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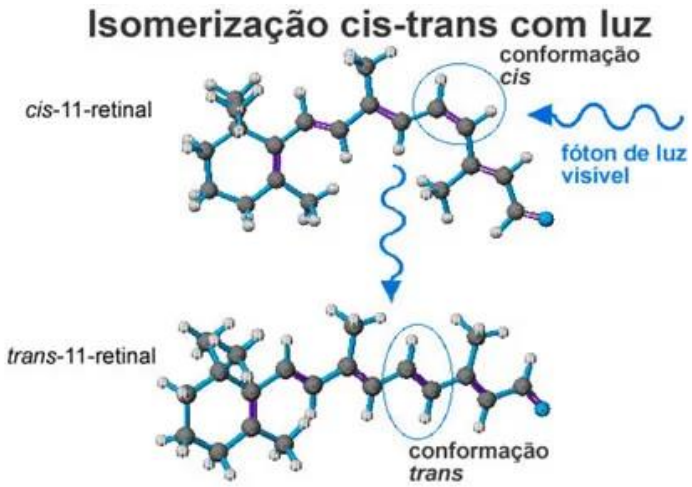
Fotoquímica de compostos de coordenação

Fotoquímica

- Fotoquímica – Reações químicas induzidas pela luz



- Vantagens
  - Energia quantizada e entregue em pacotes de energia ($E = h\nu$)

$$[Cr(NH_3)_5Br]^{2+} \begin{cases} \xrightarrow{kT} [Cr(NH_3)_5(H_2O)]^{3+} + Br^- \\ \xrightarrow{h\nu} [Cr(NH_3)_4(H_2O)Br]^{2+} + NH_3 \end{cases}$$

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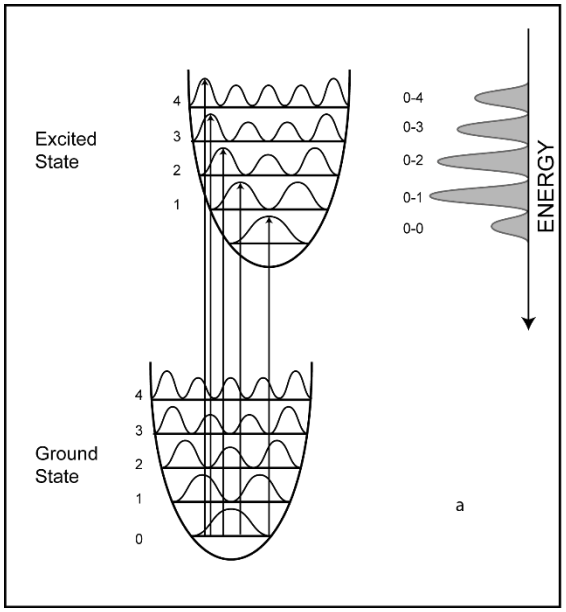
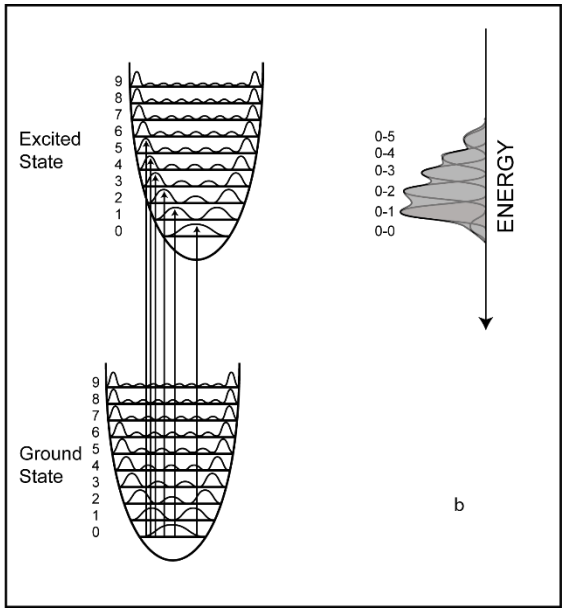
Absorção de luz





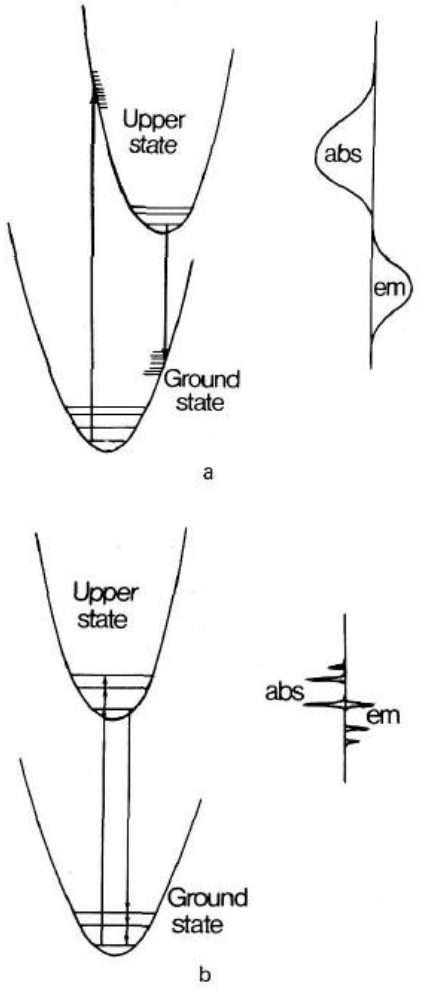
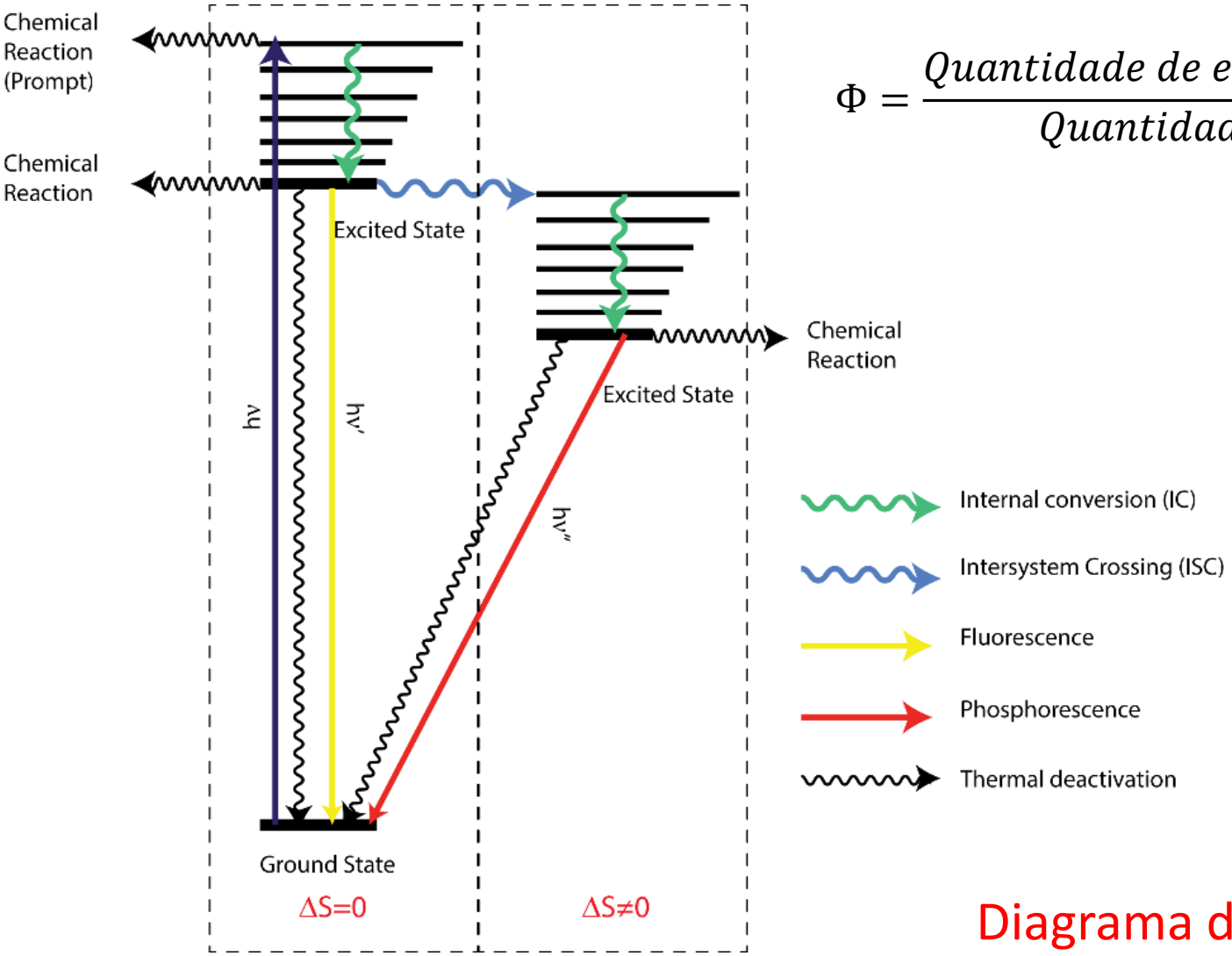


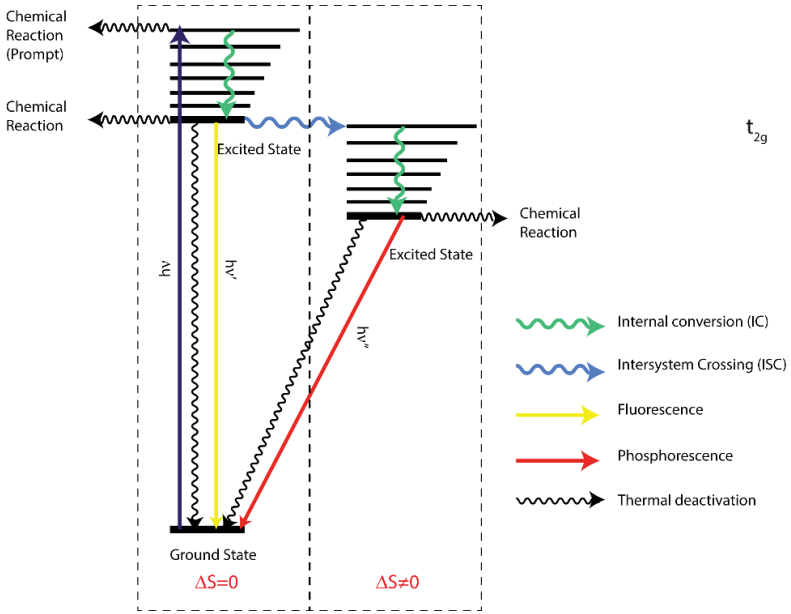
Figure 1. Franck-Condon effect for absorption and emission (a) for excited state and ground state having different internuclear distances and/or bond angles, and (b) for excited state and ground state of the same geometry and size.

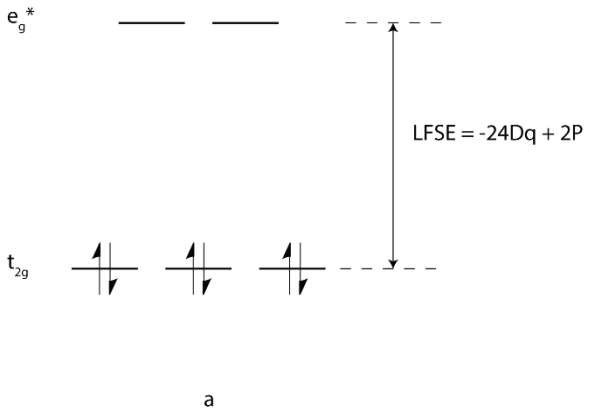
Desativando o estado excitado

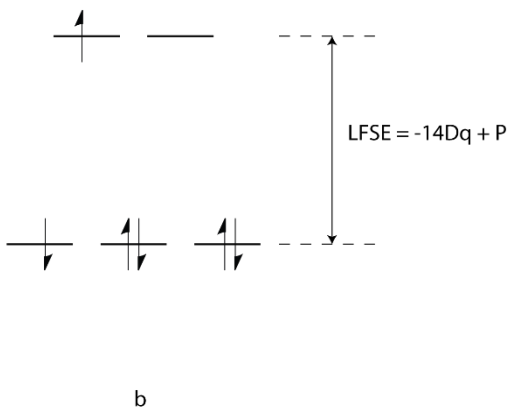


$$\Phi = \frac{Quantidade\ de\ espécies\ formadas}{Quantidade\ de\ fótons}$$

Diagrama de Jablonski


Chemical Reaction (Prompt)
Chemical Reaction
Excited State
hν
hν'
Excited State
hν''
Chemical Reaction
Ground State
ΔS=0
ΔS≠0
Internal conversion (IC)
Intersystem Crossing (ISC)
Fluorescence
Phosphorescence
Thermal deactivation


e_g*
t_{2g}
LFSE = -24Dq + 2P
a


LFSE = -14Dq + P
b

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Actinômetros químicos

A chemical actinometer or dosimeter is a chemical system (fluid, gas, solid, or in a microheterogeneous environment) that undergoes a light-induced reaction (at a certain wavelength, λ) for which the quantum yield, Φ(λ), is accurately known. Measuring the reaction rate allows the calculation of the absorbed photon flux. (CHEMICAL ACTINOMETRY - IUPAC Technical Report) Pure Appl. Chem., Vol. 76, No. 12, pp. 2105–2146, 2004.

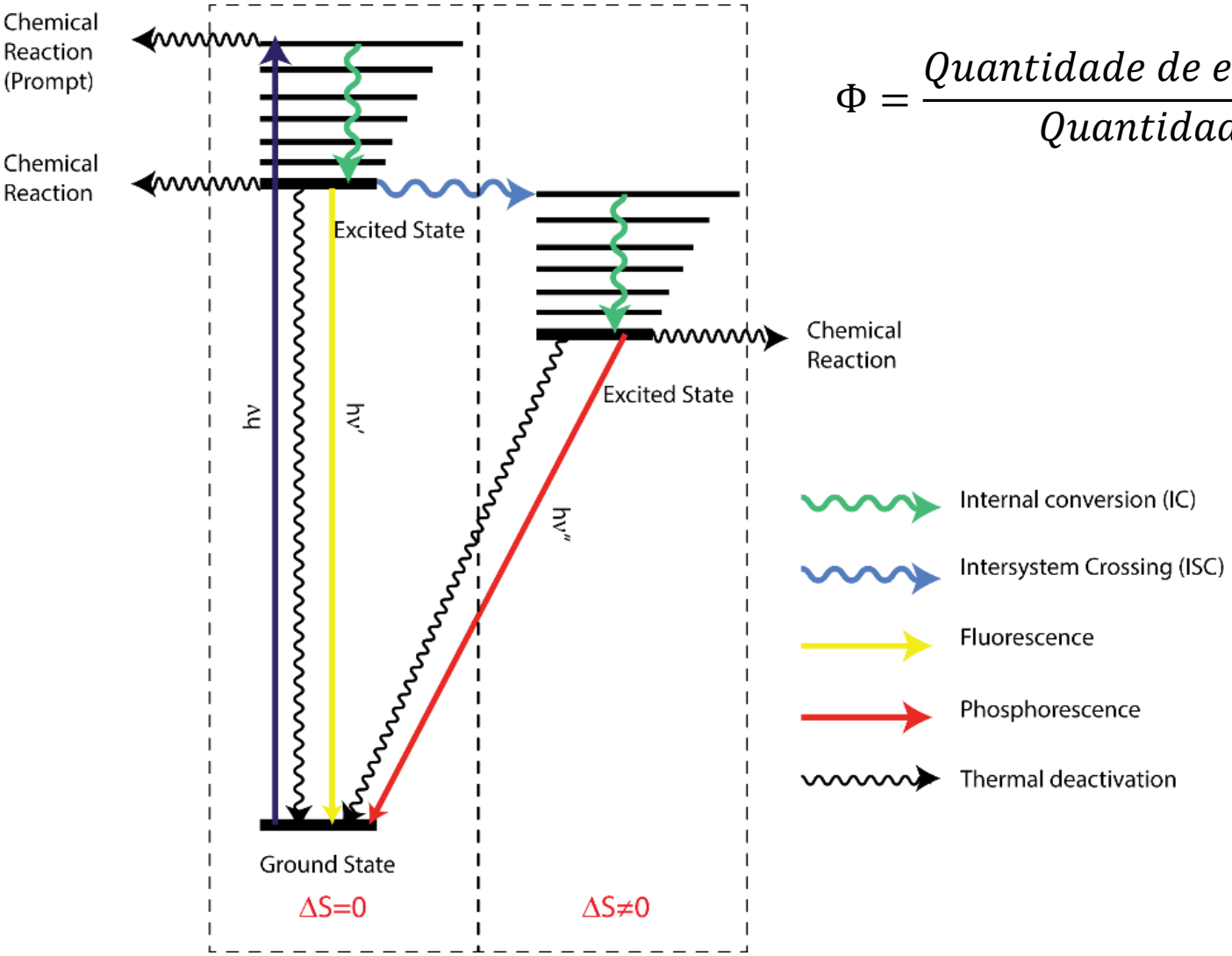
- Características fundamentais dos AQs
- The photochemical system should **be simple and well studied**. The photoreaction must be reproducible under well-defined and easily controllable experimental conditions.
- Quantum yields **should be accurately known for a large number of wavelengths**. A wide usable spectral range and wavelength-independent quantum yields are desired.
- The chemical components should be thermally stable to exclude complications due to dark reactions.
- The **analytical methods should be simple**. Direct spectrophotometric analysis is preferred.
- The system should display **large sensitivity**.
- The **handling of the photochemical system** and the evaluation of the number of photons absorbed **should be simple and straightforward**.
- The **actinometric material should be easy to synthesize and purify**. Preferably, it should be commercially available. Disposal of the waste should be straightforward.
- Each system suffers also from disadvantages, and a careful selection among the CAs is appropriate, depending on the intended experiment

Um exemplo de actinômetro químico

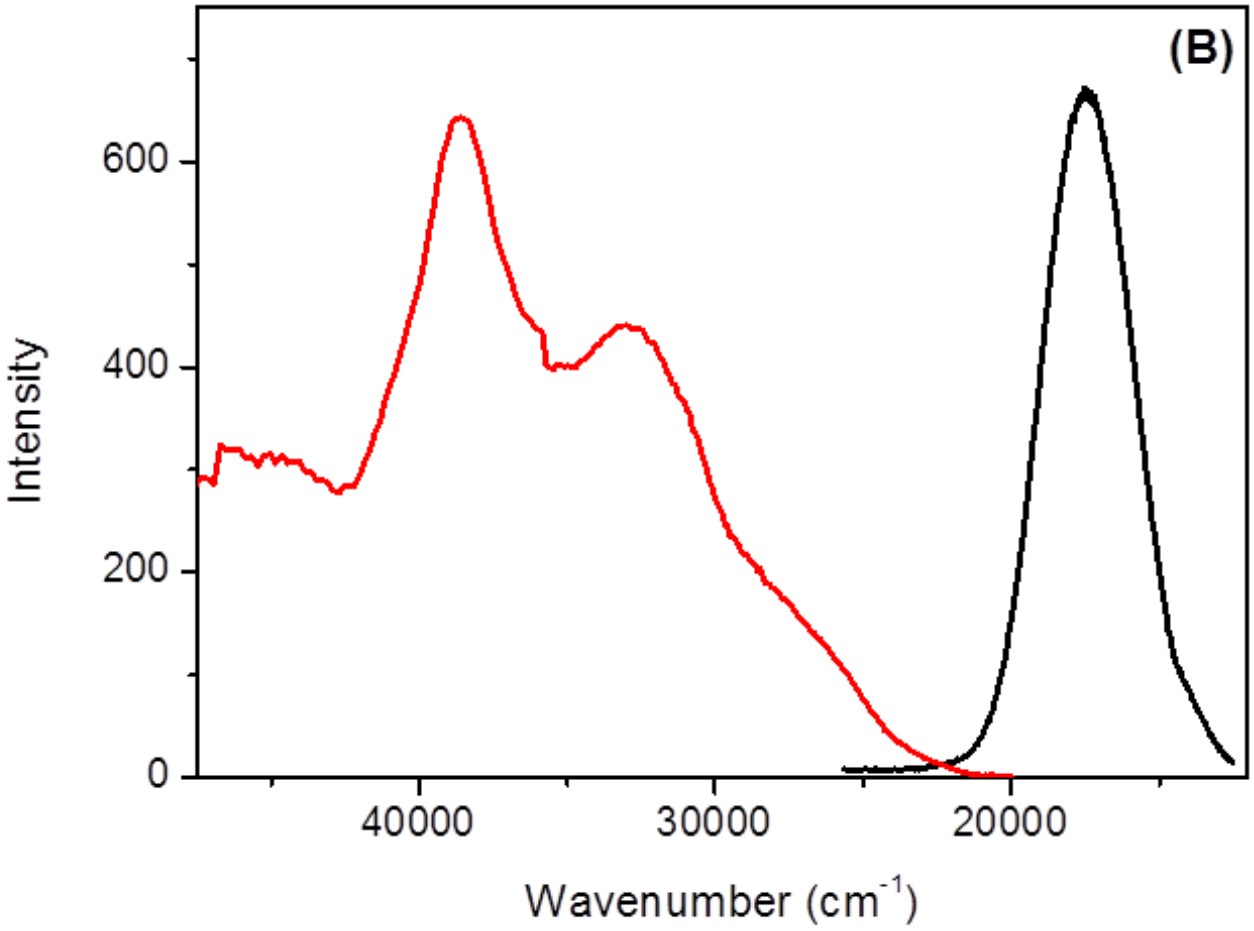
- Potassium ferrioxalate, $K_3[Fe(C_2O_4)_3].3H_2O$ [potassium tris(oxalato)ferrate(III) trihydrate] photoreduction (Hatchard–Parker actinometer).
- The most widely accepted standard actinometer, commonly called ferrioxalate actinometer.
- WR: 250–500 nm; Φ = 1.25–0.9
- AM: absorbance at 510 nm of Fe(II)-1,10-phenanthroline complex [tris(1,10-phenanthroline)iron(II)] in buffered acidic solution

$$\Phi = \frac{Quantidade\ de\ espécies\ formadas}{Quantidade\ de\ fótons}$$

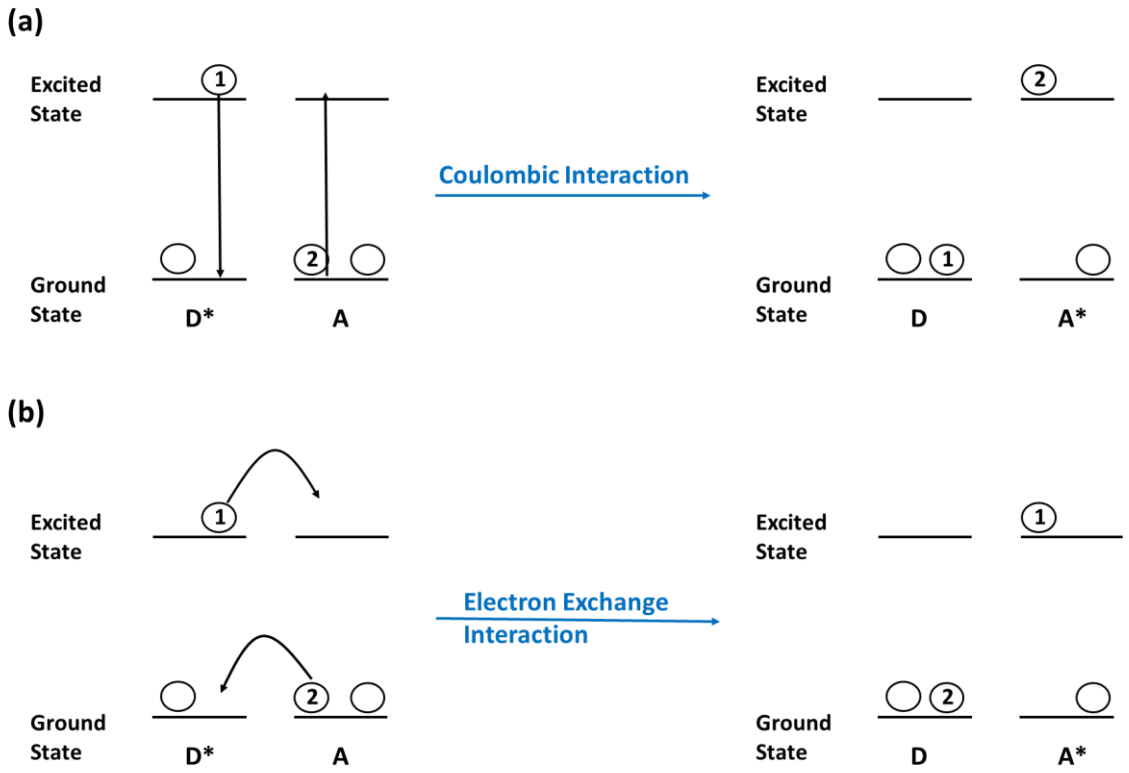
Desativando o estado excitado



$$\Phi = \frac{Quantidade\ de\ espécies\ formadas}{Quantidade\ de\ fótons}$$

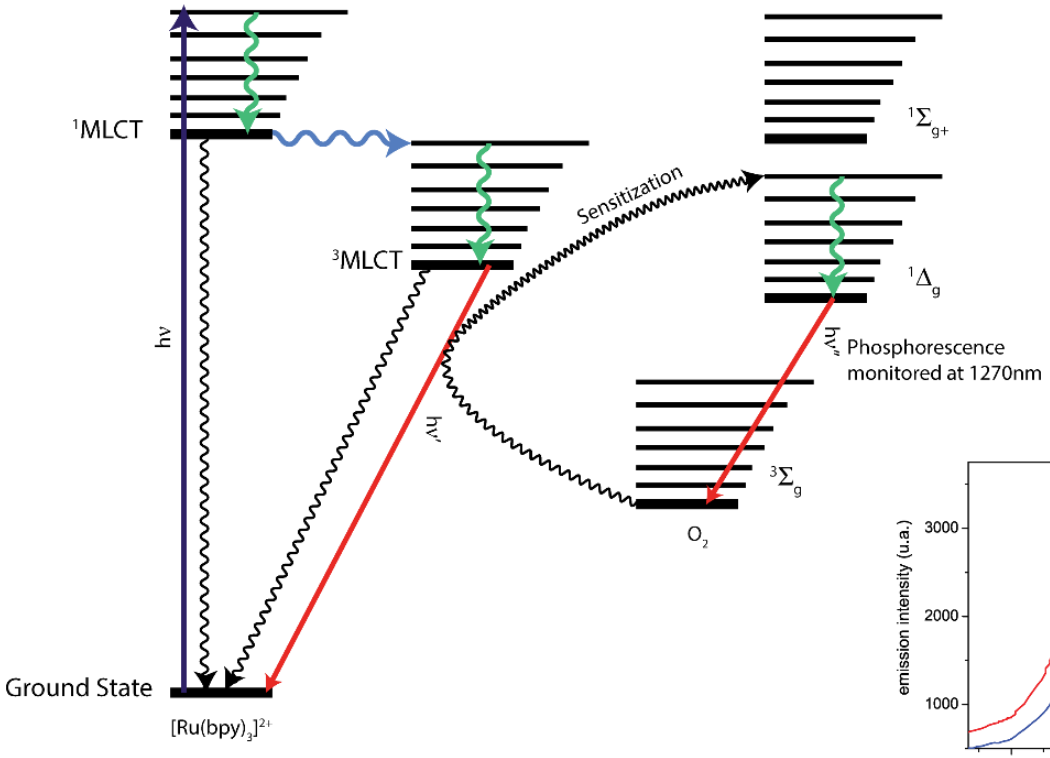


Excitation (red line) and emission (black line) spectra of fac-[Re(CO)$_3$Cl(bpy)] (B) in CH$_3$CN.

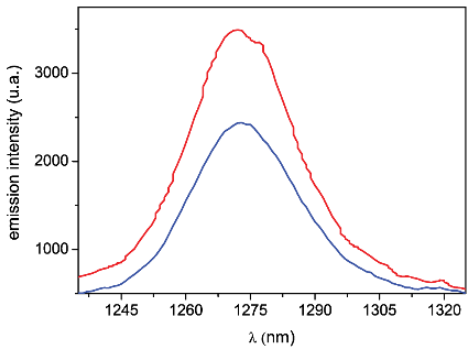


Simplified diagram representation of energy transfer by Coulombic (a) and Electron exchange interaction (b).

(A)


^{1}MLCT
^{3}MLCT
hν
hν'
Sensitization
$^1\Sigma_{g+}$
$^1\Delta_g$
hν''
Phosphorescence
monitored at 1270nm
$^3\Sigma_g$
O_2
Ground State
$[Ru(bpy)_3]^{2+}$

(B)


emission intensity (u.a.)
3000
2000
1000
1245
1260
1275
1290
1305
1320
λ (nm)