

SPECTROSCOPY

Presented By

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Electronic Spectroscopy

- Ultraviolet (UV) and visible (vis) spectroscopy:
- This is the earliest method of molecular spectroscopy.
- A phenomenon of interaction of molecules with UV and visible lights.
- Absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state to higher electronic states.

UV and Visible Spectroscopy

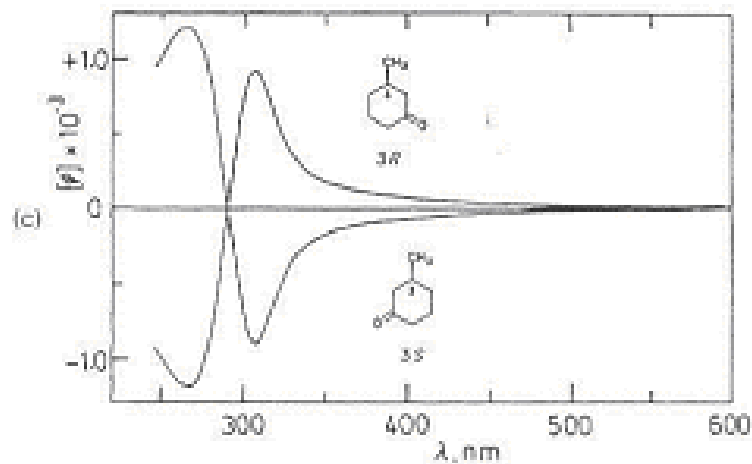
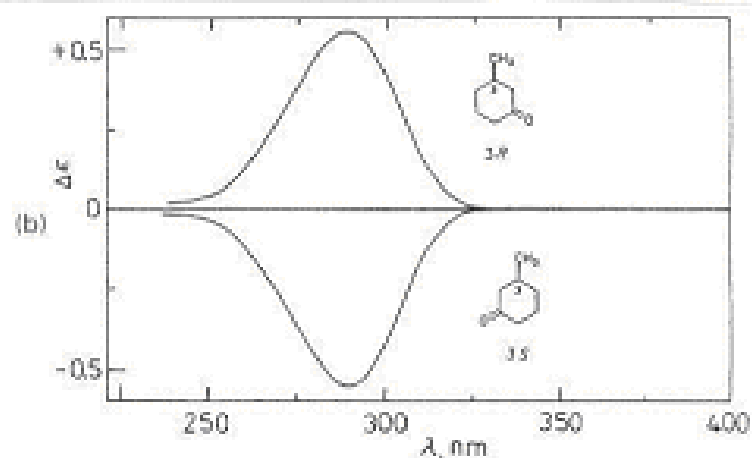
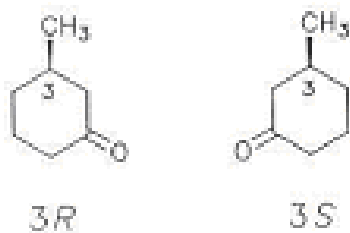
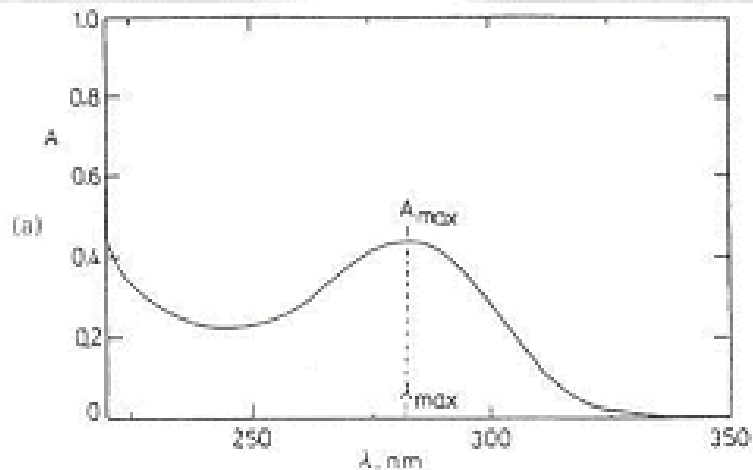
- In structure determination : UV-vis spectroscopy is used to detect the presence of chromophores like dienes, aromatics, polyenes, and conjugated ketones, etc.
- Also very useful in quantitative analysis of compounds with chromophores.
- Chiroptical spectroscopy- Optical rotary dispersion/ORD and Circular dichroism/CD : the *difference* in the refraction (ORD) or absorption (CD) of left and right circularly polarized light is measured, or absorptivity (CD) between left and right circularly polarized light .

Chiroptical Spectroscopy

- Chiroptical properties reflect stereochemical arrangement of atom in a molecule. Both CD and ORD show sense of handedness in reflecting the handedness of nonsuperimposable mirror-image molecule (enantiomer). So their curves appear as positive or negative peaks of Cotton effects reflecting the difference in chirality of molecule.

Display of spectra

- Horizontal scale (abscissa): all three methods use wavelength, λ , in nm (nanometer) unit.
- Vertical scale (ordinate):
- UV-vis: absorbance, A , or molar absorptivity, ϵ .
- CD: difference in molar absorptivity, $\Delta\epsilon$, or molar ellipticity, $[\theta]$.
- ORD: molar rotation, $[\varphi]$.



UV: A vs. λ (nm), the same curve for 3*R*-, 3*S*-isomer, and racemate.

CD: $\Delta\epsilon$ vs. λ , + Cotton effect for 3*R*-isomer, and - Cotton effect for 3*S*-isomer.

ORD: $[\phi]$ (molar rotation) vs. λ , + C. E. for 3*R*-isomer and - C. E. for 3*S*-isomer.

Origin of electronic spectra

- Absorptions of UV-vis light photons by molecule results in electronic excitation of molecule with chromophore.
- The electronic transition involves promotion of electron from a electronic ground state to higher energy state, usually from a molecular orbital called HOMO to LUMO.

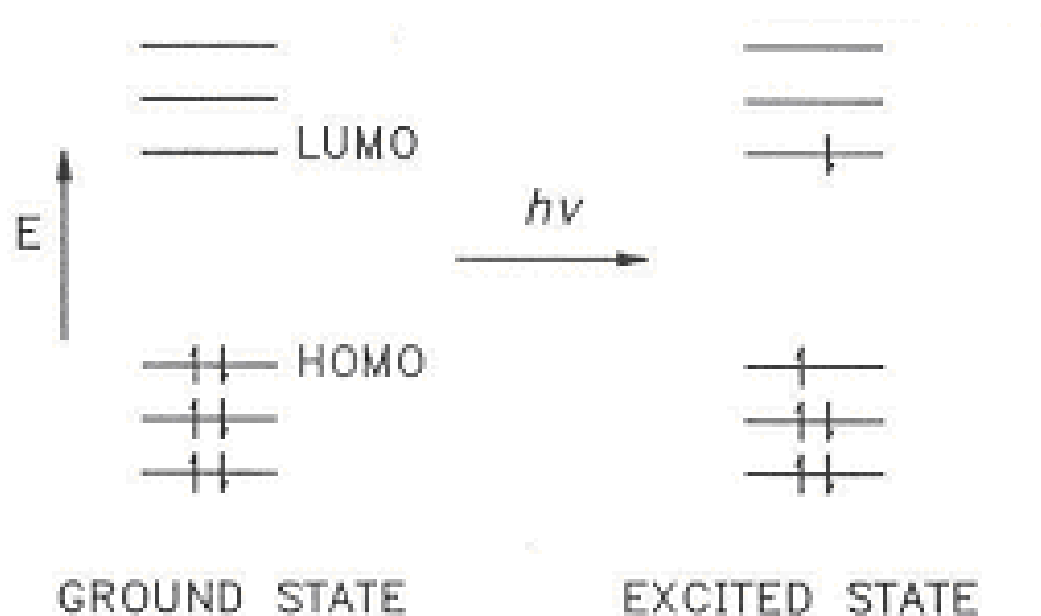
Electronic transition

- HOMO: Highest Occupied Molecular Orbital
- LUMO: Lowest Unoccupied Molecular Orbital
- Electronic transition usually originates from valence electrons in a chromophore, such as the nonbonding (n) or π electrons in unsaturated functions.

Electronic transition

- Can be assigned to different transition types according to the molecular orbital involved, such as $\pi \rightarrow \pi^*$ (in alkenes or benzene), $n \rightarrow \pi^*$ (in keto group).
- Due to their symmetry property in MO's, such transition can be allowed (high intensity) or forbidden (low intensity).
- Absorptions with high ϵ are allowed transitions, and low ϵ absorptions are forbidden transition.

UV Spectral Origin

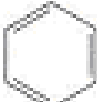
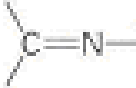


Transition of an electron from HOMO to LUMO
by light photon

UV Absorptions for some isolate chromophores

TABLE 10-1

Electronic Absorption Data for Isolate Chromophores*

Chromophore	Example	Solvent	λ_{\max} (nm) [†]	ϵ (liter mol ⁻¹ cm ⁻¹)
C=C	1-Hexene	Heptane	180	12,500
—C≡C—	1-Butyne	Vapor	172	4,500
	Benzene	Water	254	205
	Toluene	Water	203.5	7,400
			261	225
			206.5	7,000
C=O	Acetaldehyde	Vapor	298	12.5
	Acetone	Cyclohexane	182	10,000
	Camphor	Hexane	190	22
—COOH	Acetic acid	Hexane	295	14
—COCl	Acetyl chloride	Ethanol	204	41
—COOR	Ethyl acetate	Heptane	240	34
—CONH ₂	Acetamide	Water	204	60
—NO ₂	Nitromethane	Methanol	205	160
		Hexane	279	15.8
=N ⁺ =N ⁻	Diazomethane		202	4,400
—N=N—	<i>trans</i> -Azomethane	Diethyl ether	417	7
	C ₂ H ₅ CH—NC ₆ H ₅	Water	343	25
		Isooctane	238	200

* From J.B. Lambert, H.F. Shurvell, L. Verbit, R.G. Cooks, and G.H. Stout, *Organic Structural Analysis*, Macmillan Publishing, New York, 1976.

† Chromophores often have more than one absorption band.

Measurement of UV-vis absorption

- The electromagnetic radiation may be described by the wavelength λ (nm), by the frequency ν (s^{-1}), or by the wavenumber, $\bar{\nu}$ (cm^{-1}), related by energy difference as following relationships:

$$\lambda \nu = c \quad \bar{\nu} = \frac{1}{\lambda}$$

λ wave length in nm
 ν frequency in cyc/s
 $\bar{\nu}$ wave number in 1/cm

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{28636}{\lambda} \text{ kcal/mol} = \frac{119809}{\lambda} \text{ kJ/mol}$$

UV regions

- The UV region is divided to two parts:
- a. the near UV region: 190-400 nm.
- b. The far or vacuum UV region: below 190 nm.

The far UV region has interference due to absorption of oxygen, which must be removed or flushed with nitrogen in the spectrometer to obtain the spectra of sample.

Measurement of Absorbance

- The absorbance (A) or molar absorptivity (ϵ) of an UV band is calculated according to the **Beer-Bouguer-Lambert Law**:

I_0 : the intensity of incident light

$$I = I_0 e^{-kl}$$

I : the intensity of transmitted light

$$I = I_0 10^{-\epsilon cl}$$

l : the path length in cm

$$\log \frac{I_0}{I} = \epsilon cl$$

c : the concentration in mol L⁻¹

k : the absorption coefficient

ϵ : the molar extinction coefficient or molar absorptivity in cm² mol⁻¹ or L mol⁻¹ cm⁻¹.

Absorbance

- The relationship between k and ϵ is $k \approx 2.303 \epsilon c$
- Since absorbance $A = \log \frac{I_0}{I}$, and A is the actual quantity measured, the following eqn. relates A with ϵ : $A = \epsilon c l$
- For i absorbing species : $A = l \sum_i \epsilon_i c_i$
- The actual quantity measured is the relative intensities of the light beam transmitted by a reference cell containing pure solvent and an identical cell containing sample solution.

Absorbance

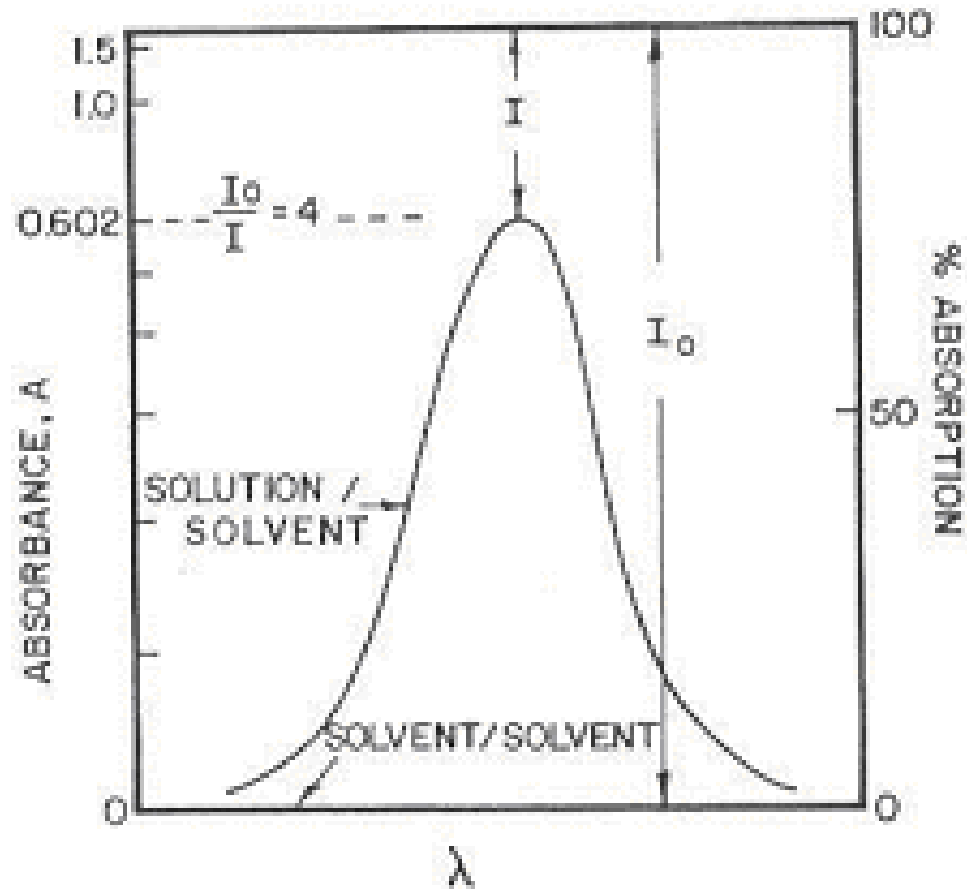


Figure 10-3 Measurement of solute absorbance A by a double-beam spectrophotometer.

Frank-Condon Principle

- The broadened bands of UV curve indicate wide distribution of energies, due to superimposition of several vibrational levels on the electronic level.
- From the P.E. diagram of a diatomic system, the G.S. has lower energy, shorter r_{equil} (bond length), while the E.S. has higher energy, longer r_{equil} (bond weaker). Each of this electronic state has many vibrational states in it.

Frank-Condon Principle

- It is the transitions between the lowest vibrational state ($v = 0$) in G.S. to various vib. levels in E.S. that determine the shape and intensity of a UV band.
- So it is determined by the spacing of the vibrational levels and the distribution and contribution of each vibrational subband to the total band intensity.
- This is governed by the **Frank-Condon Principle** stated as following:

Frank-Condon Principle

- “The nuclear motion (10^{-13} s) is much slower as compared with electronic motion in transition (10^{-16} s), so it is negligible during the time required for an electronic excitation.”
- Since the nucleus does not move during the excitation, the internuclear distance keeps the same, and “the most probable component of a electronic transition involves only the vertical transitions”.

Frank-Condon Principle

- The excitation going from $v = 0$ (G.S.) to $v = 3$ (E.S.) is the most probable one for vertical transition because it falls on the highest point in the electron probability curve for $v = 3$ in E.S.
- Other vertical transitions ($0 \rightarrow 2$, $0 \rightarrow 1$, ..., $0 \rightarrow 4$, $0 \rightarrow 5$, ...) are smaller in their probabilities of transition as revealed in the composite fine structure of vibronic broad band.

Frank-Condon principle

Figure 10-4 Potential energy diagram for a diatomic molecule illustrating Franck-Condon excitation. The equilibrium separation is longer in the excited than in the ground state.

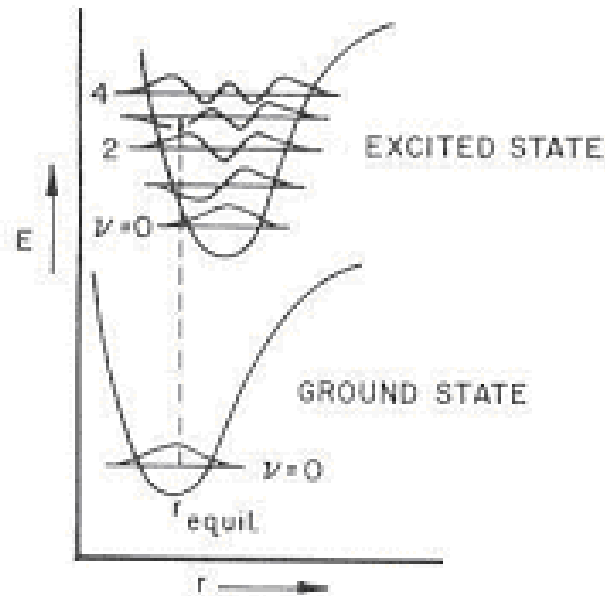
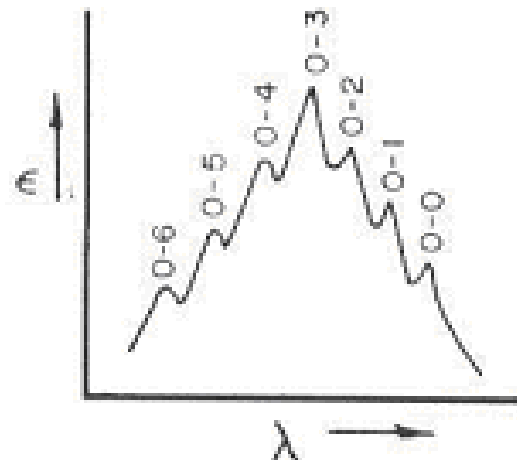


Figure 10-5 Intensity distribution among vibronic bands as determined by the Franck-Condon principle.

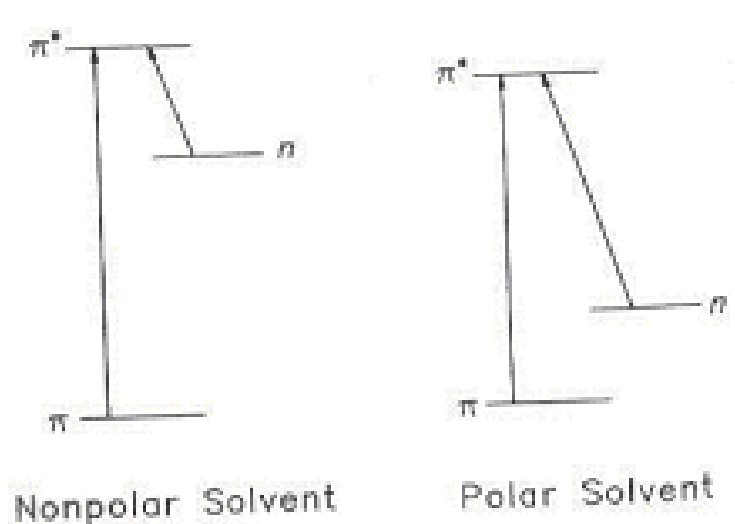


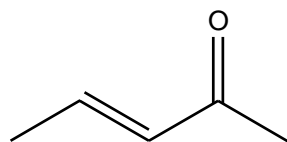
Solvent effects

- Promotion of electron from G.S. to E.S. leads to more polar excited state that is more easily stabilized by polar solvent associations (H-bonds). In going from nonpolar to polar solvents the fine vibronic structure is smoothed into a broad band.
- For $\pi \rightarrow \pi^*$ transition, the π^* state is more polar and stabilized more in polar solvent relative to nonpolar one, thus in going from nonpolar to polar solvent there is a red shift or bathochromic shift (increase in λ_{max} , decrease in ΔE).

Solvent effects

- For $n \rightarrow \pi^*$ transition, the n state is much more easily stabilized by polar solvent effects (H-bonds and association), so in going from nonpolar to polar solvent there is a blue shift or hypsochromic shift (decrease in λ_{\max} , increase in ΔE).

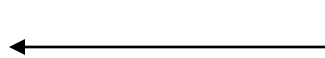




methanol



Hypsochromic shift



heptane

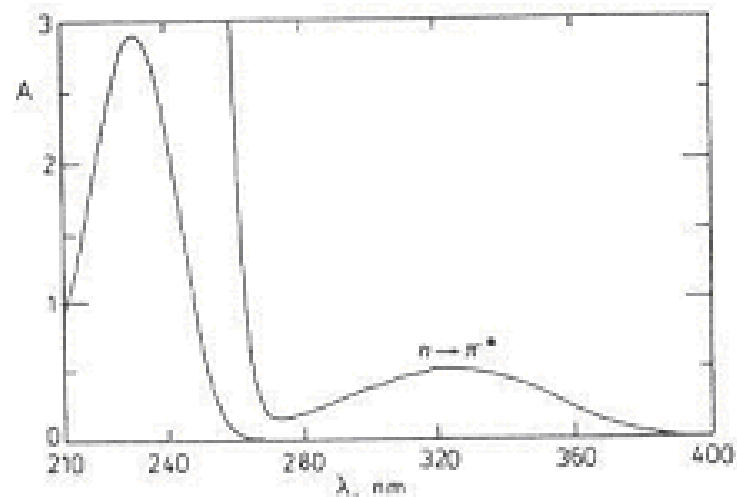
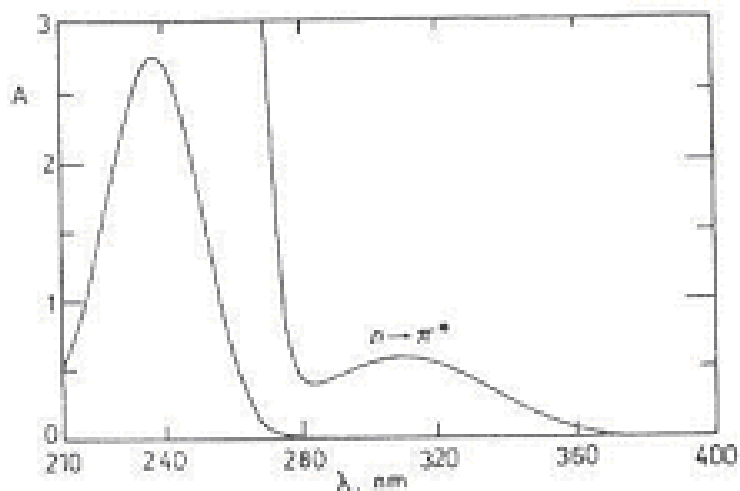


Figure 10-6 UV-vis absorption spectra of 4-methyl-3-penten-2-one (mesityl oxide) in (left) methanol and (right) heptane. Spectra in methanol were run in a 1 cm cuvette at 0.0105 M and 2.63×10^{-4} M concentrations. Spectra in heptane were run at 0.014 M and 2.8×10^{-4} M concentrations. The vertical axis is in absorbance units. The ~ 320 nm absorption is the $n \rightarrow \pi^*$ transition, the ~ 240 nm is mainly $\pi \rightarrow \pi^*$. (Spectra run by Portia Mahal Sabido.)

Solvent Effects

TABLE 10-4

Influence of Solvent on the UV λ_{\max} and ϵ_{\max} of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Excitations of 4-Methyl-3-penten-2-one (Mesityl Oxide)*



Solvent	$\pi \rightarrow \pi^*$ Transition		$n \rightarrow \pi^*$ Transition	
	λ_{\max} (nm)	ϵ_{\max} (liter mol ⁻¹ cm ⁻¹)	λ_{\max} (nm)	ϵ_{\max} (liter mol ⁻¹ cm ⁻¹)
Hexane	229.5	12,600	327	97.5
Diethyl ether	230	12,600	326	96
Ethanol	237	12,600	325	78
Methanol	238	10,700	312	74
Water	244.5	10,000	305	60

*From H.H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley & Sons, Inc., New York, 1962.

Electronic transition

- Electronic transition (UV) measure the probability and energy of exciting a molecule from G.S. to E.S. (or promoting electron from HOMO to LUMO).
- For each energy state both singlet (S) and triplet (T) states are possible. In singlet state the spins of electron pair are antiparallel; if the spins are parallel, three states are possible and are jointly called triplet state.
- $M = 2S + 1$ M: multiplicity
- S: total spin

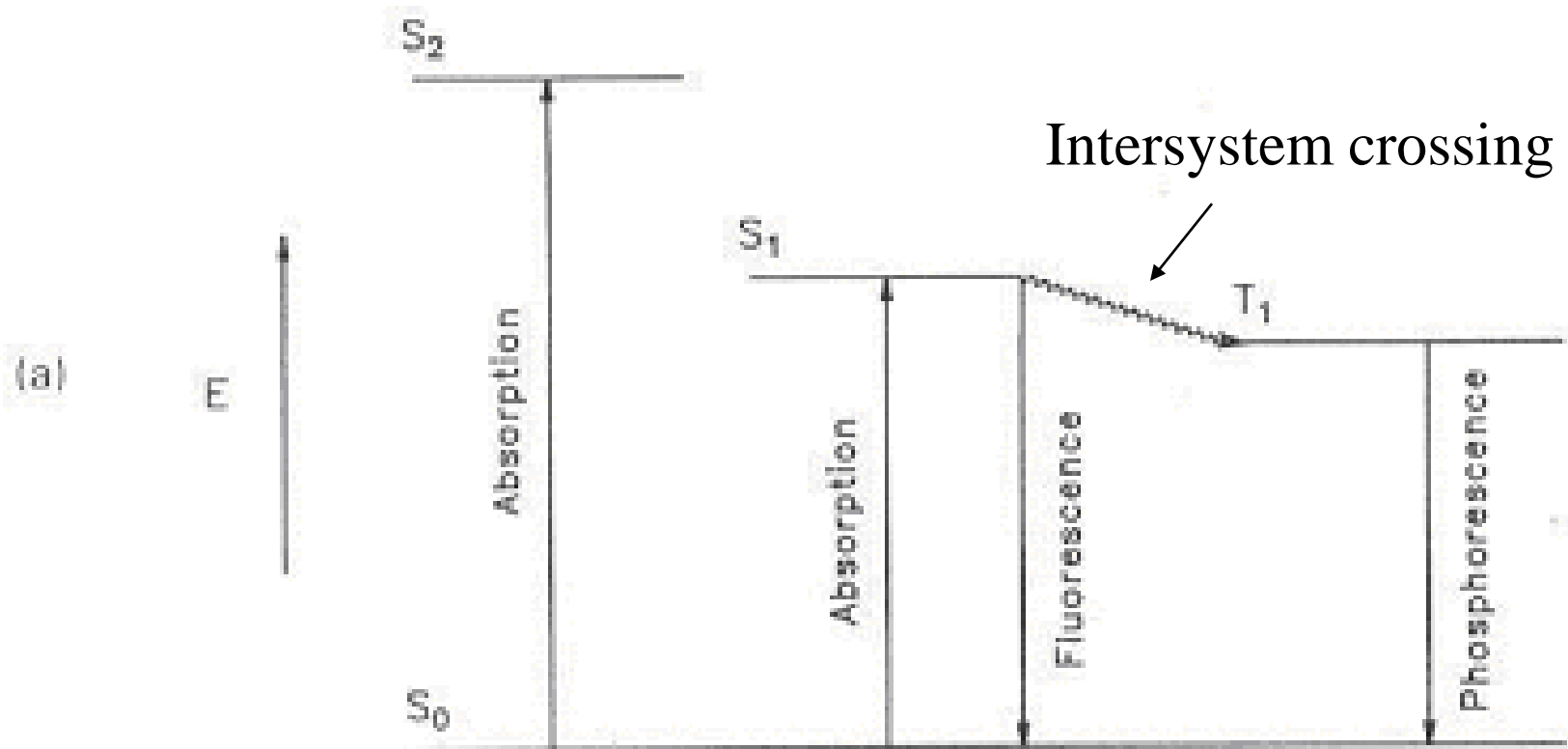
Electronic transitions

- **Selection rules:** allow $S \rightarrow S$, and $T \rightarrow T$ processes but not $S \rightarrow T$ and $T \rightarrow S$. Ground states are usually singlets; thus most excitations are to singlet excited states, like $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, ...
- Triplet states are usually formed by intersystem crossing from an excited singlet state, such as S_1 , rather than by direct excitation from the S_0 ground state.

Electronic transitions

- The electronically excited states may decay unimolecularly back to the ground state by photophysically emitting energy of fluorescence (from an excited singlet state) or of phosphorescence (from an excited triplet state).
- Alternatively, it might decay photochemically to a different ground state of different structure. One can thus measure the absorption and emission from molecules.
- The λ_{\max} of an absorption band correspond to the excitation energy, and ϵ_{\max} to the intensity of transition, a measure of the probability of promoting an electron, given the excitation energy.

Electronic transitions



Electronic activation and decay mode of a chromophore.

Classification of Electronic Transitions

- The wavelength of an electronic transition depends on the energy difference between the G.S. and the E.S. It is a useful approximation to consider the λ of to be determined by the ΔE of MO originally occupied by the e's at G.S. and the higher excited MO in E.S.
- The order: $\sigma \rightarrow \pi \rightarrow n \rightarrow \pi^* \rightarrow \sigma^*$

Different type of UV transitions

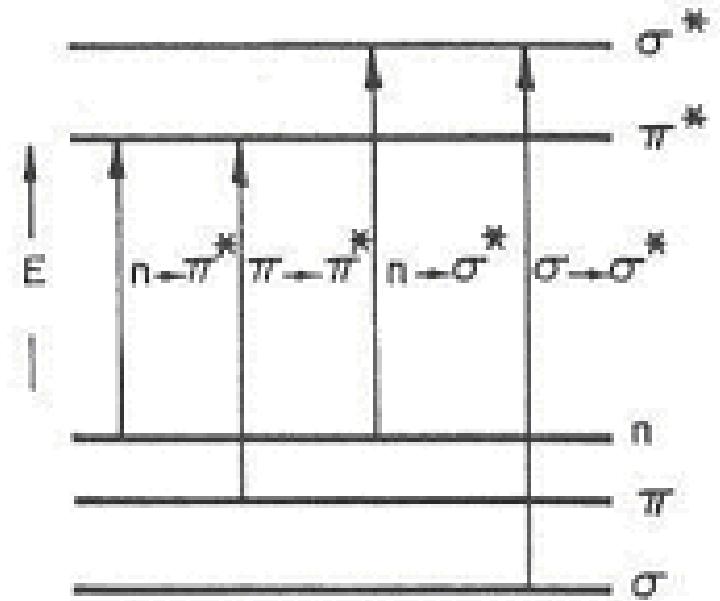


Figure 11-2 Relative electronic orbital energies and selected transitions in order of increasing energy.

UV transition type

- **$1.\sigma \rightarrow \sigma^*$ transitions:** for cpds. with σ bond only, high ΔE , short λ (< 200 nm).
- Appears in satd. hydrocarbons with σ orbital and transition to antibonding σ^* or to molecular Rydberg orbital (higher valence shell orbitals, 3s, 3p, 4s, ...), and involves large ΔE , and small λ_{\max} that appears in far-UV region.
- Ex. cyclopropane λ_{\max} 190 nm.
- cycloalkane λ_{\max} 135 nm. (vacuum UV)

UV transition type

- **2. $n \rightarrow \pi^*$ transitions** : the excitation of an electron on a nonbonding orbital, such as unshared pair e's on O, N, S,..to an antibonding π^* , usually in a double bond with hetero atoms, such as C=O, C=S, N=O, etc. A sym. forbidden and low intensity transition.
- Ex. satd. aldehydes and ketones : λ_{\max} at 185-300 nm.

UV transition type

- **$3.\pi \rightarrow \pi^*$ transitions** : for cpds. containing double, triple bonds, or aromatic rings; a π electron is excited to an antibonding π^* orbital. This is usually a sym. allowed and high intensity transition.
- Ethylene : absorbs at 162 nm (10000), in vacuum UV. Extended conjugation lowers, ΔE , and increase in λ_{\max} , if extended beyond 5 double bonds then getting into visible region.

UV transition type

- **4. $n \rightarrow \sigma^*$ transitions:** excitation from nonbonding orbital to an antibonding σ^* orbital.

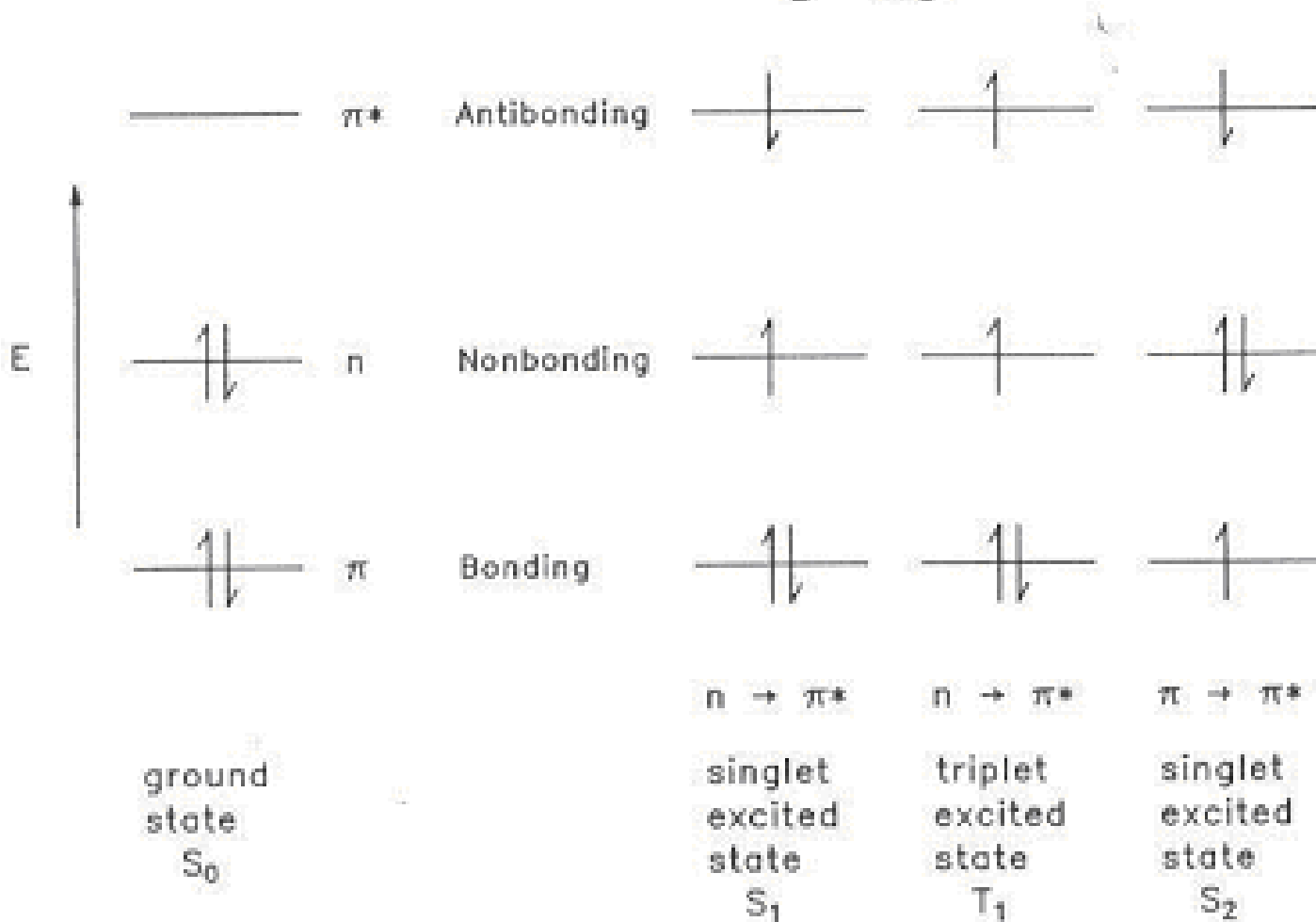
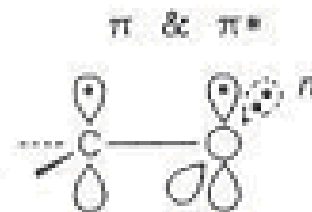
Ex. $\text{CH}_3\text{OH}(\text{vap.})$ 183 nm (ϵ 150)

$\text{NEt}_3(\text{vap.})$ 227 nm (900)

$\text{MeI}(\text{hexane})$ 258 nm (380)

- **5. Rydberg transition:** mainly to higher excited states. For most organic molecules occurs at λ below 200 nm. Part of a series of molecular electronic transitions occurs with narrowing spacing nearing the ionization potential of organic molecule.

Carbonyl chromophore of 3-methylcyclohexanone



Orbital Spin and E states

- Diagram showing the ground state and excited state configuration of carbonyl chromophore.
- Singlet state (S) have electron spin paired and triplet state (T) have two spins parallel.
- n orbital containing two electrons is perpendicular to π or π^* orbitals.
- Subscript 0 refers to G.S., 1 to 1 st. E.S., 2 to 2 nd. E.S.

Terms describing UV absorptions

- 1. **Chromophores**: functional groups that give electronic transitions.
- 2. **Auxochromes**: substituents with unshared pair e's like OH, NH, SH ..., when attached to π chromophore they generally move the absorption max. to longer λ .
- 3. **Bathochromic shift**: shift to longer λ , also called red shift.
- 4. **Hysochromic shift**: shift to shorter λ , also called blue shift.
- 5. **Hyperchromism**: increase in ϵ of a band.
- 6. **Hypochromism**: decrease in ϵ of a band.

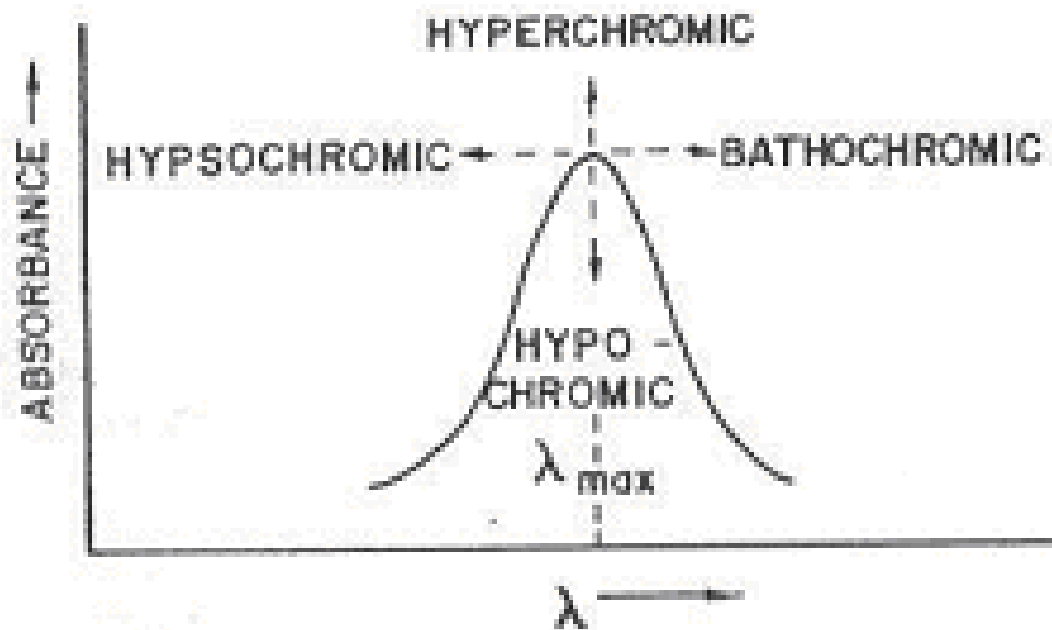


Figure 11-3 Terminology of shifts in the position of an absorption band.

Orbital Spin States

- **Singlet state (S):** Most molecules have G.S. with all electron spin paired and most E.S. also have electron spin all paired, even though they may be one electron each lying in two different orbital. Such states have zero total spin and spin multiplicities of 1, are called singlet (S) states.

Total Spin

$$\Delta S = +\frac{1}{2} - \frac{1}{2} = 0$$

Multiplicities

$$M = 2\Delta S + 1 = 2 \times 0 + 1 = 1$$

Orbital Spin States

- If an external magnetic field is applied to the singlet spin system, there is only one zero angular momentum in the field direction.
- For some of the excited states, there are states with a pair of electrons having their spins parallel (in two orbitals), leading to total spin of 1 and multiplicities of 3.

Total spine

$$\Delta S = +\frac{1}{2} + \frac{1}{2} = 1$$

Multiplicities

$$M = 2\Delta S + 1 = 2 \times 1 + 1 = 3$$

Orbital Spin States

- For triplet state: Under the influence of external field, there are three values (i.e. 3 energy states) of $+1, 0, -1$ times the angular momentum. Such states are called triplet states (T).
- According to the selection rule, $S \rightarrow S, T \rightarrow T$, are allowed transitions, but $S \rightarrow T, T \rightarrow S$, are forbidden transitions.

Selection Rules of electronic transition

- Electronic transitions may be classed as intense or weak according to the magnitude of ϵ_{\max} that corresponds to *allowed* or *forbidden* transition as governed by the following **selection rules** of electronic transition:
 1. **Spin selection rule:** there should be no change in spin orientation or no spin inversion during these transitions. Thus, $S \rightarrow S$, $T \rightarrow T$, are allowed, but $S \rightarrow T$, $T \rightarrow S$, are forbidden.

Selection Rules of electronic transition

- **2. Angular momentum rule:** the change in angular momentum should be within one unit (0 or ± 1).
- **3. Symmetry rule:** the product of the electric dipole vector and the group theoretical representations of the two states is totally symmetric.
- The spin selection rule simply states that transitions between states of different multiplicities are forbidden.

Selection Rules of electronic transition

- The second rule agrees with the fact most states are within one unit of angular momentum of each other.
- The symmetry rule indicates that group representation of initial and final states should be the same as the representations of axes system they belong to. If they are different then the transition moment of that transition is zero and the transition is thereby forbidden.
- Group representation is the symmetry property of the orbitals.

Allowed and Forbidden transitions

- Forbidden transition: The $n \rightarrow \pi^*$ transition of saturated ketones, where a carbonyl n electron is promoted to an orthogonal π^* orbital ($n \perp \pi^*$); there is no orbital overlap for such 90° movement of charge and the transition moment is zero.
- Allowed transition: For $\pi \rightarrow \pi^*$ transition in double bond, the symmetry of initial and final states are the same and a large transition moment occurs to give high intensity of the band.

Allowed and Forbidden transitions

- Forbidden transition: The $n \rightarrow \pi^*$ transition of keto group is still observable with low intensity, this is due to the vibronic states in the transition. Symmetry of orbital changed by C=O vibration that allow some overlap of orbital and the transition to occur.

Absorption Intensity

- Shape of electronic absorption band arises from various vibronic sublevels. The band intensity is described by ϵ_{\max} in UV. This quantity can not be calculated theoretically, but can be calculated by the wave-length weighted area under the absorption band.
- In UV curve it is called dipole strength D :

$$D = 9.184 \times 10^{-39} \int_0^{\infty} \frac{\epsilon}{\lambda} d\lambda \quad \text{in erg cm}^3, \text{ (range } 10^{-34} \sim 10^{-38}\text{)}$$

Dipole strength

- Dipole strength represents electronic transition probability of the absorption band.
- As electron is promoted from low to high E. states, a momentary electric dipole is generated, called the electric transition dipole moment μ , which is related to D by:
- $D = \mu \bullet \mu$ D is a dot product of μ .

Dipole strength

- The following relations calculate D in terms of $\Delta\lambda$ (the bandwidth at $\varepsilon_{\max}/2$), ε_{\max} , and λ_{\max} :

$$D \approx 9.188 \times 10^{-39} (\varepsilon_{\max}) \Delta\lambda / \lambda_{\max}$$

SPECTROSCOPY

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