

Lecture 38 — Electronic Transitions & the Franck-Condon Principle

Reading: Engel 4th ed., Chapter 14 (Sections 14.1–14.4)

Learning Objectives

- Classify electronic transitions ($\sigma \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, etc.)
 - Apply symmetry selection rules to predict allowed electronic transitions
 - State the Franck-Condon principle and explain its physical basis
 - Interpret UV-Vis absorption spectra including band shapes and vibrational fine structure
 - Relate absorption wavelength to molecular structure (chromophores)
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1. Types of Electronic Transitions

When a molecule absorbs UV or visible light, an electron is promoted from an occupied MO to an unoccupied MO:

Transition	Energy	Wavelength	Example
$\sigma \rightarrow \sigma^*$	Very high	< 150 nm (vacuum UV)	C–C, C–H bonds
$n \rightarrow \sigma^*$	High	150–250 nm	Alcohols, amines
$\pi \rightarrow \pi^*$	Moderate	200–500 nm	Alkenes, aromatics
$n \rightarrow \pi^*$	Low	250–600 nm	Carbonyls, azo compounds

Chromophores

A **chromophore** is the functional group responsible for UV-Vis absorption:

Chromophore	Transition	λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
C=C	$\pi \rightarrow \pi^*$	170	15,000

Chromophore	Transition	λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
C=O (aldehyde)	$n \rightarrow \pi^*$	290	10
C=O (aldehyde)	$\pi \rightarrow \pi^*$	180	10,000
Benzene	$\pi \rightarrow \pi^*$	254	200
Conjugated diene	$\pi \rightarrow \pi^*$	217	21,000

[!NOTE] **Concept Check 38.1** Which electronic transition typically requires the highest energy (shortest wavelength): $\sigma \rightarrow \sigma^*$ or $n \rightarrow \pi^*$? Briefly explain why based on the types of orbitals involved.

2. Selection Rules for Electronic Transitions

Symmetry Selection Rule

A transition from state Ψ_i to Ψ_f is allowed if the transition dipole moment is nonzero:

$$\vec{\mu}_{fi} = \langle \Psi_f | \hat{\mu} | \Psi_i \rangle \neq 0$$

This requires:

$$\Gamma_f \otimes \Gamma_\mu \otimes \Gamma_i \supseteq A_1 \text{ (totally symmetric)}$$

Spin Selection Rule

$$\Delta S = 0$$

Singlet \rightarrow triplet (or vice versa) transitions are **spin-forbidden**. They occur only weakly via spin-orbit coupling.

Orbital Symmetry (Laporte Rule)

For centrosymmetric molecules: only $g \rightarrow u$ or $u \rightarrow g$ transitions are allowed.

This means $d \rightarrow d$ transitions in octahedral complexes are (strictly) Laporte-forbidden — they gain intensity through vibronic coupling (vibrations that temporarily remove the inversion center).

3. The Franck-Condon Principle

Statement

Electronic transitions occur so rapidly ($\sim 10^{-15}$ s) compared to nuclear motion ($\sim 10^{-13}$ s) that the nuclear positions and momenta are essentially unchanged during the transition.

This is the **vertical transition** approximation — on an energy diagram, the transition is represented as a vertical arrow.

Consequences

1. The molecule is promoted to a vibrational level of the excited electronic state that has the **maximum overlap** with the ground vibrational wavefunction
2. The transition probability is proportional to the **Franck-Condon factor**:

$$\text{FC factor} = |\langle \chi_{v'}^{\text{excited}} | \chi_{v''}^{\text{ground}} \rangle|^2$$

3. If the excited-state equilibrium geometry is similar to the ground state: $v'' = 0 \rightarrow v' = 0$ is strongest (narrow band)
4. If the equilibrium geometries differ significantly: $v'' = 0 \rightarrow v' > 0$ transitions are strong (broad band with vibrational progression)

Vibrational Fine Structure

UV-Vis bands often show vibrational progressions — a series of peaks separated by the excited-state vibrational frequency $\tilde{\nu}'$:

$$\tilde{\nu}_{\text{absorption}} = \tilde{\nu}_{0-0} + v' \tilde{\nu}' \quad (v' = 0, 1, 2, \dots)$$

The $0 - 0$ band corresponds to zero vibrational quanta in both states.

[!NOTE] **Concept Check 38.2** According to the Franck-Condon principle, why are electronic transitions represented as "vertical" lines on a potential energy diagram? What assumption is made about the relative speed of electrons vs. nuclei?

4. Beer-Lambert Law

The absorbance A is related to concentration and path length:

$$A = \epsilon c l = -\log_{10}(I/I_0)$$

Quantity	Units
ϵ (molar absorptivity)	$\text{L mol}^{-1} \text{cm}^{-1}$
c (concentration)	mol L^{-1}
l (path length)	cm

Oscillator Strength

The dimensionless oscillator strength connects to the integrated absorption:

$$f = \frac{4m_e c \ln 10}{N_A e^2} \int \epsilon(\tilde{\nu}) d\tilde{\nu}$$

For fully allowed transitions: $f \sim 0.1\text{--}1.0$ For forbidden transitions: $f \ll 0.01$

5. Effect of Conjugation

Extended conjugation shifts λ_{\max} to longer wavelength (**bathochromic shift or red shift**):

System	λ_{\max} (nm)
Ethylene	170
1,3-Butadiene	217
1,3,5-Hexatriene	258
β -Carotene (11 conjugated C=C)	450 (orange!)

This is exactly the particle-in-a-box / FEMO model from Lecture 13 — longer conjugation = larger "box" = smaller ΔE .

Key Equations Summary

Equation	Expression
Transition dipole	$\vec{\mu}_{fi} = \langle \Psi_f \hat{\mu} \Psi_i \rangle$
Selection rules	$\Delta S = 0; \Gamma_f \otimes \Gamma_\mu \otimes \Gamma_i \supseteq A_1$
Franck-Condon factor	$\ \langle \chi'_v \chi''_{v''} \rangle \ ^2$
Beer-Lambert	$A = \epsilon cl$
FEMO trend	$\lambda_{\max} \propto L^2$ (box length)

Recent Literature Spotlight

"Attosecond Delays in X-Ray Molecular Ionization" *H. J. Wörner, M. Vacher, A. Schneider, et al.*, *Nature*, **2024**, 632, 762–767. [DOI](#)

This experiment used attosecond soft X-ray pulses from a free-electron laser to measure photoionization delays in NO molecules. The observed delays — up to 700 attoseconds — arise from shape resonances and Auger-Meitner electron scattering within the molecular Franck-Condon region. This real-time probe of electronic excitation dynamics directly visualizes the vertical transitions between molecular potential energy surfaces taught in this lecture.

Practice Problems

- 1. Symmetry selection rules.** Using the C_{2v} character table, determine whether the $n \rightarrow \pi^*$ transition in formaldehyde ($A_1 \rightarrow A_2$) is symmetry-allowed. What about the $\pi \rightarrow \pi^*$ transition ($A_1 \rightarrow B_1$)?
- 2. Franck-Condon.** Sketch potential energy curves for a molecule where the excited-state bond is significantly longer than the ground state. On your diagram, show the most probable vertical transition and the resulting vibrational progression in the absorption spectrum.
- 3. Conjugation effect.** Using the FEMO model, predict the ratio $\lambda_{\max}(\text{hexatriene})/\lambda_{\max}(\text{butadiene})$. Compare with the experimental values above.

Next lecture: Fluorescence, Phosphorescence & Photochemistry