

# 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)

## 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	$\lambda_{\max}$ (nm)	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )
C=C	$\pi \rightarrow \pi^*$	170	15,000

Chromophore	Transition	$\lambda_{\text{max}}$ (nm)	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )
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  $\Psi_i$  to  $\Psi_f$  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

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#### 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

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The absorbance  $A$  is related to concentration and path length:

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

Quantity	Units
$\epsilon$ (molar absorptivity)	$\text{L mol}^{-1} \text{cm}^{-1}$
$c$ (concentration)	$\text{mol L}^{-1}$
$l$ (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:  $f \ll 0.01$

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## 5. Effect of Conjugation

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

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

This is exactly the particle-in-a-box / FMO model from Lecture 13 — longer conjugation = larger "box" = smaller  $\Delta E$ .

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## Key Equations Summary

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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

- 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 ( $A_1 \rightarrow B_1$ )?
- 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.
- 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*