Chem 241

Lecture 14

Homework

Finish reading chapter 19 – 19.3, 19.4, 19.6 (a lot on p-chem.)

Exercises: 1, 2, 4, 5, 7, 8, 24

Problem : 3, 8

Recap

MOT for O_h

Ligand Field Theory

A good σ-donor should result in a strong metal-ligand overlap, hence a more strongly anti-bonding e_g set and a larger value of Δ_o.

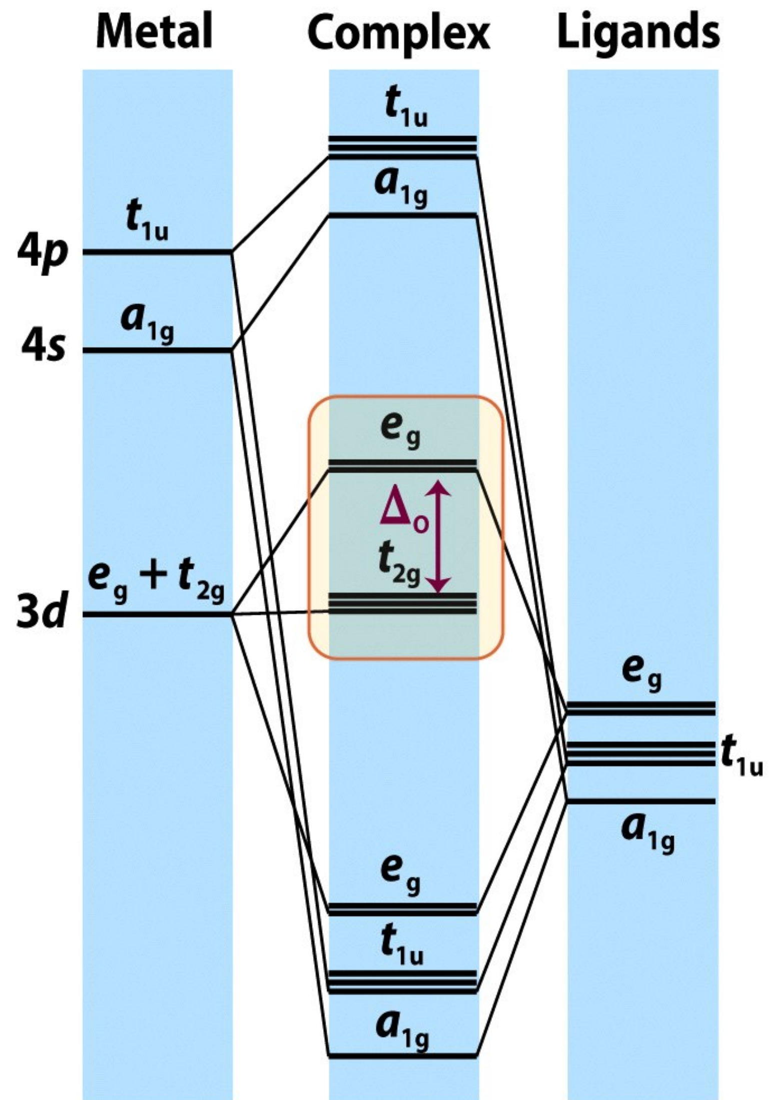
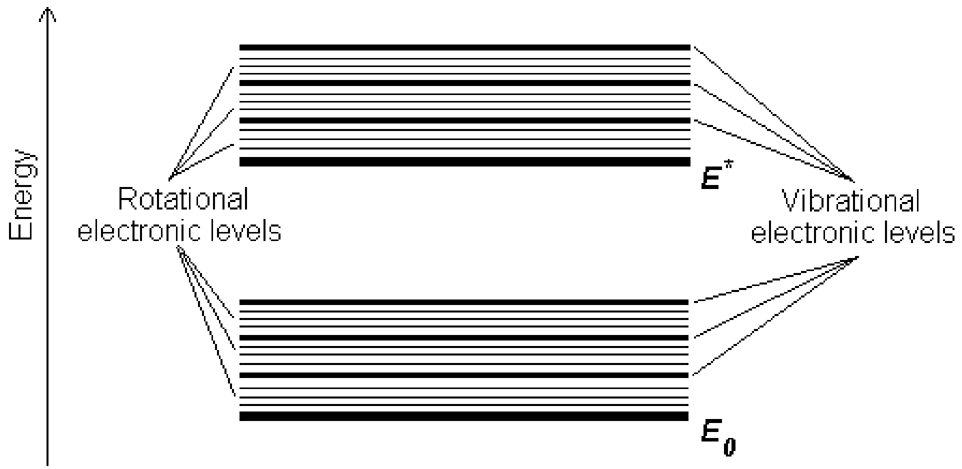
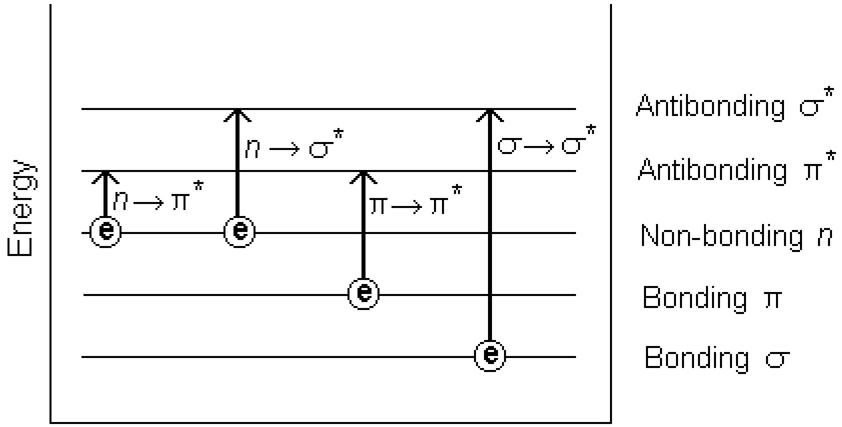


Figure 19-13
Shriver & Atkins Inorganic Chemistry, Fourth Edition
…kins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Absorption

Ultravoilet-visible spectroscopy is the observation of the abosoption of electromagnetic radiation in the ultraviolet and visible (UV) regions of the spectrocopy.





Absorption of a Metal Complex

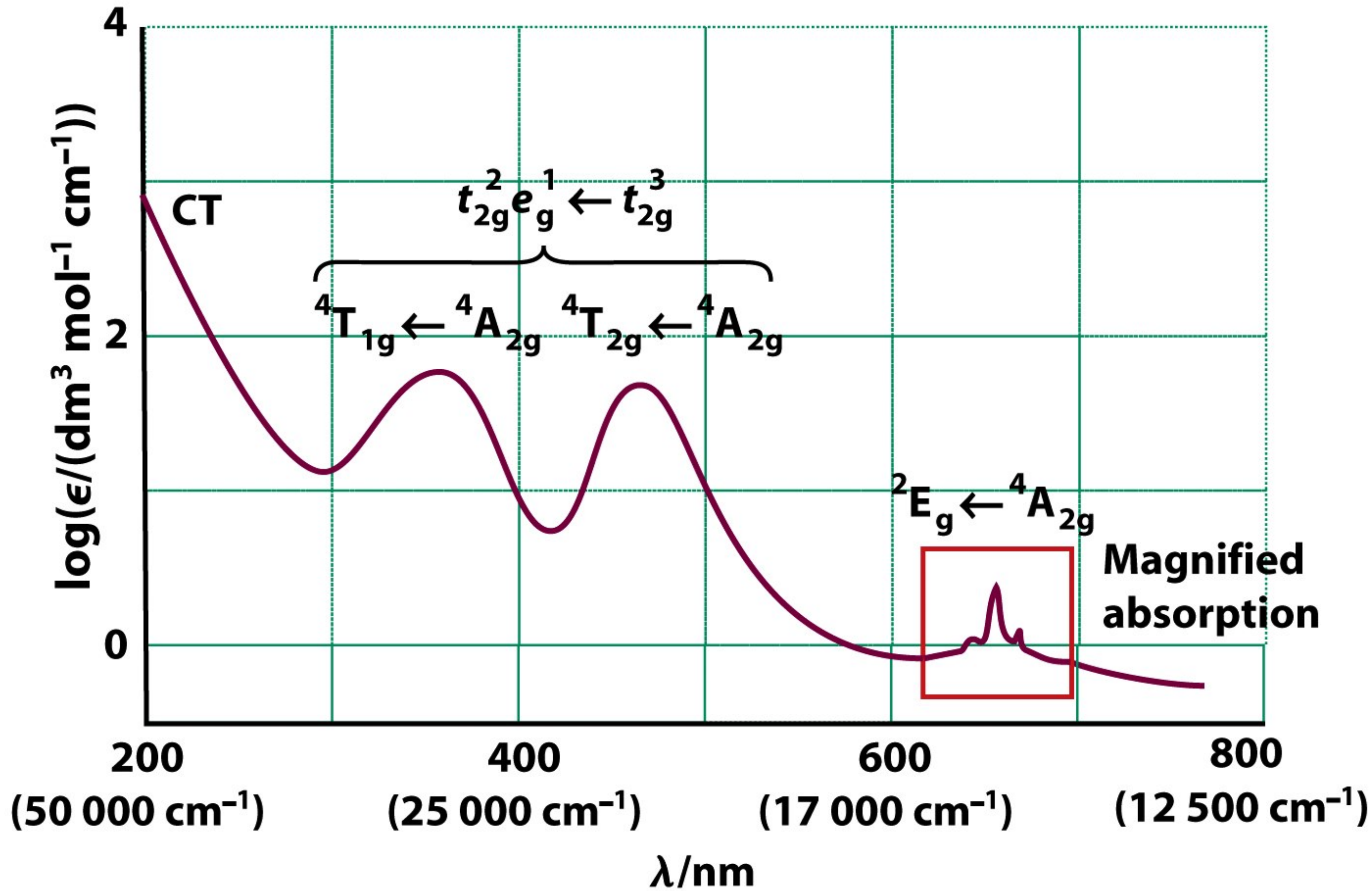


Figure 19-19
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Absorption

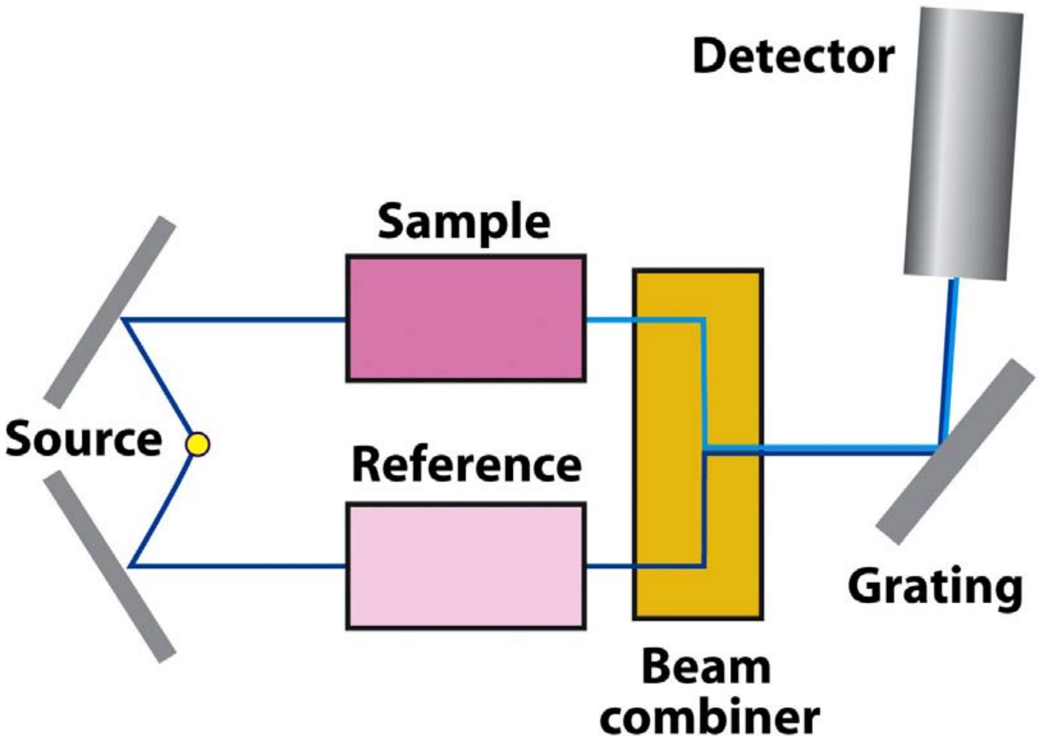


Figure 6-4
Shriver & Atkins Inorganic Chemistry, Fourth Edition

$\underline{A = \log (I_0/I)}$

I_o = Light In

I = Light abs.

$\underline{A = \varepsilon B[C]}$

ε = molar abs.

B = Path length

[C] = concentration

Consider π-orbitals

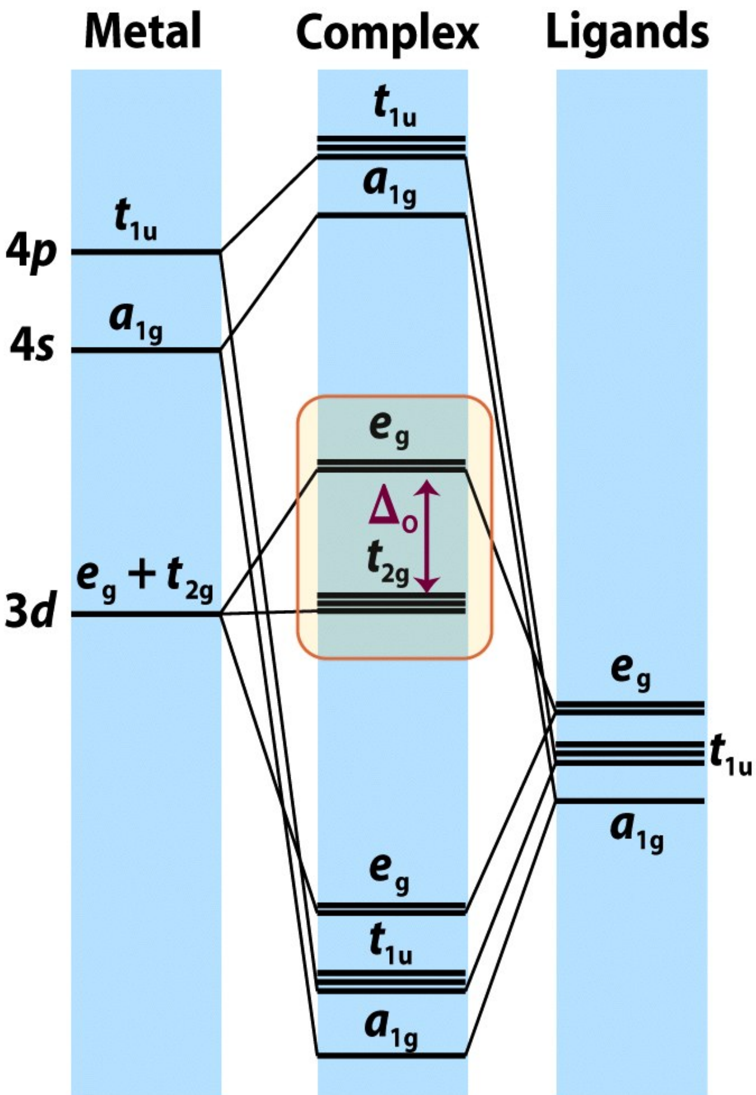
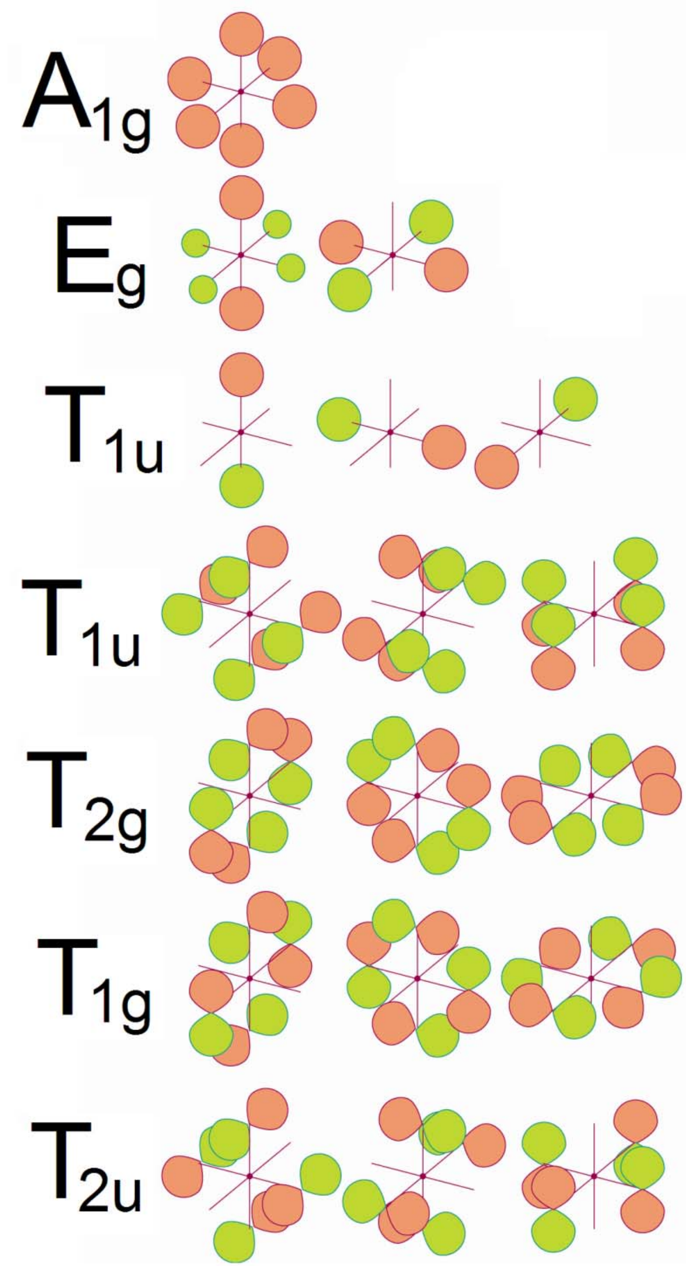


Figure 19-13
Shriver & Atkins Inorganic Chemistry, Fourth Edition



Consider π-orbitals

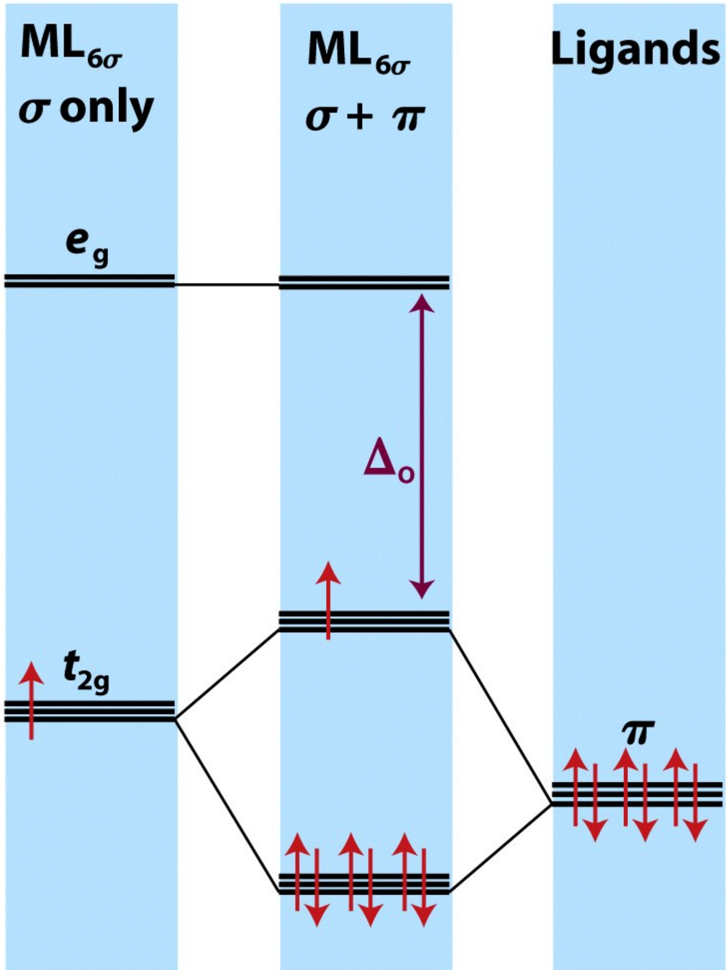


Figure 19-17
Shriver & Atkins Inorganic Chemistry, Fourth Edition

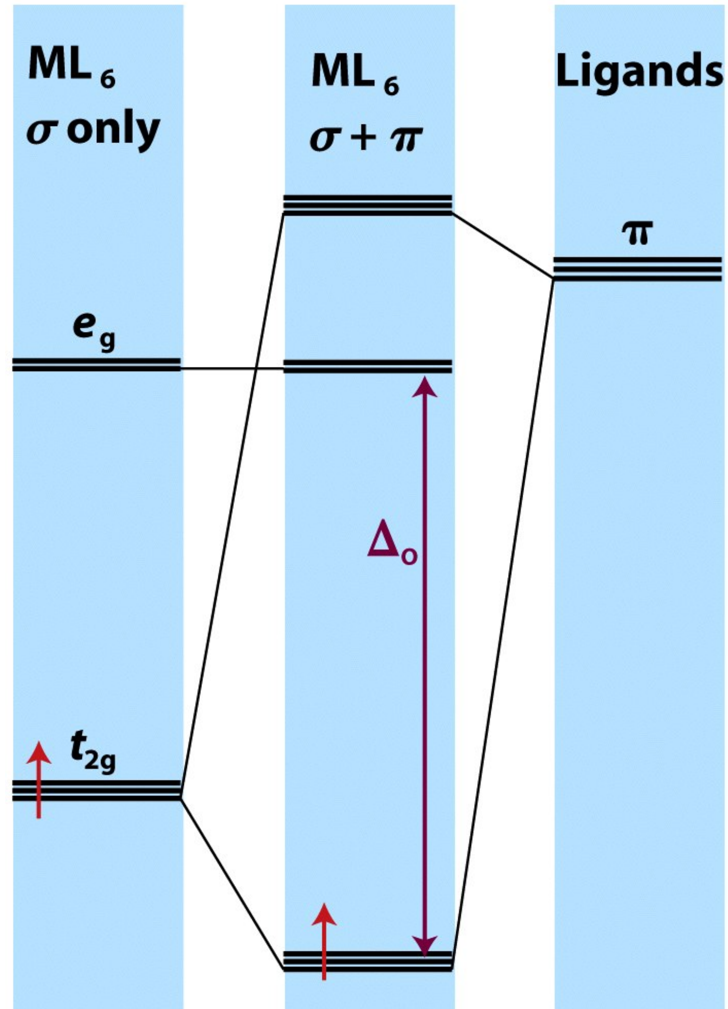


Figure 19-18
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Coordination compounds

We are now in a position to understand the spectrochemical series.

- Δ_o: I^- < Br^- < S^{2-} < $-SCN^-$ < Cl^- < $-O_2N^-$ < N_3^- < F^- < OH^- < ox^{2-} < H_2O < $-NCS^-$ < CH_3CN < py < NH_3 < en < bipy < phen < $-NO_2^-$ < PPh_3 < CN^- < CO

Δ_o: σ + π-donors < σ-donors < σ-donors + π-acceptors

Charge Transfer

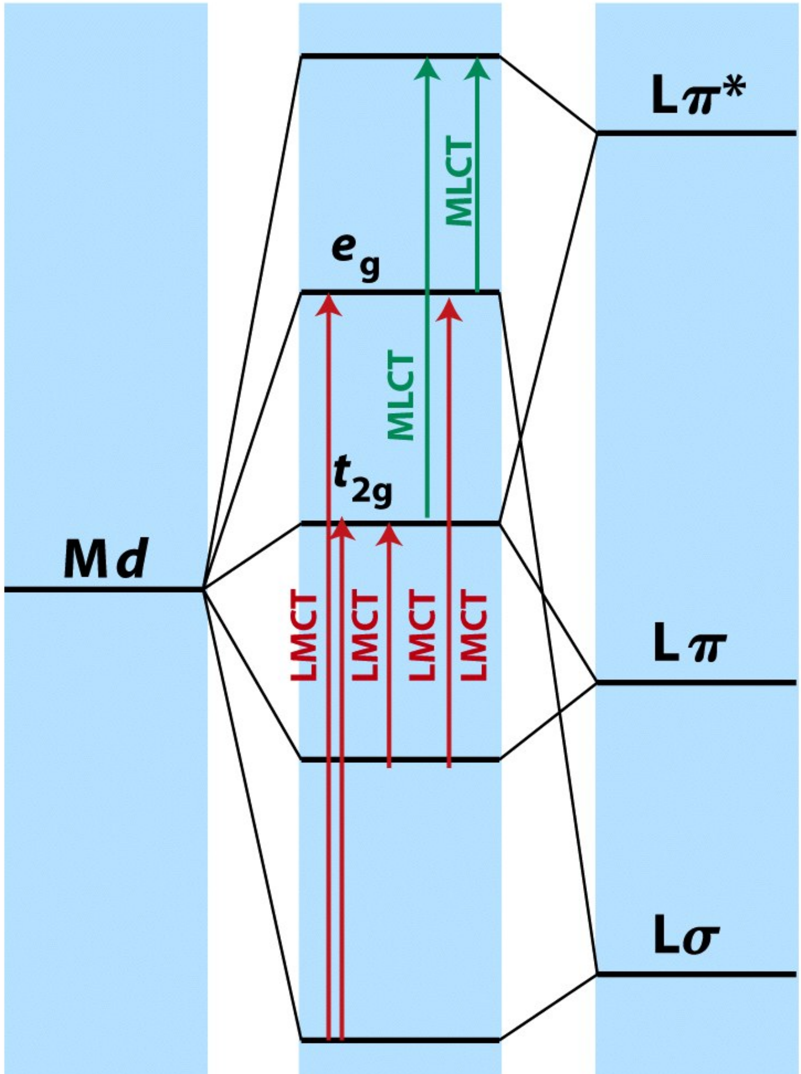


Figure 19-28
Shriver & Atkins Inorganic Chemistry, Fourth Edition

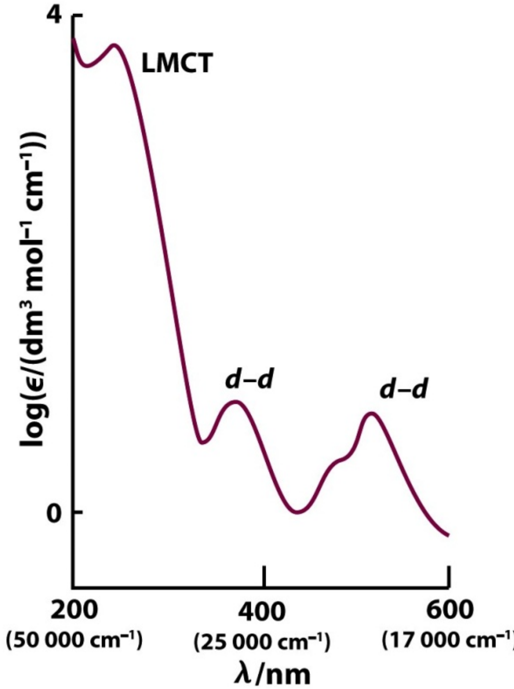
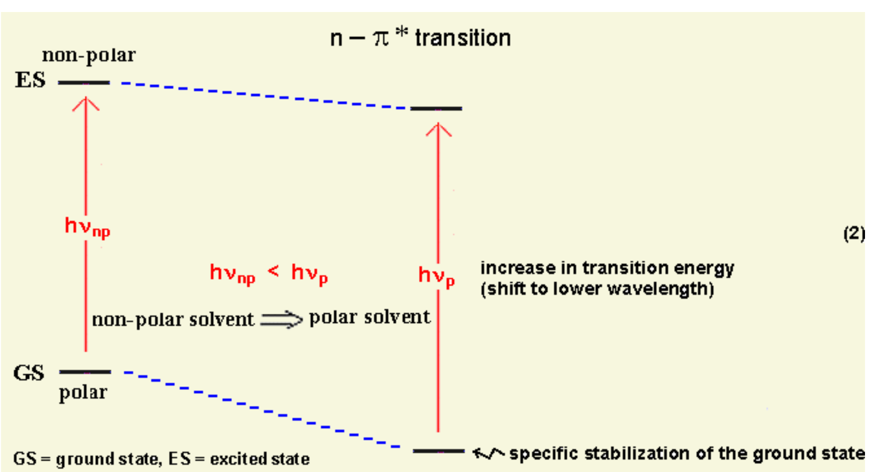
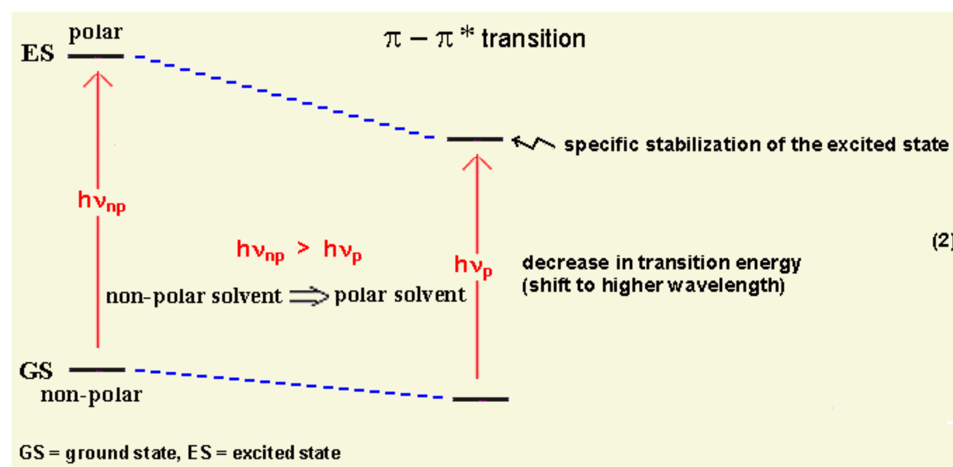


Figure 19-29
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Solvatochromism

- Negative solvatochromism corresponds to <u>hypsochromic shift</u>,
- Positive solvatochromism corresponds to <u>bathochromic shift</u> with increasing solvent polarity.



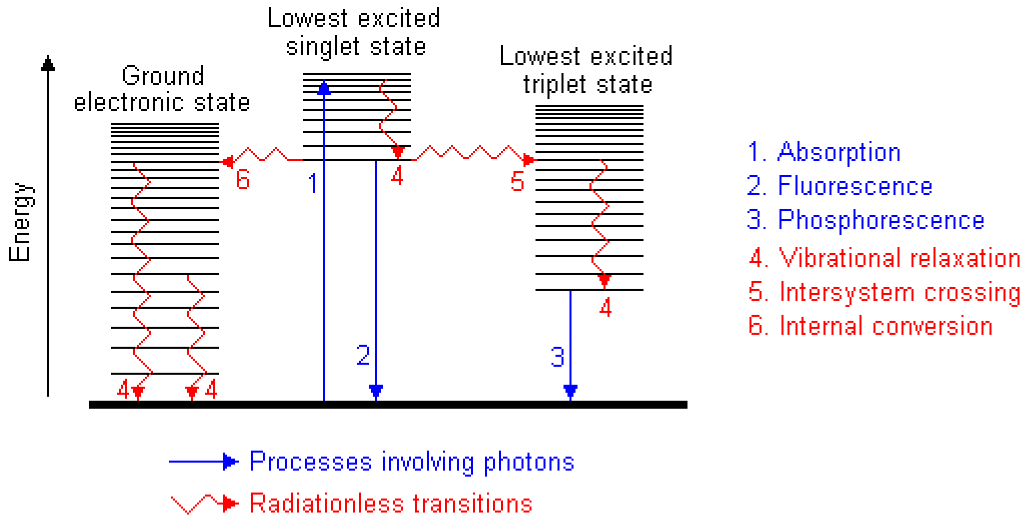


Pottery, Glass and Gems

Fluorescence and Phosphorescence

Fluorescence – is radiative decay from an excited state of the **same** multiplicity as the ground state.

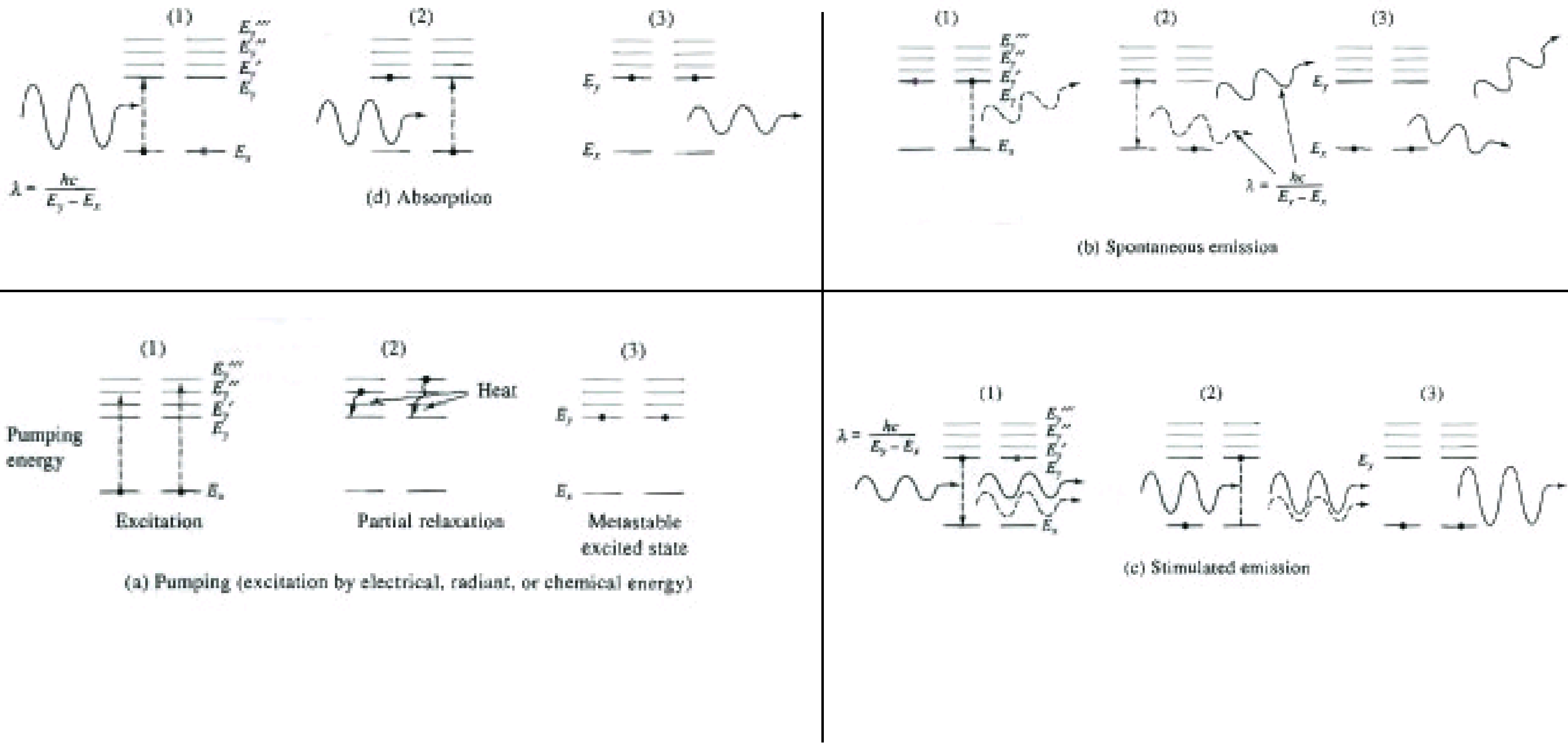
Phosphorescence - is radiative decay from an excited state of the **different** multiplicity as the ground state.



2S + 1

Laser

Light **A**mplification by **S**timulated **E**mission of **R**adiation

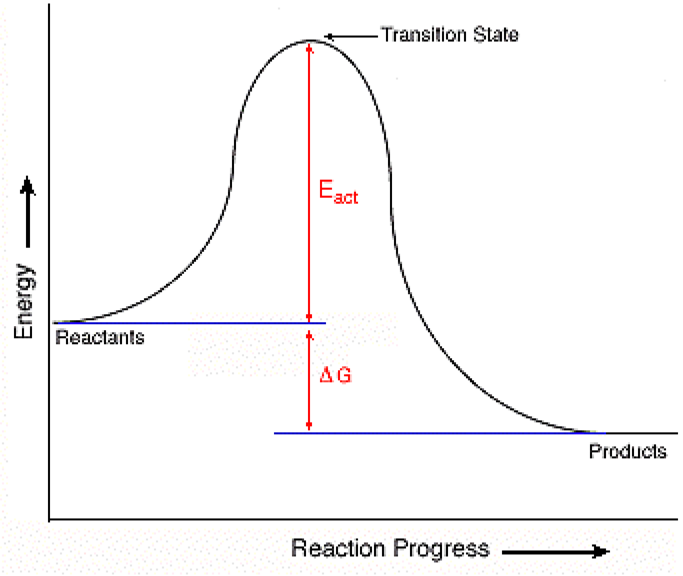


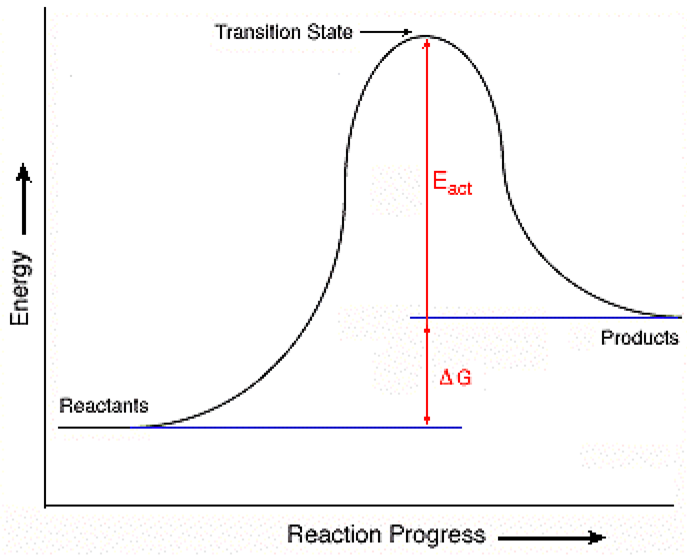
Reactions

Ligand substitution

Y + M-X → M-Y + X

Kinetics v Thermodynamic





Formation Constant

$M + L \rightleftharpoons ML$ $$K_1 = \frac{[ML]}{[M][L]}$$

$ML + L \rightleftharpoons ML_2$ $$K_2 = \frac{[ML_2]}{[ML][L]}$$

$M + nL \rightleftharpoons ML_n$ $$B_n = \frac{[ML_n]}{[M][L]^n}$$

Dissociation Constant

$$ML \rightleftharpoons M + L \qquad K_d = \frac{[M][L]}{[ML]}$$

Table 20.1 Formation constants for the reaction $[M(H_2O)_n]^{m+} + L \rightleftharpoons [M(L)(OH_2)_{n-1}]^{m+} H_2O$

Ion	Ligand	K_f	log K_f	Ion	Ligand	K_f	log K_f
Mg^{2+}	NH_3	1.7	0.23	Pd^{2+}	Cl^-	1.25×10^5	6.1
Ca^{2+}	NH_3	0.64	−0.2	Na^+	SCN^-	1.2×10^4	4.08
Ni^{2+}	NH_3	525	2.72	Cr^{3+}	SCN^-	1.2×10^3	3.08
Cu^+	NH_3	8.50×10^5	5.93	Fe^{3+}	SCN^-	234	2.37
Cu^{2+}	NH_3	2.0×10^4	4.31	Co^{2+}	SCN^-	11.5	1.06
Hg^{2+}	NH_3	6.3×10^8	8.8	Fe^{2+}	pyridine	5.13	0.71
Rb^+	Cl^-	0.17	−0.77	Zn^{2+}	pyridine	8.91	0.95
Mg^{2+}	Cl^-	4.17	0.62	Cu^{2+}	pyridine	331	2.52
Cr^{3+}	Cl^-	7.24	0.86	Ag^+	pyridine	93	1.97
Co^{2+}	Cl^-	4.90	0.69				

Trends in formation Constants

General Trends

$K_1 > K_2 > K_3 \ldots$

Chelating Effect – Greater stability once coordinated

Higher K formation because of entropy.

Rings

5 and 6 membered rings tend to be more stable

The Irving-William Series

Summarize stability of complexes based on electrostatic effects and LFSE

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn$

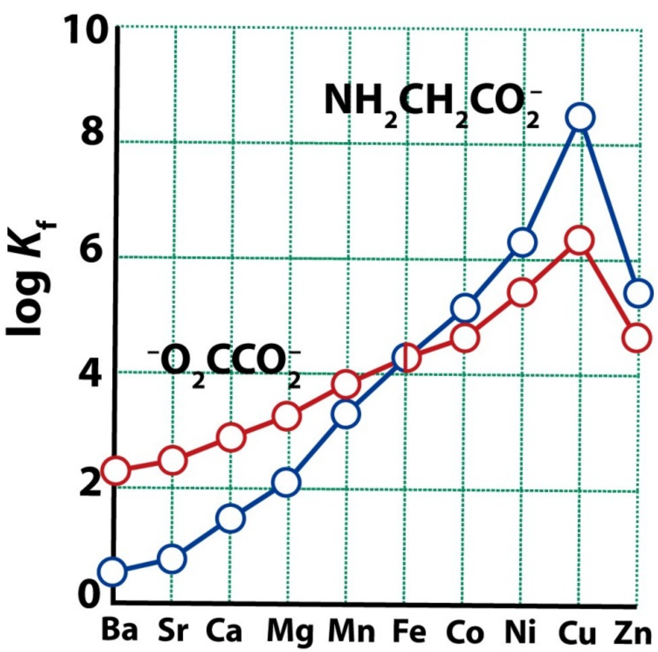
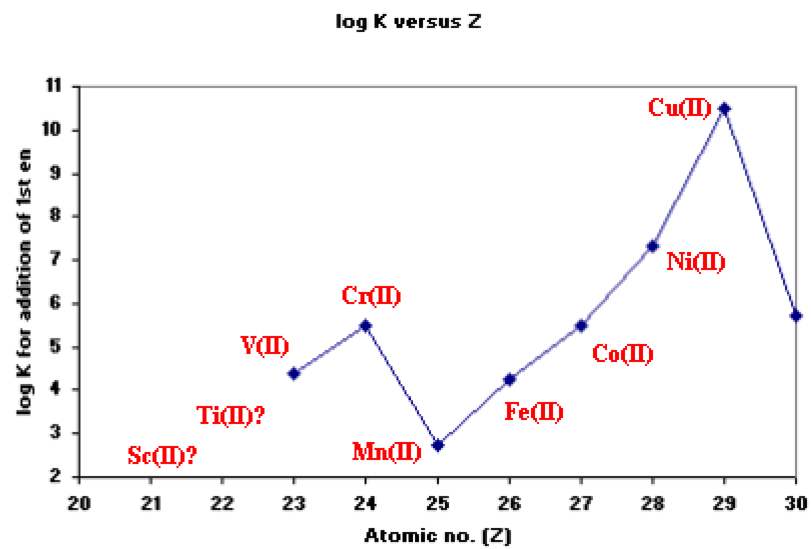


Figure 20-1
Shriver & Atkins Inorganic Chemistry, Fourth Edition



Ligand substitution

Complexes that lose their ligands easily = Labile
Complexes that keep their ligands = Nonlabile or Inert

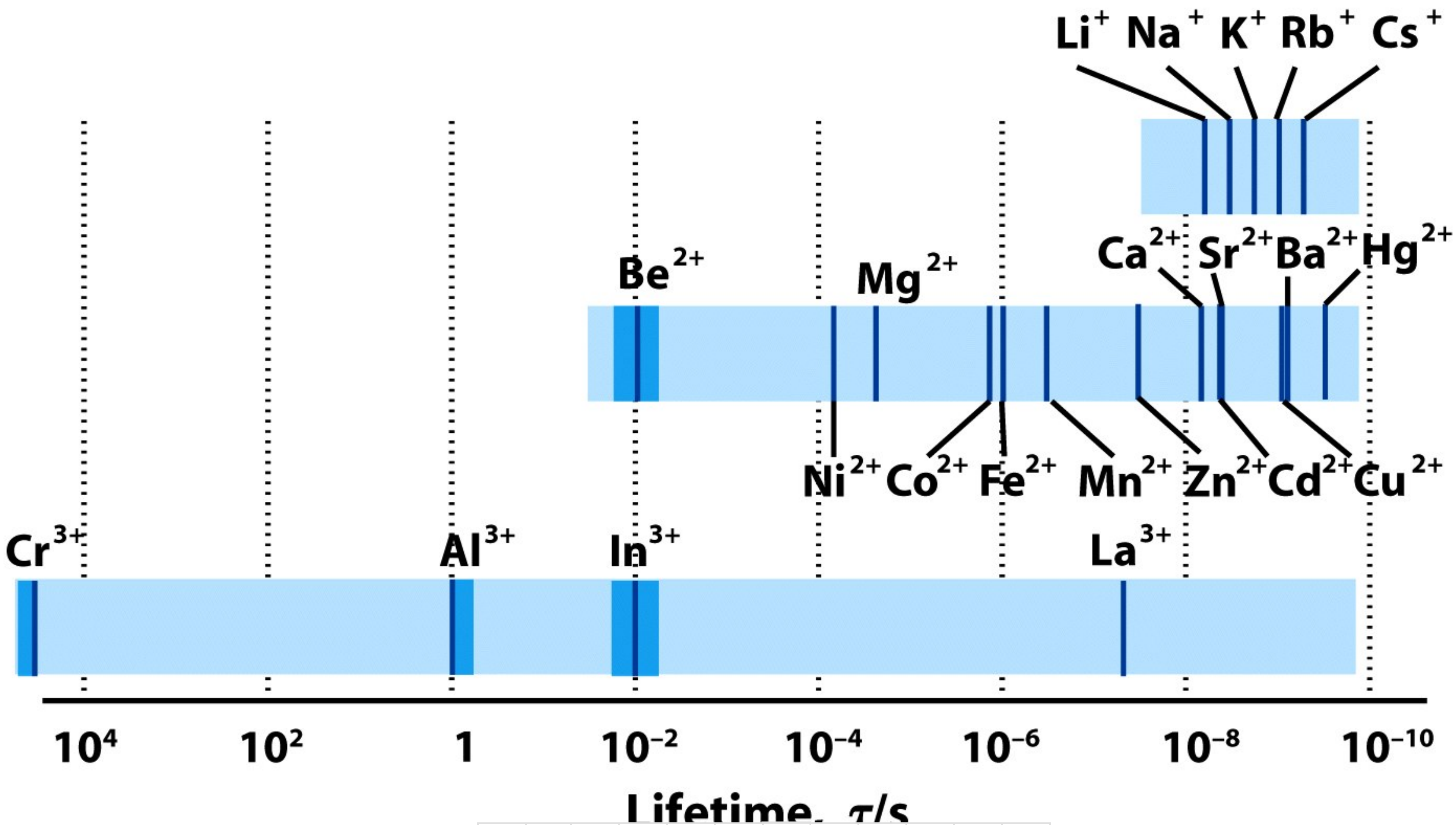


Figure 20-2