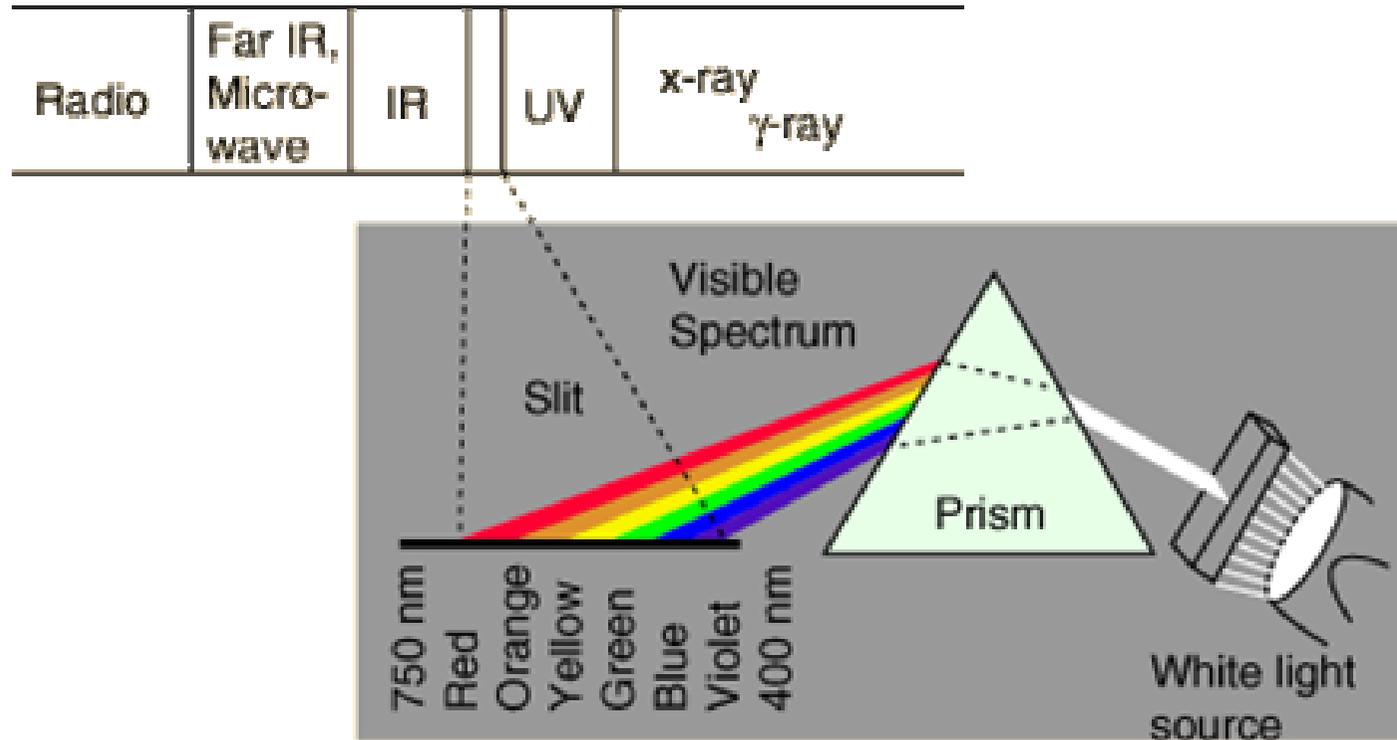


# Cor em Vidros

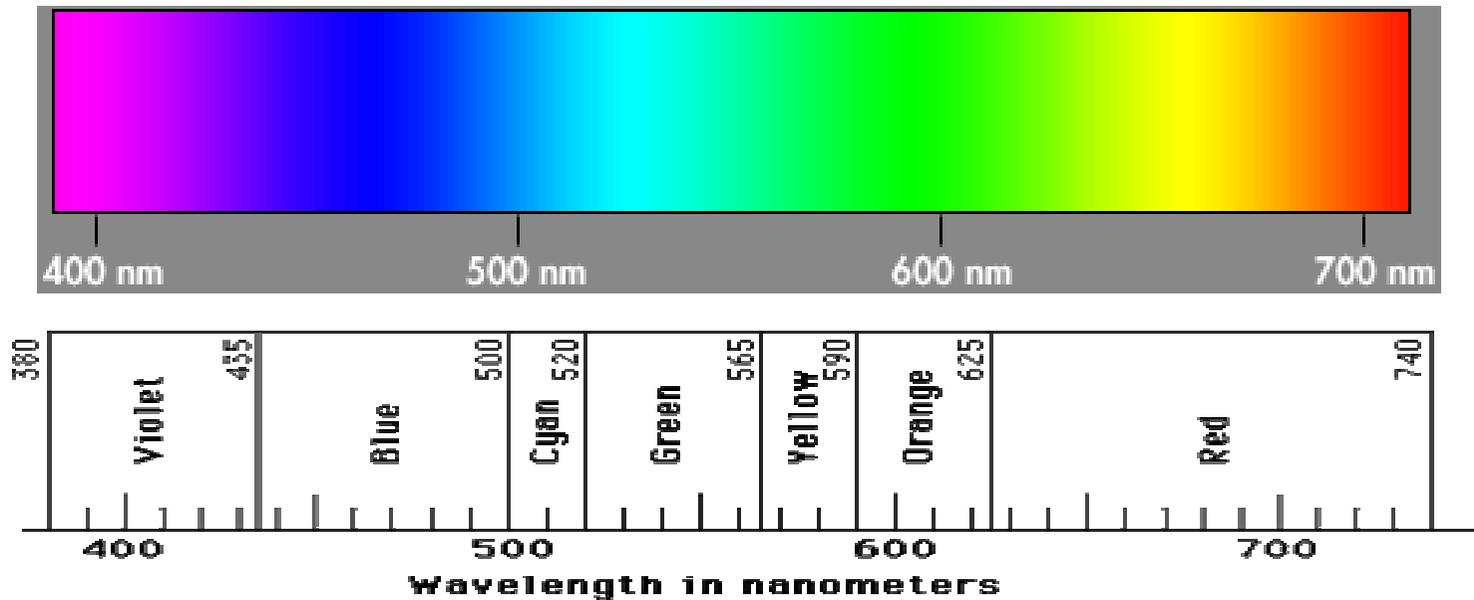
# Cor e Transições Eletrônicas



As cores no espectro eletromagnético

<http://hyperphysics.phy-astr.gsu.edu/hbase/ems3.html#c2>

# Cores e Faixas de Comprimento de Onda



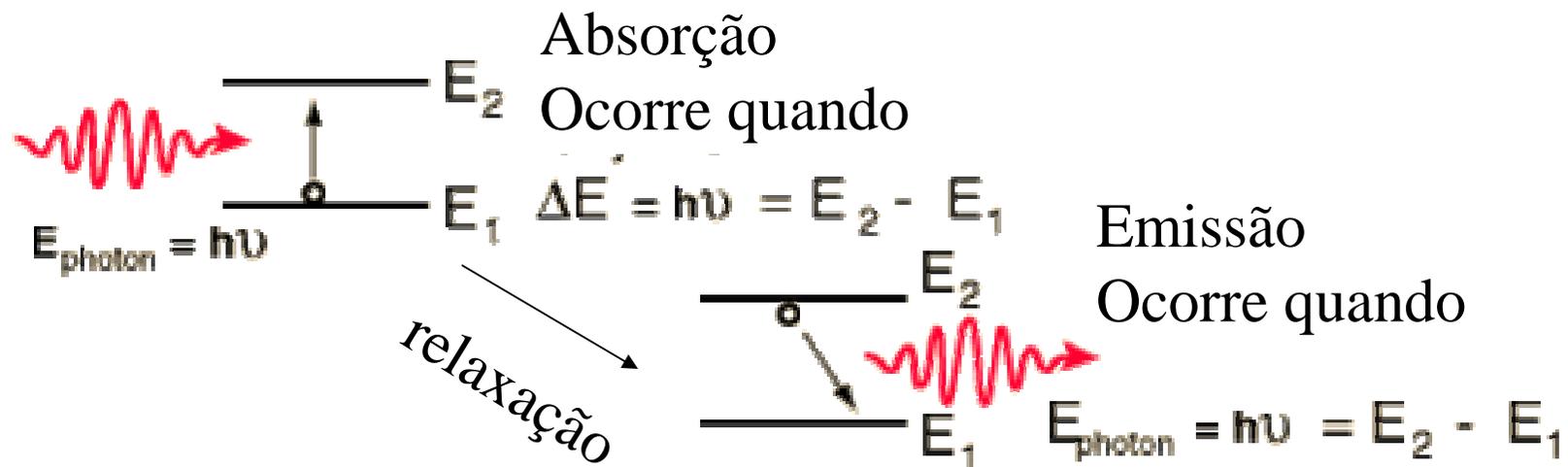
- ✓ A cada cor esta associada uma faixa de comprimentos de onda.
- ✓ A cor de um objeto depende da faixa de comprimentos de onda refletidos por ele, ou seja, daquilo que não é absorvido.
- ✓ As cor ou as cores absorvida(s) dependem de um fenômeno físico chamado de transição entre os estados eletrônicos da molécula, ou seja, a energia da transição eletrônica depende da diferença de energia entre os estados eletrônico inicial (geralmente o fundamental) e a energia do estado eletrônico final (dito excitado).

# Cor e Comprimento de Onda

- **Violeta:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Azul:** 440 - 490 nm
- **Verde:** 490 - 570 nm
- **Amarelo:** 570 - 585 nm
- **Laranja:** 585 - 620 nm
- **Vermelho:** 620 - 780 nm

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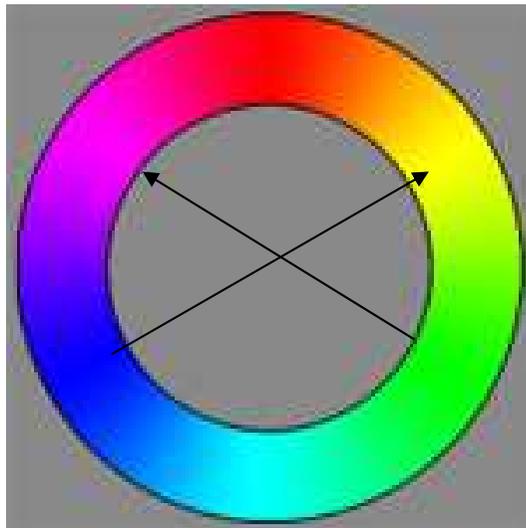
# Transições Eletrônicas e Estados Eletrônicos como Origem da Cor



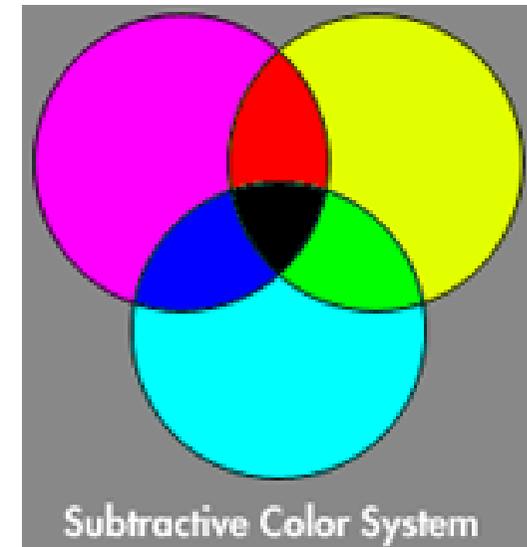
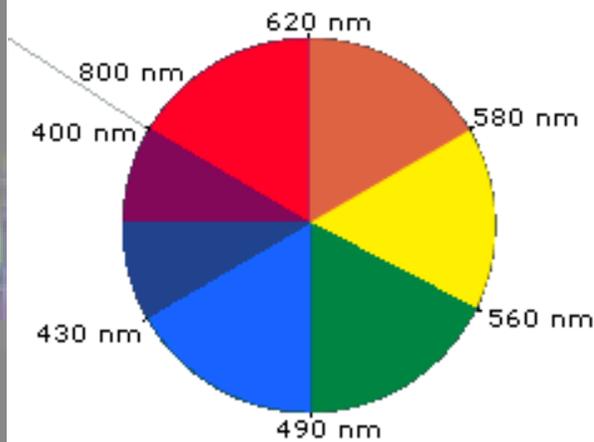
$E_1$  representa a energia de um estado eletrônico fundamental  
 $E_2$  representa a energia de um estado eletrônico excitado

# A cor dos Objetos Reflexão

- As cores refletidas são complementares àquelas absorvidas.



Disco de Cores



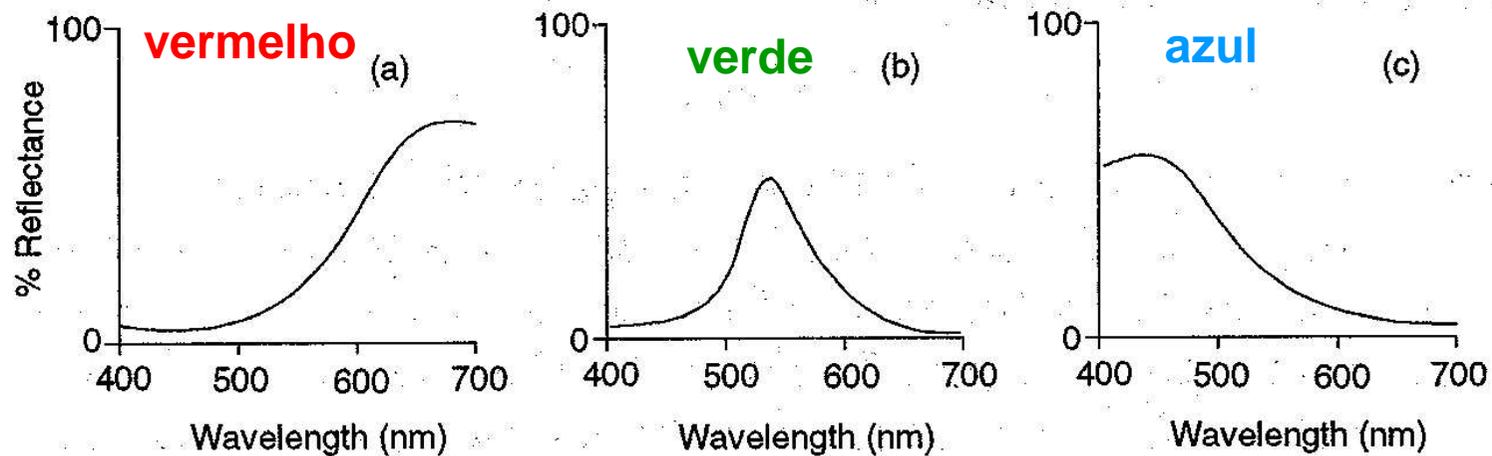
Quando mais de uma cor é refletida, então usamos o Padrão de cores subtrativas

# Relação de Cores Complementares

**Table 2.1** *Complementary colour relationships*

<i>Wavelength range (nm)</i>	<i>Colour</i>	<i>Complementary colour</i>
400–435	Violet	Greenish-yellow
435–480	Blue	Yellow
480–490	Greenish-blue	Orange
490–500	Bluish-green	Red
500–560	Green	Purple
560–580	Yellowish-green	Violet
580–595	Yellow	Blue
595–605	Orange	Greenish-blue
605–750	Red	Bluish-green

# Espectro Eletrônico e Cor



**Figure 2.4** *Visible reflectance spectra of (a) red, (b) green and (c) blue surfaces.*

# Intensidade da Cor

- A intensidade da cor esta relacionada a intensidade da banda de absorção quando a cor é fruto de uma absorção de luz.

$$\log \frac{I_0}{I} = A = \varepsilon.d.c$$

$$f = (4,32 \times 10^{-9}) \int_{\nu_1}^{\nu_2} \varepsilon d\nu \propto \text{area sob a banda de absorção no espectro}$$

# Intensidade e Regras de Seleção

- Laporte
  - O produto triplo das representações de simetria do estado final pelo momento de dipolo elétrico pelo estado final não deve ser zero.

$$\int \Psi^* \hat{\mu} \Psi d\tau \approx \Gamma_{\Psi^*} \Gamma_{\mu} \Gamma_{\Psi} \neq 0$$

- Spin
  - Não pode haver mudança de multiplicidade (2S+1).

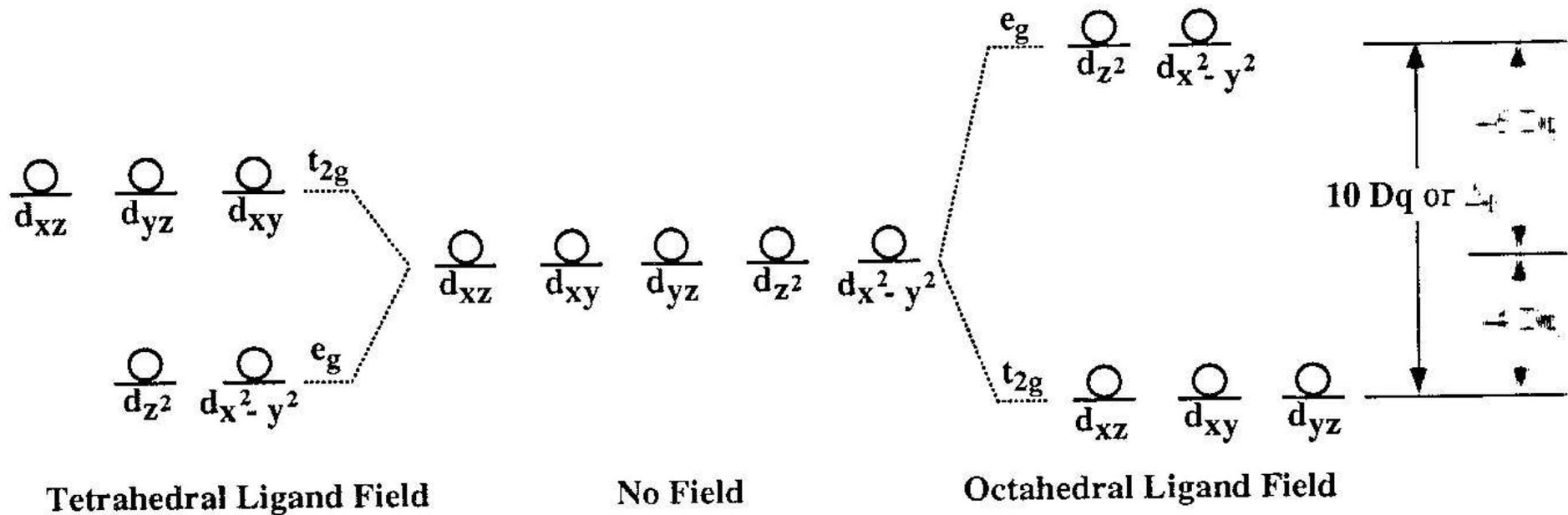
# Intensidade e Regras de Seleção

Table 7.10  
Representative values for the intensities of bands of various types in transition metal complexes.

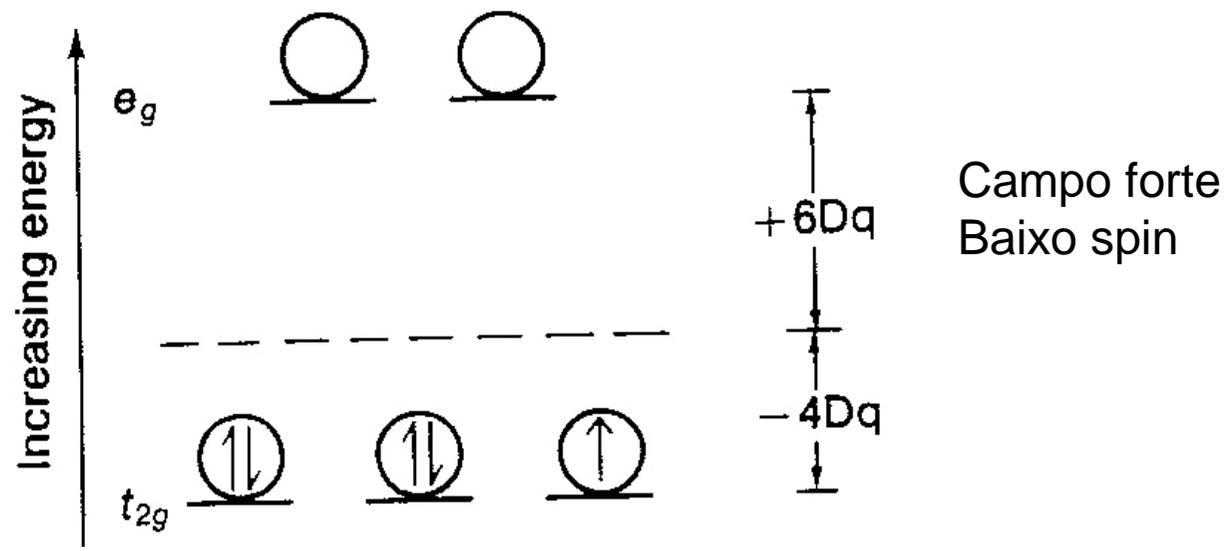
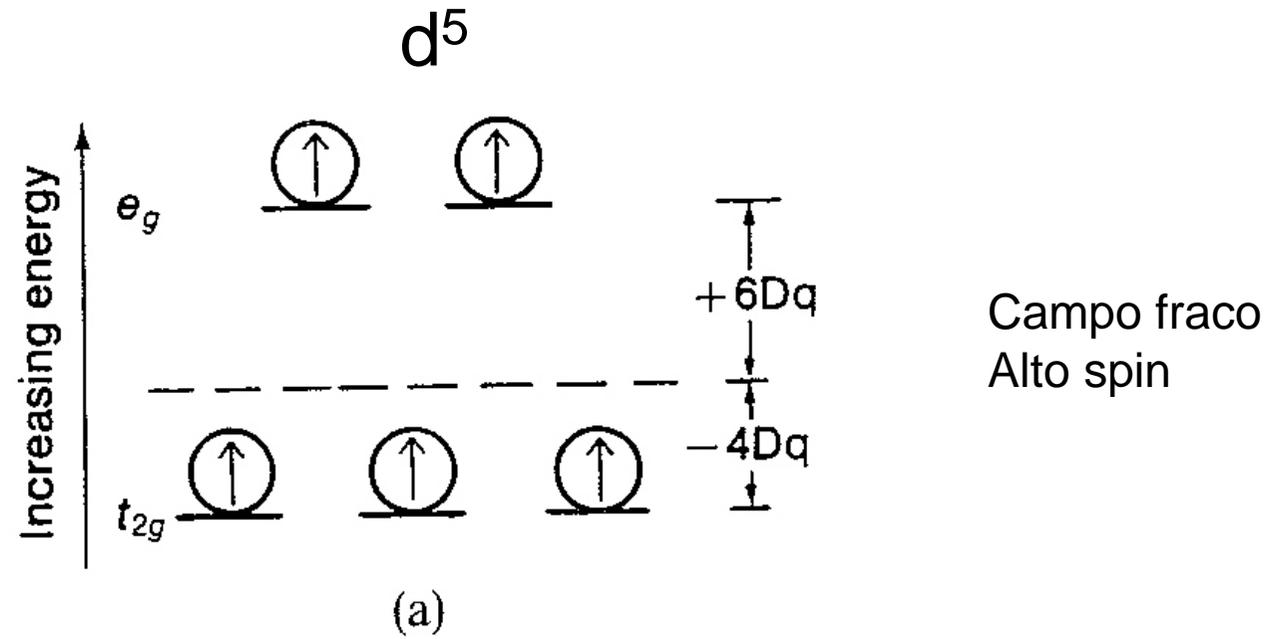
<i>Type of transition</i>	<i>Approximate <math>f</math></i>	<i>Approximate <math>\epsilon</math></i>
Spin-forbidden, Laporte-forbidden	$10^{-7}$	0.1
Spin-allowed, Laporte-forbidden	$10^{-5}$	10
Spin-allowed, d-p mixing	$10^{-3}$	100
Spin-allowed, intensity stealing	$10^{-2}$	1 000
Spin-allowed, Laporte-allowed (charge transfer)	$10^{-1}$	10 000

# Cor e Íons de Metais de Transição

## Desdobramento do Campo Cristalino



**Figure 19-3.** Energy levels of the  $d$ -orbitals in octahedral and tetrahedral fields.



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# Diagrama de OM

## $[\text{Co}(\text{NH}_3)_6]^{3+}$

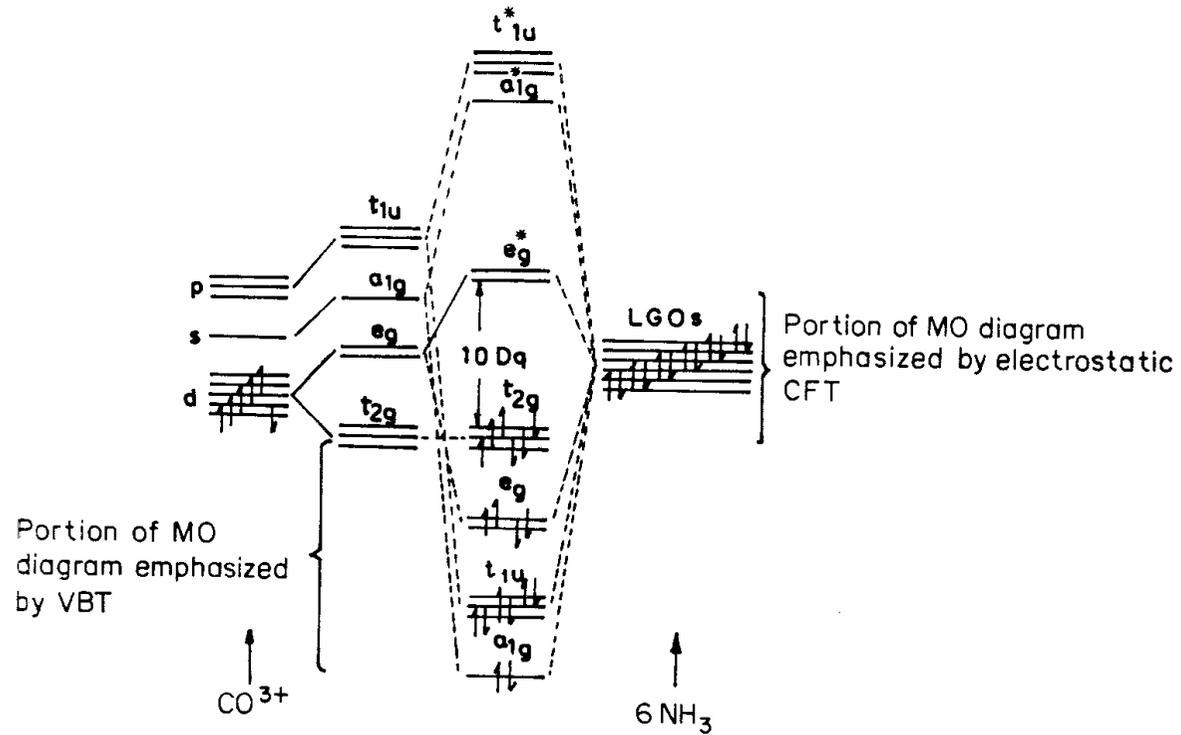


Fig. 7.10 MO energy level diagram of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  illustrating electron distribution and relation between MOT (Molecular Orbital Theory), CFT (Crystal Field Theory), and VBT (Valence Bond Theory).

# Estados de Energia Metais de Transição Externa

Table 7.7  
For octahedral symmetry

Configuration	Transition	Energy
$d^1, d^6$ $d^4, d^9$ $d^2, d^7$	$T_2 \rightarrow E$	$10 Dq$
	$E \rightarrow T_2$	$10 Dq$
	$T_1(F) \rightarrow T_1(P)$	$(225 B^2 + 180 B \cdot Dq + 100 Dq^2)^{1/2}$
	$\rightarrow A_2(F)$	$-\frac{15}{2} B + 15 Dq + \frac{1}{2}(x)^{1/2}$
$d^3, d^8$	$\rightarrow T_2(F)$	$-\frac{15}{2} B + 5 Dq + 1/2(x)^{1/2}$
	$A_2(F) \rightarrow T_1(F)$	$\frac{15}{2} B + 15 Dq - 1/2(x)^{1/2}$
	$\rightarrow T_1(P)$	$\frac{15}{2} B + 15 Dq + 1/2(x)^{1/2}$
	$\rightarrow T_2(F)$	$10 Dq$

where  $x = (225 B^2 + 180 B \cdot Dq + 100 Dq^2)$ .

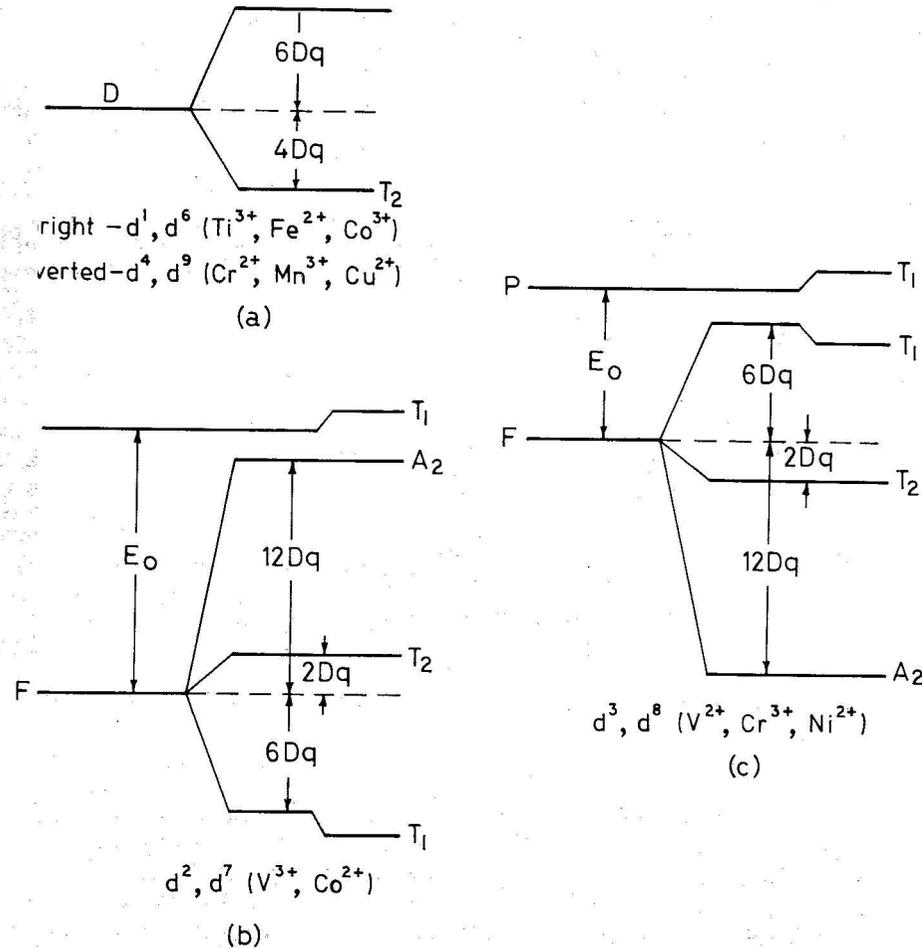
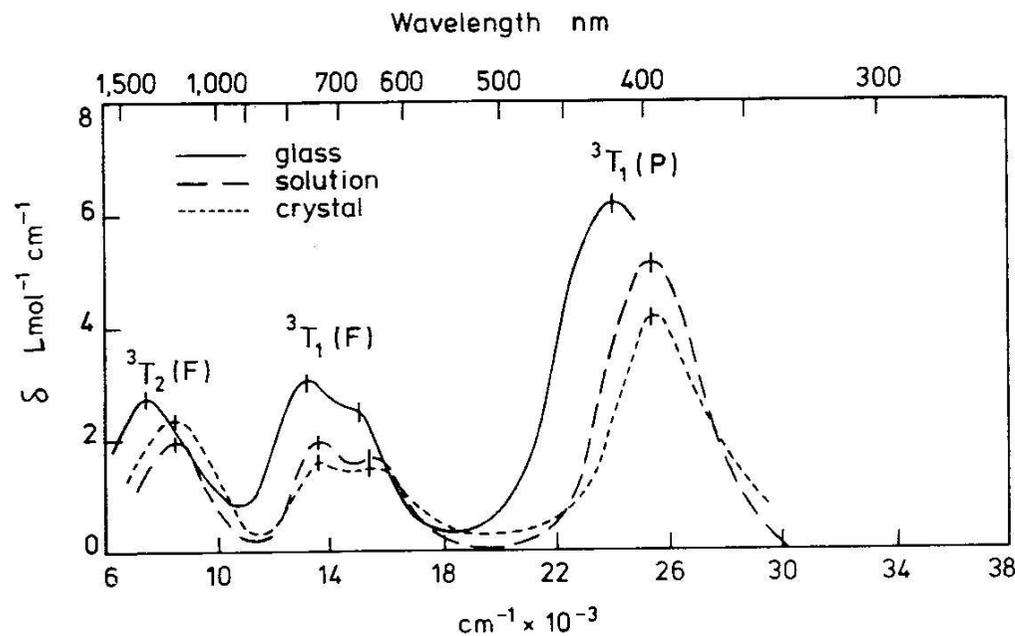
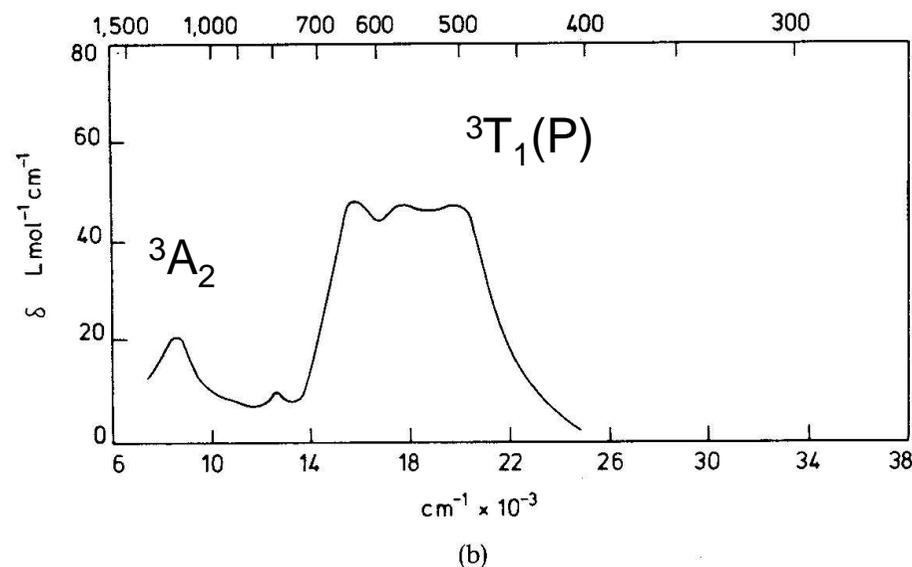


Fig. 7.5 The splitting of d orbitals (a) for D-state, (b), (c) for P and F states. The diagrams are appropriate for octahedral fields and when inverted apply to tetrahedral or cubic coordination.





Os espectros ao lado mostram as bandas correspondentes às bandas permitidas por spin para o íon  $\text{Ni}^{2+}$  em ambientes de simetria  $O_h$ . O espectro em linha cheia é do  $\text{Ni}^{2+}$  em vidro borato alcalino, baixo teor de álcali.



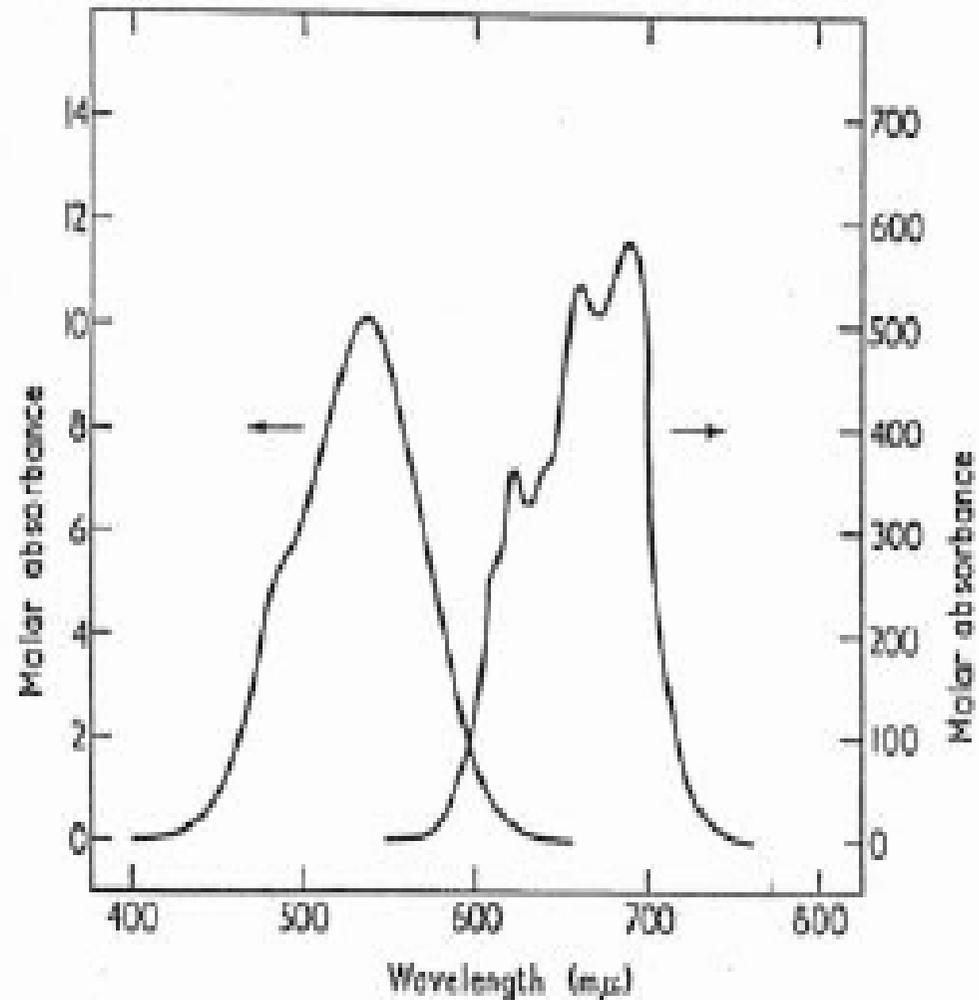
O espectro do íon  $\text{Ni}^{2+}$  no vidro de borato alcalino, alto teor de álcali, possui um padrão diferente mais condizente com o  $\text{Ni}^{2+}$  em simetria  $T_d$ .

**Tendência: quanto maior o teor de álcalis nestes vidros a base de borato mais o metal de transição tende a  $T_d$ .**

**Figure 19-6.** Absorption spectra (a) octahedrally coordinated  $\text{Ni}^{2+}$  in various media, (b)  $\text{Ni}^{2+}$  in high-alkali borate glass. (Adapted from Bates [6], Fig. 37, p. 248, and Fig. 38, p. 249. Reproduced with permission of Butterworth-Heinemann Ltd.,

# Simetria e Cor

- Co(II) apresenta cores diferentes quando em simetria octaédrica e tetraédrica como pode ser visto no espectro eletrônico obtido em modo de transmissão ao lado.



# Cobalto

## $O_h$ vs $T_d$

COLOURED GLASSES

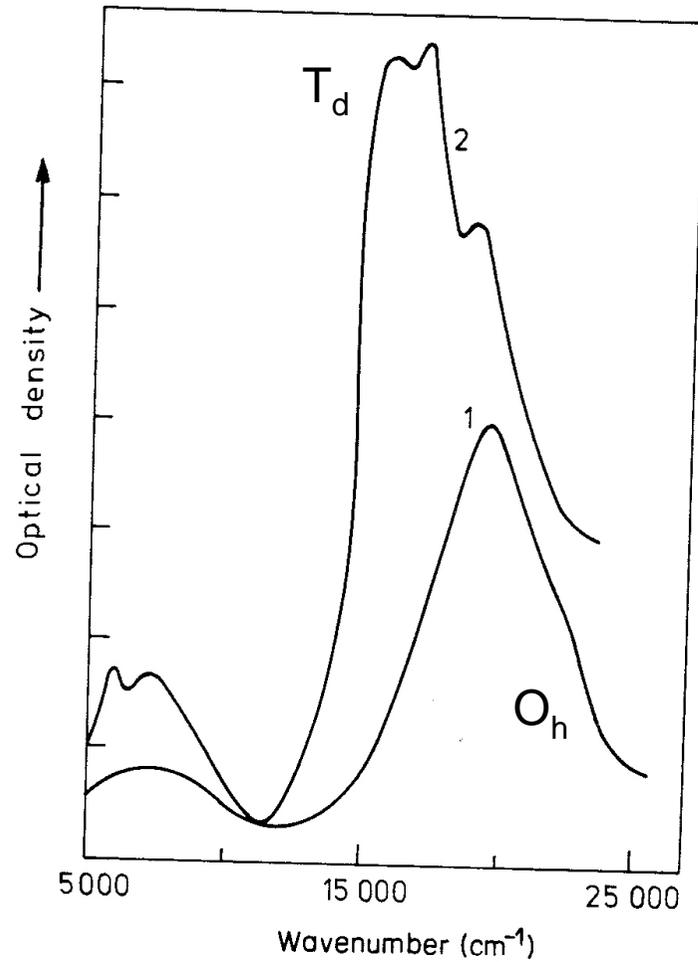


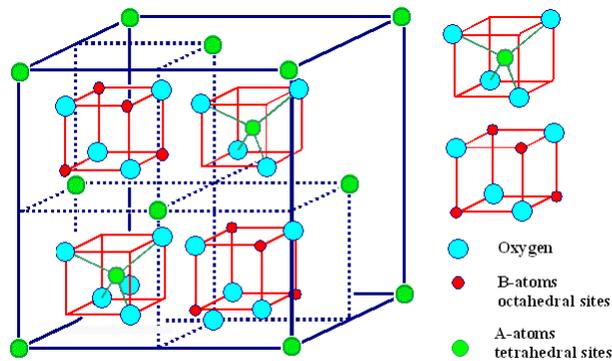
Fig. 7.18 Optical absorption spectra of cobalt (II) in binary sodium-borate glasses.  
(1) 10 mol%  $Na_2O$  (2) 30 mol%  $Na_2O$ .

**Table 19-1.** Colors Generated by Transition-Metal and Rare-Earth Ions in Glass

Transition metal ions			Rare earth ions		
Configuration	Ion	Color	Configuration	Ion	Color
$d^0$	Ti <sup>4+</sup>	Colorless	$4f^0$	La <sup>3+</sup>	None
	V <sup>5+</sup>	Faint yellow to colorless		Ce <sup>4+</sup>	Weak yellow
	Cr <sup>6+</sup>	Faint yellow to colorless		Ce <sup>3+</sup>	Weak yellow
$d^1$	Ti <sup>3+</sup>	Violet-purple	$4f^1$	Pr <sup>3+</sup>	Green
	V <sup>4+</sup>	Blue	$4f^2$	Nd <sup>3+</sup>	Violet-pink
	Mn <sup>6+</sup>	Colorless	$4f^4$	Pm <sup>3+</sup>	None
$d^2$	V <sup>3+</sup>	Yellow-green	$4f^5$	Sm <sup>3+</sup>	None
	Cr <sup>3+</sup>	Green	$4f^6$	Sm <sup>2+</sup>	Green
$d^3$	Cr <sup>3+</sup>	Green	$4f^7$	Eu <sup>3+</sup>	None
$d^4$	Cr <sup>2+</sup>	Faint blue		Eu <sup>2+</sup>	Brown
$d^5$	Mn <sup>3+</sup>	Purple	$4f^8$	Gd <sup>3+</sup>	None
	Mn <sup>2+</sup>	Light yellow	$4f^9$	Tb <sup>3+</sup>	None
$d^6$	Fe <sup>3+</sup>	Faint yellow	$4f^{10}$	Dy <sup>3+</sup>	None
	Fe <sup>2+</sup>	Blue-green	$4f^{11}$	Dy <sup>2+</sup>	Brown
$d^7$	Co <sup>3+</sup>	Faint yellow		$4f^{12}$	Ho <sup>3+</sup>
	Co <sup>2+</sup>	Blue-pink	$4f^{13}$	Er <sup>3+</sup>	Weak pink
$d^8$	Ni <sup>2+</sup>	Brown-purple	$4f^{14}$	Tm <sup>3+</sup>	None
$d^9$	Cu <sup>2+</sup>	Blue-green		Tm <sup>2+</sup>	None
$d^{10}$	Cu <sup>+</sup>	Colorless		Yb <sup>3+</sup>	None
				Lu <sup>3+</sup>	None

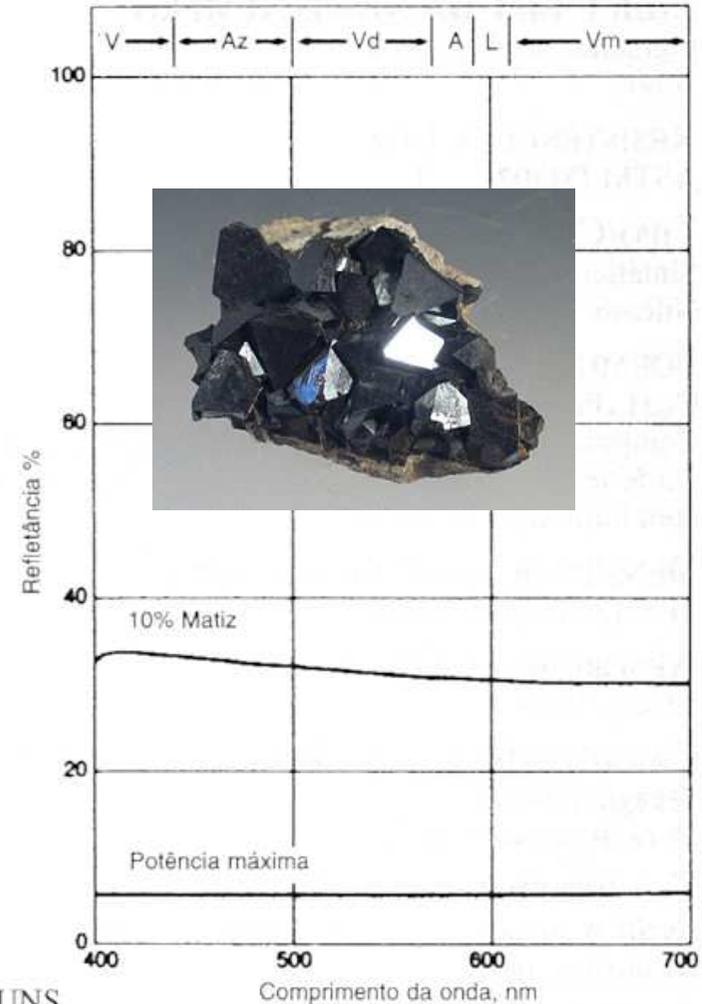
# Pigmento Negro

- Ao lado é mostrado um espectro eletrônico em modo de refletância do  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  ou  $\text{Fe}_3\text{O}_4$  (magnetita), espinélio de formula  $(A)[B_2]O_4$  onde A é um sitio tetraédrico e B octaédrico.



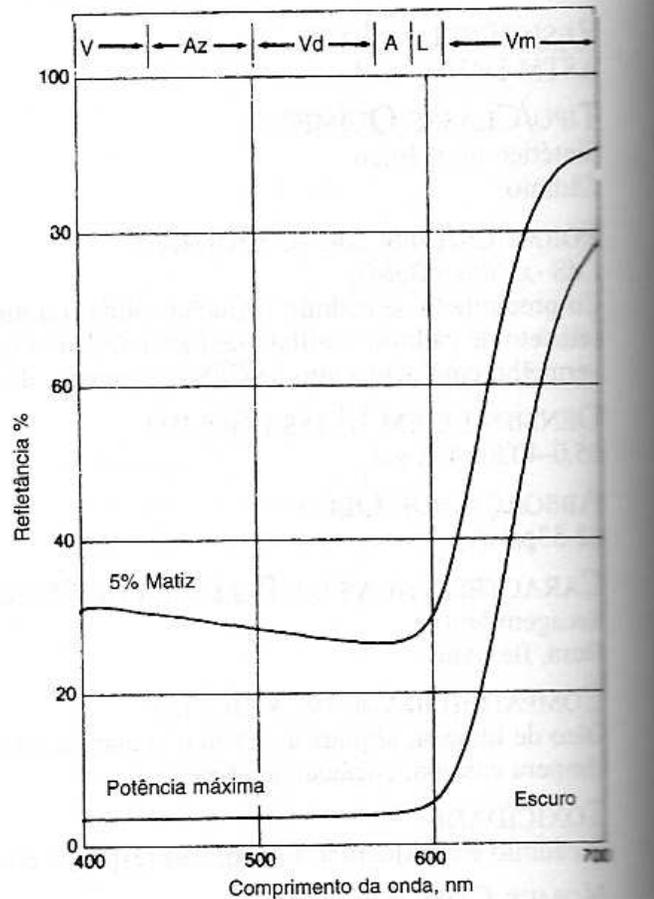
$\text{AB}_2\text{O}_4$  spinel The red cubes are also contained in the back half of the unit cell

CURVAS ESPECTRAIS REPRESENTATIVAS



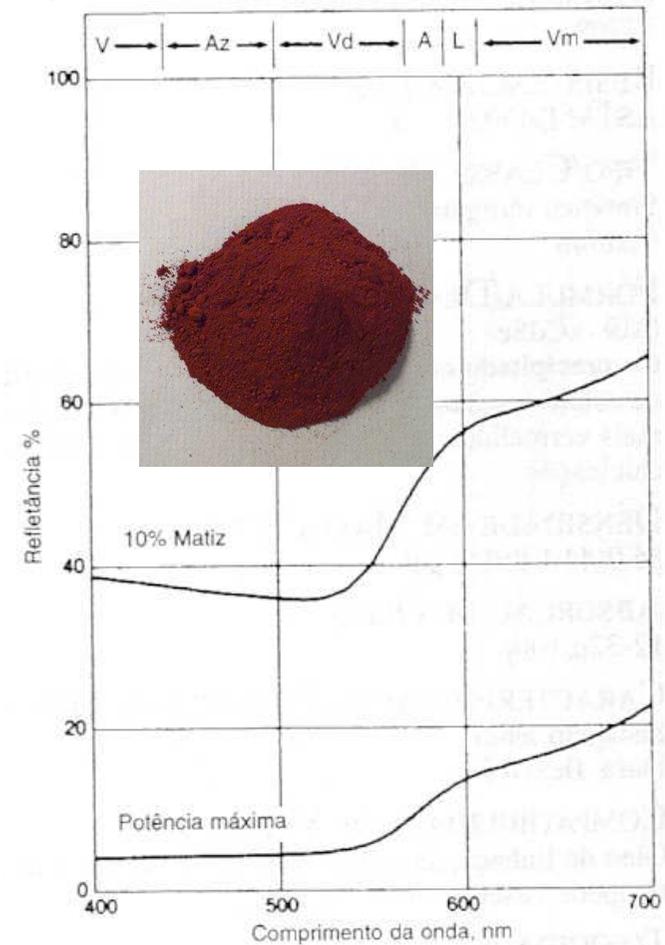
# Pigmento Vermelho

CURVAS ESPECTRAIS REPRESENTATIVAS



- Espectro eletrônico em modo de refletância da HgS.CdS. Ubirajara Pereira Rodrigues Filho

CURVAS ESPECTRAIS REPRESENTATIVAS

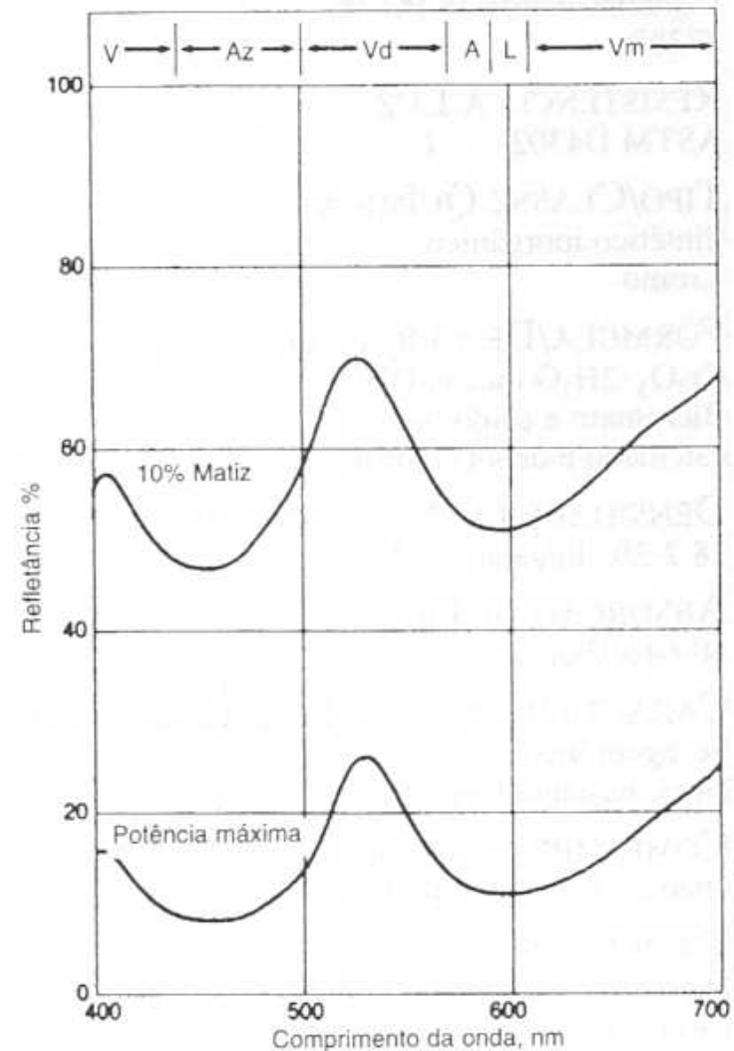


- Espectro eletrônico em modo de refletância da  $Fe_2O_3$ .

# Pigmento Verde

- Ao lado é mostrado um espectro eletrônico em modo de refletância do  $\text{Cr}_2\text{O}_3$ .

CURVAS ESPECTRAIS REPRESENTATIVAS



Ubirajara Pereira

# Cores nos Vidros



Vidro com Fe(III),  
ambar, e  
Fe(III) e BaO, verde.



Vidro com Mn(III)



Vidro com Cr(III)

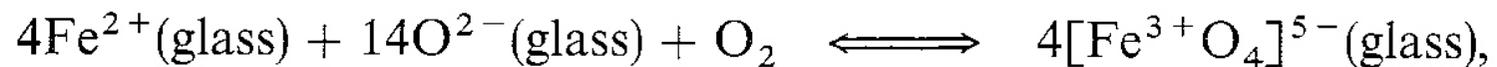


Vidro com Cu(II)



Vidro com Co(II)

# Oxidação e Cor



such that the rate constant is given by

$$K = \frac{[a_{\text{Fe}^{3+}\text{O}_4(\text{glass})}]^4}{[a_{\text{Fe}^{2+}(\text{glass})}]^4 [a_{\text{O}^{2-}(\text{glass})}]^{14} p_{\text{O}_2(\text{glass})}}.$$

A quantidade de Fe(II) e Fe(III) dependem do teor de O<sub>2</sub> dissolvido no vidro e no fundente.

# Diagrama de Tanabe-Sugano $d^6$

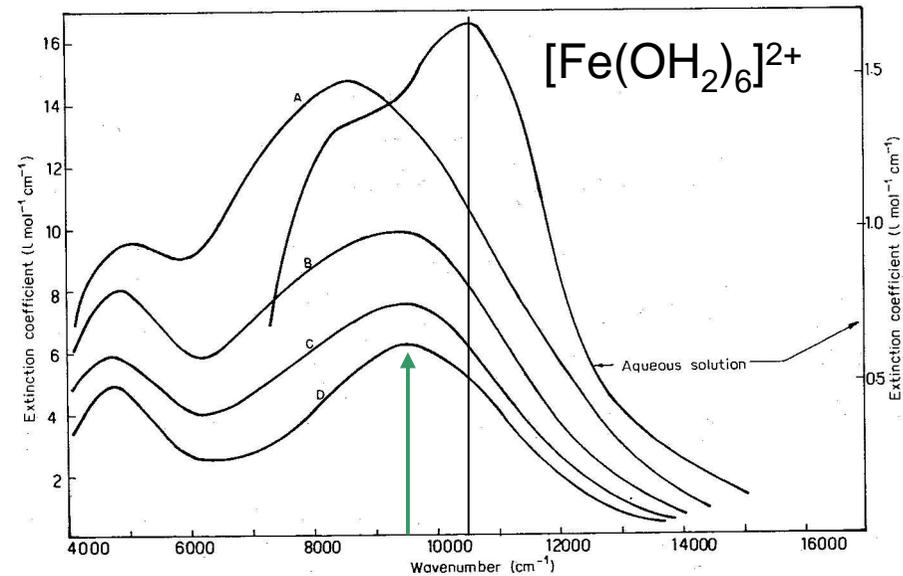
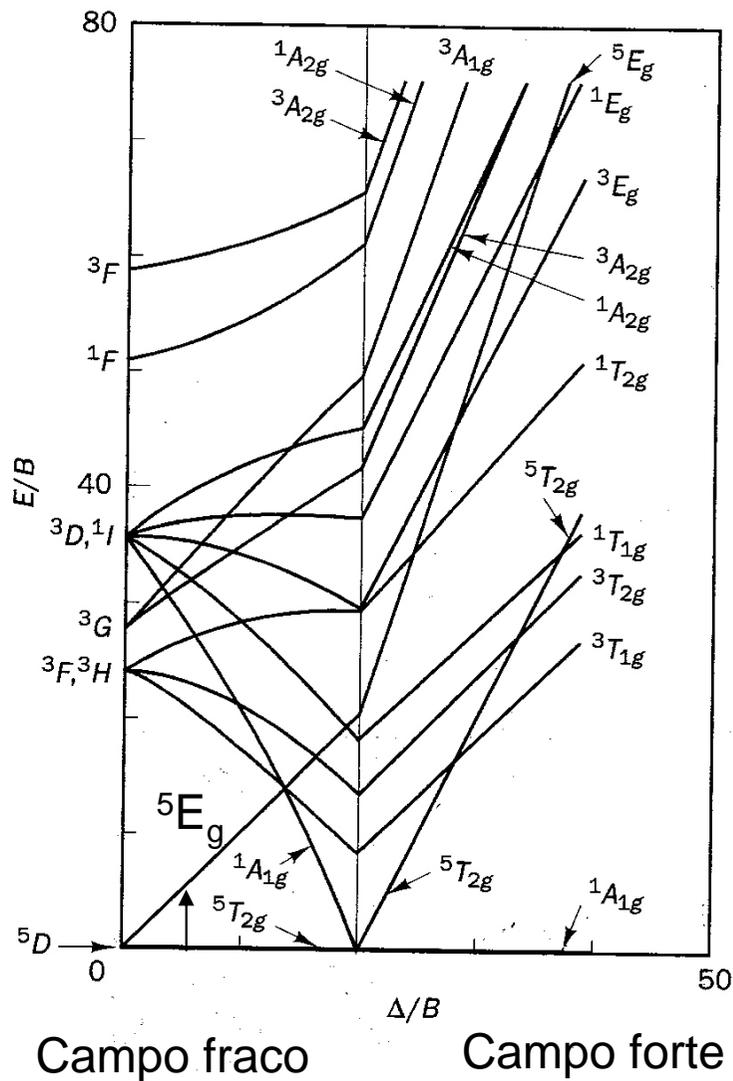


Fig. 7.17 Optical absorption spectra of iron(II) in aqueous solution and in some binary alkaline-earth-phosphate glasses.

- (A)  $MgO-P_2O_5$
- (B)  $CaO-P_2O_5$
- (C)  $SrO-P_2O_5$
- (D)  $BaO-P_2O_5$

Principal transição:  $5E_g \leftarrow 5T_{2g}$

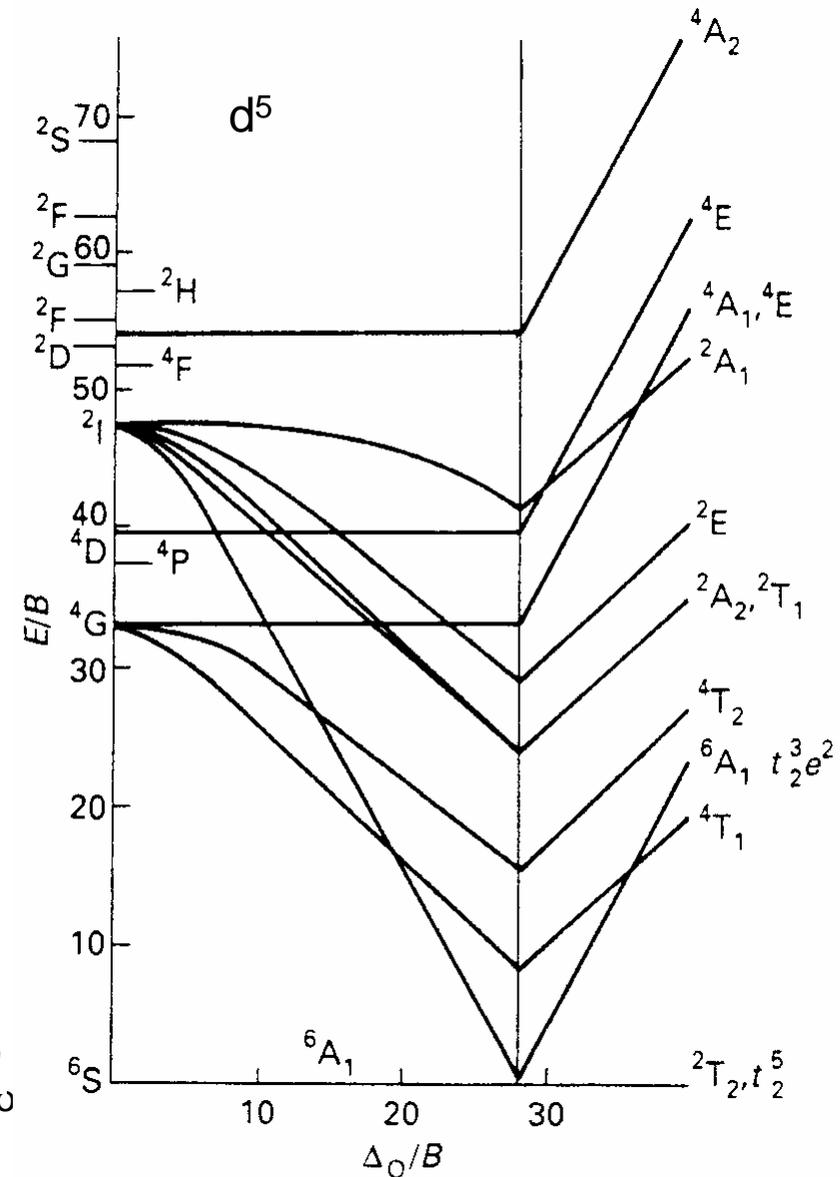
odrigues Filho

# Diagrama de Tanabe-Sugano $d^5$

Table 1. Tanabe-Sugano expressions for the ligand field state energies of octahedral  $Fe^{3+}$  (from Lever, 1968). The terms which are quadratic in  $B$  describe the configurational interaction and are derived assuming  $C = 4B$ . The quantities designated by  $x$  in the expressions for the  ${}^4T_2({}^4D)$  and  ${}^4T_1({}^4P)$  state energies arise from off-diagonal elements in the Tanabe-Sugano matrices; these quantities are neglected in the calculations of the spectroscopic state energies (Table 2).

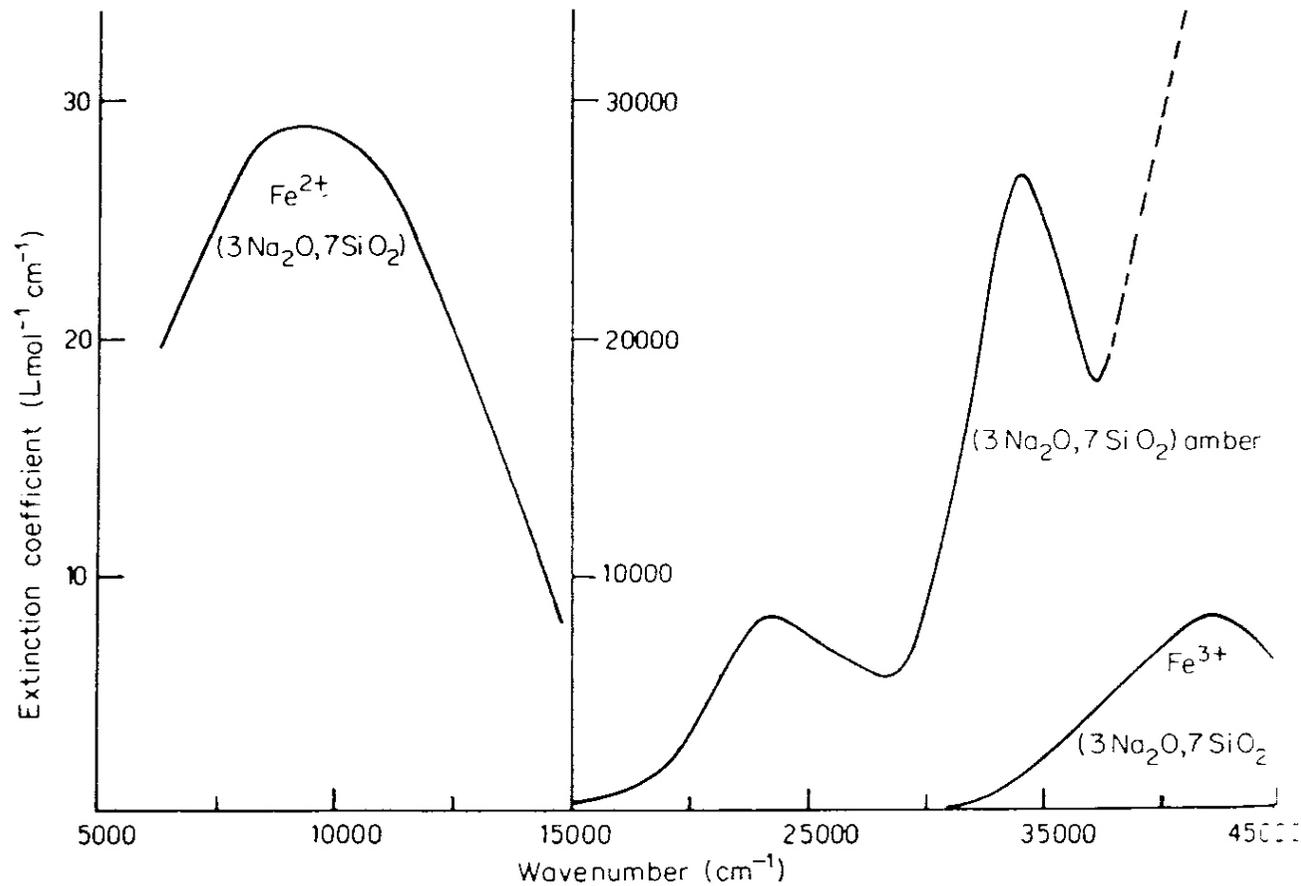
State	Configuration	Energy
${}^4T_1({}^4G)$	$(t_{2g})^4(e_g)^1$	$-100q + 10B + 6C - 26B^2/100q$
${}^4T_2({}^4G)$	$(t_{2g})^4(e_g)^1$	$-100q + 18B + 6C - 38B^2/100q$
${}^4E, {}^4A_1({}^4G)$	$(t_{2g})^3(e_g)^2$	$10B + 5C$
${}^4T_2({}^4D)$	$(t_{2g})^3(e_g)^2$	$13B + 5C + x$
${}^4E({}^4D)$	$(t_{2g})^3(e_g)^2$	$17B + 5C$
${}^4T_1({}^4P)$	$(t_{2g})^3(e_g)^2$	$19B + 7C - x$
${}^4A_2({}^4F)$	$(t_{2g})^3(e_g)^2$	$22B + 7C$

Ubirajara Pereira KO



# Vidros com Óxidos de Ferro

Vidro ambar de embalagem

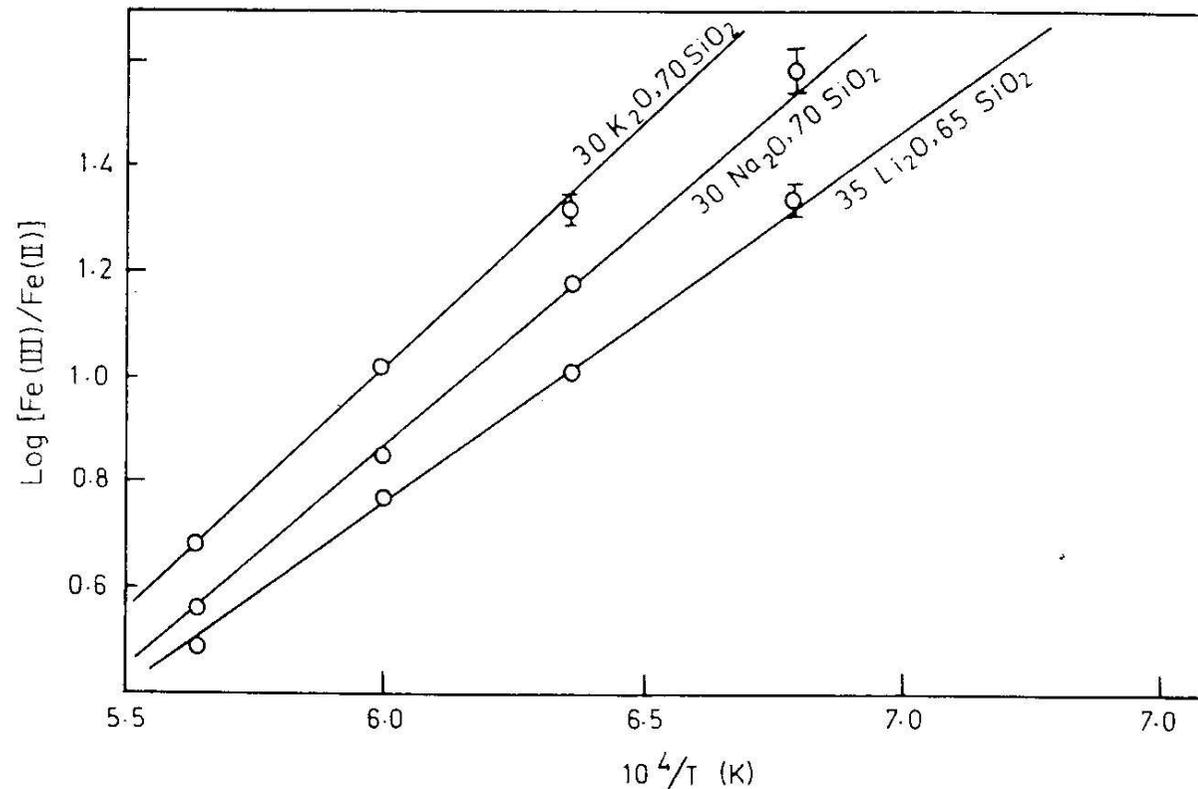


**Figure 19-8.** Absorption spectra of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and “carbon–sulfur amber.” (After Paul [7], Fig. 9.31, p. 330. Reproduced with permission of Chapman & Hall.)

# Razão entre Fe(II) e Fe(III)

472

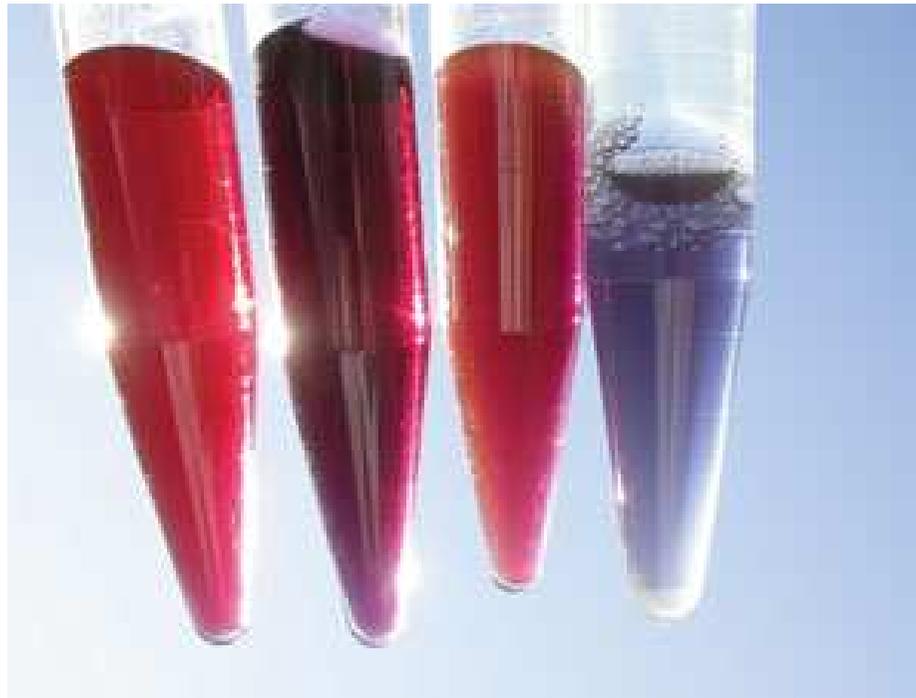
Fundamentals of Inorganic Glasses



**Figure 19-7.** Variation of  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$  equilibrium with temperature in some binary alkali silicate melts. (After Paul [7], Fig. 7.6, p. 233. Reproduced with permission of Chapman & Hall.)

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# Nanopartículas e Cor



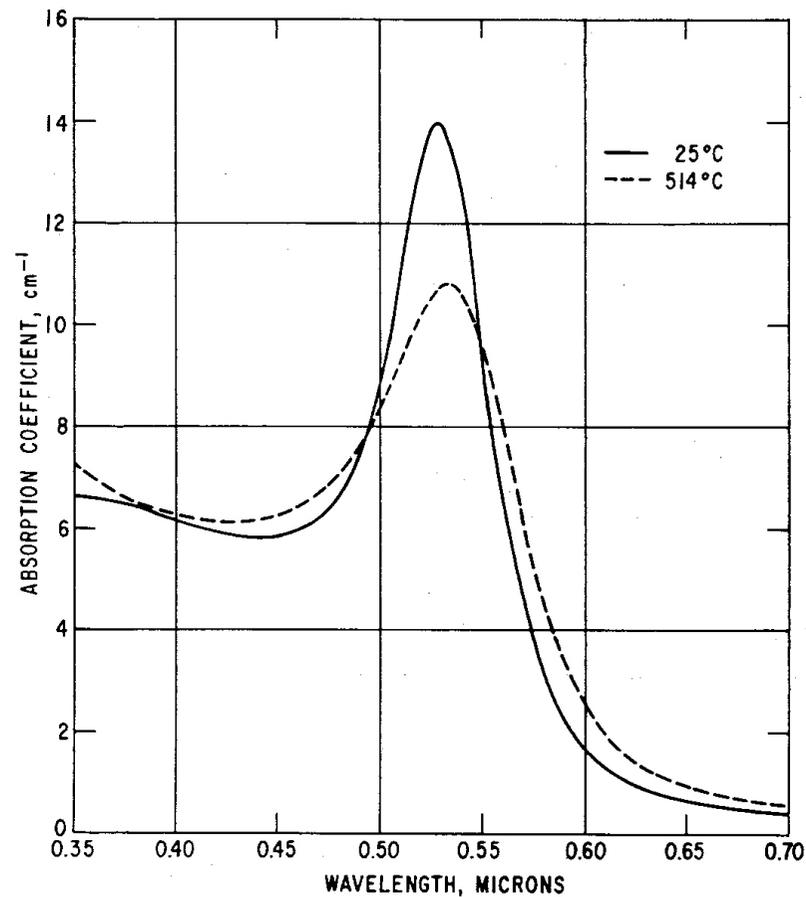
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# Ruby Gold

Quando vidros contendo pequenos teores de Au, 0,001-0,002%, junto com agentes redutores tais como SnO<sub>2</sub> ou ZnO são resfriados e reaquecidos acima da T<sub>g</sub> leva ao aparecimento de uma cor rubi intensa devido a presença de nanopartículas de c.a. 200Å.

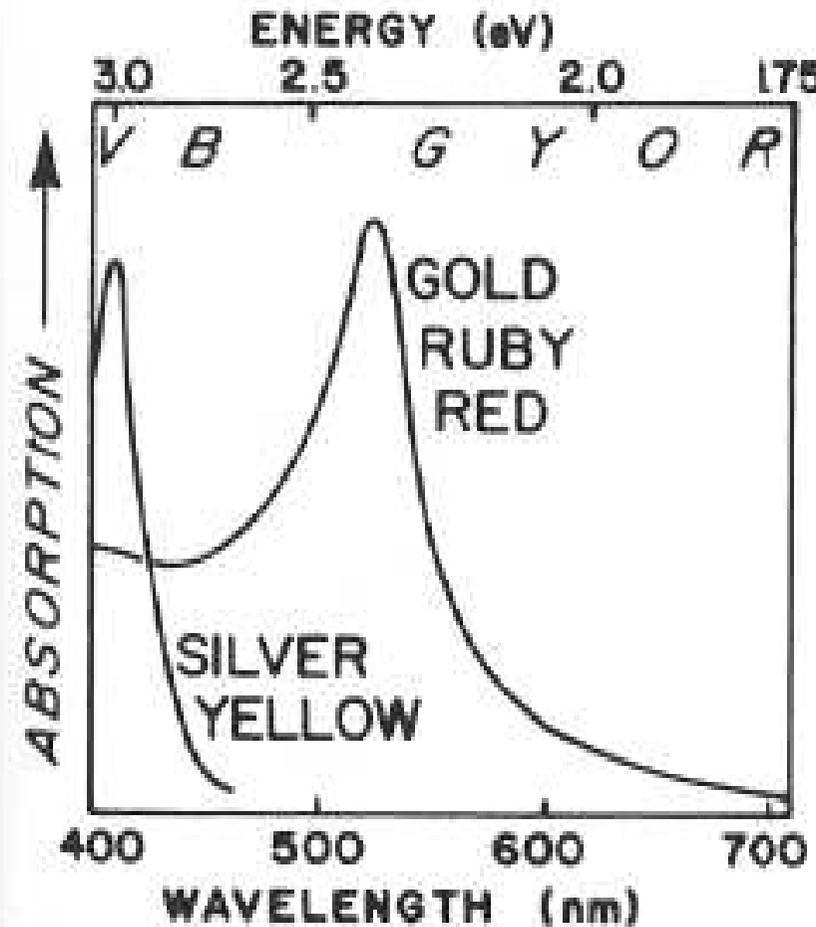


# Ressonância de Plasma e Cor Partículas Metálicas



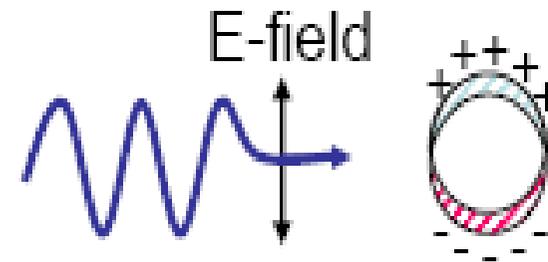
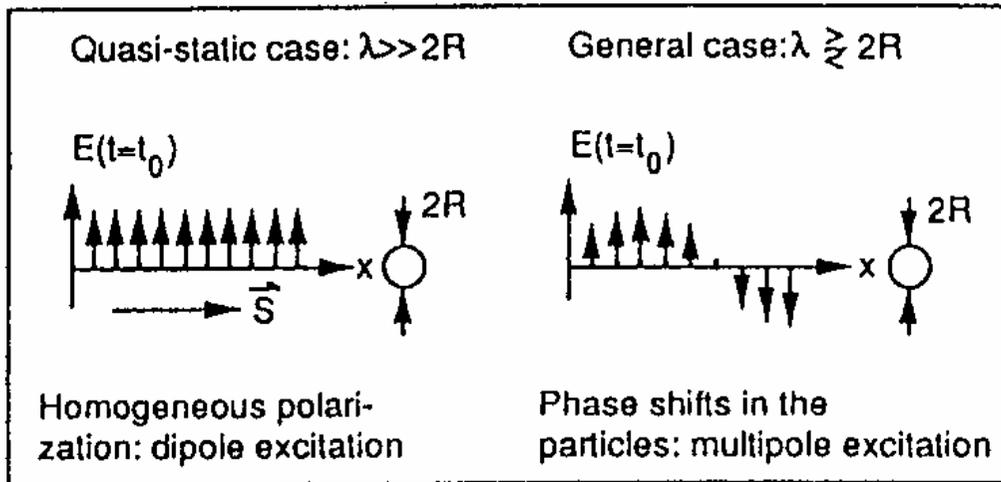
**Figure 19-9.** Absorption spectrum of gold particles about 200 Å diameter in glass. (After Doremus [3]. Reproduced with permission of American Institute of Physics.)

# Cor e Ressonância de Plasmon



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# Ressonância de Plasmon



Raio do Cluster $R$	$R < 10 \text{ nm}$	$R > 10 \text{ nm}$
Electrodinâmica da teoria de Mie função Dielétrica sofre dependência do tamanho	Independente de $R$  $\epsilon = \epsilon(R)$ intrinseco	$f(R)$  independente de $R$ extrinseco

# Ressonância de Plasmon

## Teoria de Espalhamento de Mie

$$a = \frac{18\pi N V n_0^3 \varepsilon''}{\left[ \lambda \left\{ (\varepsilon' + 2n_0^2) + \varepsilon''^2 \right\} \right]}$$

$a$  = coeficiente de extinção

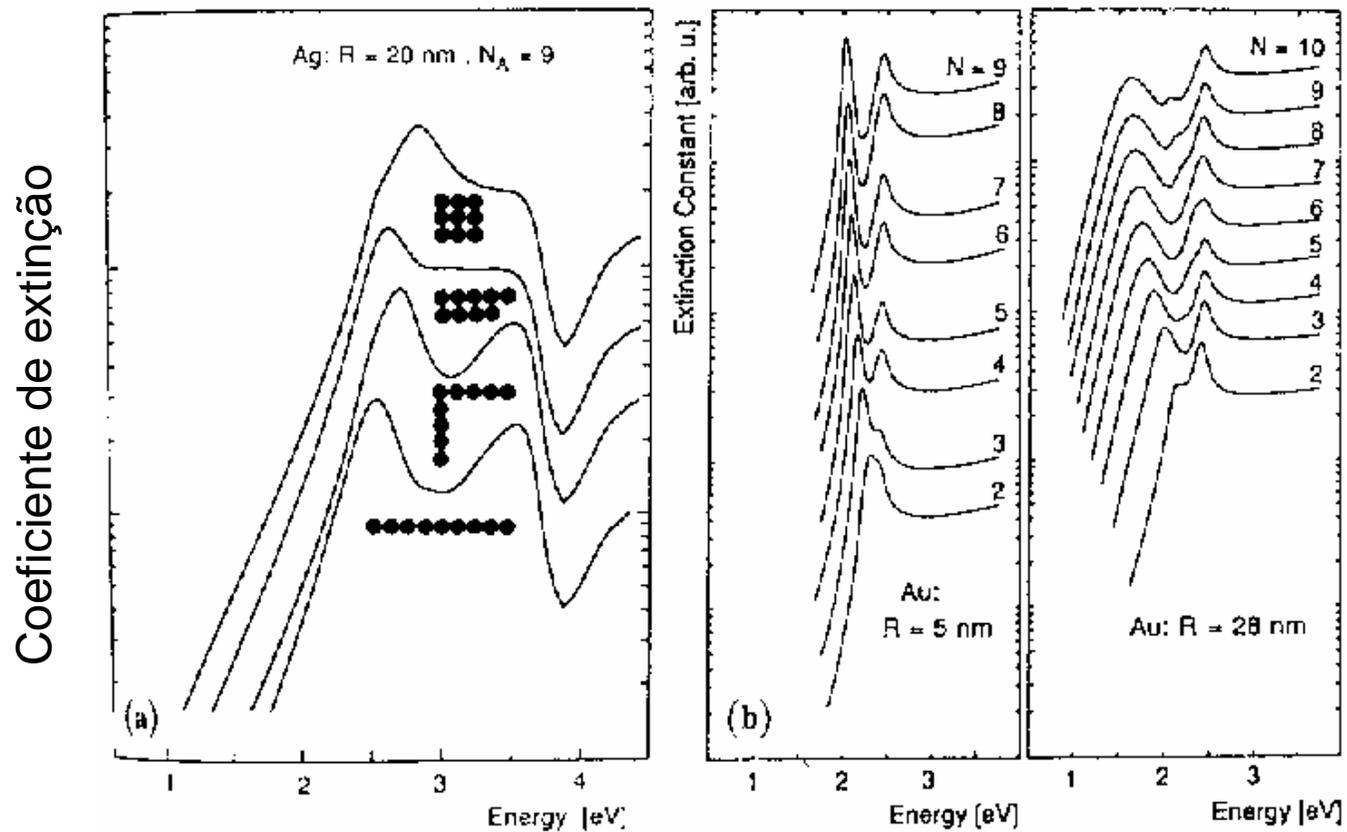
$n_0$  = índice de refração do vidro

$\lambda$  = comprimento da radiação incidente

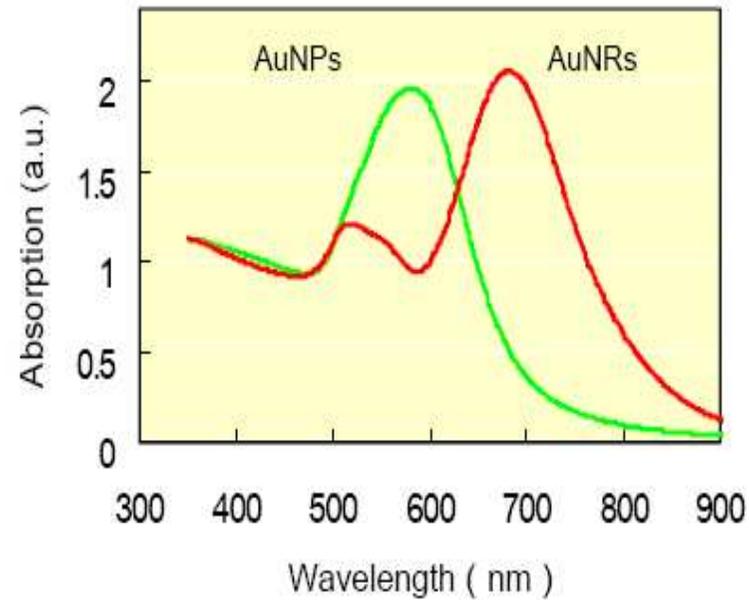
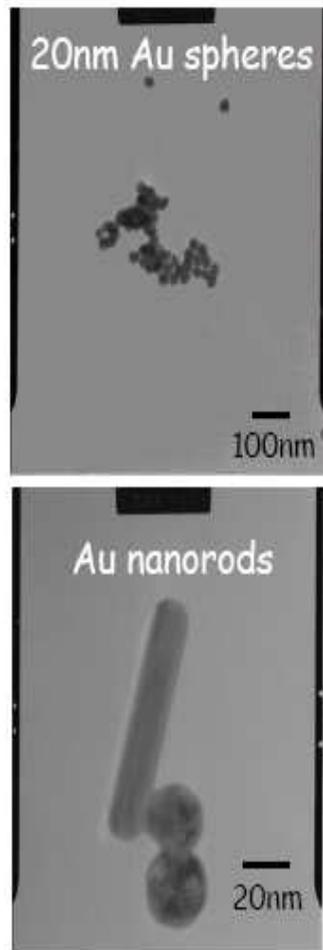
$N$  = numero de esferas de volume  $V$  e cte dielétrica  $\varepsilon^* = \varepsilon' - j\varepsilon''$

$$j = \sqrt{-1}$$

# Dependência da Formação de Aglomerados e sua Simetria

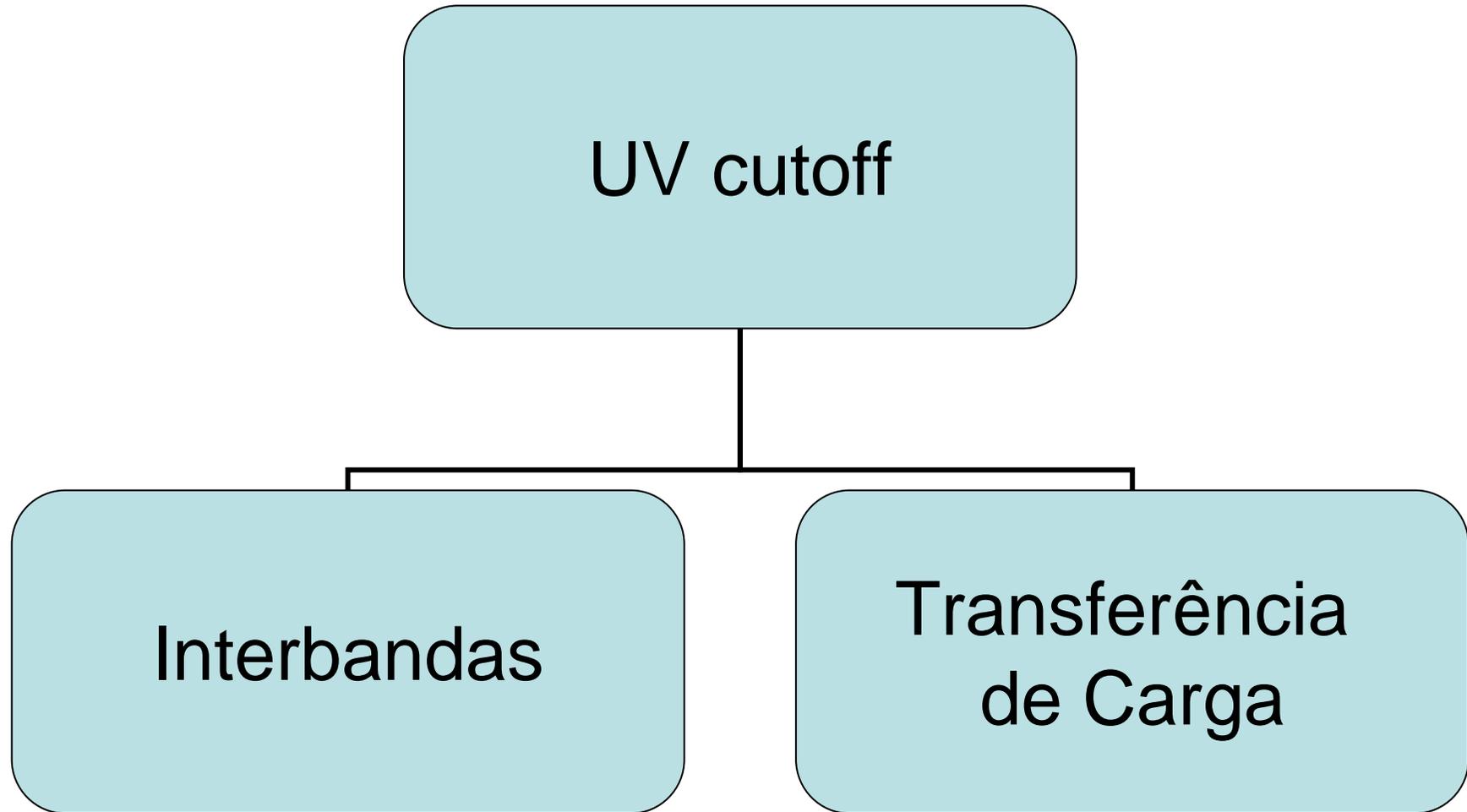


# Influência da Forma Ressonância de Plasmon



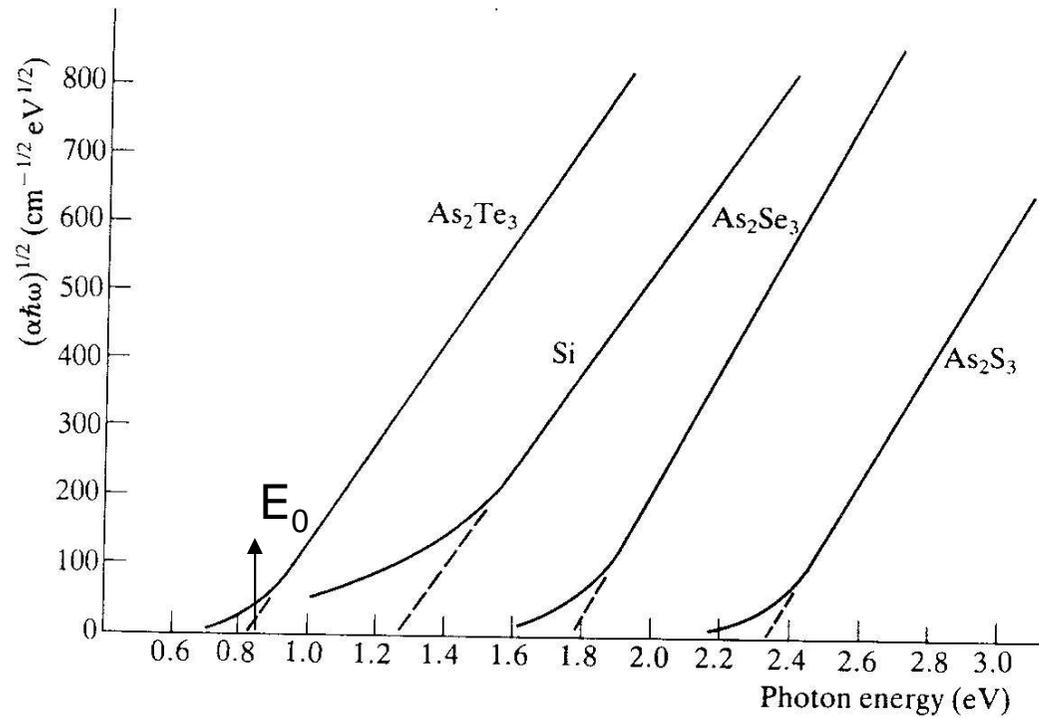
# Filtros de UV

## Transição Interbandas

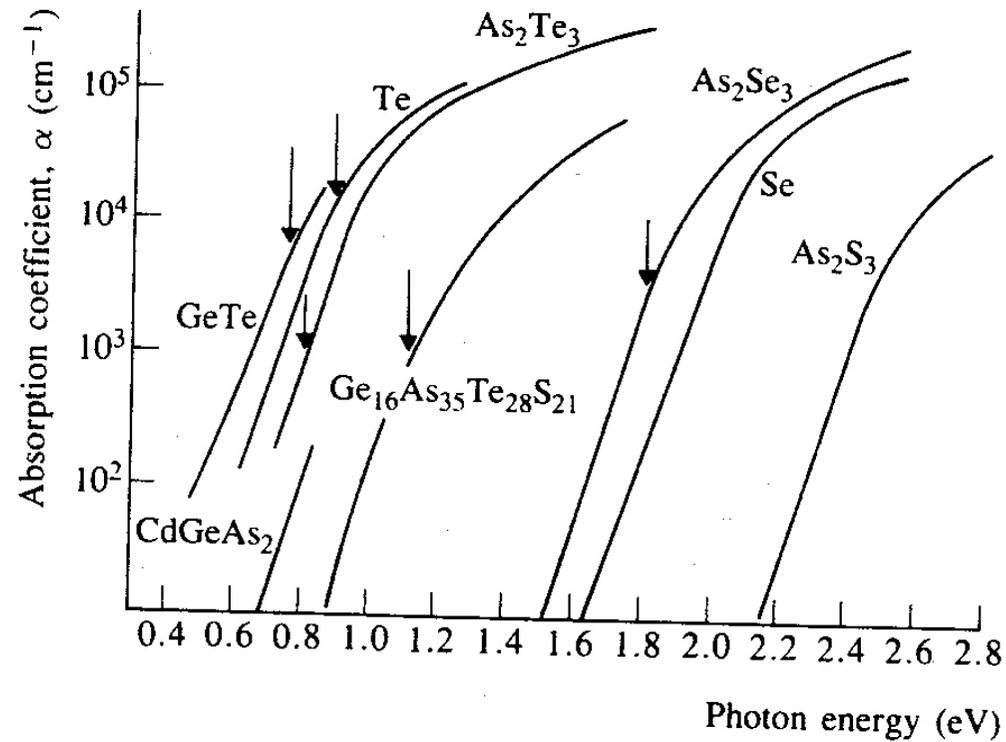


# Transição Interbandas Band Gap

$$\lambda_c = \frac{hc}{E_g}$$



**Figure 19-10.** Optical absorption edges of some materials. Extrapolation of the linear regime yields the “optical gap.” (After N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials*, 2nd Ed. Oxford University Press, 1979. Reproduced with permission of Oxford University Press.)



**Figure 19-11.** Optical absorption edges for several chalcogenide glasses at room temperature, showing Urbach behavior. (After N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials*, 2nd Ed., Oxford University Press, 1979. Reproduced with permission of Oxford University Press.)

# Transferência de Carga

- Bandas muito intensas por serem totalmente permitidas.

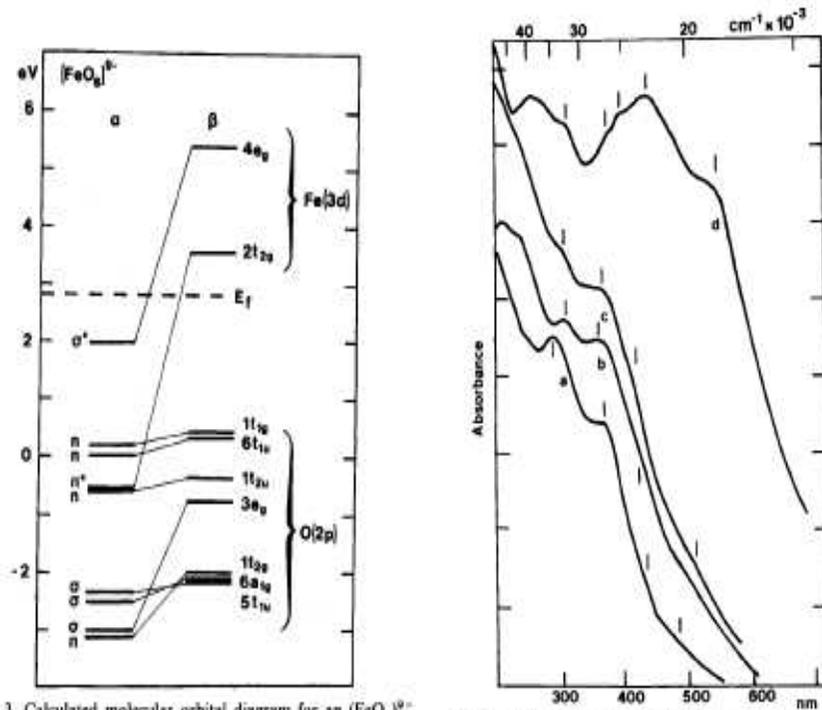


Fig. 3. Calculated molecular orbital diagram for an  $(\text{FeO}_4)^{9-}$  cluster with an Fe-O bond length of 2.05 Å (from Sherman, 1985). The  $\alpha$  and  $\beta$  symbols refer to levels with spin-up ( $\alpha$ -spin) or spin-down ( $\beta$ -spin).  $E_f$  is the Fermi energy, below which all orbitals are occupied in the ground state.

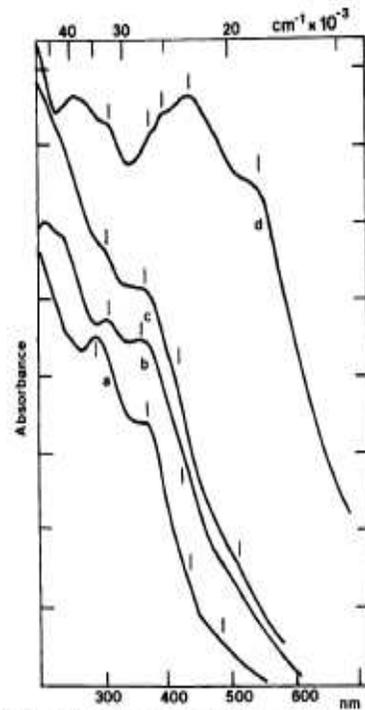


Fig. 5. Visible and near-ultraviolet absorption spectra of (a) goethite (b) lepidocrocite (c) maghemite and (d) hematite. Absorption bands near 430, 360–380, and 290–310 nm correspond to the  ${}^6A_1 \rightarrow {}^4E$ ,  ${}^6A_1 \rightarrow {}^4G$ ,  ${}^6A_1 \rightarrow {}^4E({}^4D)$ , and  ${}^6A_1 \rightarrow {}^4T_1({}^4P)$  ligand field transitions of  $\text{Fe}^{3+}$ . A feature near 485–550 nm is assigned to the  ${}^6A_1 + {}^6A_1 \rightarrow {}^4T_1({}^4G) + {}^4T_1({}^4G)$  excitation of an Fe-Fe pair. Higher energy features, at wavelengths below 270 nm, are assigned to ligand-to-metal charge-transfer transitions.

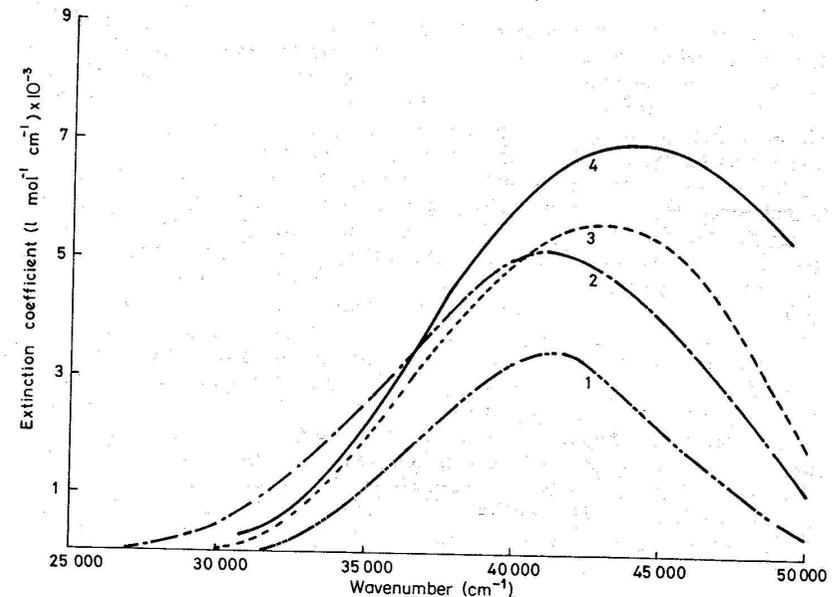
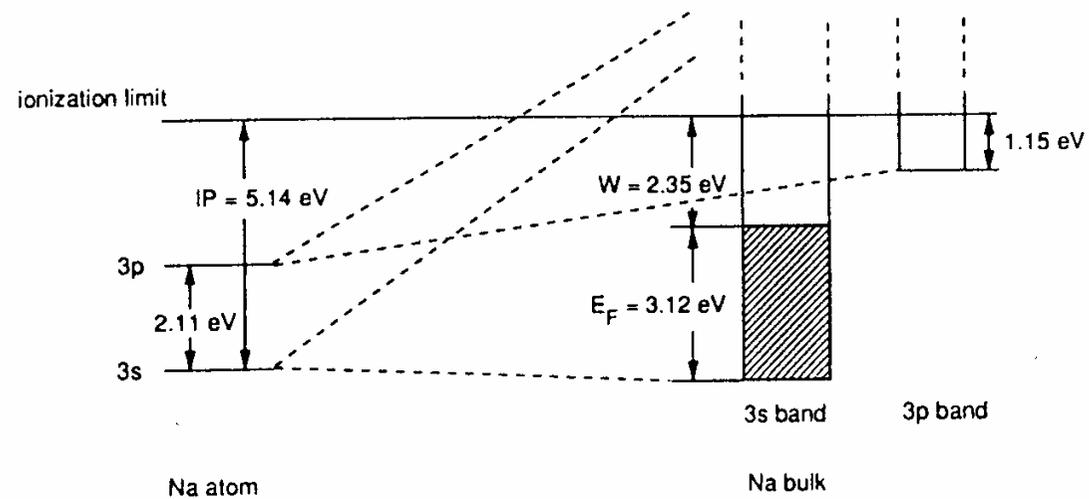
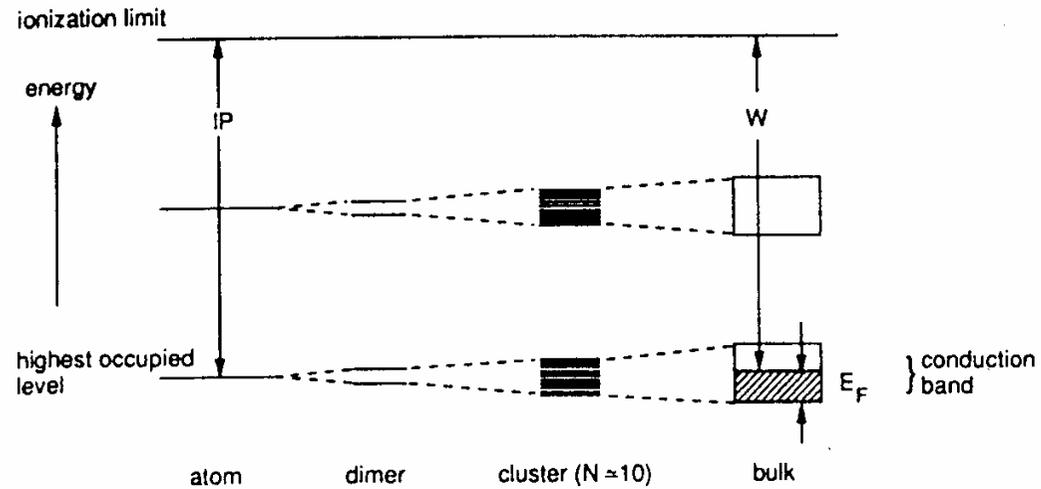


Fig. 7.23 Ultraviolet absorption of iron(III) in:  
 (1) 4.6 molar perchloric acid  
 (2)  $\text{MgO-P}_2\text{O}_5$  glass  
 (3)  $\text{CaO-P}_2\text{O}_5$  glass  
 (4)  $\text{Na}_2\text{O-SiO}_2$  glass

# Estrutura de Bandas



# Cor e Emissão

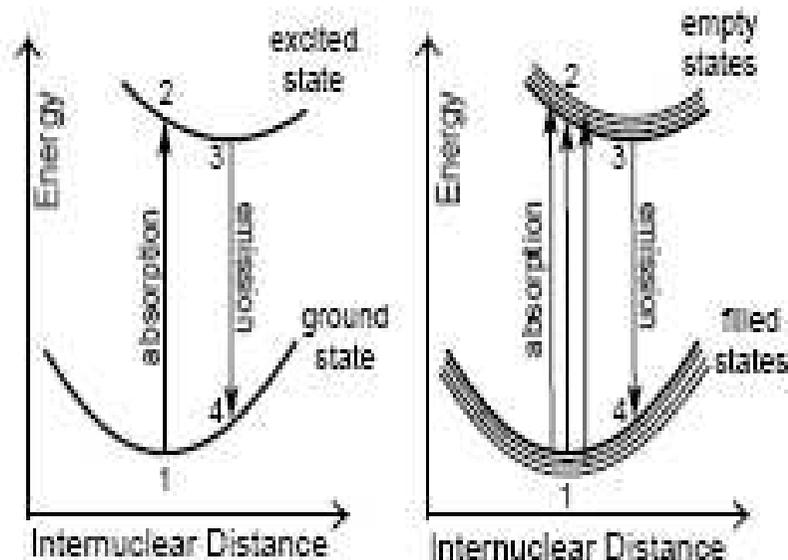


Figure 6. Relationship between absorption and emission energies for discrete molecules (left) and for semiconductor nanoparticles (right). When a photon is absorbed thereby exciting an electron from the ground state (1) to an excited state (2) the bond order decreases and the atoms relax to a longer internuclear distance (3) before emission of a photon (4) and relaxation to the ground state (1). In semiconductor nanoparticles the process is the same (steps 1–4) but there are more possibilities for the energy of the excitation photon to match an electronic energy transition.

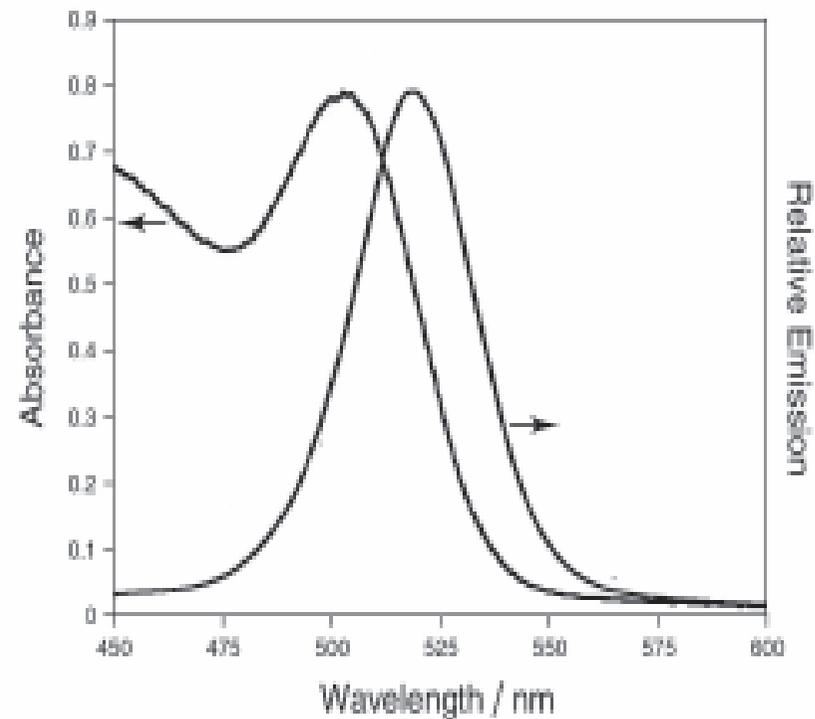


Figure 4. For a given size quantum dot the absorption maximum (peak at left) occurs at higher energy than the emission maximum

# Cor e Emissão

## Nanopartículas de CdSe

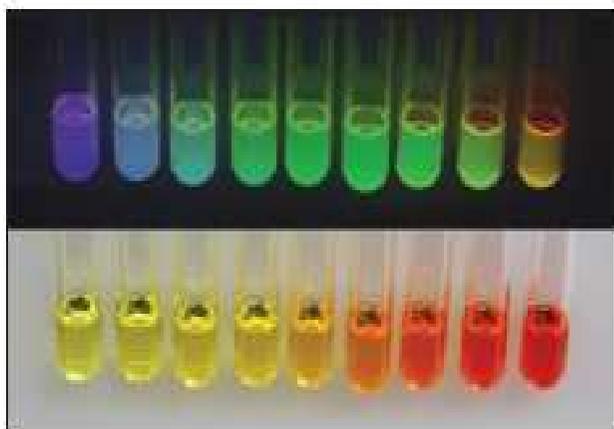


Figure 1. Colloidal suspensions of CdSe quantum dots of increasing size from left (approximately 1.8-nm diameter) to right (approximately 4.0-nm diameter). Bottom: Samples viewed in ambient light vary in color from green-yellow to orange-red. Top: The same samples viewed under long-wave ultraviolet illumination vary in color from blue to yellow.

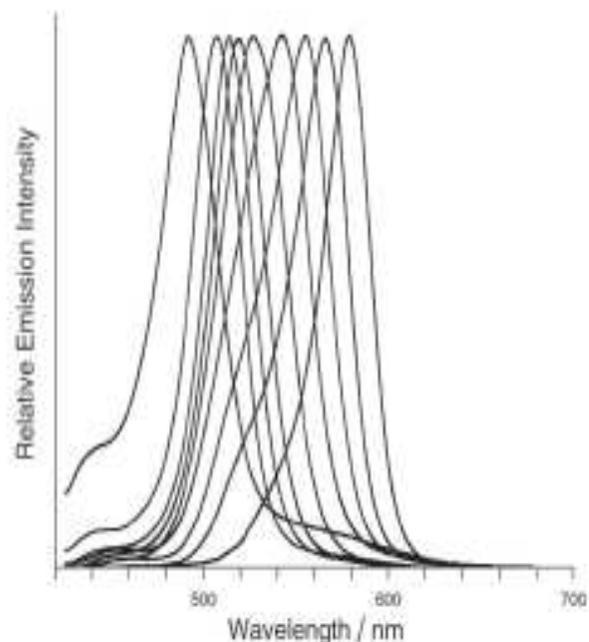


Figure 2. Normalized emission spectra of the samples in Figure 1 using 400-nm excitation. The samples were withdrawn from the reaction mixture in order from left to right at an initial time of 8 seconds after selenium addition to a final time of about two minutes after addition. Longer wavelength, smaller energy emission corresponds with larger particle sizes.

# Emissão em Partículas Metálicas

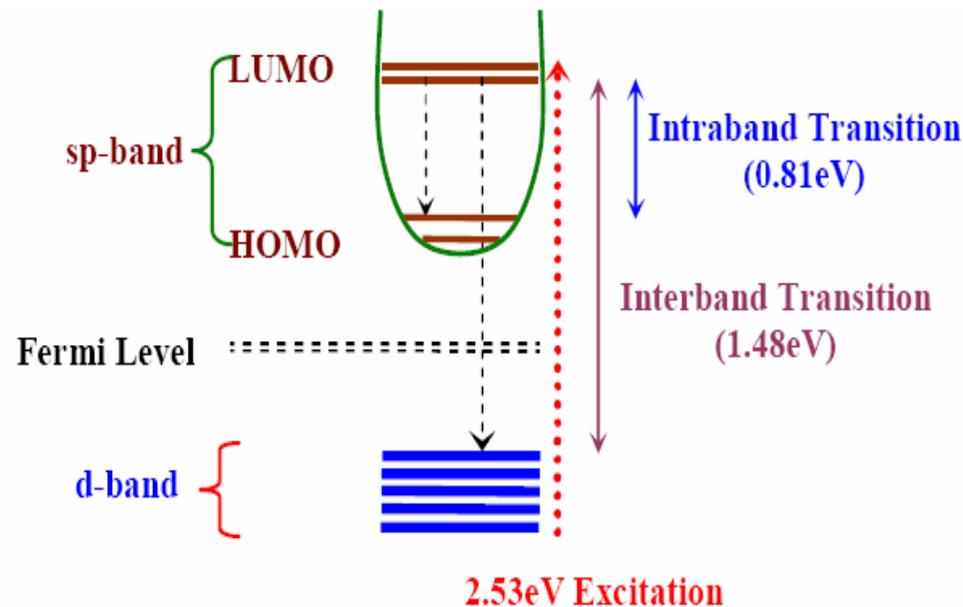
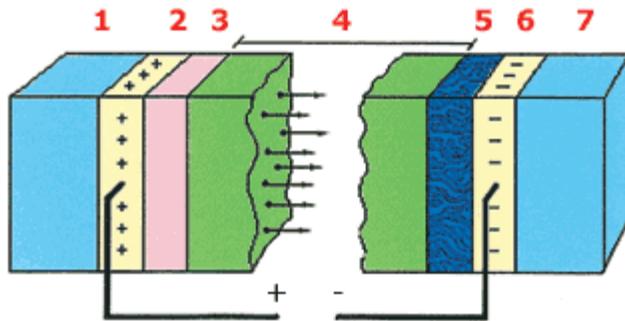


Fig. 4. Solid-state model for the origin of the two PL bands: The high energy band is proposed to be due to radiative interband recombination between the sp and d-bands while the low energy band is thought to originate from radiative intraband transitions within the sp-band cross the HOMO-LUMO gap. Note that intraband recombination has to involve prior nonradiative recombination of the hole in the d-band created after excitation with an (unexcited) electron in the sp-band.

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# Vidros Eletrocrômicos



Material	Cor
$\text{WO}_3$	azul
$\text{Nb}_2\text{O}_5$	azul
$\text{V}_2\text{O}_5$	Verde, amarelo, vermelho
$\text{TiO}_2$	cinza
$\text{TiO}_2\text{-Al}_2\text{O}_3$	azul
$\text{TiO}_2\text{-Cr}_2\text{O}_3$	azul

**Figura 1 - Esquema de janela eletrocrômica**

1. e 7. Vidro 2. e 6. Condutor transparente 3. Reservatório de íons 4. Eletrólito 5. Filme eletrocrômico



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