Lecture 6: Physical Methods II

UV-Vis (electronic spectroscopy)

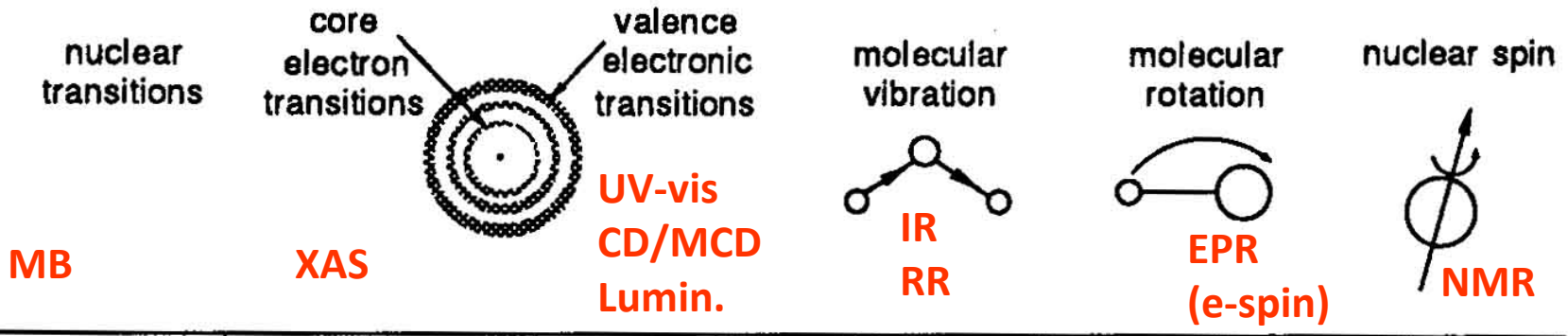
Electron Spin Resonance

Mossbauer Spectroscopy

Physical Methods used in bioinorganic chemistry

- X-ray crystallography
- X-ray absorption (XAS)
  - **Extended X-ray Absorption Fine Structure (EXAFS)**
  - **X-ray Absorption Near Edge Structure**
- Magnetic Resonance
  - **Electron paramagnetic resonance (EPR)**
  - **Nuclear magnetic resonance (NMR)**
- Mössbauer (MB)
- Optical Spectroscopy:
  - **Electronic absorption (UV-vis)**
  - **Circular dichroism (CD)**
  - **Magnetic circular dichroism (MCD)**
  - **Luminescence (fluorescence & phosphorescence)**
  - **Infrared (IR)**
  - **Resonance Raman (RR)**
- Electrochemistry

Spectrum of Electromagnetic Radiation



γ-ray	x-ray	uv	visible	IR	microwave	radio
λ(m) 10^{-12}—10^{-10}	10^{-10}—10^{-8}	10^{-8}—10^{-6}		10^{-6}—10^{-4}	10^{-4}—10^{-2}	10^{-2}—10^{2}
ν(Hz) 10^{18}—10^{20}	10^{16}—10^{18}	10^{14}—10^{16}		10^{12}—10^{14}	10^{10}—10^{12}	10^{6}—10^{10}
E(J) 10^{9}—10^{11}	10^{7}—10^{8}	10^{5}—10^{6}		10^{4}—10^{5}	10^{2}—10^{4}	10^{-3}—10^{2}

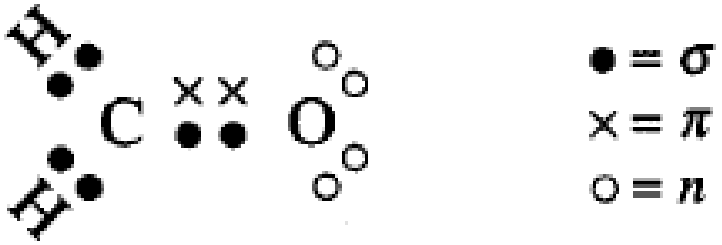
Figure 2.2 Spectrum of electromagnetic radiation. The boundaries between domains are not sharp, and each region is not shown to scale. The visible domain actually forms an extremely small part (~350–750 nm) of the electromagnetic spectrum.

A Reminder:

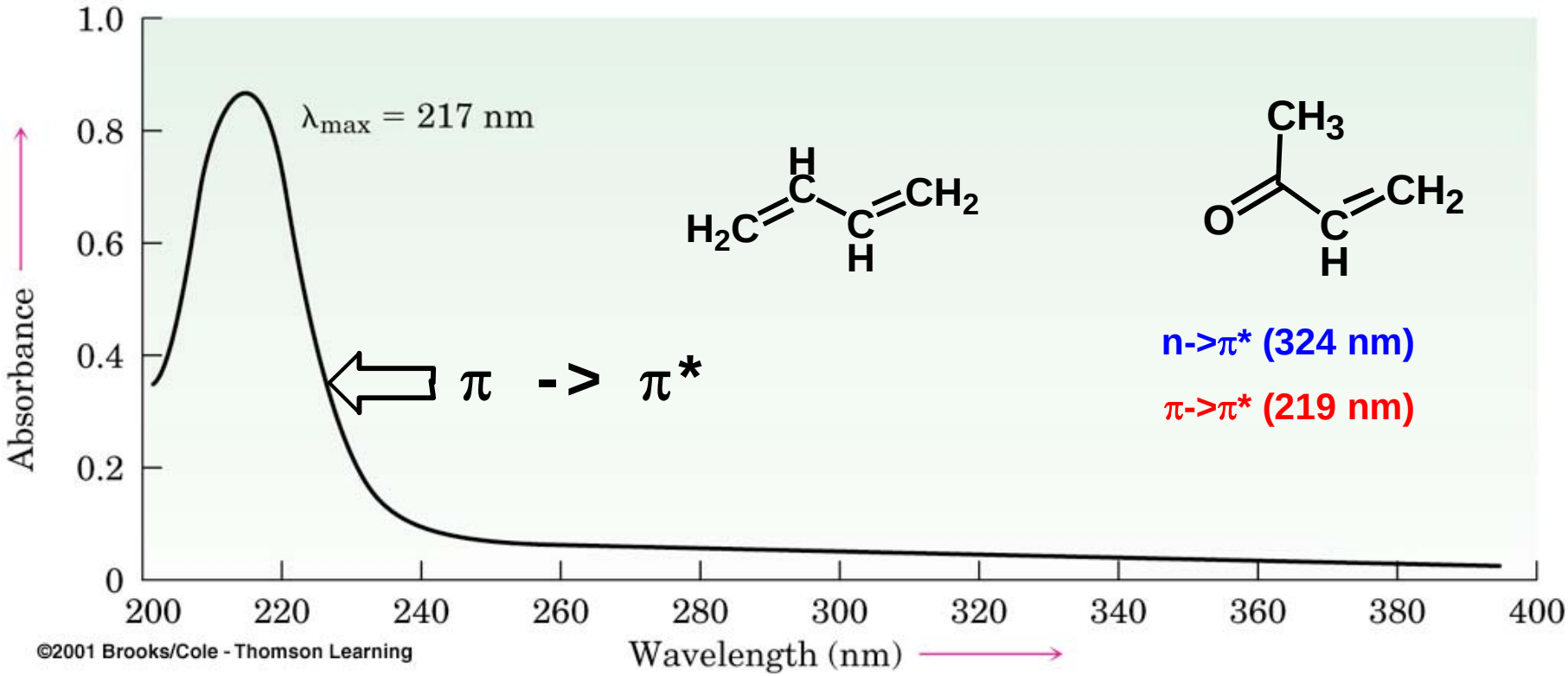
UV-Visible Spectroscopy

- Absorption of UV-vis results in transitions of electrons from a lower energy occupied MO to a higher energy unoccupied MO
- Widely used method for identification of inorganic and organic species

- Electronic transitions
  - π, σ, and n electrons
  - d and f electrons
  - Charge transfer reactions
- π, σ, and n (non-bonding) electrons



Chromophore - part of a molecule that absorbs UV/Vis light



n->π* (324 nm)

π->π* (219 nm)

Vacuum UV : 10 – 200 nm
Normal : 200 – 400 nm
Visible : 380 – 780 nm

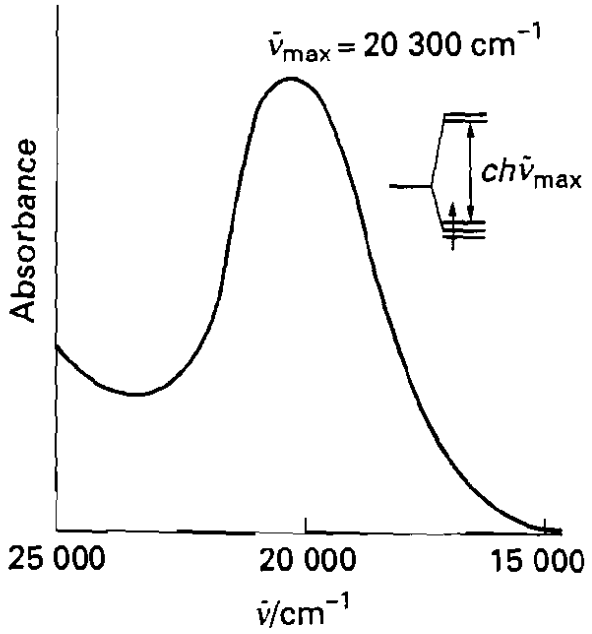
176 nm

178 nm

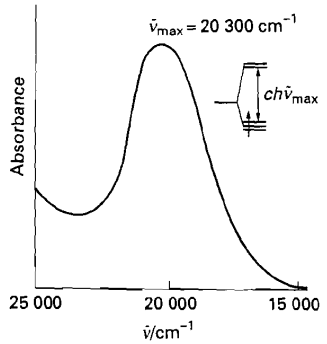
223 nm

$E = h\upsilon = hc/\lambda$

$E \propto 1/\lambda$ = wavenumber (cm^{-1})



7.10 The optical absorption spectrum of $[Ti(OH_2)_6]^{3+}$.



7.10 The optical absorption spectrum of $[Ti(OH_2)_6]^{3+}$.

Table 7.3 Ligand-field splitting parameters Δ_O of ML_6 complexes*

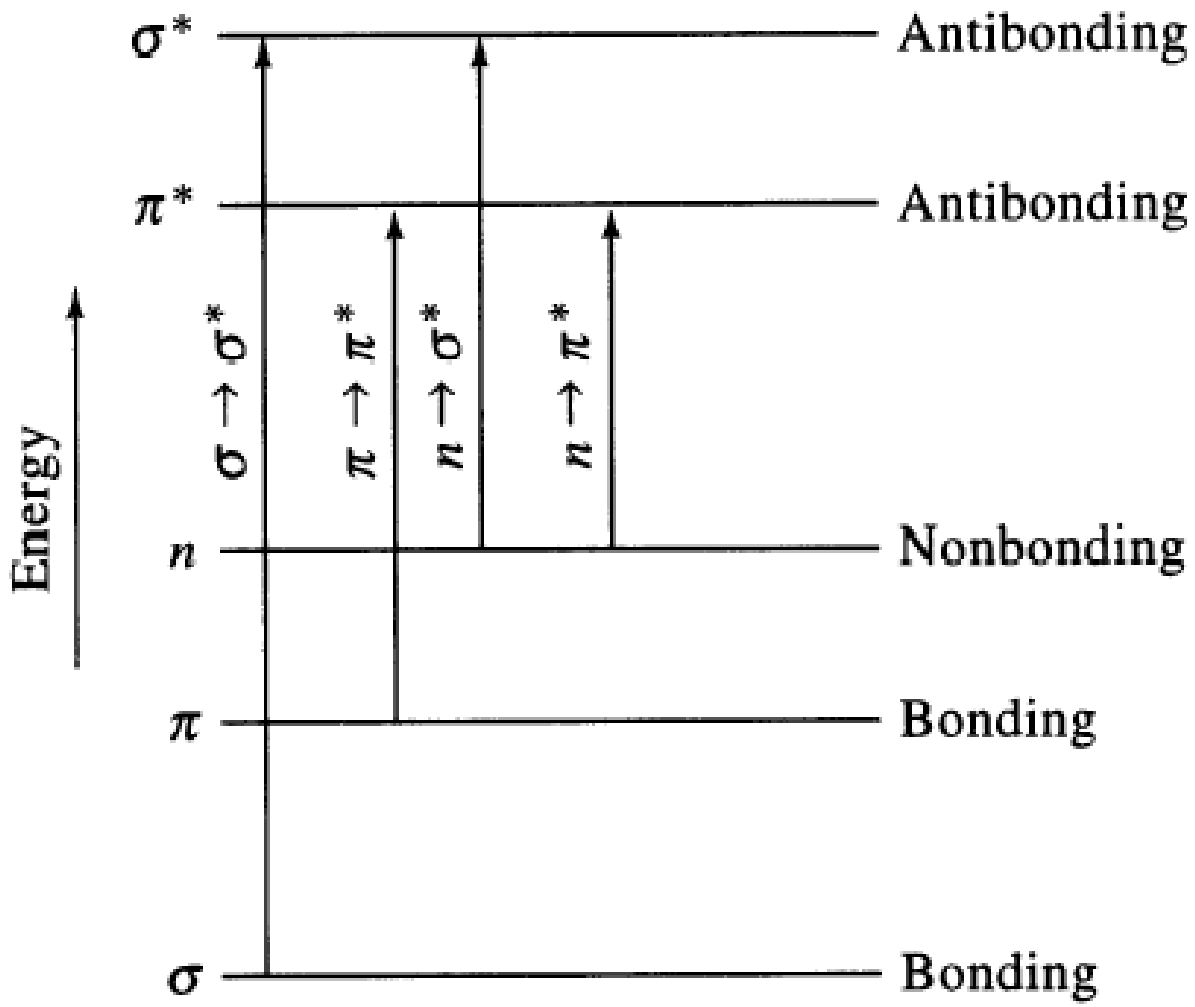
	Ions	Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13.7	17.4	21.5	21.9	26.6
d^5	Mn^{2+}	7.5	8.5		10.1	30
	Fe^{3+}	11.0	14.3			(35)
d^6	Fe^{2+}		10.4			(32.8)
	Co^{3+}		(20.7)	(22.9)	(23.2)	(34.8)
	Rh^{3+}	(20.4)	(27.0)	(34.0)	(34.6)	(45.5)
d^8	Ni^{2+}	7.5	8.5	10.8	11.5	

*Values are in multiples of 1000 cm^{-1}; entries in parentheses are for low-spin complexes.
Source: H.B. Gray, *Electrons and chemical bonding.* Benjamin, Menlo Park (1965).

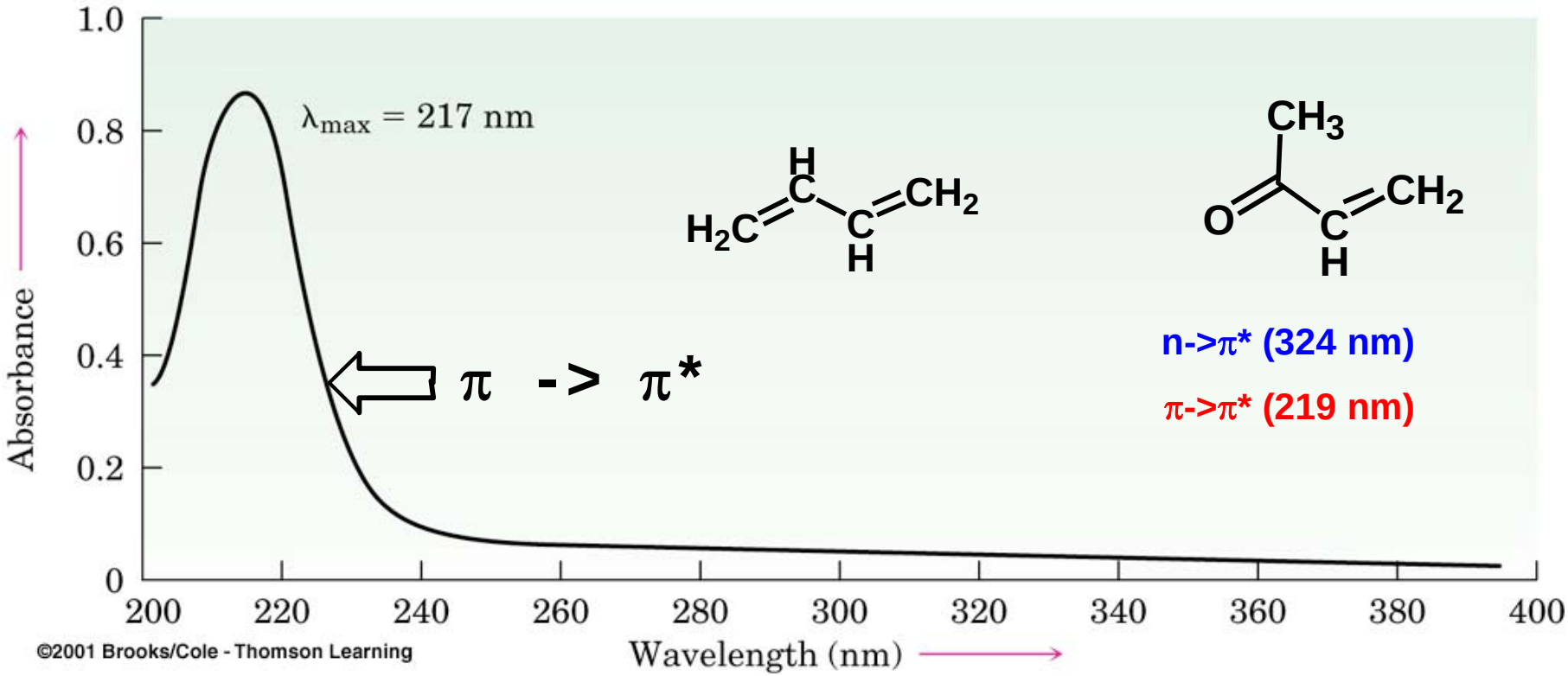
d-d transitions

- **Δ value dependent upon ligand field strength**
  - $Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O$ $< SCN^- < NH_3 < en < NO_2^- < CN^-$
  - Δ increases with increasing field strength
- **Δ increases with increasing charge on TM**
- **Δ increases with 2 and 3rd row TM**

Electron transitions



Chromophore - part of a molecule that absorbs UV/Vis light



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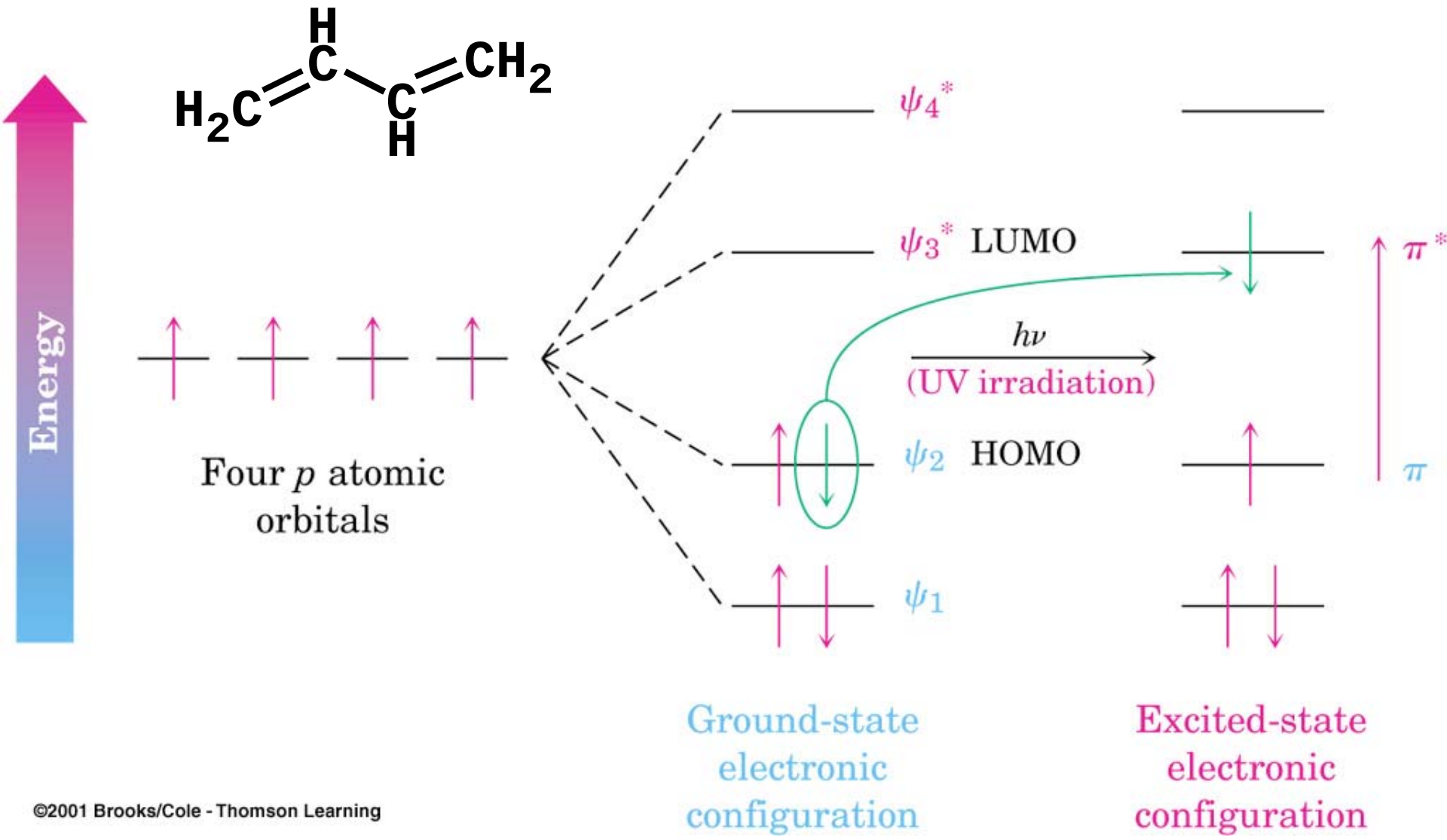
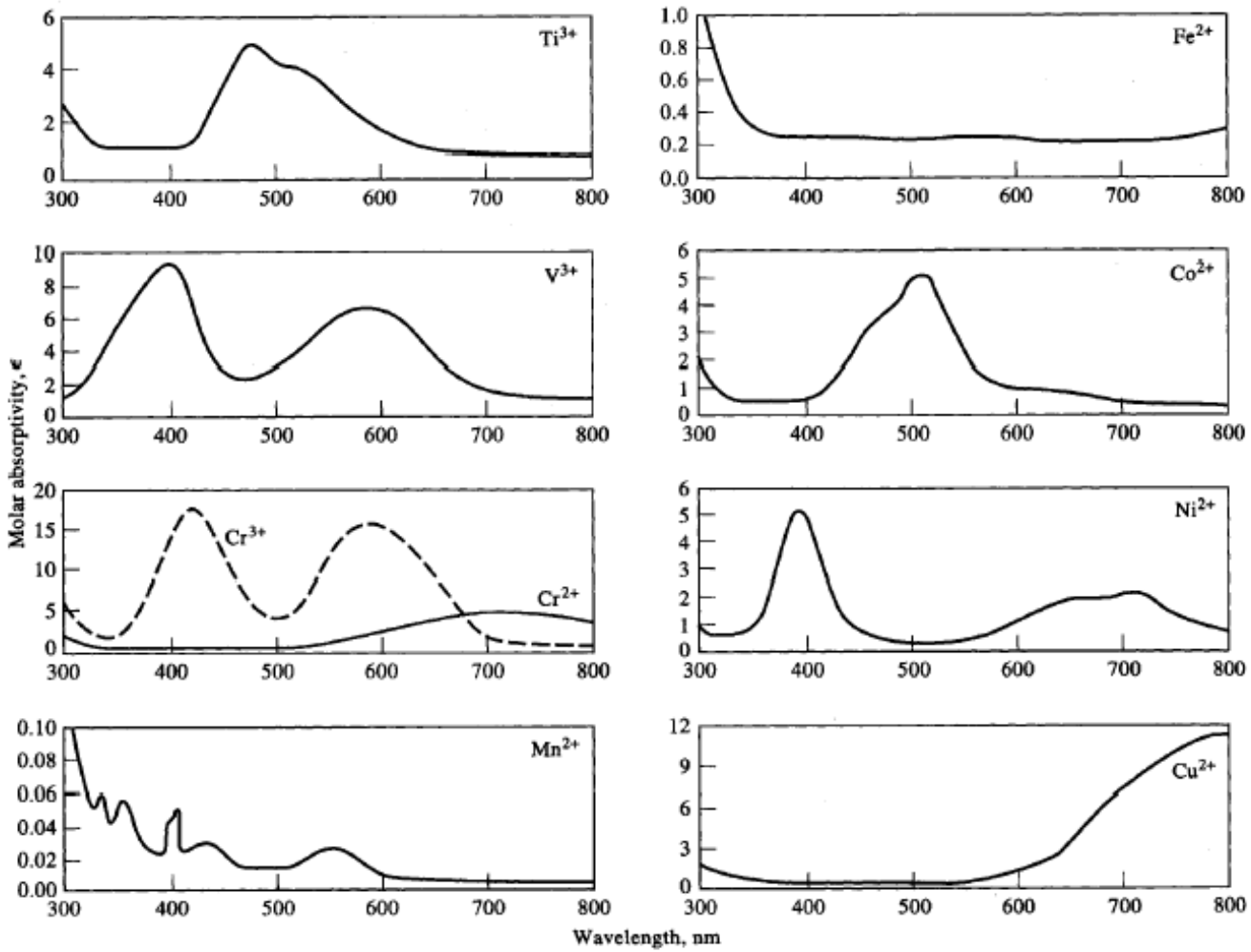


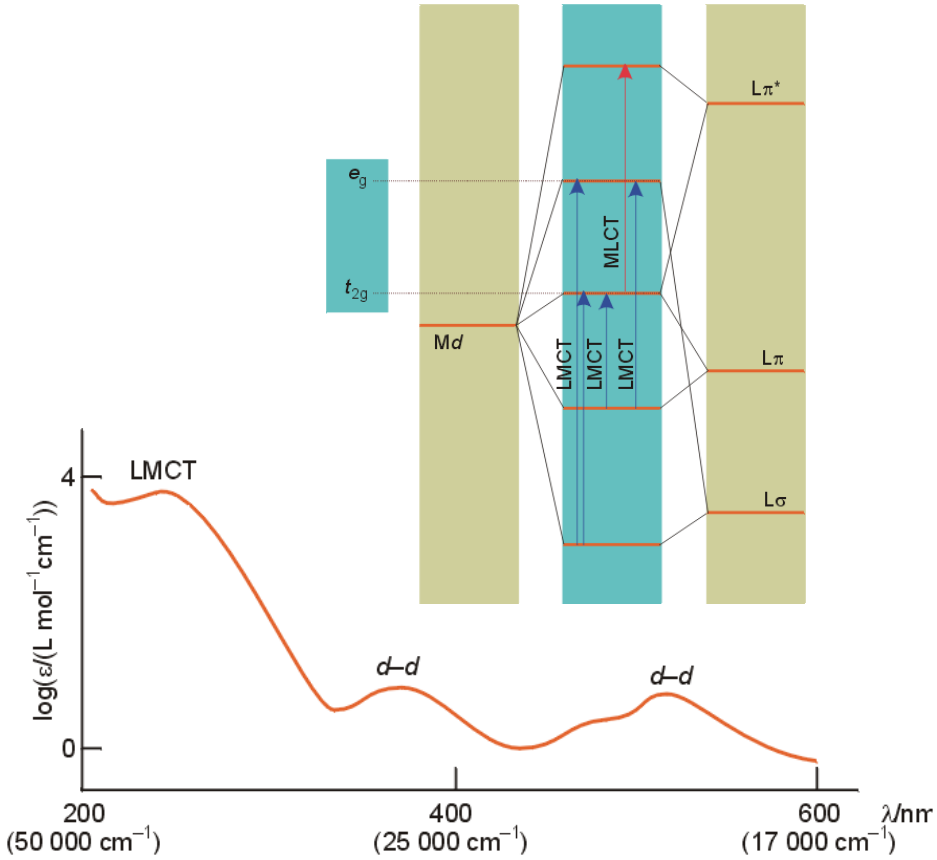
d-d transitions

- 3d and 4d 1st and 2nd transition metal series
- Broad transitions; small molar absorptivity coefficients (these transitions are formally “forbidden”)



Charge transfer bands

- High energy absorbance
  - Energy greater than d-d transition
    - Electron moves between orbitals
      - Metal to ligand
      - Ligand to metal
    - Sensitive to solvent
- LMCT
  - High oxidation state metal ion
  - Lone pair ligand donor
- MLCT
  - Low lying pi, aromatic
  - Low oxidation state metal
    - High d orbital energy



Metal-based UV-vis terms

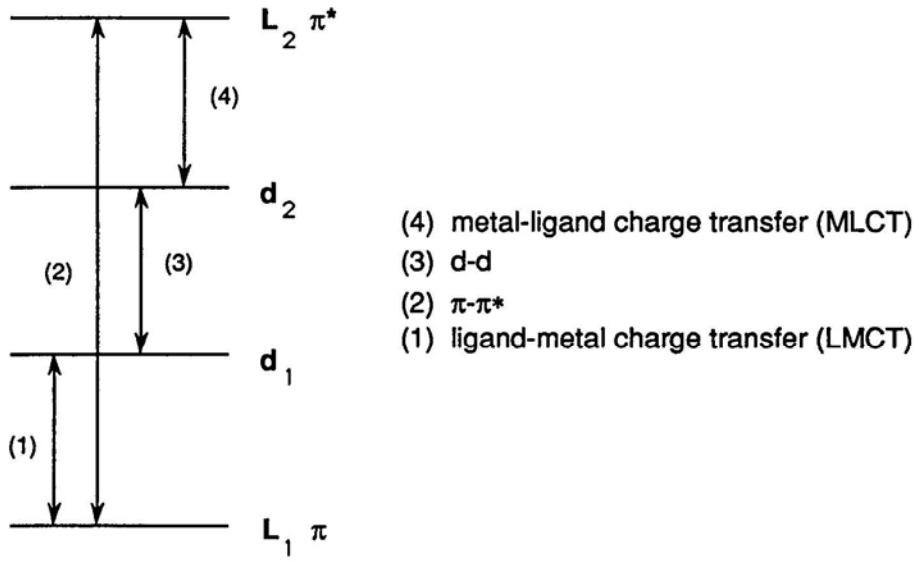


Figure 2.4 Electronic transitions commonly observed in metal complexes. Only *d*–*d* absorption bands are formally symmetry forbidden. The symbols d_1, d_2, L_1, and L_2 represent metal centered *d*-orbitals and ligand π-orbitals, respectively. Typical extinction coefficients are noted in Table 2.1.

Table 2.1 Summary of Extinction Coefficients for Metal and Ligand Transitions in First-Row Transition Metal Complexes

	Type of Electronic Transition	ε (M^{-1} cm^{-1})
Ligand	MLCT, LMCT, π–π*	$10^3 - 10^4$
Metal (*d*–*d*)	Tetrahedral (allowed)	10^2-10^3
	Octahedral (forbidden)	$(M^{2+}) \sim 10$, $(M^{3+}) \sim 50$
	Spin forbidden[a]	$10^{-3} - 10^{-2}$

[a] Common examples include high-spin Mn^{2+} (d^5), high-spin Fe^{3+} (d^5), low-spin Co^{3+} (d^6).

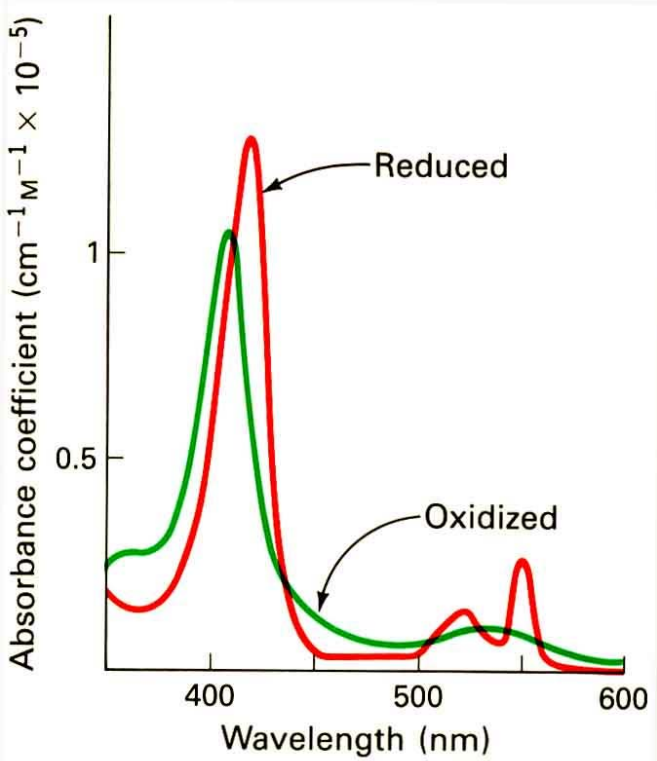
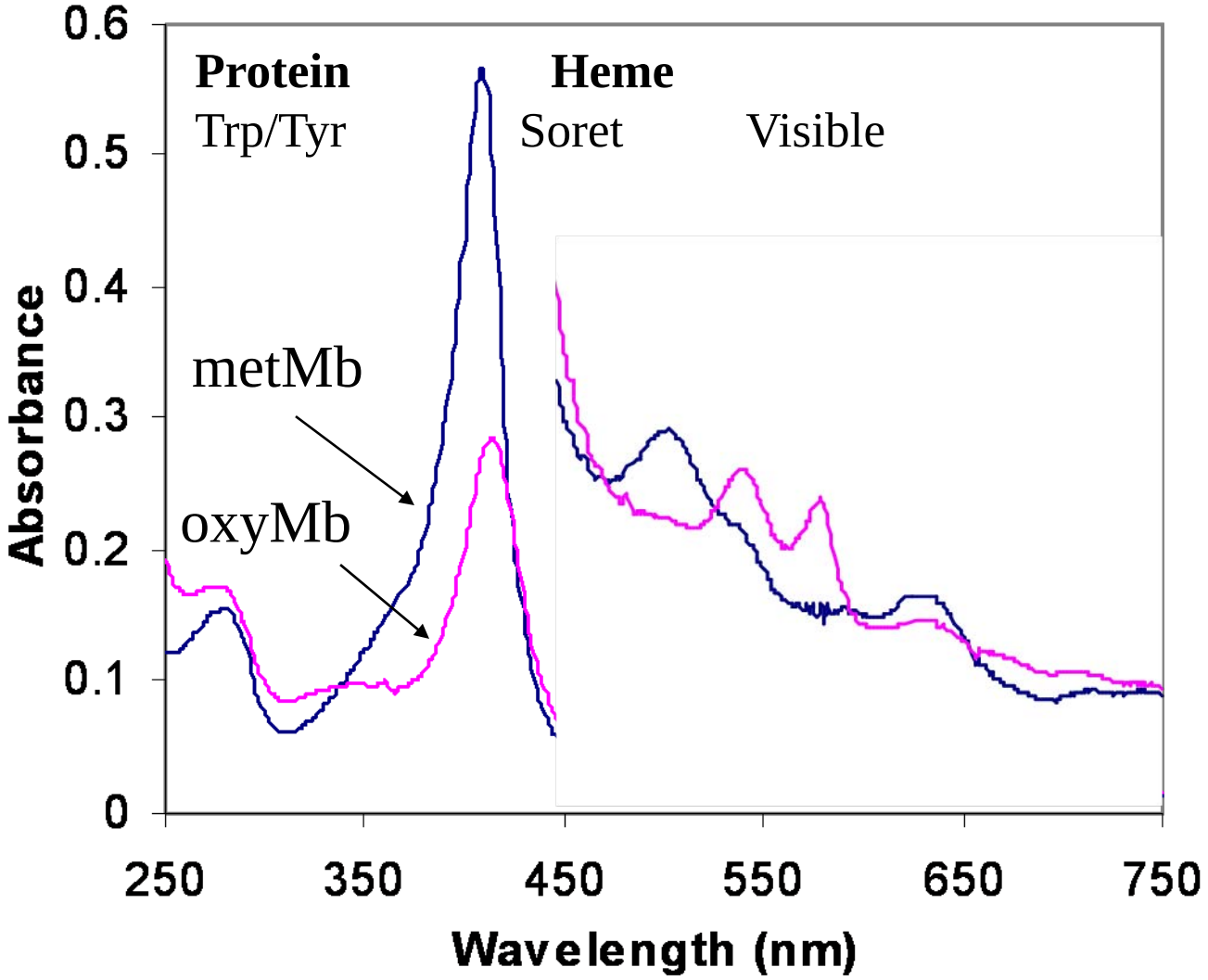
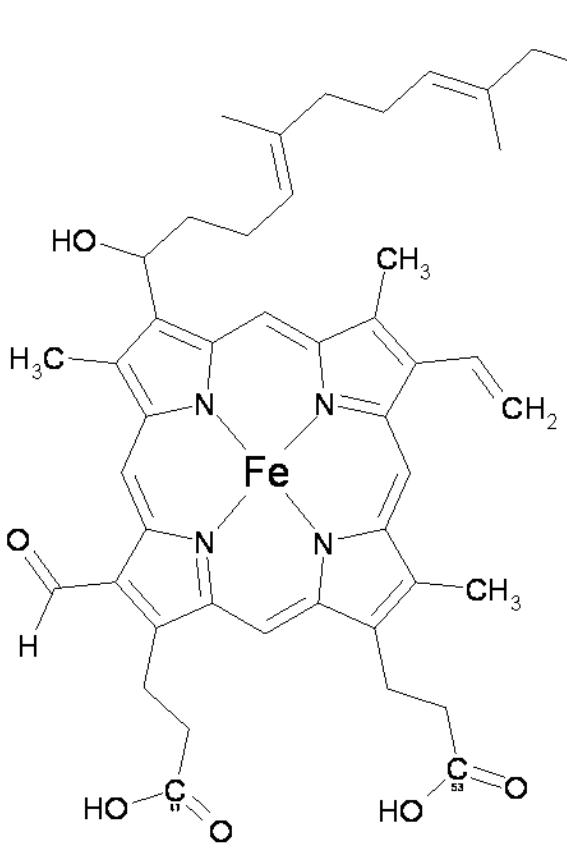


Figure 17-22
Absorption spectra of the oxidized and reduced forms of cytochrome *c*.

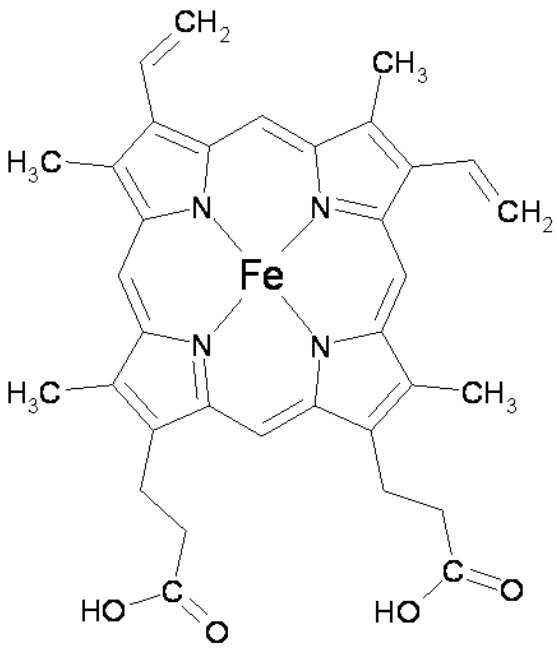
UV-vis Spectral Characteristics of Heme Proteins



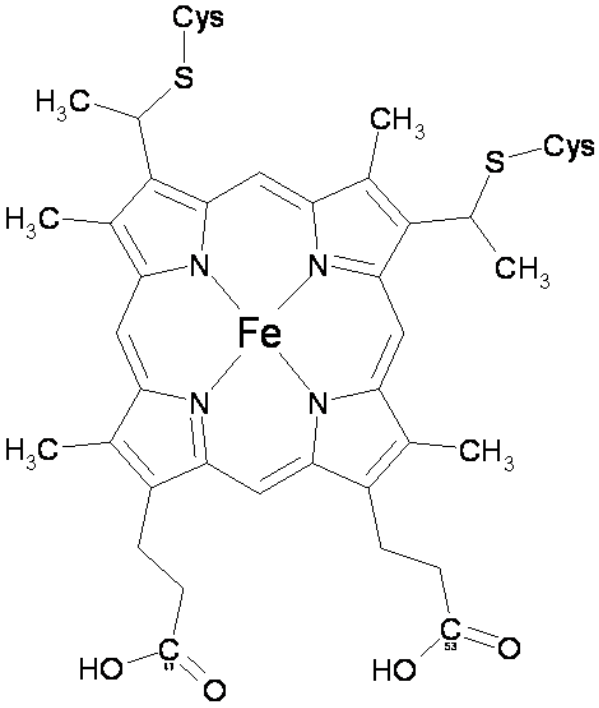
Different types of hemes



heme a



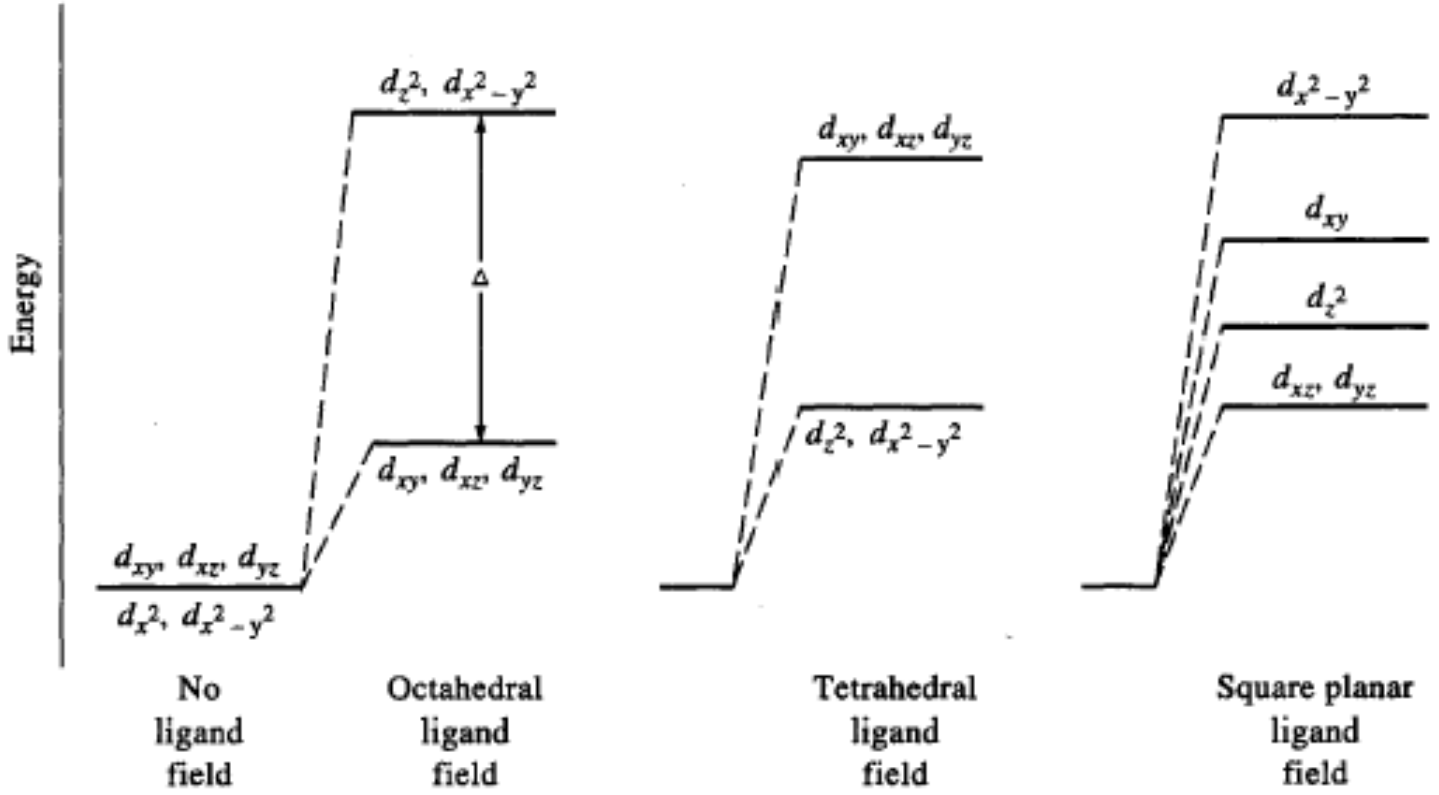
heme b



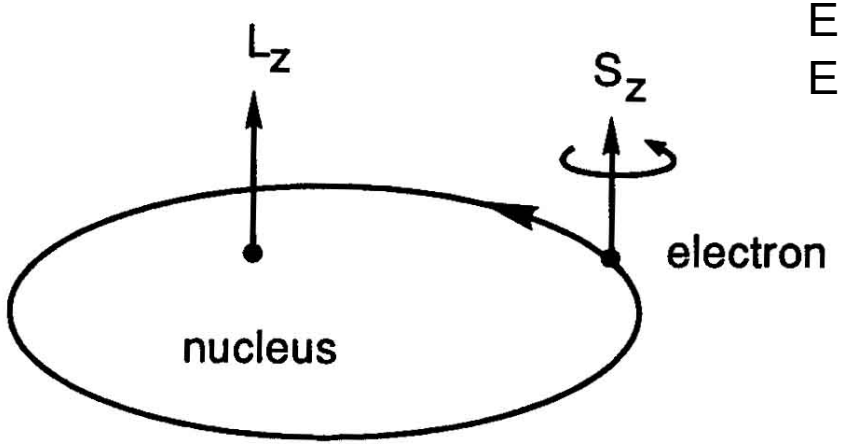
heme c

d -d transitions

- Binding ligands on axis has greater effect on



Electron Paramagnetic Resonance (EPR)

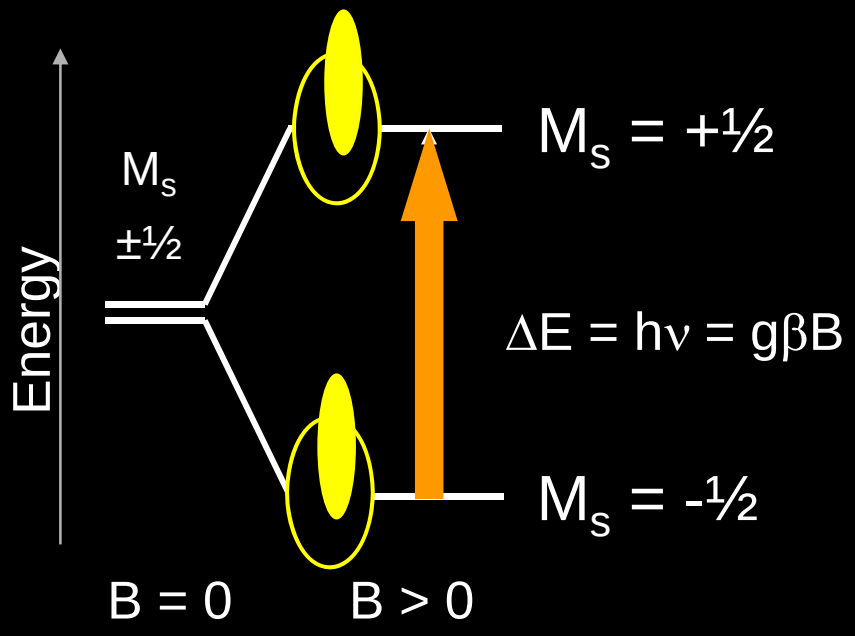


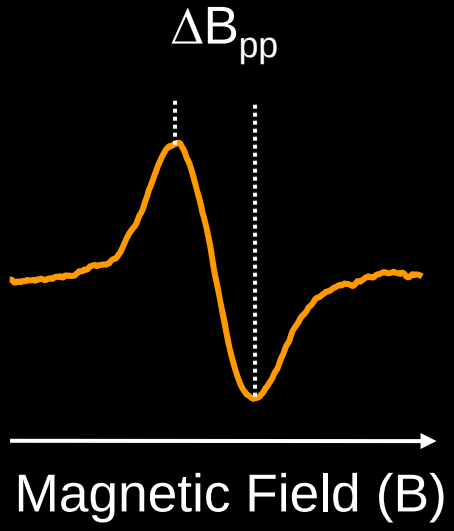
Electron Spin Resonance (ESR)
Electron Magnetic Resonance (EMR)
EPR ~ ESR ~ EMR

Molecules with one or more unpaired electron

- Quantum mechanics: unpaired electrons have spin and charge and hence magnetic moment
- Electronic spin can be in either of two directions (formally *up* or *down*)
- The two spin states under normal conditions are energetically degenerate
- Energy degeneracy lost when exposed to an external magnetic field

www.healthcare.uiowa.edu/research/sfrbm/Papers/Sunrise%20Papers/Workshop%20Papers/2005/Gunther%202005.ppt
www.mcw.edu/FileLibrary/Groups/FreeRadicalResearchCenter/otherfile/EPRBasics.ppt





- h Planck's constant 6.626196 x 10^{-27} erg.sec
- ν frequency (GHz or MHz)
- g g-factor (approximately 2.0)
- β Bohr magneton (9.2741 x 10^{-21} erg.Gauss^{-1})
- B magnetic field (Gauss or mT)

$h\nu = g\beta B$

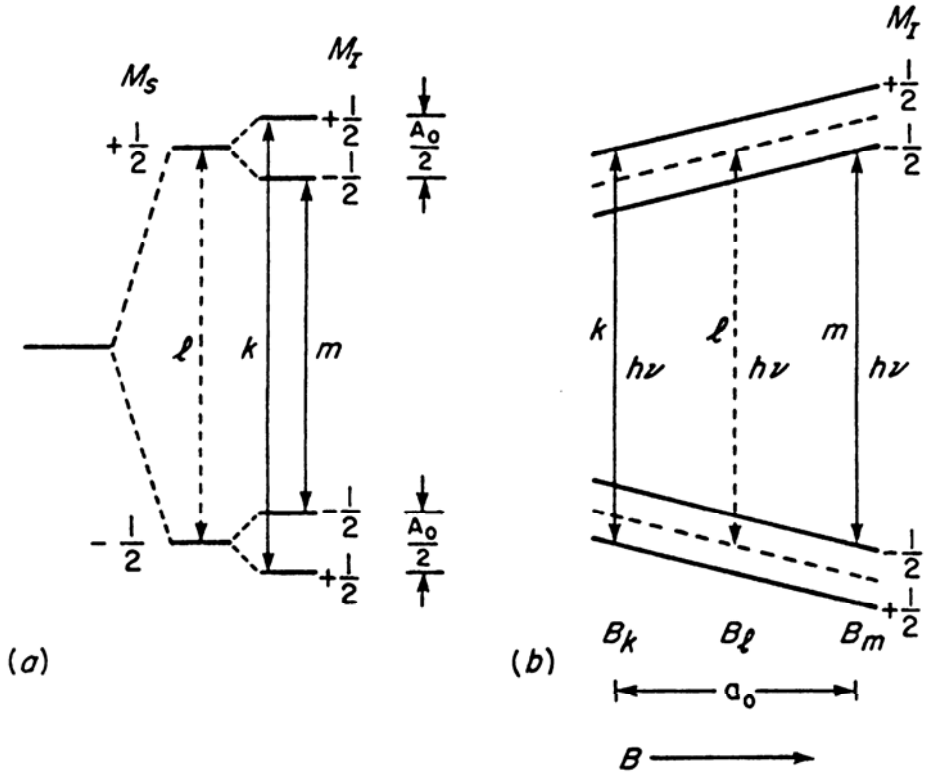
$\nu = (g\beta/h)B = 2.8024 \times B$ MHz

for B = 3480 G ν = 9.75 GHz (X-band)
for B = 420 G ν = 1.2 GHz (L-band)
for B = 110 G ν = 300 MHz (Radiofrequency)

EPR is the resonant absorption of microwave radiation by paramagnetic systems in the presence of an applied magnetic field

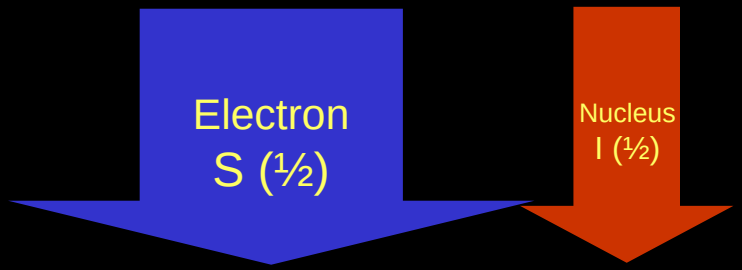
The hyperfine effect

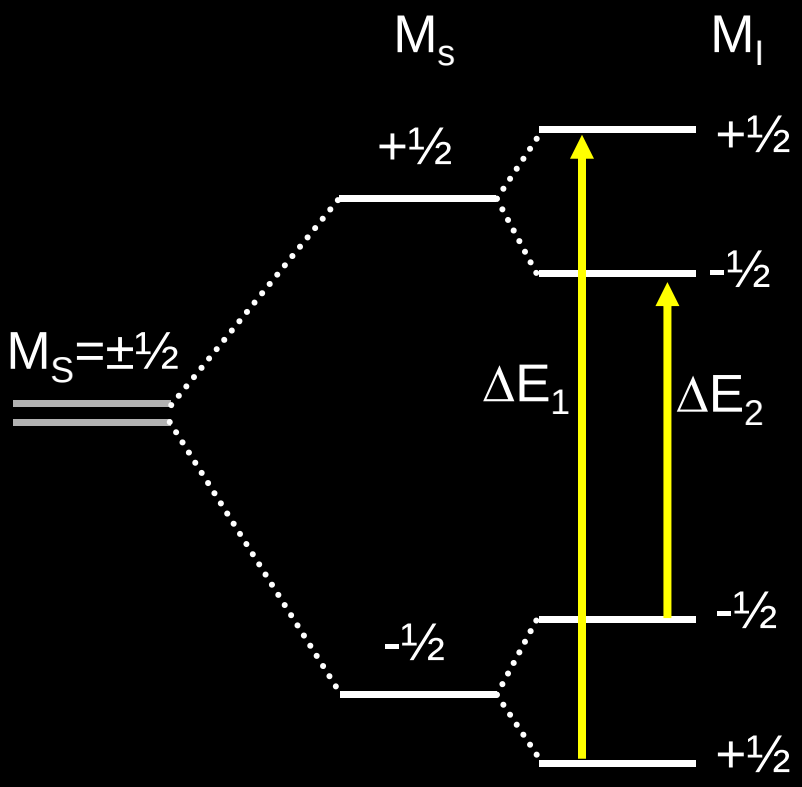
- The magnetic field experienced by the unpaired electron is affected by nearby nuclei with non-zero nuclear spin

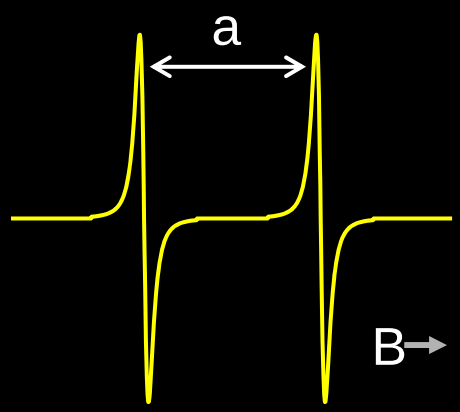


Weil, Bolton, and Wertz, 1994, “Electron Paramagnetic Resonance”, New York: Wiley Interscience.

Hyperfine Coupling







"doublet"

$E = g\beta BS_z + (hA_0)S_zI_z$

$E = g\beta BS_z + (a)S_zI_z$

(hA_0 (Hz) -> a (G) via g-factor)

Selection Rule

$\Delta M_S = \pm 1$ (electron)

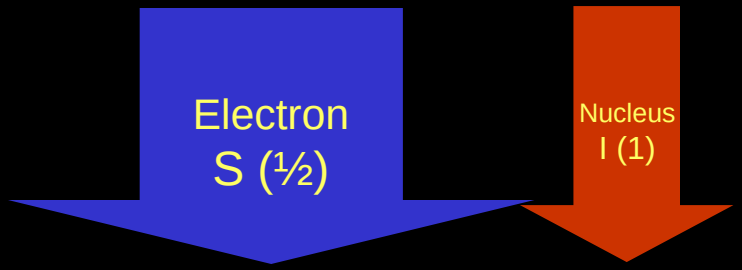
$\Delta M_I = 0$ (nuclear)

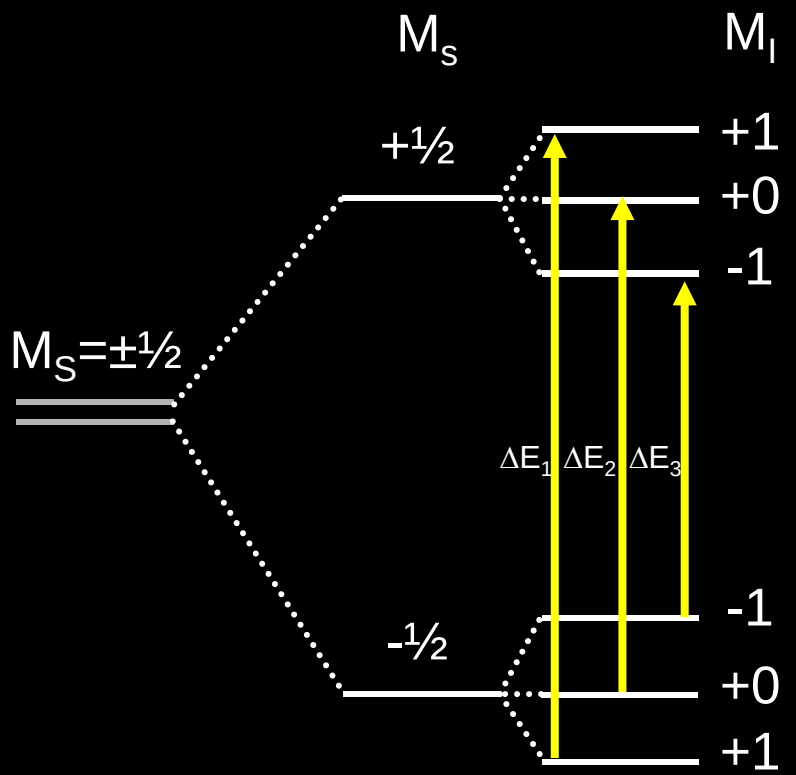
$\Delta E_1 = g\beta B + a/2$

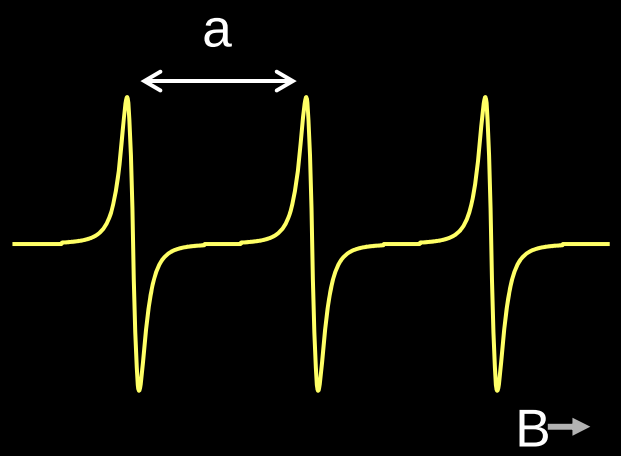
$\Delta E_2 = g\beta B - a/2$

$\Delta E_1 - \Delta E_2 = a$

Hyperfine Coupling





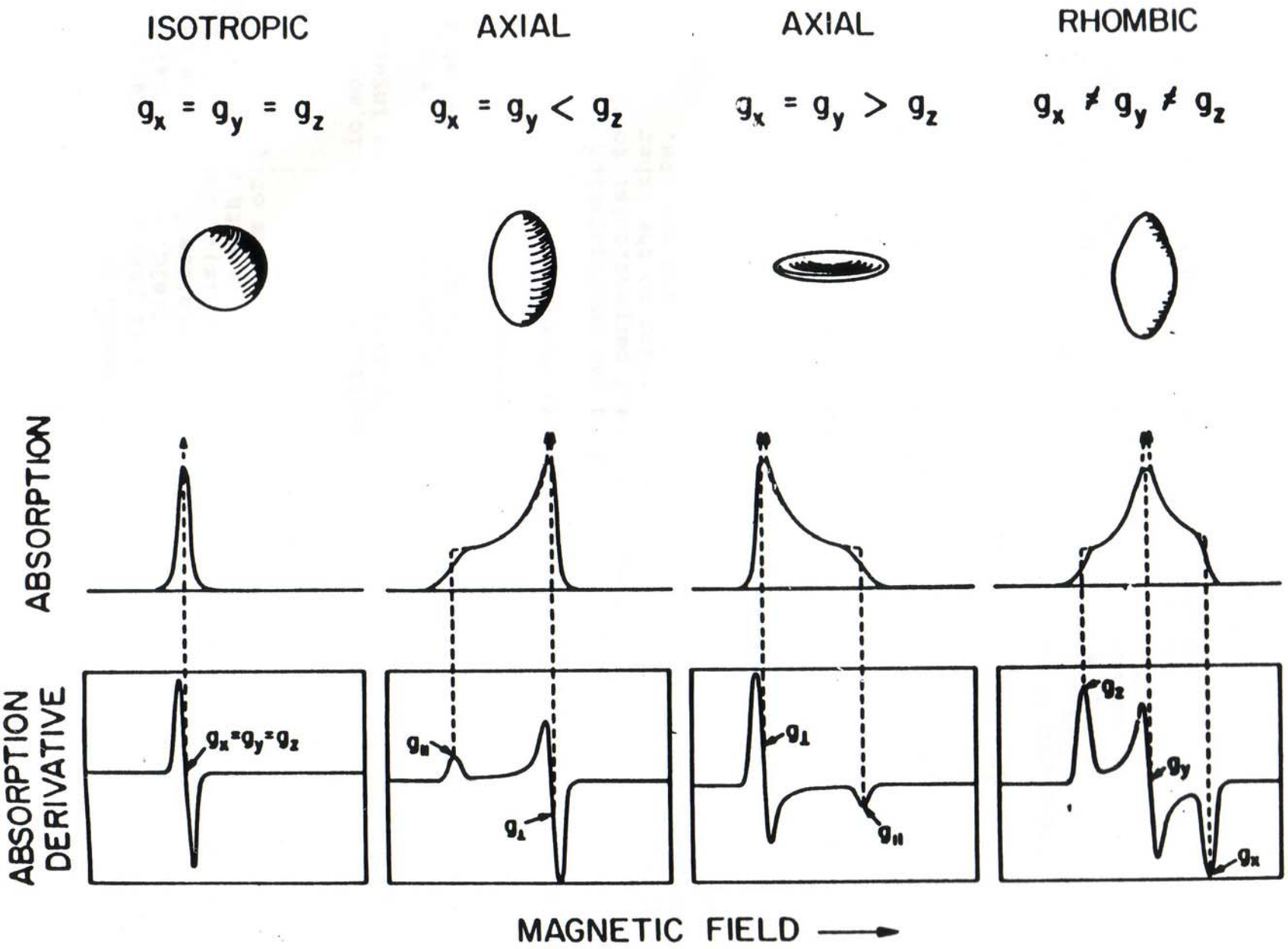


"triplet"

$E = g\beta BS_z + (hA_0)S_zI_z$
$E = g\beta BS_z + (a)S_zI_z$
(hA_0 (Hz) -> a (G) via g-factor)

Selection Rule
$\Delta M_S = \pm 1$ (electron)
$\Delta M_I = 0$ (nuclear)

$\Delta E_1 = g\beta B + a$
$\Delta E_2 = g\beta B$
$\Delta E_3 = g\beta B - a$


ISOTROPIC
AXIAL
AXIAL
RHOMBIC
$g_x = g_y = g_z$
$g_x = g_y < g_z$
$g_x = g_y > g_z$
$g_x \neq g_y \neq g_z$
ABSORPTION
ABSORPTION DERIVATIVE
$g_x = g_y = g_z$
$g_{\parallel}$
$g_{\perp}$
$g_{\perp}$
$g_{\parallel}$
g_z
g_y
g_x
MAGNETIC FIELD

EPR

Table 2.3 Spin States for Transition Metal Ions Commonly Studied by EPR

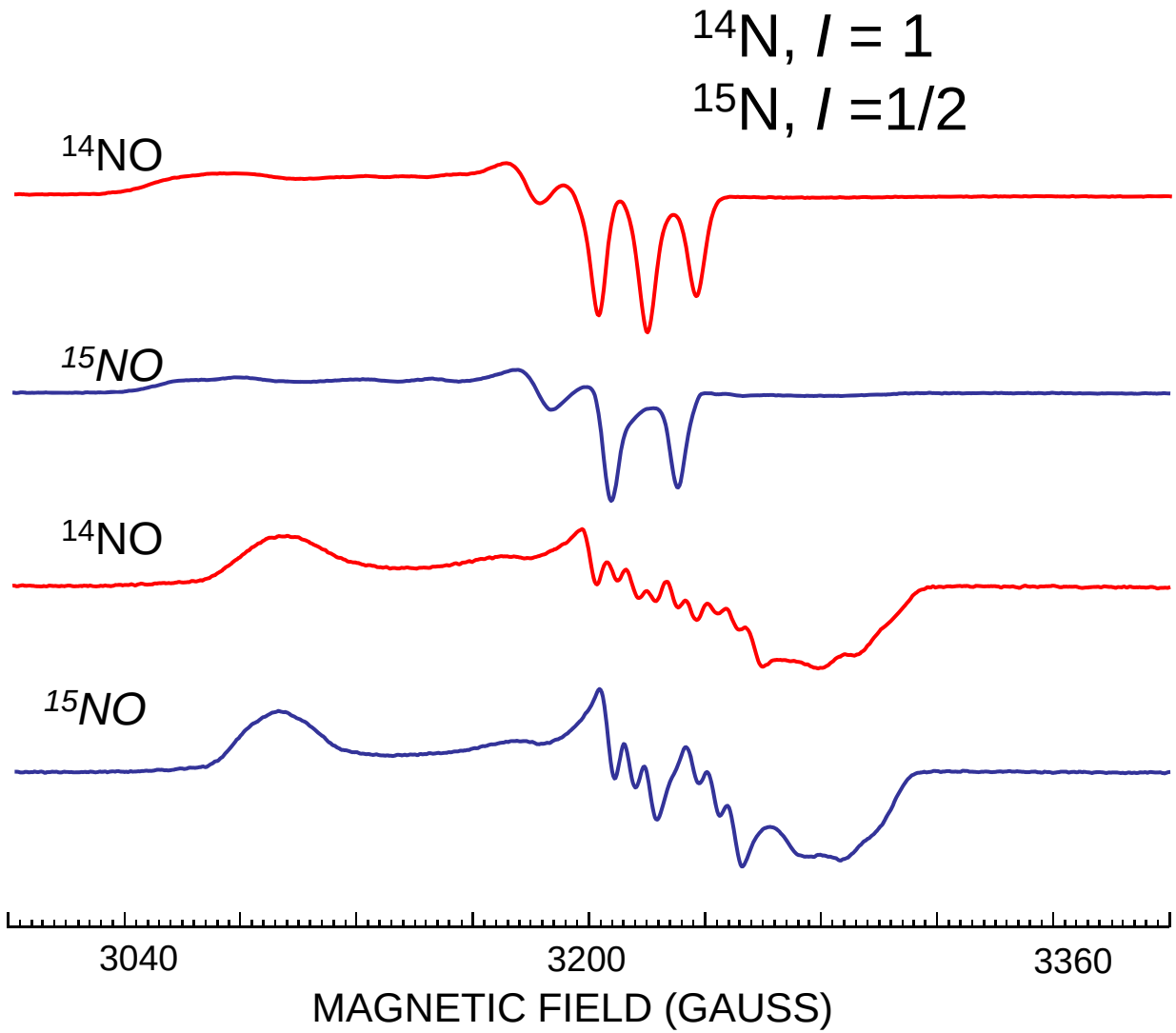
Ion	d^n	Spin (S)
Mo^{5+}	$4d^1$	$\frac{1}{2}$
Fe^{3+}	$3d^5$	$\frac{5}{2}$ (high spin), $\frac{1}{2}$ (low spin)
		$\frac{3}{2}$ (intermediate)
Mn^{2+}	$3d^5$	$\frac{5}{2}$ (high spin)
Fe^{2+}	$3d^6$	2 (high spin), 0 (low spin)
Co^{2+}	$3d^7$	$\frac{3}{2}$ (high spin), $\frac{1}{2}$ (low spin)
Cu^{2+}	$3d^9$	$\frac{1}{2}$

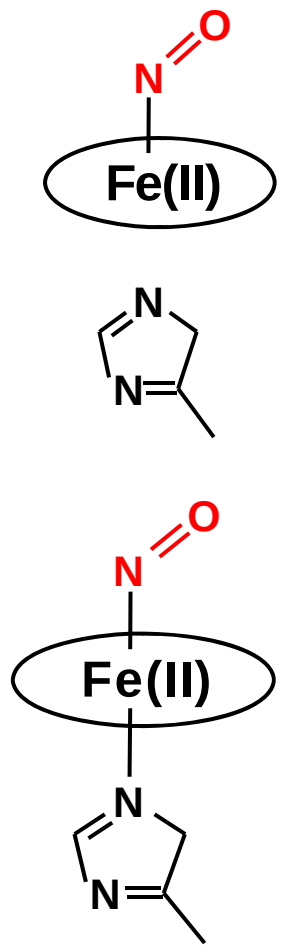
Ferromagnetic coupling: $S = S_1 + S_2$

Antiferromagnetic coupling: $S = S_1 - S_2$

Which one is EPR active: Fe(III)-NO or Fe(II)-NO?

EPR Spectra of Ferrous Porphyrin-Fe-NO

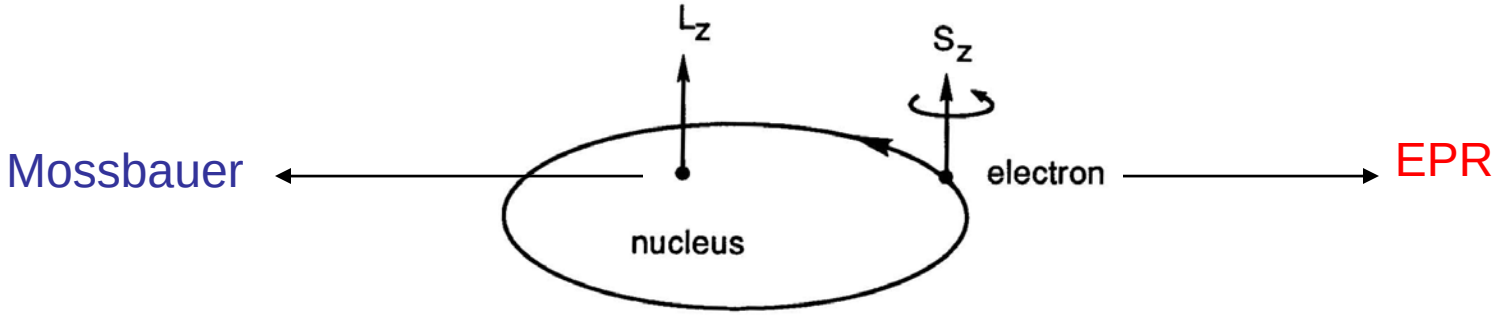




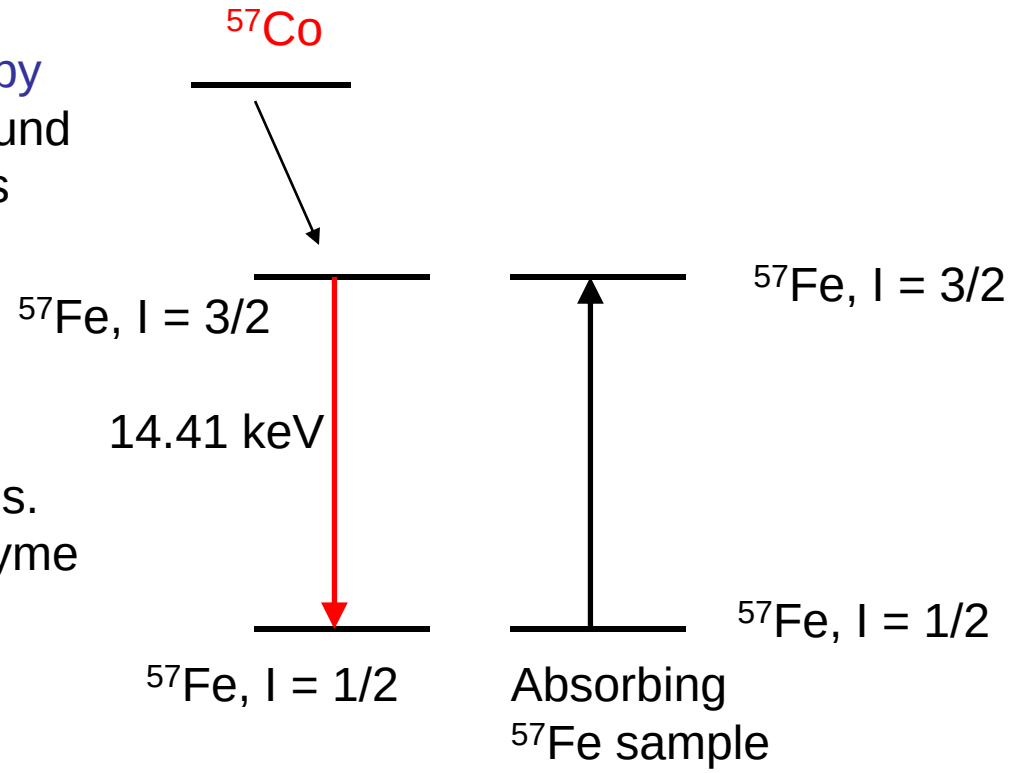
6 Coord.

Zhao, X.; Yeung, N.; Russell, B.S.; Garner, D.K.; Lu, Y. *J. Am. Chem. Soc.*, *126*, 6766-6767 (2006).

Mössbauer Spectroscopy (Nuclear Gamma Ray Resonace)



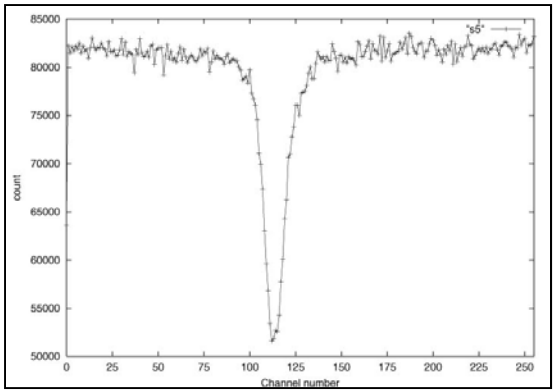
Mossbauer: a nuclear phenomena involves the absorption of photons by nuclei, causing transitions from ground nuclear spin states to excited states (e.g. I = ½ to I = 3/2 in ^{57}Fe)



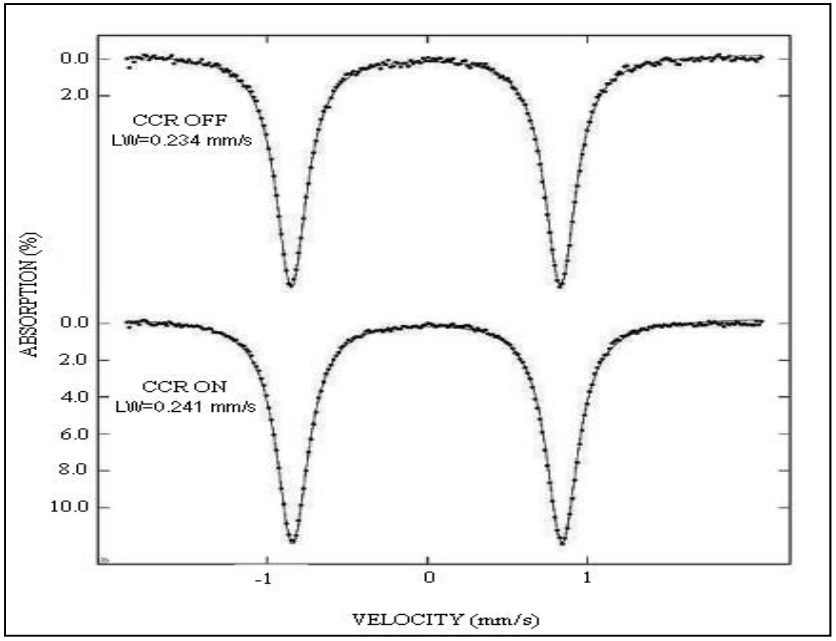
Utility:

- the oxidation states, coordination environments, spin states of iron ions.
- number of irons in a cluster or enzyme
- spin coupling phenomena in iron clusters

Isomer shift (δ, mm/s):
the energy of actual transition minus the energy at 0 mm/s;
reflects the magnitude of the electron density at the nucleus
Determined by
-oxidation state of the iron
-nature of the iron-ligand bonds
-the coordination number about the iron ion
e.g. $Fe^{2+}(SR)_4$, δ = 0.7 mm/s; $Fe^{3+}(SR)_4$, δ = 0.3 mm/s



Quadrupole splitting (ΔE_Q): the electric field gradient (EFG)
-the electrons about the nucleus, thus indirectly about the oxidation state of the Fe
-the ligand field about the nucleus



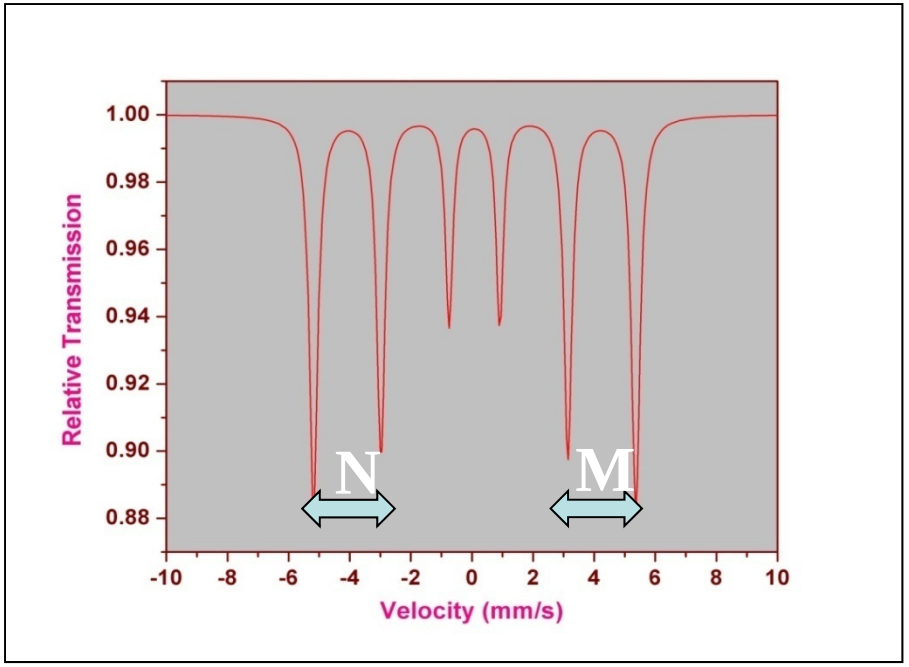
For high spin Fe(II) and Fe(III), which one has bigger ΔE_Q?

Typical ΔE_Q: for Fe(II) is 3 mm/s, for Fe(III) is 0.3 mm/s

Nuclear Zeeman Interaction:
the nuclear spin can interact with a magnetic field, like that of electron spin in EPR

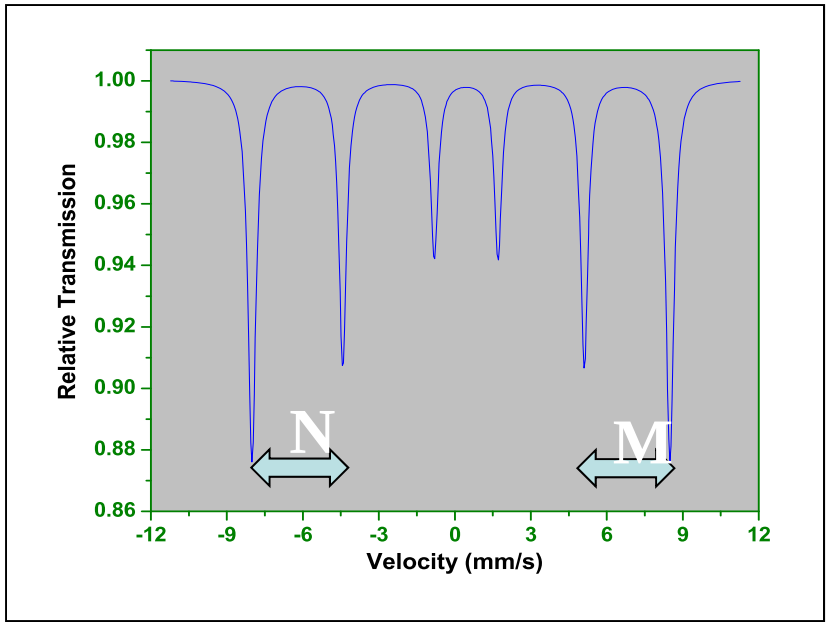
Sextet with cubic symmetry: No EFG

$$N - M = 0$$

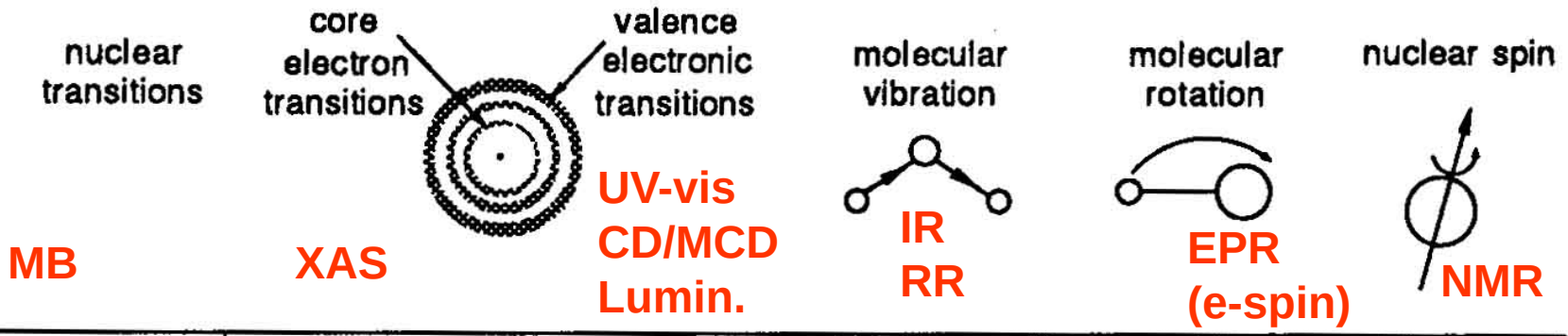


Sextet without cubic symmetry: Presence of EFG

$$N - M \neq 0$$



Spectrum of Electromagnetic Radiation



γ-ray	x-ray	uv	visible	IR	microwave	radio
λ(m) 10^{-12}—10^{-10}	10^{-10}—10^{-8}	10^{-8}—10^{-6}		10^{-6}—10^{-4}	10^{-4}—10^{-2}	10^{-2}—10^{2}
ν(Hz) 10^{18}—10^{20}	10^{16}—10^{18}	10^{14}—10^{16}		10^{12}—10^{14}	10^{10}—10^{12}	10^{6}—10^{10}
E(J) 10^{9}—10^{11}	10^{7}—10^{8}	10^{5}—10^{6}		10^{4}—10^{5}	10^{2}—10^{4}	10^{-3}—10^{2}

Figure 2.2 Spectrum of electromagnetic radiation. The boundaries between domains are not sharp, and each region is not shown to scale. The visible domain actually forms an extremely small part (~350–750 nm) of the electromagnetic spectrum.

UV-Visible Spectroscopy

- Absorption of UV-vis results in transitions of electrons from a lower energy occupied MO to a higher energy unoccupied MO
- Widely used method for identification of inorganic and organic species

- Electronic transitions
  - π, σ, and n electrons
  - d and f electrons
  - Charge transfer reactions
- π, σ, and n (non-bonding) electrons