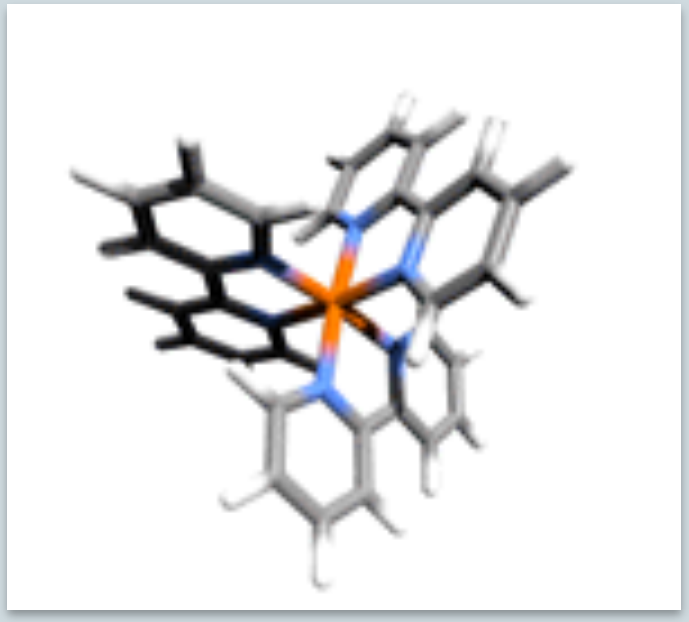
2 - Propriétés électroniques

transferts de charge



$[Ru(bpy)_3]^{2+}$

I – Transitions électroniques

I

Diamant jaune

4 – Semiconduction
bandgap

Améthyste

3 – Electrons piégés dans
les solides
centres colorés

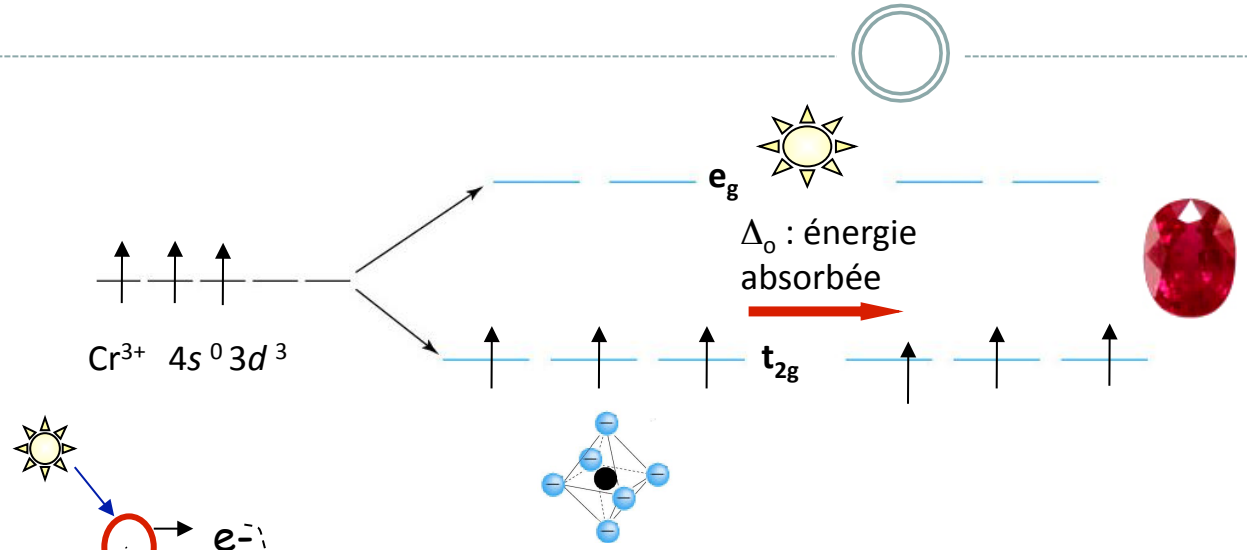
Rubis

1 - CFT/CLT
transitions *d-d*

Lapis-Lazuli

2 - Propriétés électroniques
moléculaires
transfert de charge

1. Transition *d-d vs* transfert de charge



Transition *d-d*
transition électronique entre OA d'un même atome

Transfert de charge *:*
transition électronique entre OA ou OM d'atomes différents

ligand – métal
$KMnO_4$
O → Mn

métal – ligand
$[Ru(bpy)_3]^{2+}$
Ru → bpy

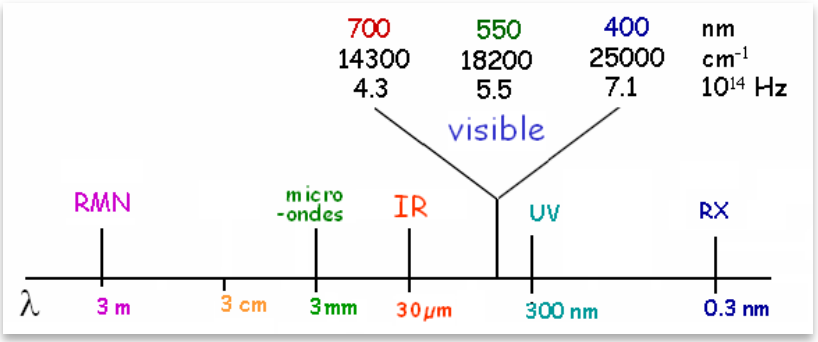
métal – métal
saphir
$Fe^{2+} \rightarrow Ti^{4+}$

ligand – ligand
Lapis-Lazuli
O → S

Energies des transitions

Mécanique quantique : quantification de l'énergie
⇨ niveaux discrets d'énergie, solutions de l'équation de mouvement de la molécule (Schrödinger)

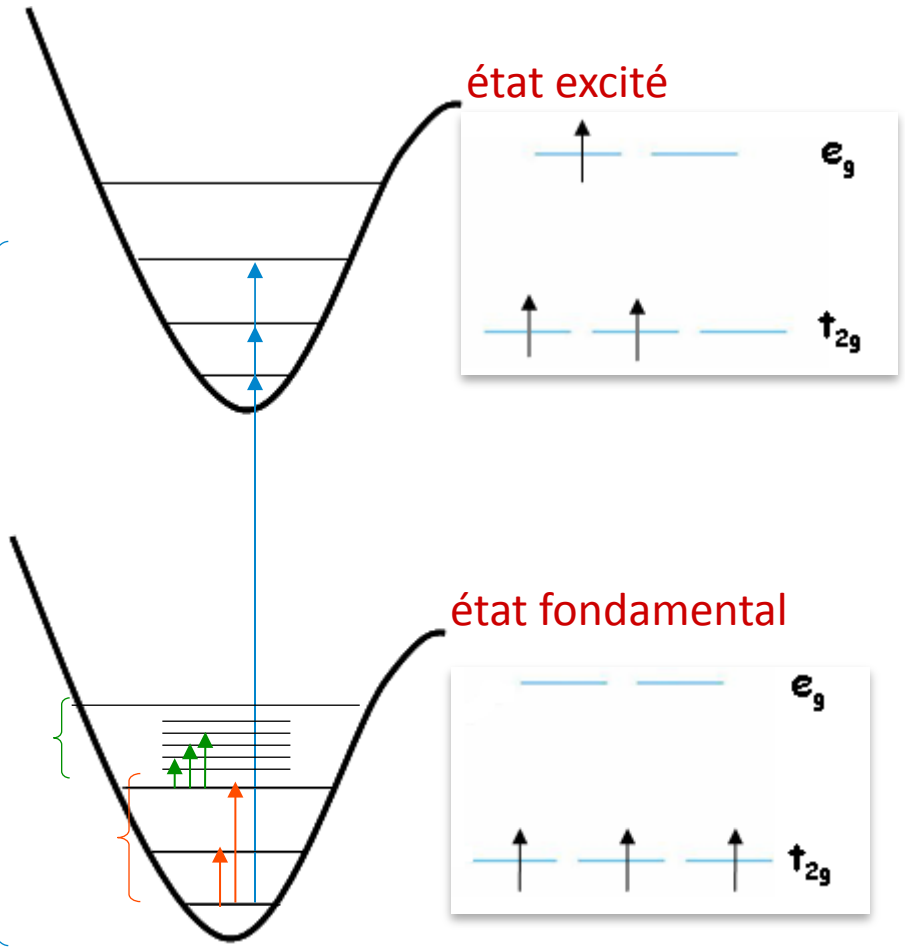
I-1



transitions électroniques
haute énergie
(100 - 10^4 kJ mol^{-1})
(8300 – 83.10^4 cm^{-1})
(1200 - 12 nm)
visible et UV

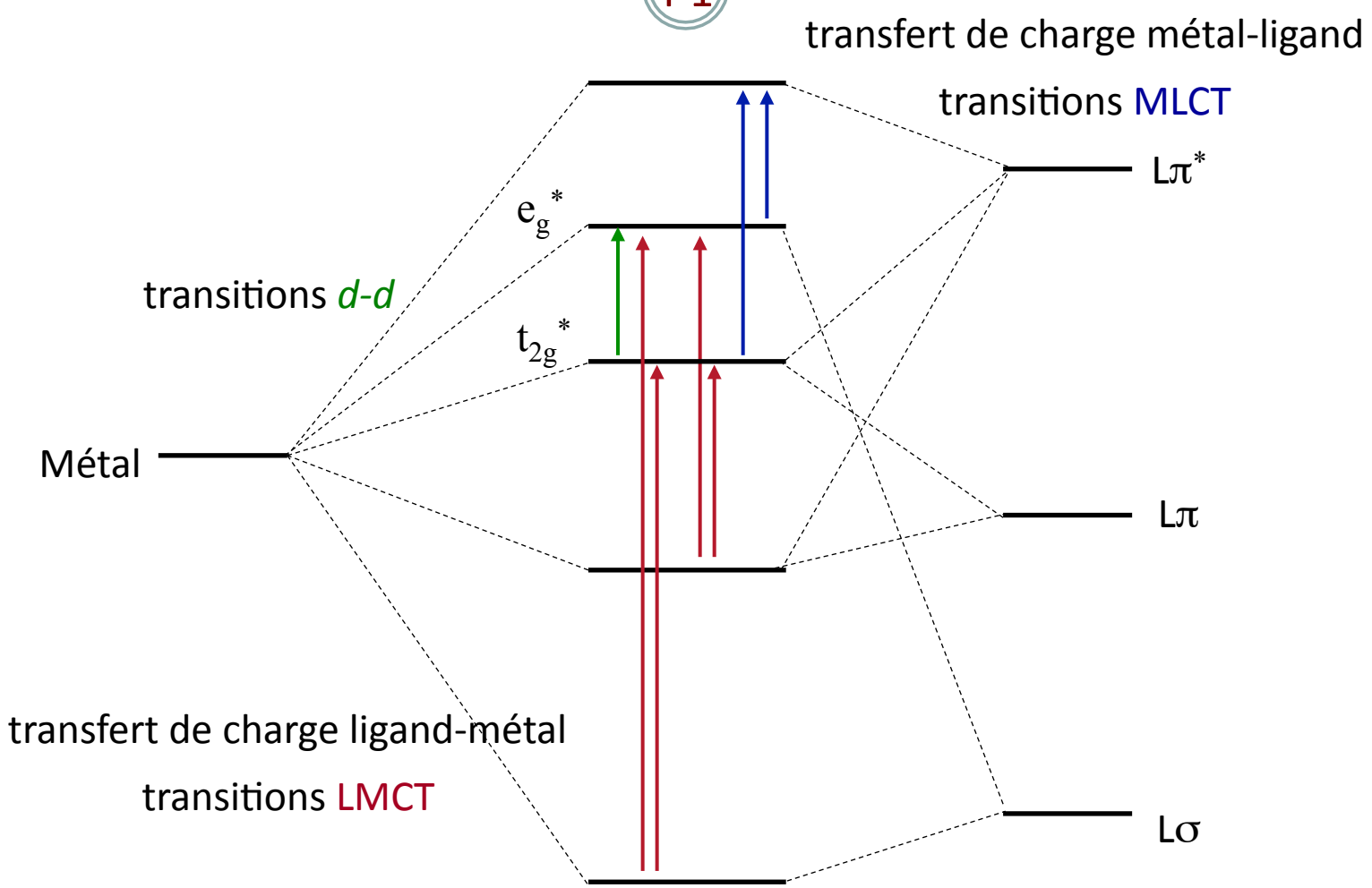
rotations moléculaires
faible énergie
(0.01 - 1 kJ mol^{-1})
(0.83 – 83 cm^{-1})
(12 – 0.12 mm)
micro-ondes

vibrations moléculaires
énergie moyenne
(1 - 120 kJ mol^{-1})
(83 – 10^5 cm^{-1})
(120 - 1 µm)
Infrarouge



Nature des transitions

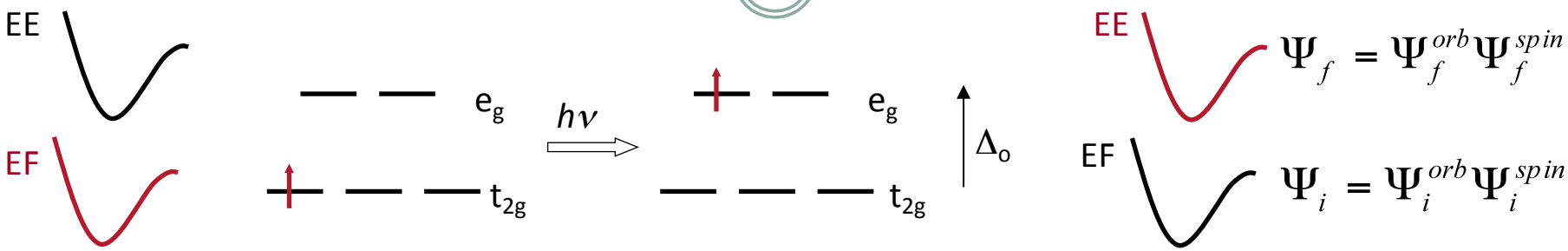
I-1



Transfert de charge + énergétique que transition *d-d*

2. Transitions permises ou interdites

I-2



Règles de sélection pour une transition dipolaire électrique

$$transition = \langle \Psi_i | \mu | \Psi_f \rangle = \langle \Psi_i^{orb} | \mu | \Psi_f^{orb} \rangle \langle \Psi_i^{spin} \| \Psi_f^{spin} \rangle \neq 0$$

μ antisymétrique

$\Delta L = \pm 1$: paire (*g*) ↔ impaire (*u*)

d → *p*, *s* → *p* … *d* (*l*=2), *p* (*l*=1), *s*(*l*=0)

Laporte

$\Delta S = 0$

$^{(2S+1)}\chi_1 \rightarrow {}^{(2S+1)}\chi_2$

Spin

Transitions *d-d* ($t_{2g} \rightarrow e_g$ dans O_h) interdites par Laporte ($\Delta l = 0$) ⇒ règle de spin (TS)

Transfert de charge CT autorisé par Laporte

Plus de détails : 5. Luminescence (SN), préceptorat Couleurs

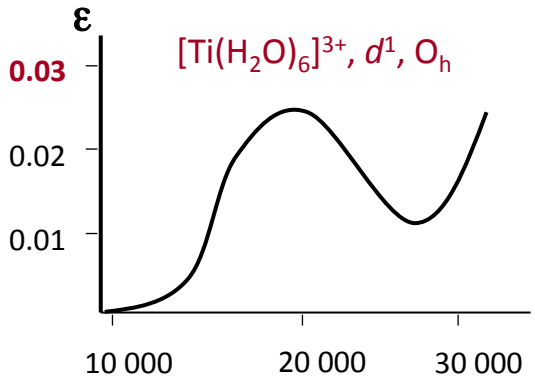
Les règles à suivre…

I-2

Les règles de sélection déterminent l'intensité des transitions électroniques

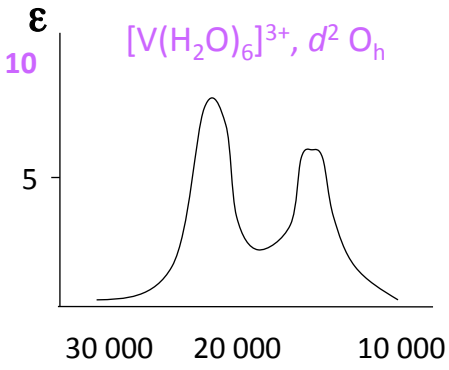
Nature de la transition : Valeur du coefficient d'extinction ε ($M^{-1}.cm^{-1}$)

Loi de Beer-lambert : $A = \log_{10}(I/I_0) = \varepsilon \times [c] \times l$



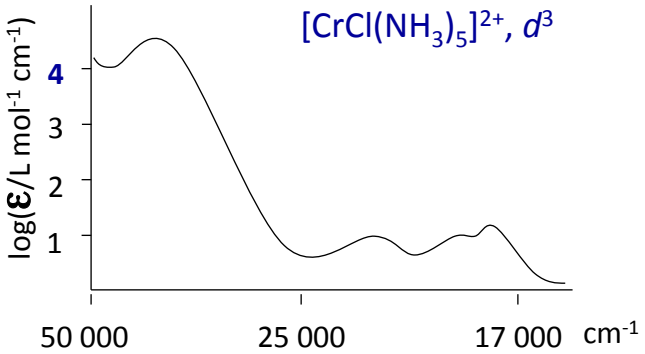
$\varepsilon < 1$

interdite Laporte & spin



$1 < \varepsilon < 10^3$

interdite Laporte



$\varepsilon > 10^3$

autorisée

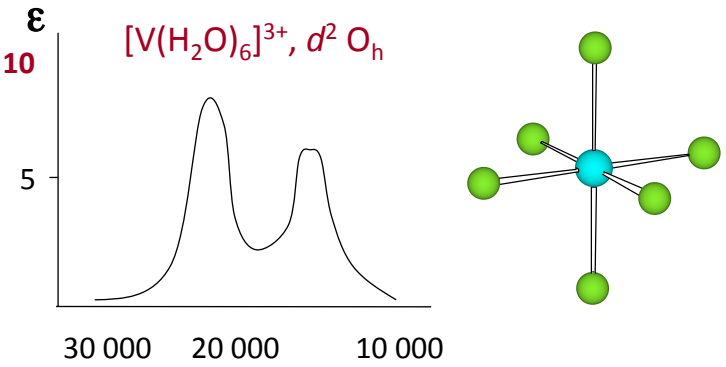
Les exceptions…

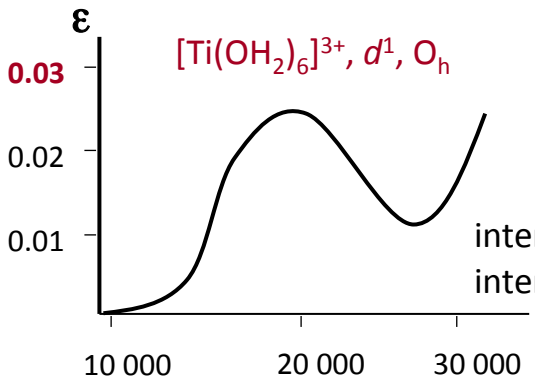
I-2

complexe octaédrique

centrosymétrique ($t_{2g} \rightarrow e_g$)

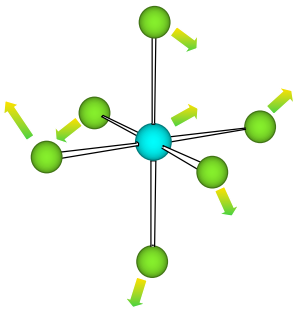
interdite Laporte





interdite Laporte

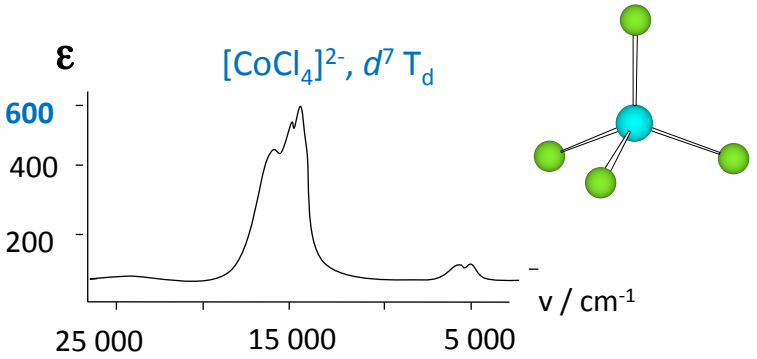
interdite Spin

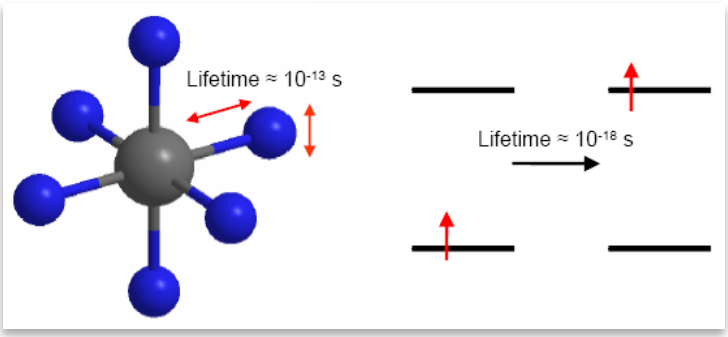


complexe tétraédrique

non-centrosymétrique ($e \rightarrow t_2$)

Laporte relaxée



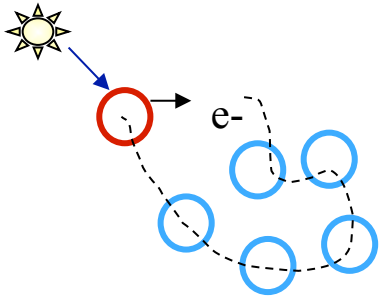


faibles transitions dues aux vibrations asymétriques

transitions vibroniques

3. Différents transferts de charge

I-3



Transfert de charge *:*

transition électronique entre OA ou OM d'atomes différents

ligand – métal

($KMnO_4$)

O → Mn

métal– ligand

($Ru(bpy)_3^{2+}$)

Ru → bpy

métal– métal

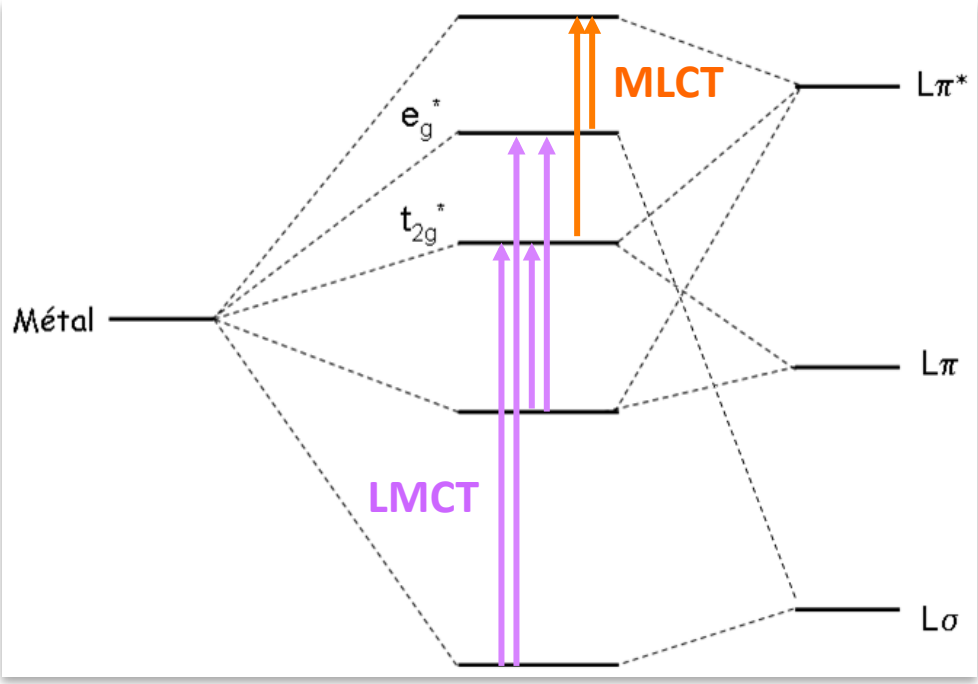
(saphir)

Fe^{2+} → Ti^{4+}

ligand – ligand

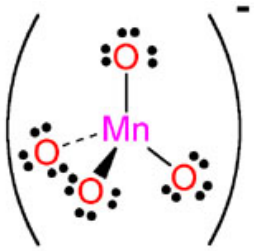
(Lapis-Lazuli)

O → S



Transfert de charge ligand/métal (LMCT)

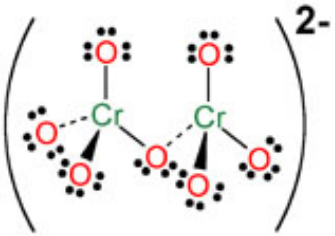
I-3



Mn^{7+} : 4*s* ^{0}3***d*** ^{0}

Transfert de charge du ligand O vers le métal

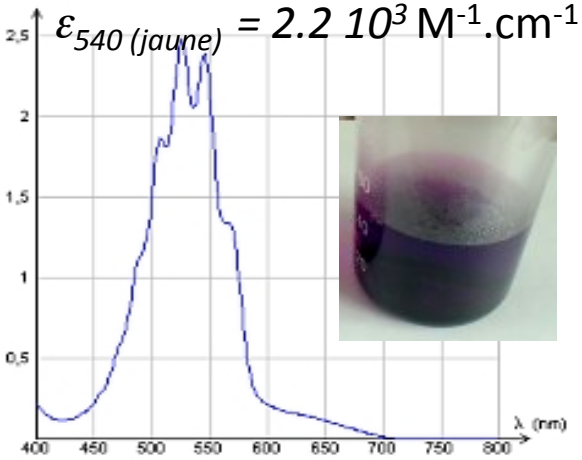
$Mn^{7+}\ O^{2-} \longrightarrow Mn^{6+}\ O^{-}$



Cr^{6+} : 4*s* ^{0}3***d*** ^{0}

$\varepsilon_{350\ (bleu/violet)} = 1.5\ 10^{3}\ M^{-1}.cm^{-1}$

$Cr^{6+}\ O^{2-} \longrightarrow Cr^{5+}\ O^{-}$



LMCT

métal pauvre en e^-, charge élevée

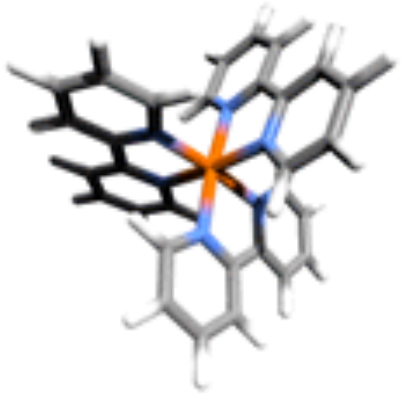
Cr(III), d^3 ; Mn(VII), d^0

ligand riche en e-

O^{2-}, Cl^-, Br^-, I^-

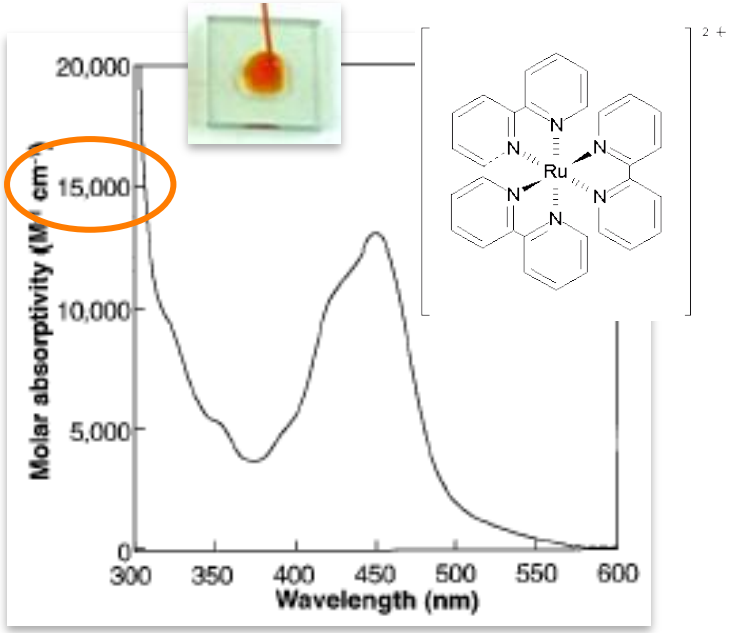
Transfert de charge métal/ligand (MLCT)

I-3



$[Ru^{II}(bpy)_3]^{2+}$ $\xrightarrow{452\ nm}$ $[Ru^{III}(bpy^{-})(bpy)_2]^{2+}$

t_{2g}^{6} $t_{2g}^{5}\ \pi^{*1}$



MLCT

- métal riche en e^-, charge faible
  - Ru(II), d^6 ; Cu(I), d^{10}
- ligand σ-donneur/π-accepteur avec OM π^* basses en énergie
  - 2,2'-bipyridine, 1,10-phénantroline

Luminescence du $[Ru(bpy)_3]^{2+}$

I-3

$[Ru^{II}(bpy)_3]^{2+}$ t_{2g}^{6} S_0

452 nm (absorption, 1)

$^{1}[Ru^{III}(bpy^{-})(bpy)_2]^{2+}$ $t_{2g}^{5}\,\pi^{*1}$ S_0

(qq fs)

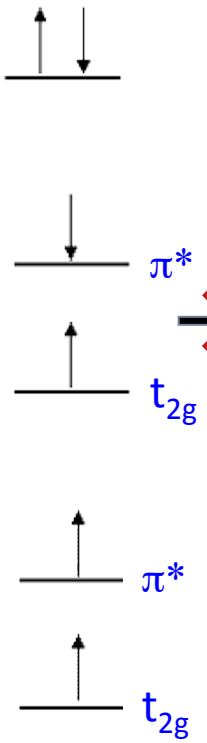
Croisement intersystème **(5)**

$^{3}[Ru^{III}(bpy^{-})(bpy)_2]^{2+}$ $t_{2g}^{5}\,\pi^{*1}$ T_1

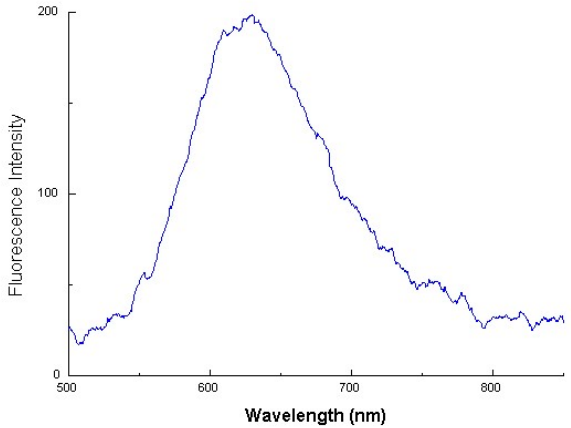
(600 ns)

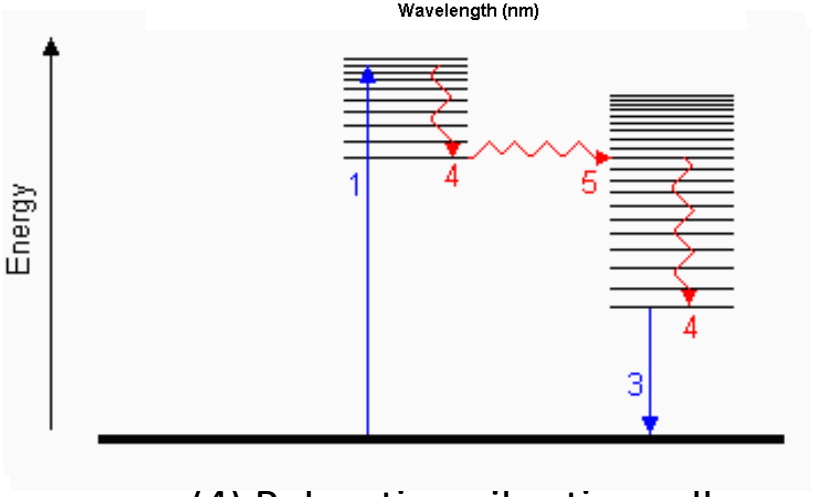
600 nm (émission)

$[Ru^{II}(bpy)_3]^{2+}$



(3) phosphorescence



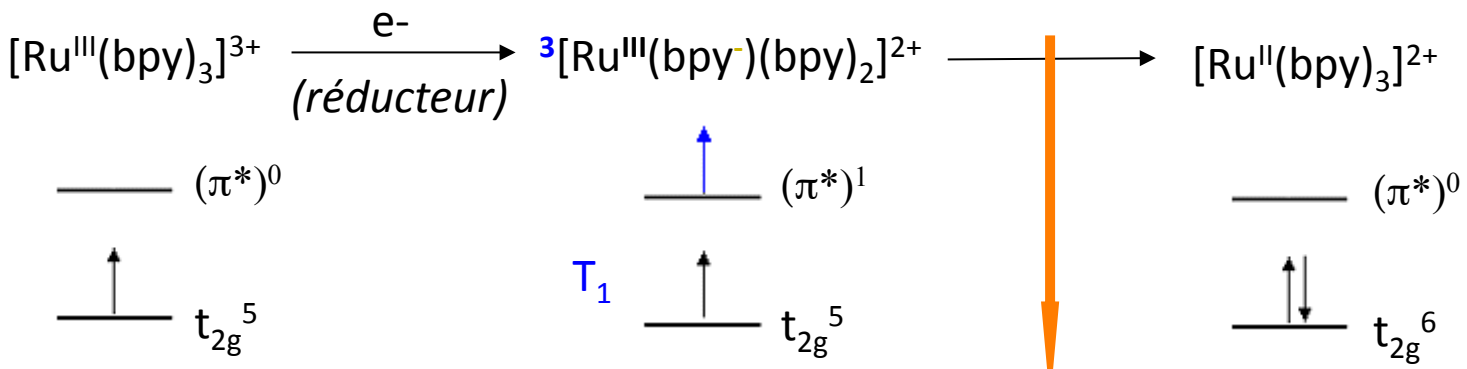


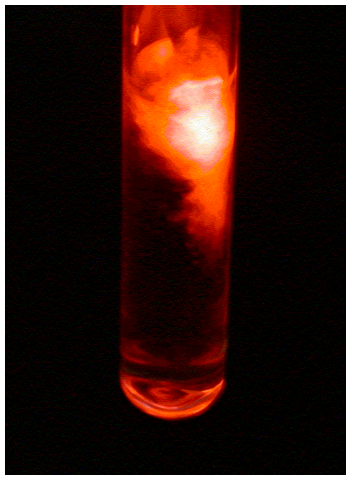
(4) Relaxation vibrationnelle

Luminescence du $[Ru(bpy)_3]^{2+}$

I-3

Mise en évidence : réduction de $[Ru^{III}(bpy)_3]^{3+}$



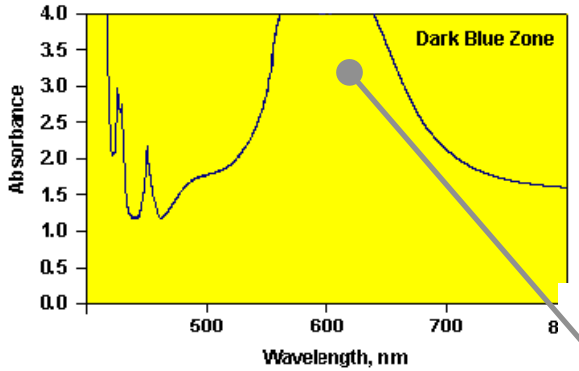


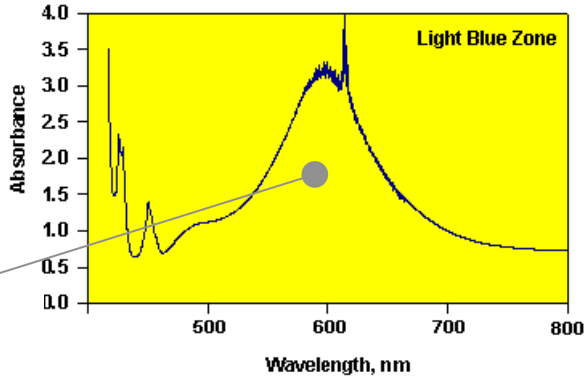
TP luminescences
cours 5. luminescence (SN)

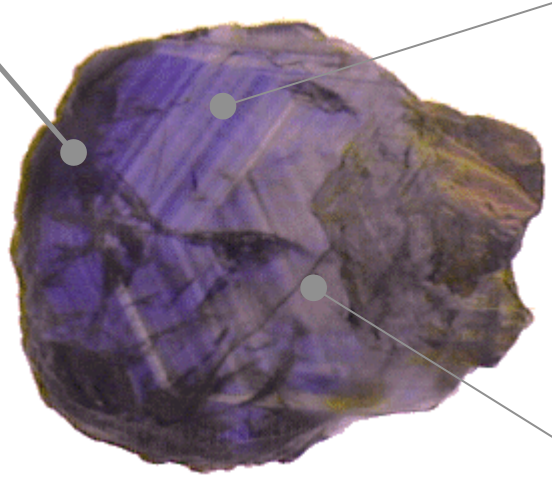
Transfert de charge métal/métal (MMCT)

I-3

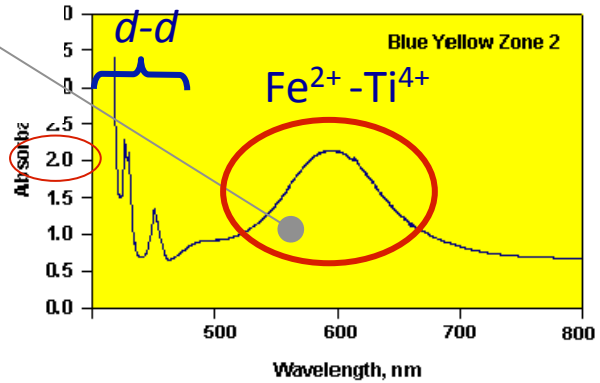
saphir bleu







impuretés colorées :
Fe^{2+} et Ti^{4+}

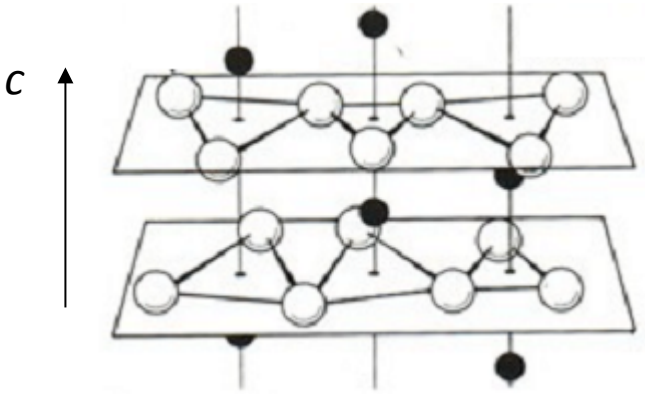


Transfert de charge d'intervalence (**ICT**)
(métal/métal) (homo ou hétéronucléaire) :

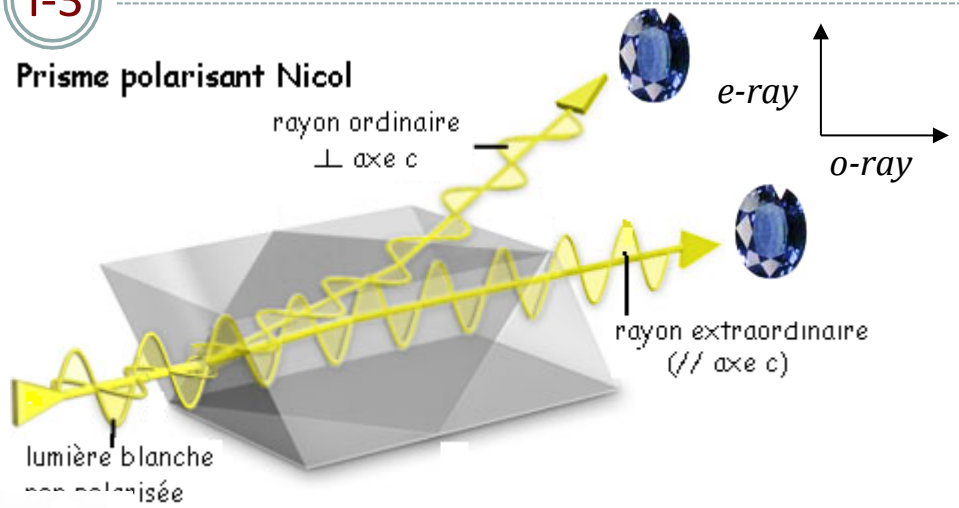
- Laporte interdite : $d\ (g, M_1) \leftrightarrow d\ (g, M_2)$
- Spin autorisée

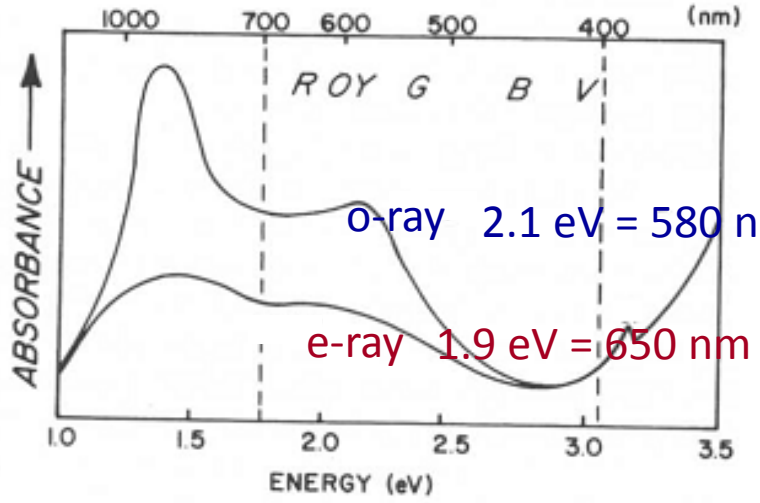
Dichroïsme et piézochromisme du saphir

I-3



Saphir (corindon)





Fe^{2+} d^6 : $t_{2g}^4 e_g^2$ → Fe^{3+} d^5 : $t_{2g}^4 e_g^1$

Ti^{4+} d^0 : $t_{2g}^0 e_g^0$ → Ti^{3+} d^1 : $t_{2g}^0 e_g^1$

→ // axe = CT – énergétique !

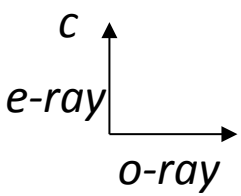
Dichroïsme et piézochromisme du saphir

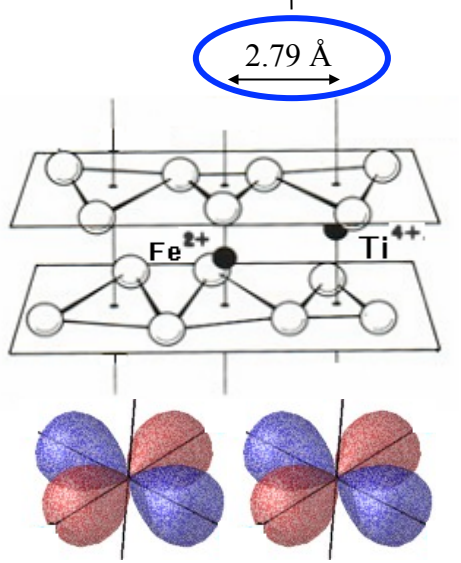
I-3

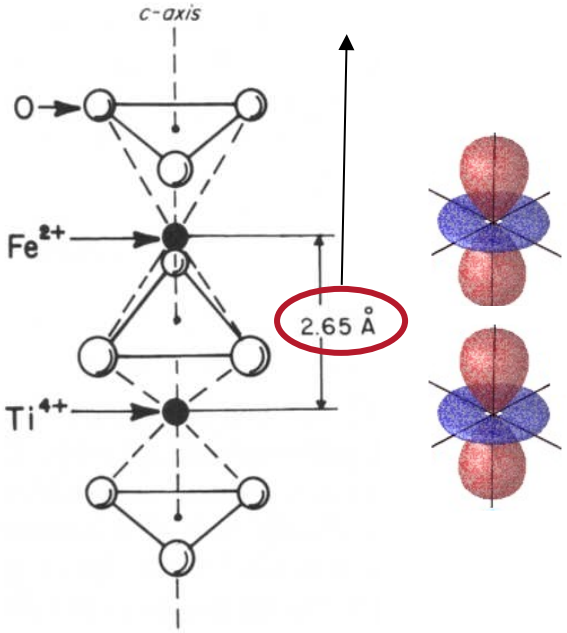
Dichroïsme bleu-vert

E_{CT} = 2.1 eV
= 580 nm (abs. jaune)

E_{CT} = 1.9 eV
= 650 nm (abs. orange/rouge)

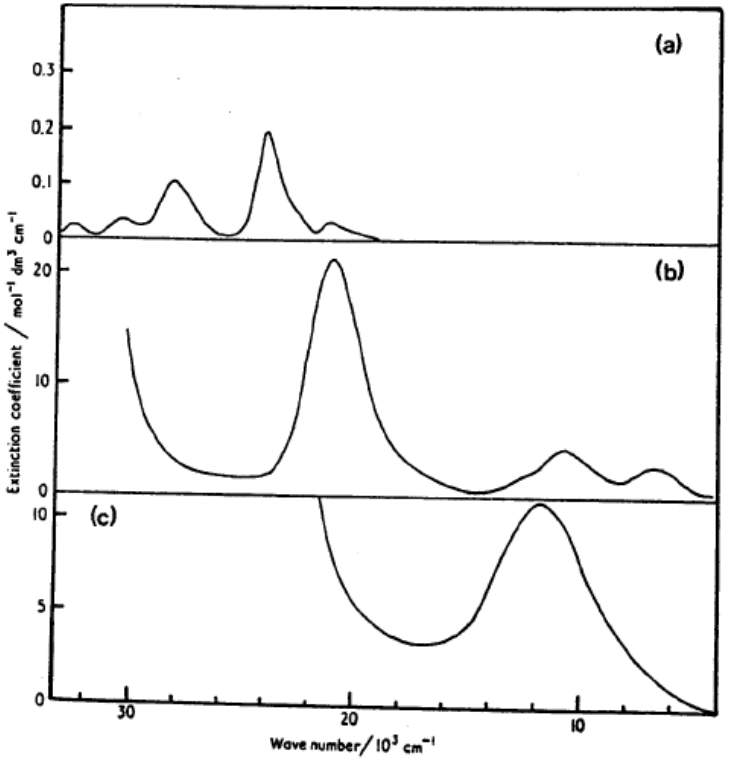






Un peu d'exercice…

1. Indiquer le degré d'oxydation des métaux.
   Identifier chaque spectre en le justifiant.



complexes $[MCl_6]^{4-}$, avec M = Cu, Ni, Mn.

2. Interpréter les spectres.