

Chapter 14. Electronic Spectroscopy

Molecular term symbols

$${}^{2S+1}\Lambda_{\text{parity}}^{\text{reflection}}$$

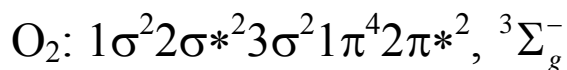
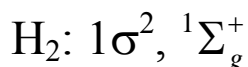
For linear molecules:

$$M_L = \sum_i m_{li}, \quad \Lambda = |M_L|,$$
$$M_S = \sum_i m_{si}, \quad S = |M_S|,$$

Λ : 0, 1, 2, ...

Symbol: Σ , Π , Δ , ...

Example:



Ground state is labeled as X , excited states are labeled by A, B, C , etc. for the same spin, and a, b, c , etc for different spins.

Electronic transitions

Selection rules:

$$\Delta\Lambda = 0, \pm 1, \quad \Delta S = 0$$

Franck-Condon principle: Nuclear positions and momenta do not change during electronic transition (because $m_n \gg m_e$).

Intensity:

$$I \propto |\mu_{fi}|^2 = \left| \int \Psi_f^*(-e\vec{r})\Psi_i d\tau \right|^2$$

Separation of motion (B-O approx.):

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi^{(e)}(\mathbf{r})\Phi^{(n)}(\mathbf{R})$$

So

$$\mu_{fi} = \int \Phi_f^{(e)*}(\mathbf{r})(-e\vec{r})\Phi_i^{(e)}(\mathbf{r})d\tau_e \int \Phi_f^{(n)*}(\mathbf{R})\Phi_i^{(n)}(\mathbf{R})d\tau_n$$

1st term determines intensity.

2nd term (Franck-Condon factor) determines vibrational structure.

Commonly seen transitions

Chromophore: functional group responsible for transition.

A. d-d transitions:

Transition metal compounds

d orbitals are not degenerate and can split into two groups, e.g. t_{2g} and e_g .

B. Charge-transfer transitions:

Transfer of e^- from ligands to *d* orbitals of metal.
Strong intensities.

MnO_4^-

C. $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions

Transitions from a bonding π orbital or a non-bonding *n* orbital to an anti-bonding π^* orbital.

$C=O$, $C=C$

Fate of excited states

Fluorescence and phosphorescence

Fluorescence: spontaneous emission immediately after absorption (0.1-1 ps).

Three steps:

- A. Absorption to excited state
- B. Radiationless decay (collisional energy transfer).
- C. Vertical transition to ground state

Phosphorescence: spontaneous emission after intersystem crossing (0.1-1 s).

Five steps:

- A. Absorption to excited state
- B. Radiationless decay
- C. Transition from excited singlet state to triplet state
- D. Radiationless decay
- E. Weak transition to ground state (spin-forbidden)

Dissociation:

- A. Transition to an excited state
- B. Above dissociation limit
- C. Via curve-crossing (predissociation)

Internal conversion:

- A. Transition to an excited singlet state.
- B. Radiationless decay
- C. Population transfer to ground singlet state (internal conversion).

Photoelectron spectroscopy (UPS and XPS)

Electrons in molecules can be ejected by photon.

$$h\nu = \frac{1}{2}m_e v^2 + I_i$$

Binding energy of e⁻ in molecule can be obtained from kinetic energy of free e⁻.

Ultraviolet photoelectron spectroscopy (UPS): eject valence electrons, used for identify MO energies

X-ray photoelectron spectroscopy (XPS): eject core electrons, mainly used in chemical analysis.