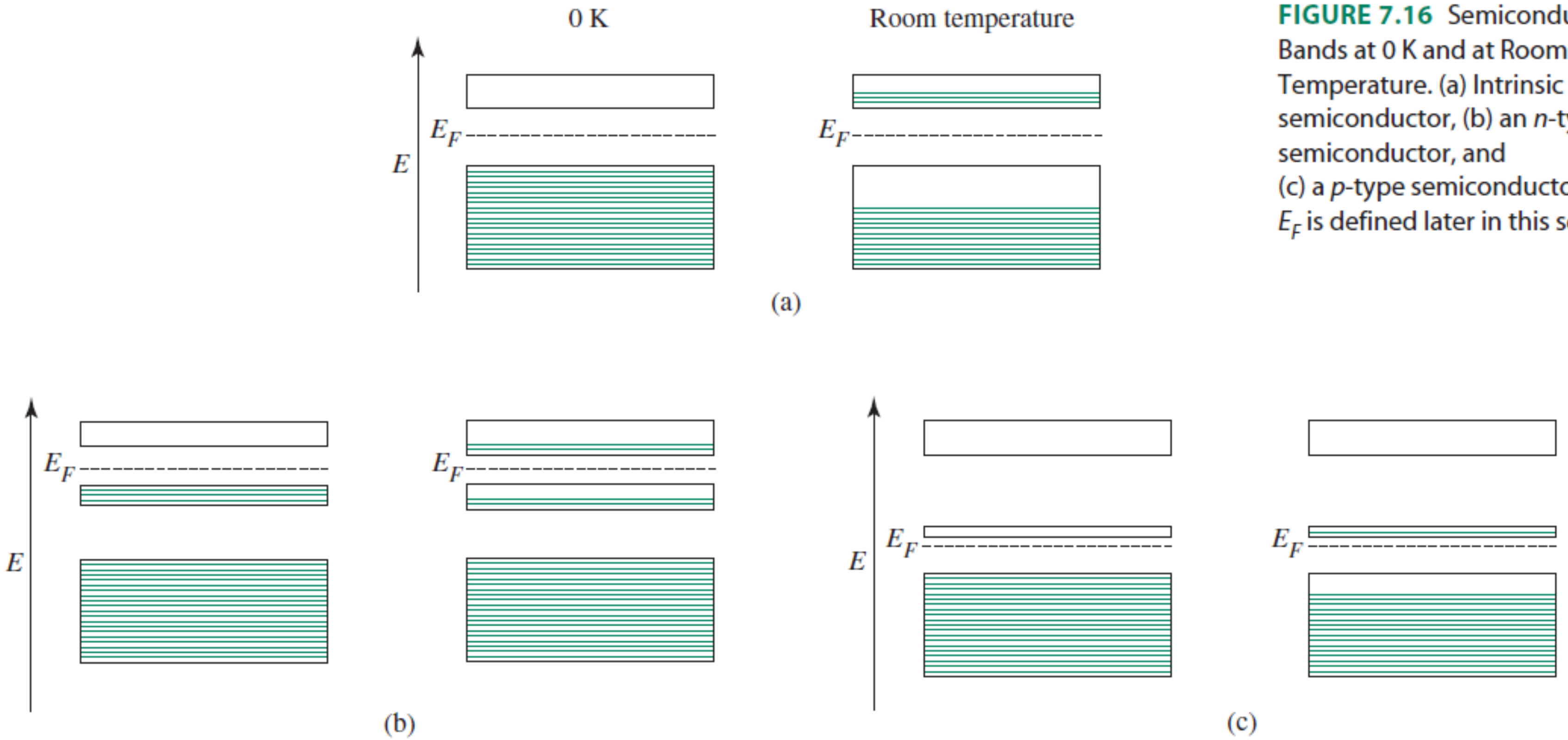

FIGURE 7.16 Semiconductor Bands at 0 K and at Room Temperature. (a) Intrinsic semiconductor, (b) an *n*-type semiconductor, and (c) a *p*-type semiconductor. E_F is defined later in this section.

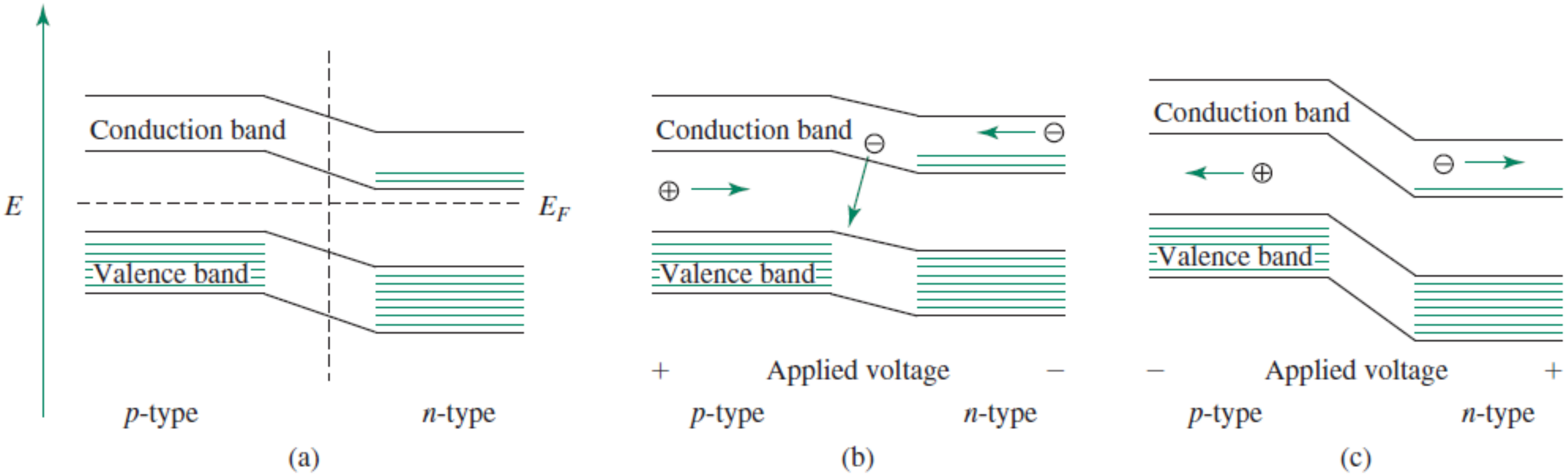

FIGURE 7.17 Band-Energy Diagram of a *p*–*n* Junction. (a) At equilibrium, the two Fermi levels are at the same energy, changing from the pure *n*-type or *p*-type Fermi levels, because a few electrons can move across the boundary (vertical dashed line). (b) With forward bias, current flows readily. (c) With reverse bias, very little current flows.

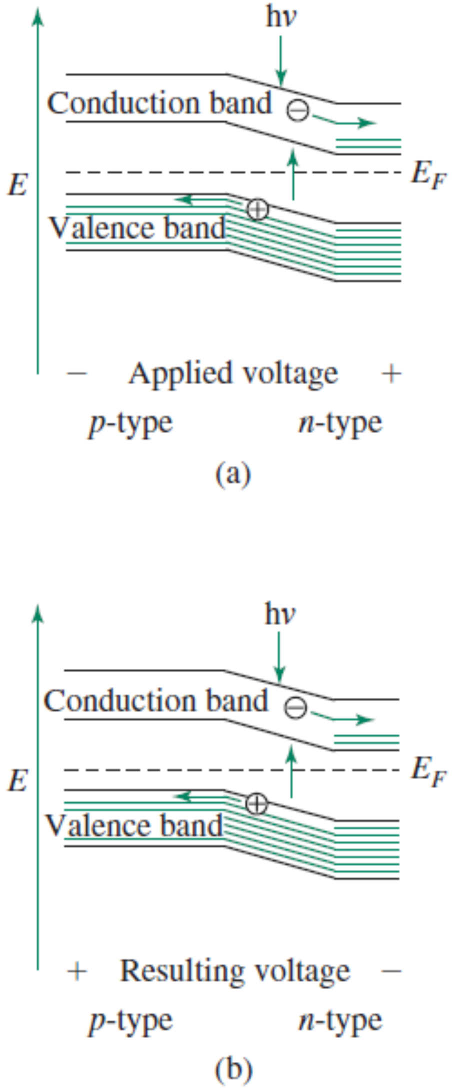

FIGURE 7.19 The Photovoltaic Effect. (a) As a light-activated switch. (b) Generating electricity. Light promotes electrons into the conduction band in the junction.

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Synthesis and properties of colloidal heteronanocrystals†

Celso de Mello Donegá*

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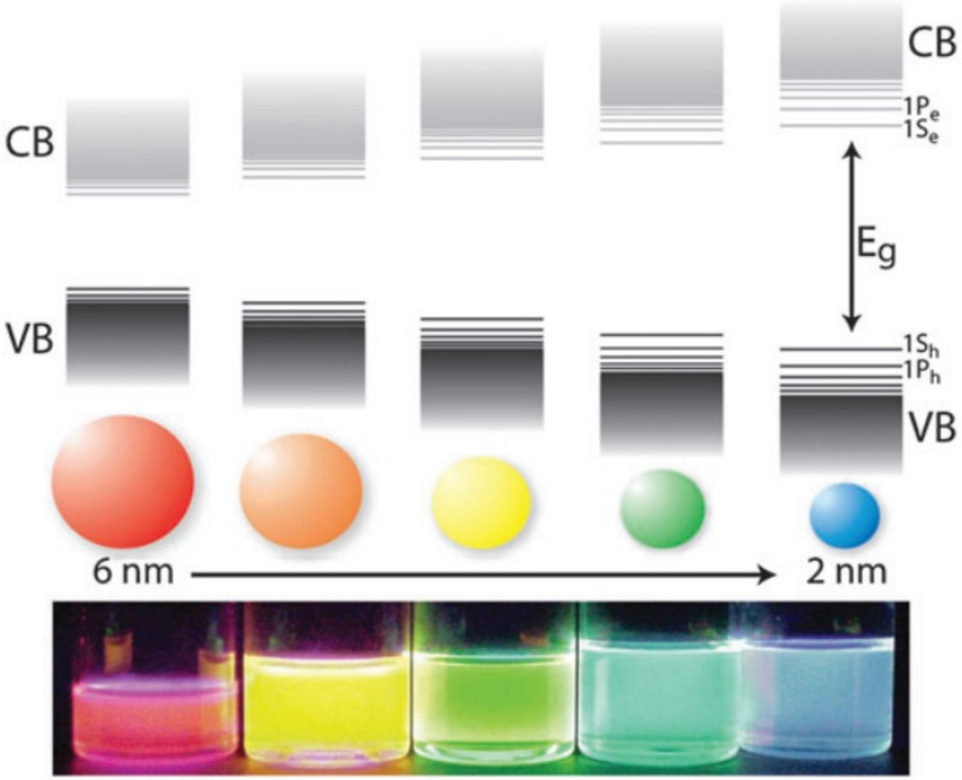
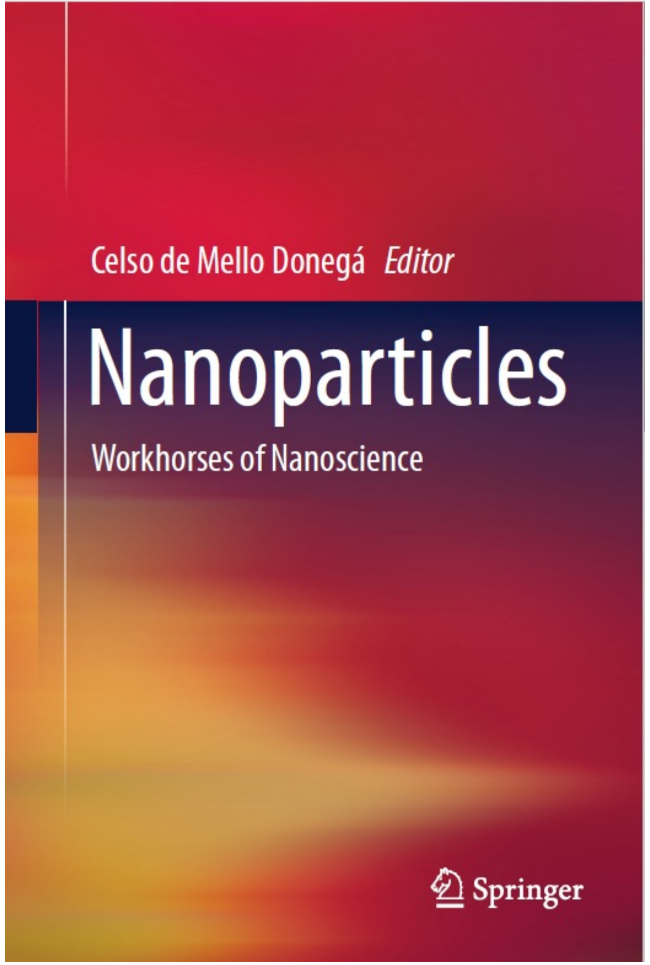


Fig. 4 Schematic representation of the quantum confinement effect on the energy level structure of a semiconductor material. The lower panel shows colloidal suspensions of CdSe NCs of different sizes under UV excitation. Courtesy of R. Koole (Philips Research Laboratories,



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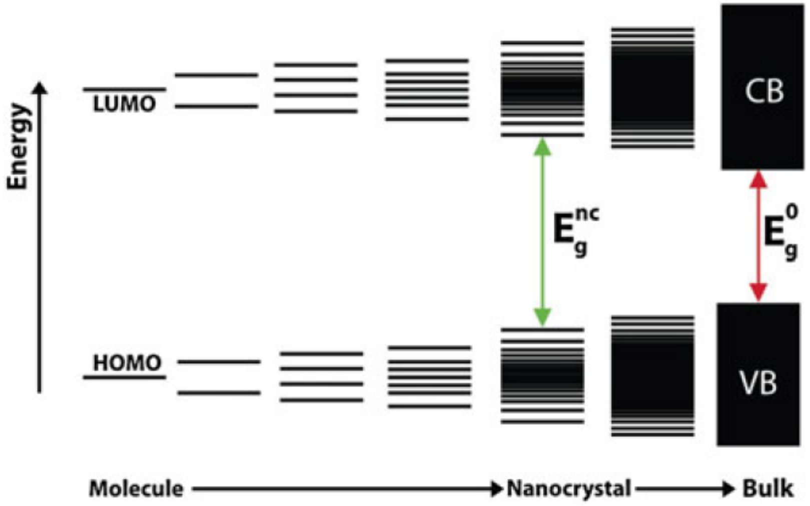

Fig. 2.12 Evolution of the energy level structure from a hypothetical diatomic molecule (*extreme left*) to a bulk semiconductor (*extreme right*). E_g^{nc} and E_g^0 indicate the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for a nanocrystal and bulk, respectively (CB = conduction band, VB = valence band). Reprinted with permission from Ref. [45]