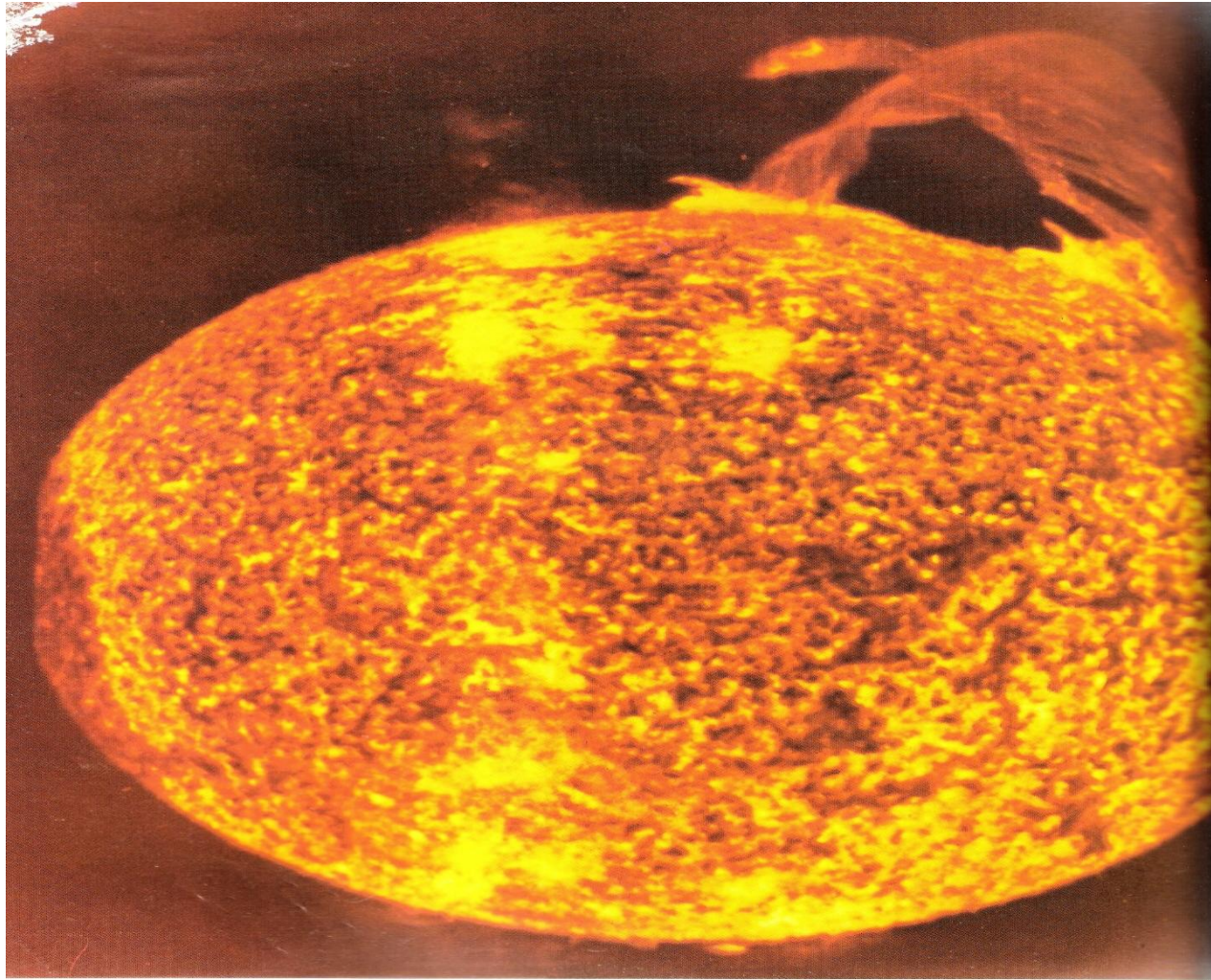# Spectroscopy

by

Dr. Anil Kumar

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University Institute of Engineering and Technology,
Panjab University, Chandigarh-160014

Ultimate source of energy ?
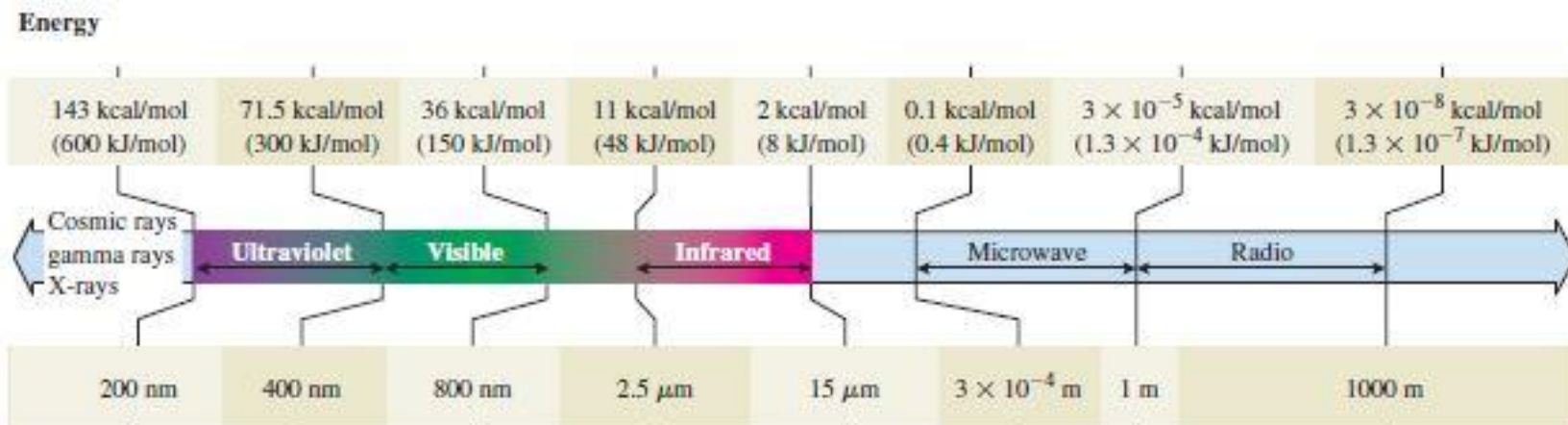
True or False

Sun rises in the East.   **False**

Spectroscopy

Interaction   of   Radiation   with   Matter

Electromagnetic Radiations

Energy

| 143 kcal/mol (600 kJ/mol) | 71.5 kcal/mol (300 kJ/mol) | 36 kcal/mol (150 kJ/mol) | 11 kcal/mol (48 kJ/mol) | 2 kcal/mol (8 kJ/mol) | 0.1 kcal/mol (0.4 kJ/mol) | 3×10^{-5} kcal/mol (1.3×10^{-4} kJ/mol) | 3×10^{-8} kcal/mol (1.3×10^{-7} kJ/mol) |

Cosmic rays
gamma rays
X-rays

Ultraviolet **Visible** **Infrared** Microwave Radio

| 200 nm | 400 nm | 800 nm | 2.5 μm | 15 μm | 3×10^{-4} m | 1 m | 1000 m |

Wavelength

Higher energy
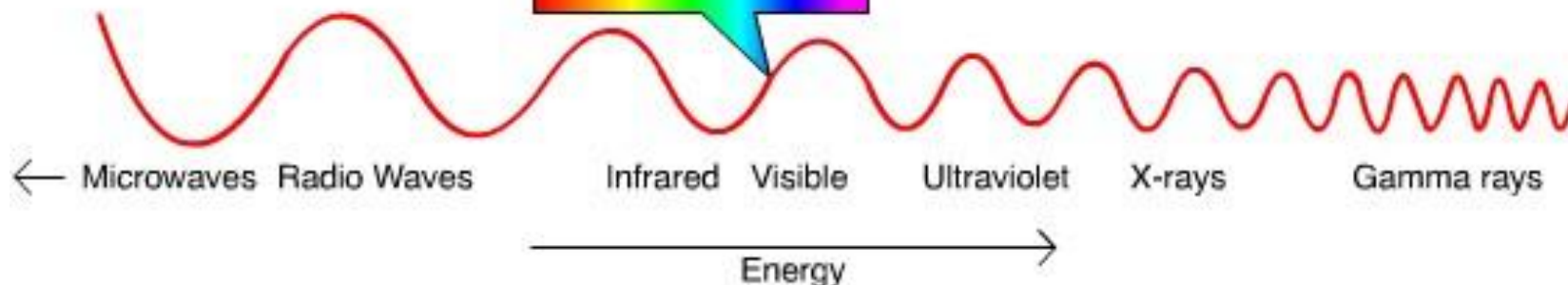Higher frequency
Shorter wavelength

Lower energy
Lower frequency
Longer wavelength

The energy of infrared light matches the ΔE between the vibrational energy levels of covalent bonds. When a molecule absorbs light, its bonds vibrate more rapidly. IR spectroscopy is discussed in this chapter.

Radar employs microwave radiation. Microwave ovens use this radiation to excite rotational energy states of water and other molecules in food.

Radio and TV broadcasts use radio frequency radiation. In addition, nuclear magnetic resonance spectroscopy, which causes transitions between nuclear spin states, uses radiation from this region. One typical NMR spectrometer operates at 2×10^{8} Hz or 200 MHz (1.9×10^{-5} kcal/mol or 8×10^{-5} kJ/mol).
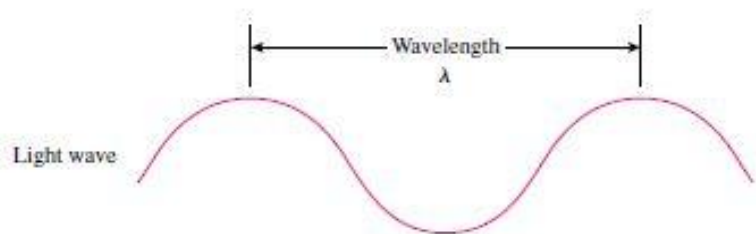
← Microwaves Radio Waves Infrared Visible Ultraviolet X-rays Gamma rays

Energy

Radiation 🤝 Matter

$$C = \lambda v$$

λ = wavelength, nm (10^{-9} m)
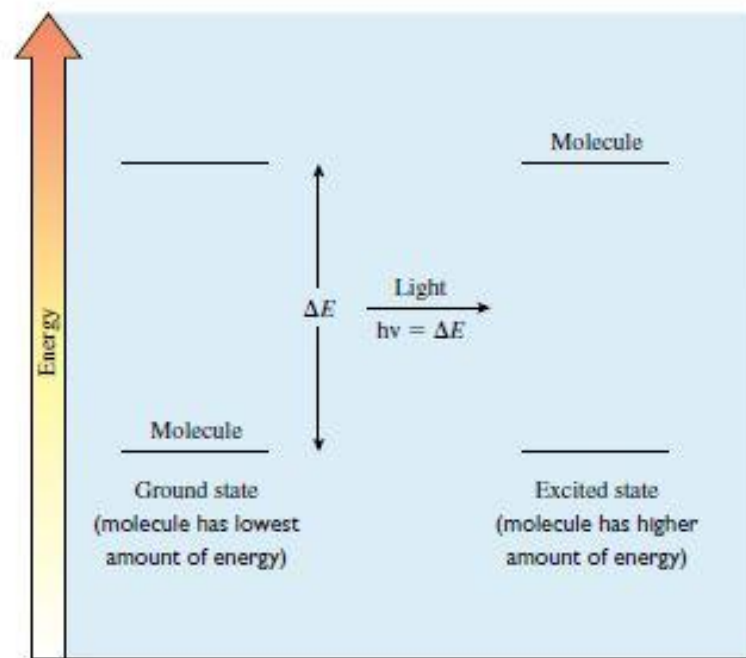v = no. of wave cycles, Hertz/cps or s^{-1}
C = velocity of light, 3×10^8 m/s
h (Plank's constant) = 6.6242×10^{-27} erg sec
= 6.63 x 10-37 k Js or 1.58×10^{-37} kcal sec

$$E = hv = hc/\lambda$$

UV-Visible = 200-800 nm (143-36 kcal/mol)

Energy is quantized

Each molecule/compound has fixed energy gap between the ground state and excited state

Energy is quantized

Spectroscopy

❖ **Why to study Spectroscopy?**
❖ **What kind of information we can get from the Spectroscopy?**

Radiation + unknown Matter = Electromagnetic Spectrum

Electromagnetic spectrum will give useful information about the structure of that matter such as atoms, no. of atoms, type of bond between atoms, conjugation, functional groups etc.

ⓑ When there are many, closely spaced sublevels in each energy level, the absorptions occur in broad bands because the individual lines are not resolved.
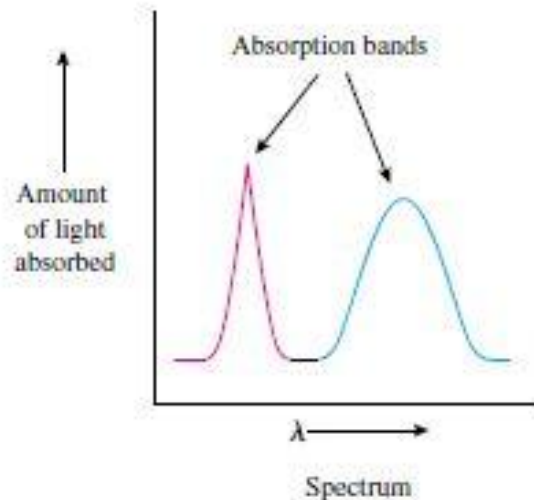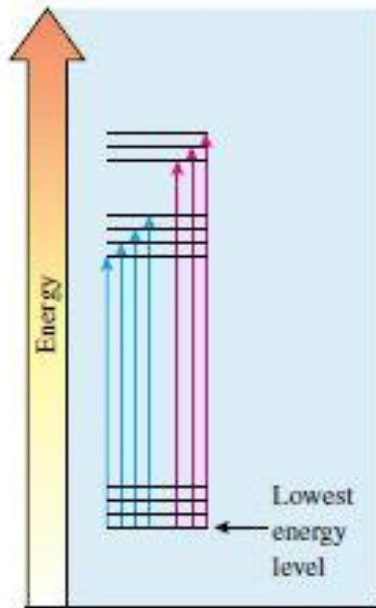
Spectroscopy

✓ **UV-Visible Spectroscopy : Gives only some basic information about the unknown matter such as type of bond, conjugation, hetero atom etc.**

✓ **Infrared Spectroscopy : Very important technique, gives information about the presence of functional groups in the unknown matter**

✓ **NMR Spectroscopy : Very useful spectroscopy. Gives no. of hydrogens and carbons (other nuclei also) present in a molecule and their environment and overall structure.**

✓ **Mass Spectroscopy : Gives exact mass of the unknown matter.**

UV-Visible Spectroscopy

Interaction of UV-Visible Radiation with Matter

UV Radiation λ = 200-400 nm
Visible Radiation λ = 400-800 nm

Matter

a

1s

Nucleus
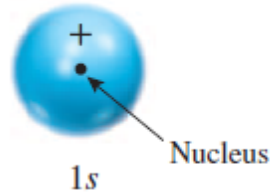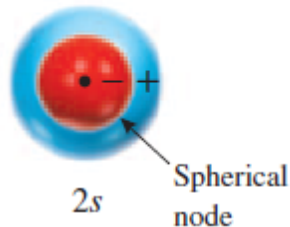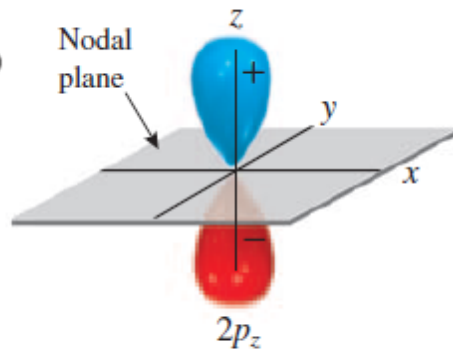
The 1s orbital is the lowest-energy atomic orbital. It has no nodes—that is, the math sign of the function is positive everywhere.

b

2s

Spherical node

The 2s orbital is the next higher-energy orbital. It is larger than the 1s orbital and has a spherical node.

c

Nodal plane

z

y

x

$2p_z$

The 2p is the next higher-energy orbital after the 2s. It has a planar node. In the orbital shown here, the $2p_z$ orbital, the x-y plane is the nodal plane—that is, the value for the wave function is zero in the x-y plane, and there is no electron density there. A 2p orbital is often drawn as shown at the left, although its actual shape is more like the computer-generated version shown at the right.
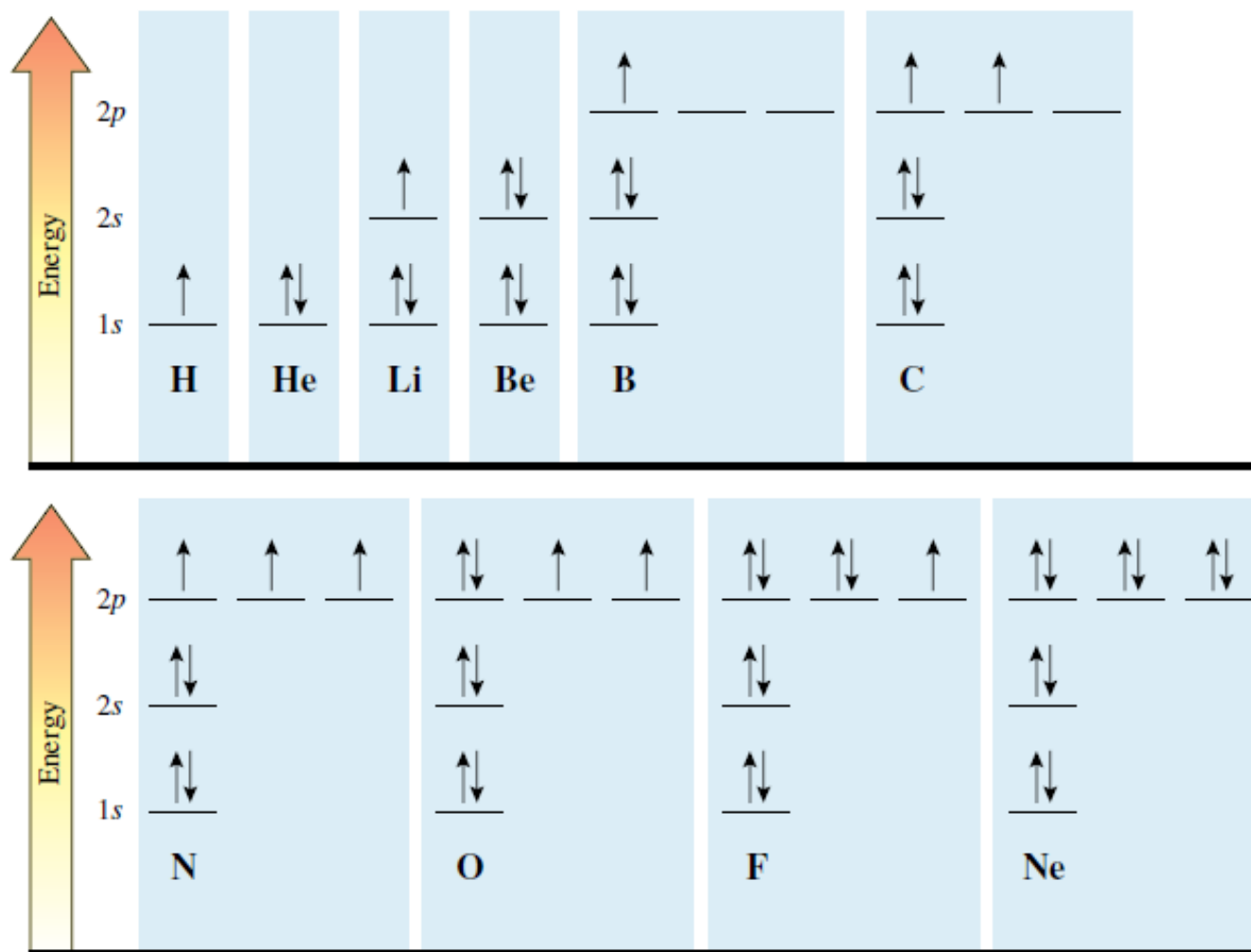
Matter

Figure 3.2

ATOMIC ORBITAL ENERGY LEVEL DIAGRAMS. To simplify these diagrams, the orbitals are shown at the same energies for different atoms. Actually, the energy of an orbital decreases as the number of protons in the atom increases. Thus the $2p$ orbitals of fluorine are lower in energy than the $2p$ orbitals of oxygen.

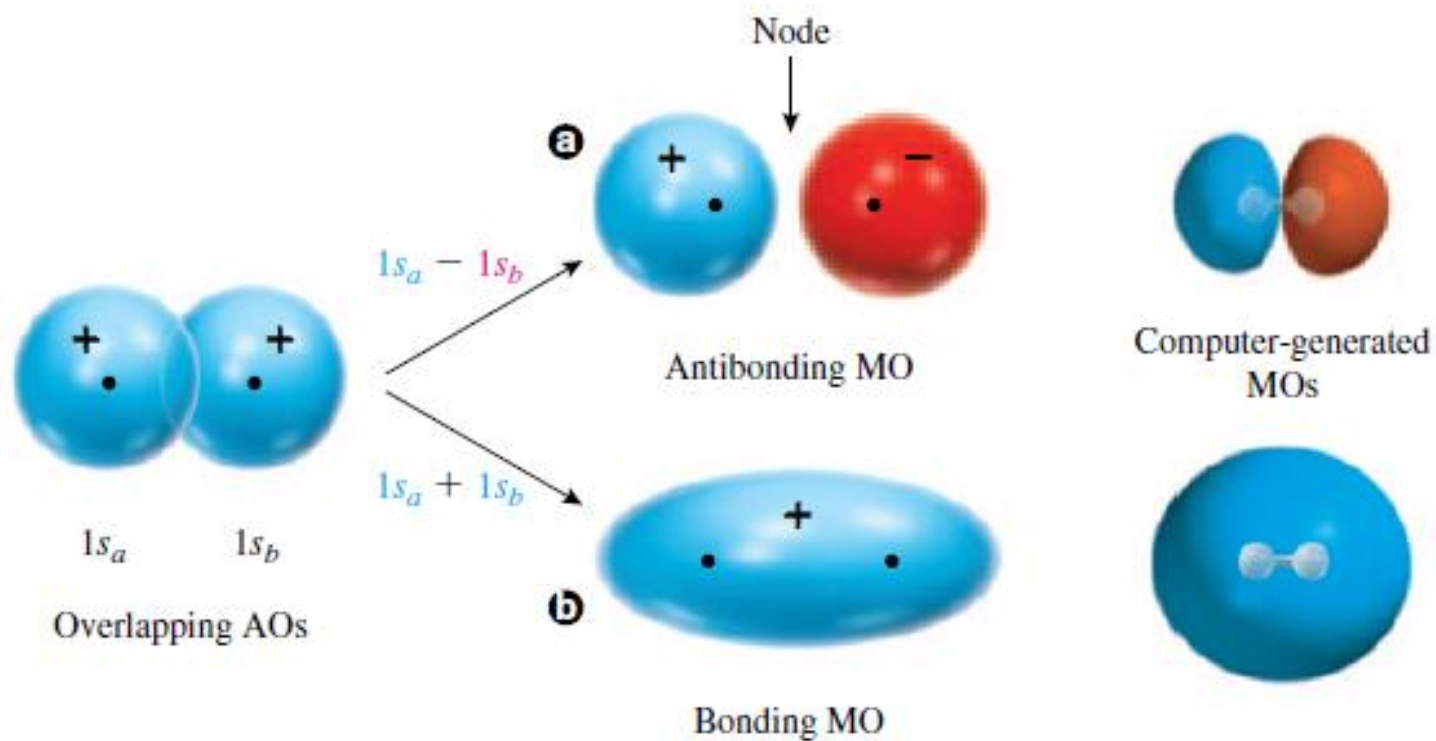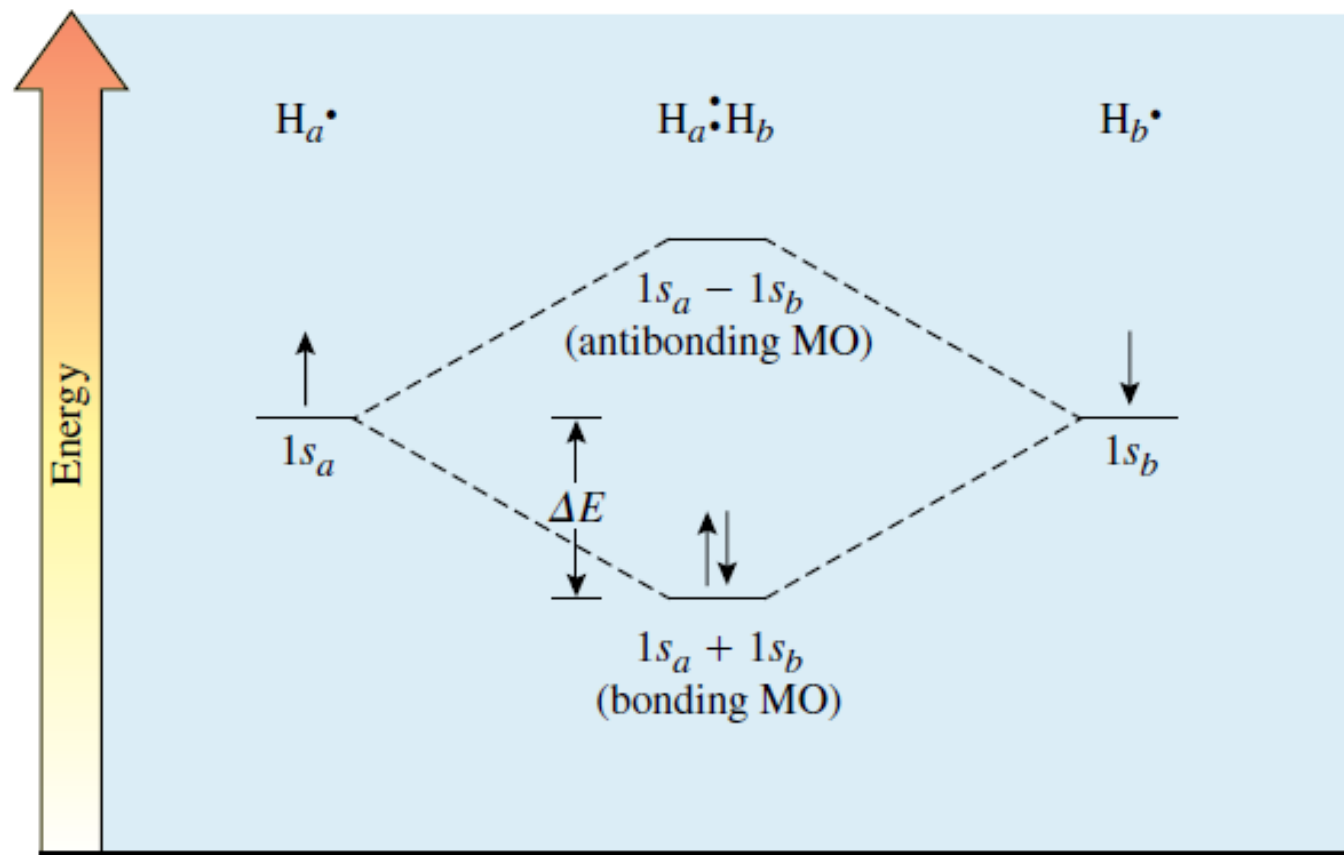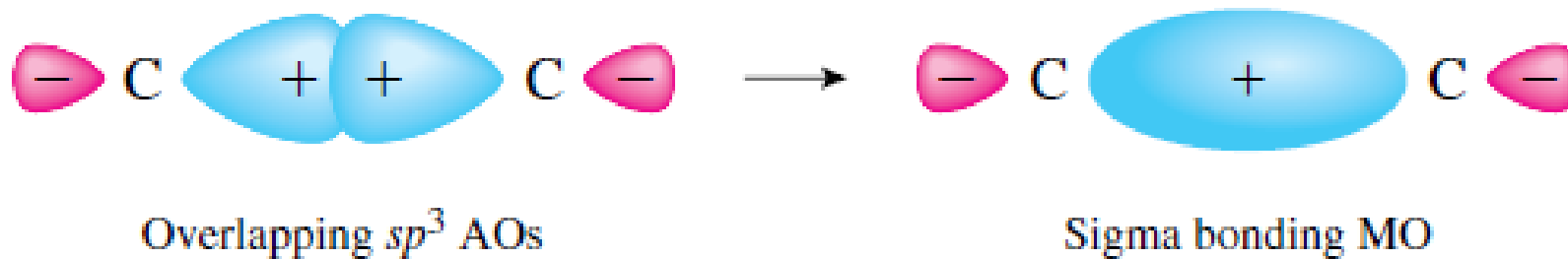# Matter

Figure 3.3

COMBINATION OF HYDROGEN 1s ATOMIC ORBITALS TO FORM MOLECULAR ORBITALS.

Matter

ENERGY LEVEL DIAGRAM FOR
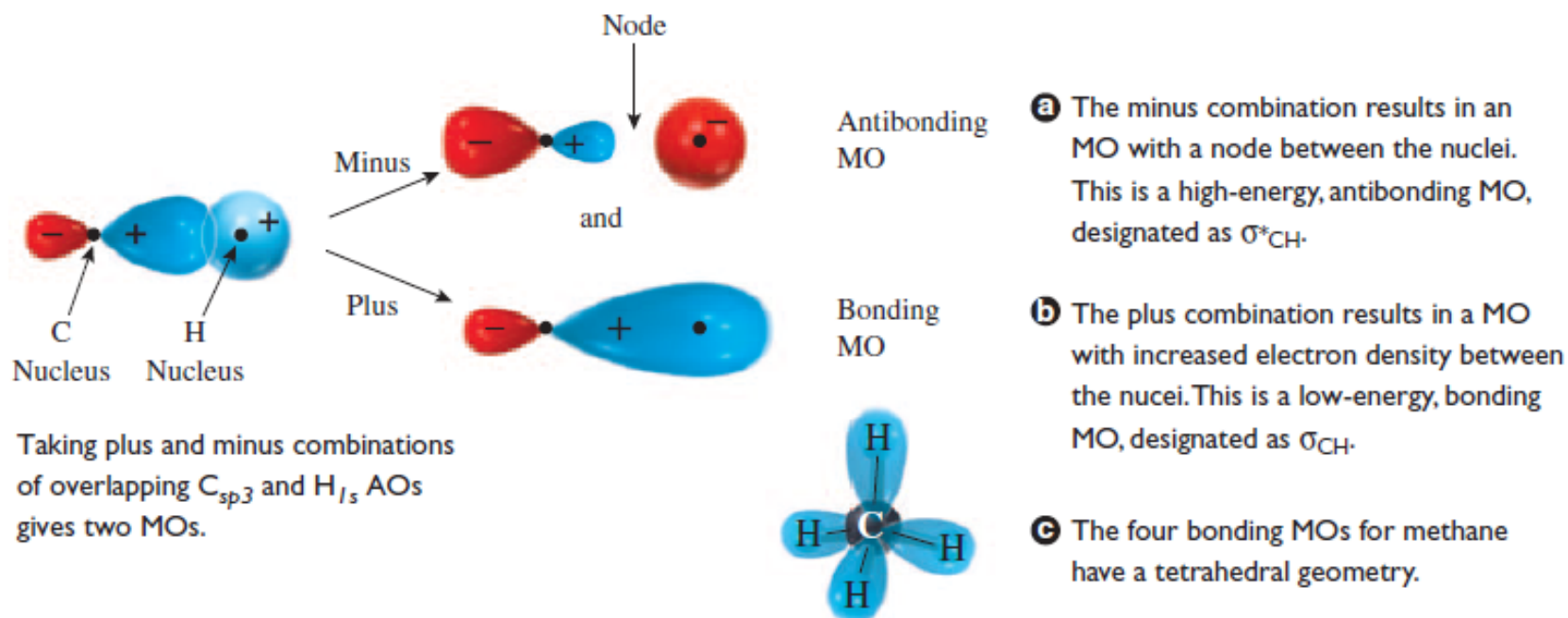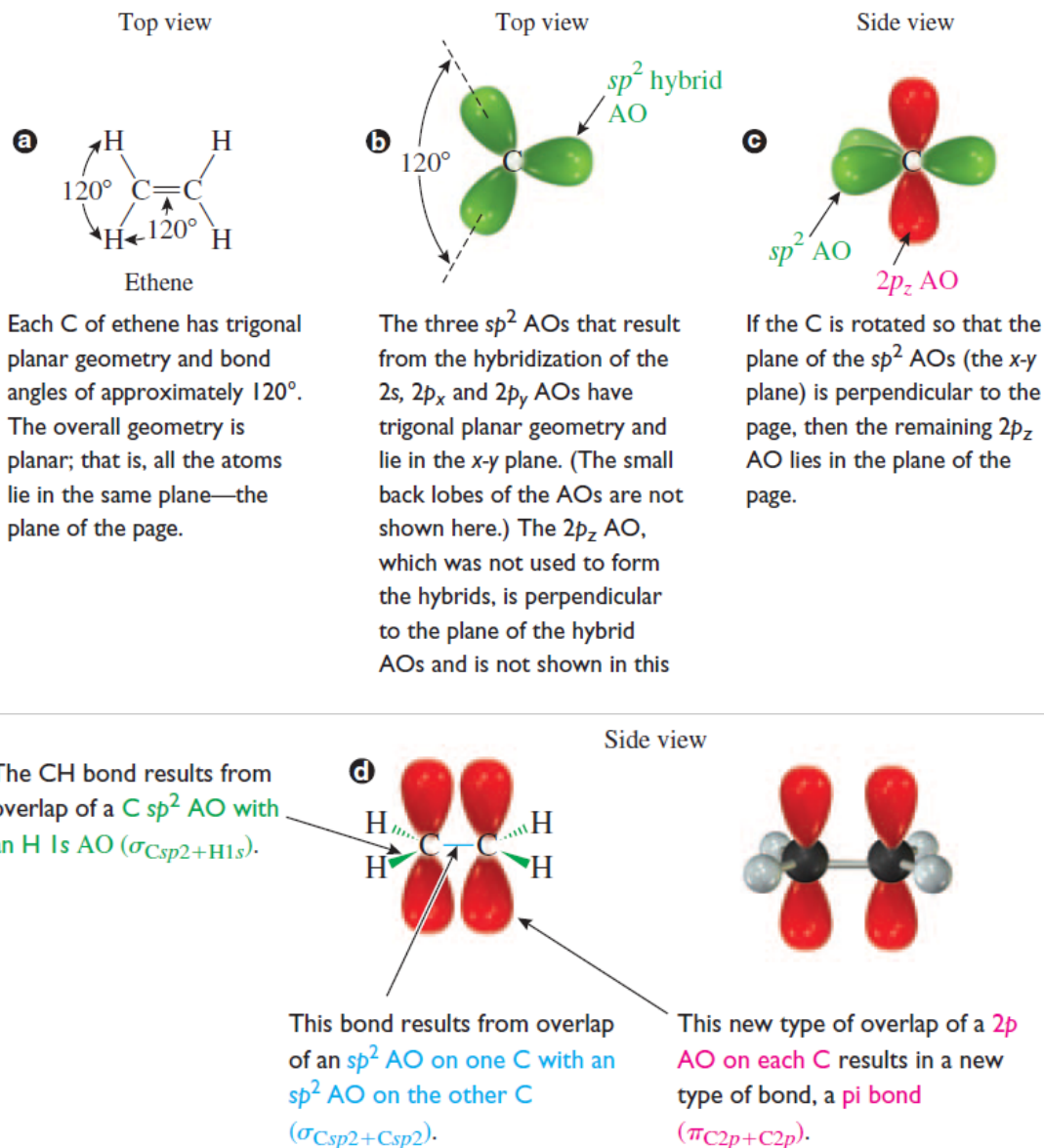H_2 MOLECULAR ORBITALS.

Matter

Overlapping sp^3 AOs → Sigma bonding MO

Matter

Node

Minus

and

Antibonding
MO

Plus

Bonding
MO

C   H
Nucleus   Nucleus

Taking plus and minus combinations
of overlapping C_{sp3} and H_{1s} AOs
gives two MOs.

ⓐ The minus combination results in an
MO with a node between the nuclei.
This is a high-energy, antibonding MO,
designated as σ^{*}_{CH}.

ⓑ The plus combination results in a MO
with increased electron density between
the nucei. This is a low-energy, bonding
MO, designated as σ_{CH}.

ⓒ The four bonding MOs for methane
have a tetrahedral geometry.

Figure 3.7

ORBITAL PICTURES FOR THE SIGMA BONDS OF METHANE. ⓐ Antibonding MO, **ⓑ** bonding MO, and **ⓒ** four
bonding MOs.

Matter

Top view

ⓐ

$120°$ $C = C$
H,$^{\wedge}$H
$120°$
H — $120°$ — H

Ethene

Each C of ethene has trigonal planar geometry and bond angles of approximately 120°. The overall geometry is planar; that is, all the atoms lie in the same plane—the plane of the page.

Top view

ⓑ $120°$

sp^2 hybrid AO

The three sp^2 AOs that result from the hybridization of the $2s$, $2p_x$ and $2p_y$ AOs have trigonal planar geometry and lie in the x-y plane. (The small back lobes of the AOs are not shown here.) The $2p_z$ AO, which was not used to form the hybrids, is perpendicular to the plane of the hybrid AOs and is not shown in this

Side view

ⓒ

sp^2 AO

$2p_z$ AO

If the C is rotated so that the plane of the sp^2 AOs (the x-y plane) is perpendicular to the page, then the remaining $2p_z$ AO lies in the plane of the page.

The CH bond results from overlap of a C sp^2 AO with an H 1s AO ($\sigma_{Csp2+H1s}$).

Side view

ⓓ

H,,,C — C,,,,H
H H

This bond results from overlap of an sp^2 AO on one C with an sp^2 AO on the other C ($\sigma_{Csp2+Csp2}$).

This new type of overlap of a $2p$ AO on each C results in a new type of bond, a pi bond ($\pi_{C2p+C2p}$).

Active Figure 3.9

ORGANIC
Chemistry ⚛ Now™

BONDING AND ORBITAL PICTURES FOR ETHENE. Test yourself on the concepts in this figure at OrganicChemistryNow.

Matter
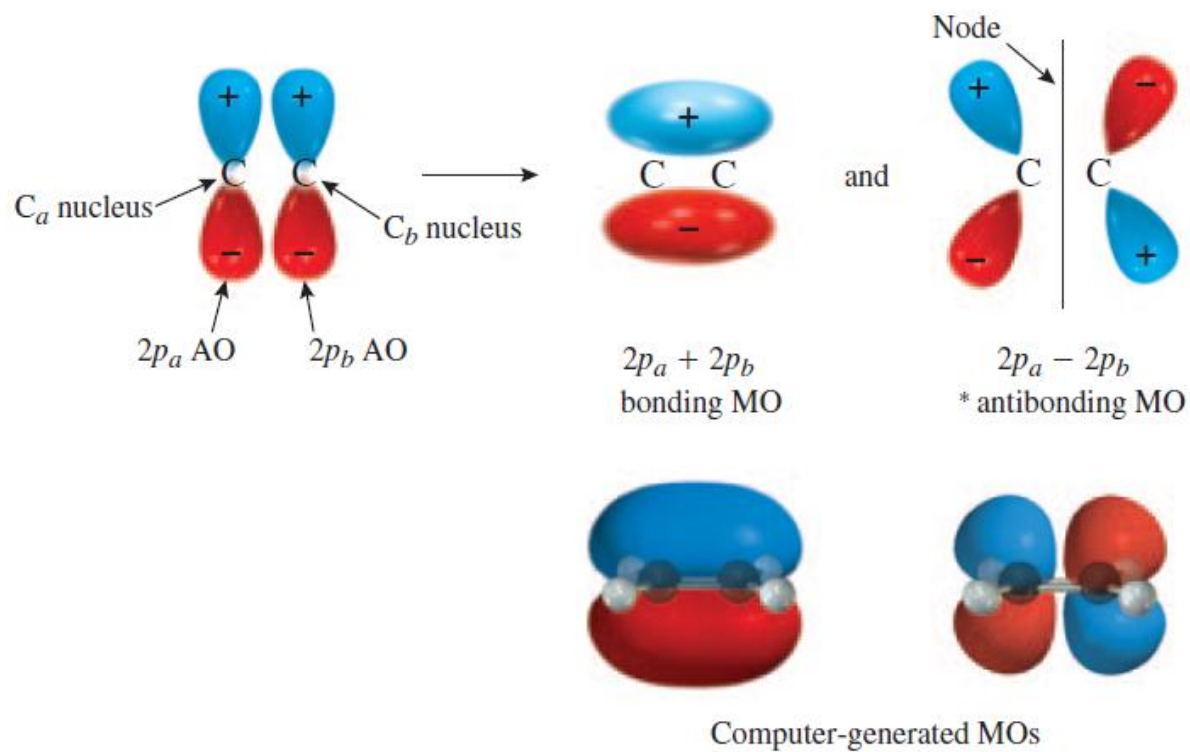
Figure 3.10

FORMATION OF PI BONDING
AND PI ANTIBONDING
MOLECULAR ORBITALS.

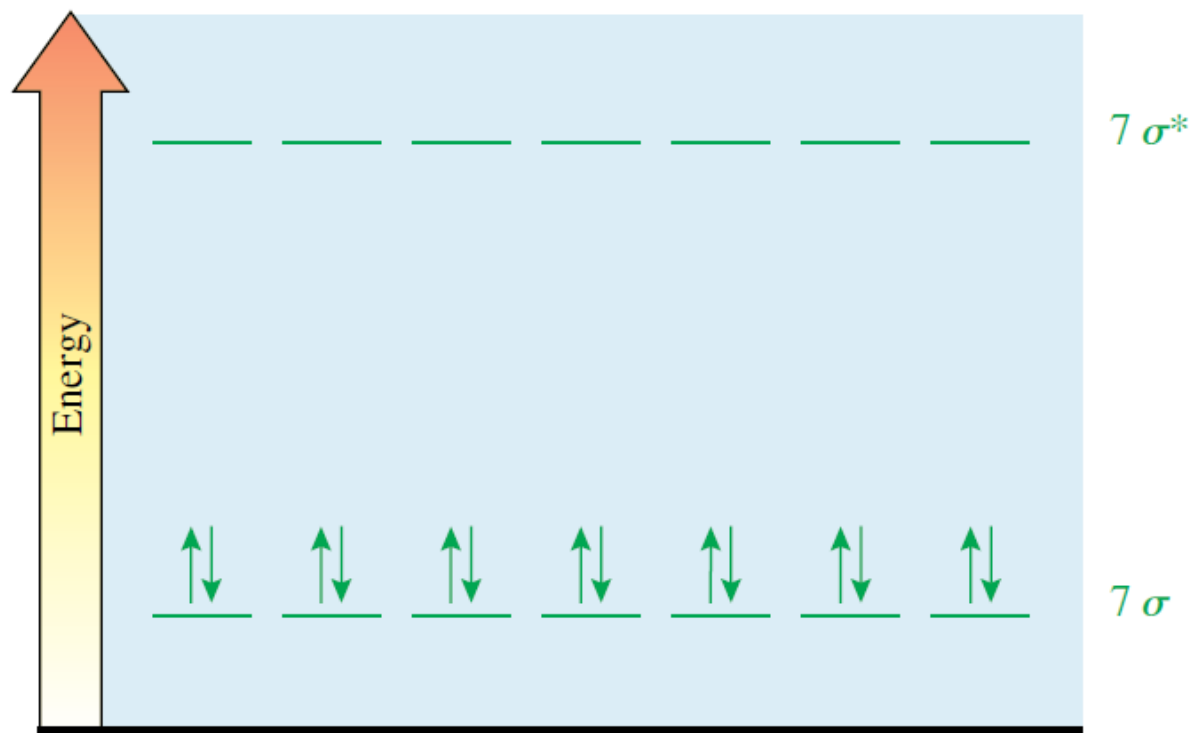C_a nucleus

C_b nucleus

$2p_a$ AO $2p_b$ AO

Node

and

$2p_a + 2p_b$
bonding MO

$2p_a - 2p_b$
* antibonding MO

Computer-generated MOs
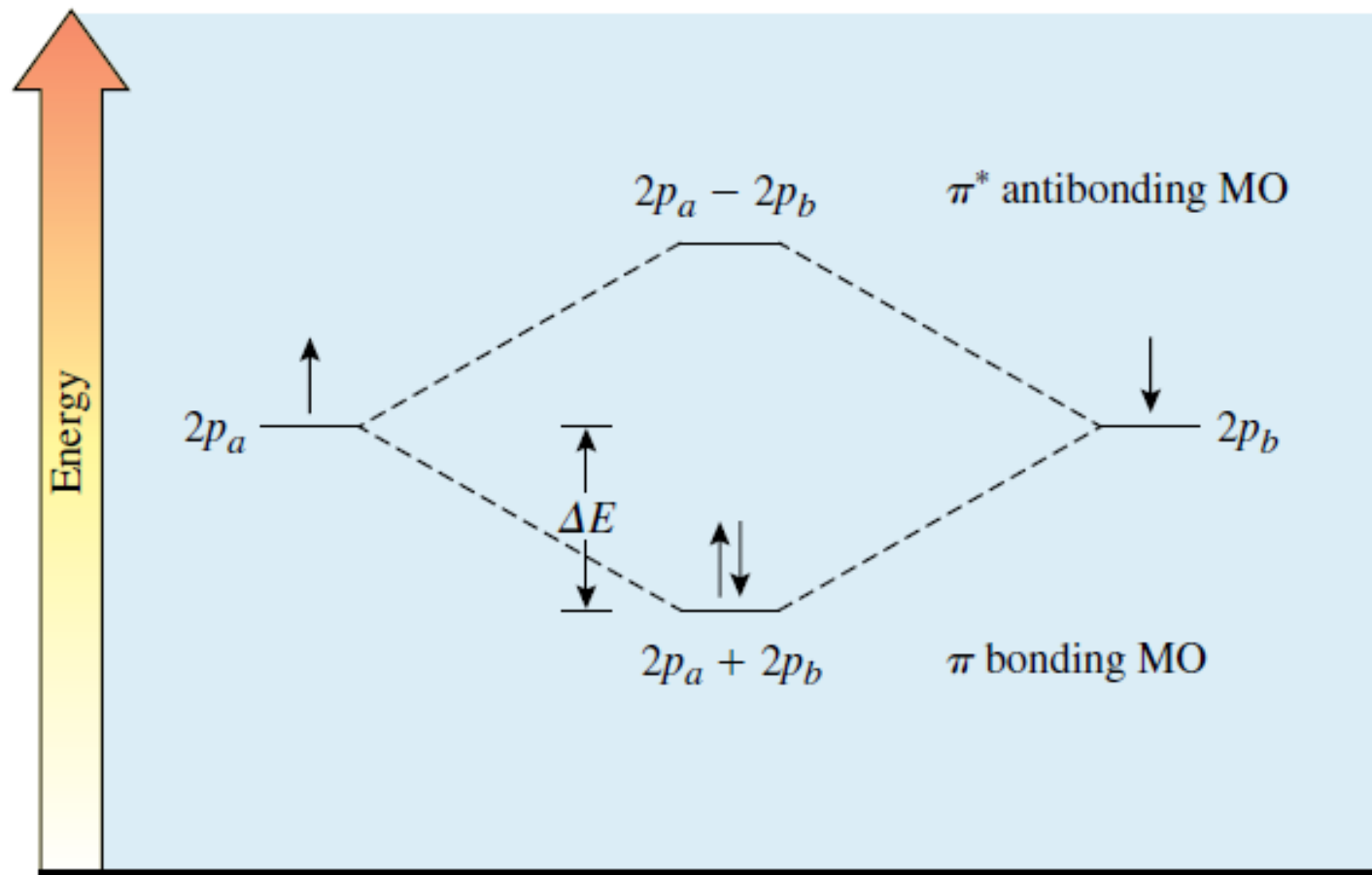
Matter

ENERGIES OF THE PI
BONDING AND ANTIBONDING
MOLECULAR ORBITALS.
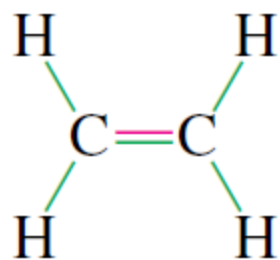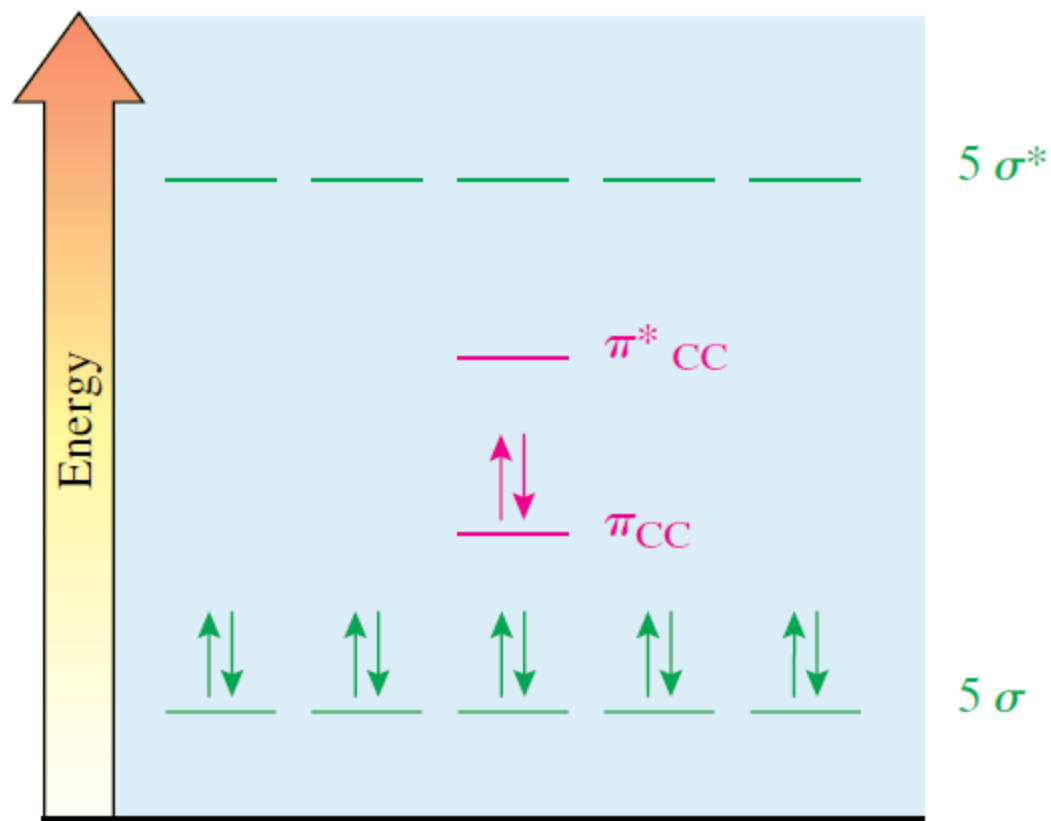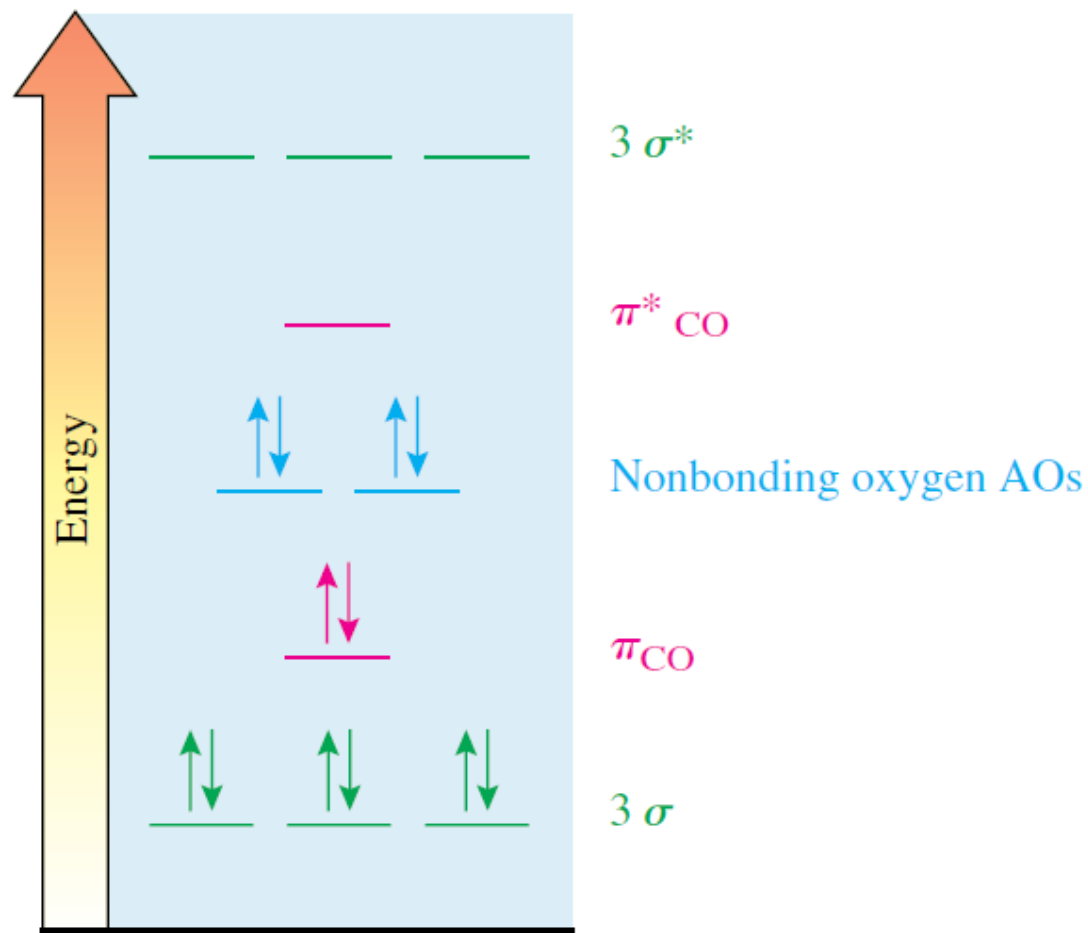
Matter

Ethane

Energy

$7\,\sigma^*$

$7\,\sigma$
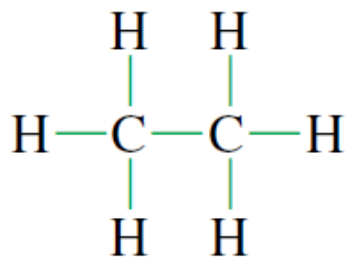
MOLECULAR ORBITAL
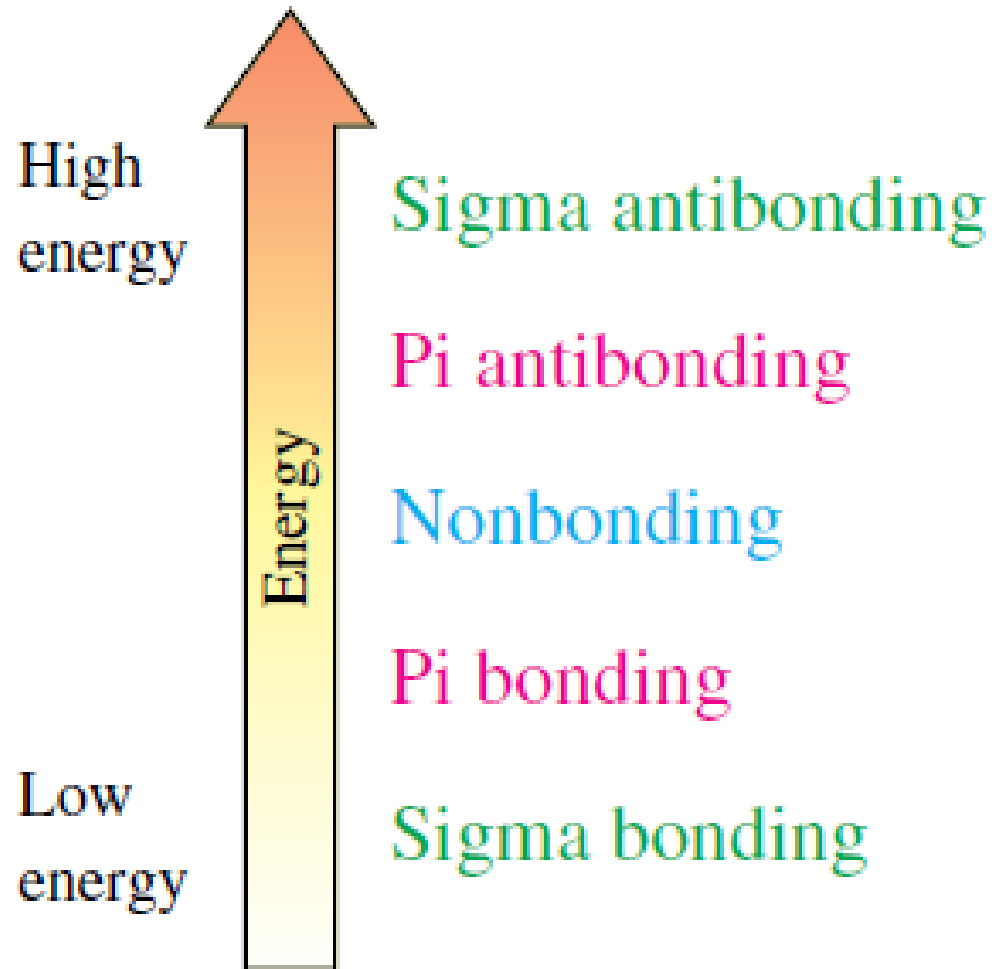ENERGY LEVEL DIAGRAM
FOR ETHANE, C_2H_6.

Matter

Ethene

MOLECULAR ORBITAL
ENERGY LEVEL DIAGRAM
FOR ETHENE, C_2H_4.

Matter
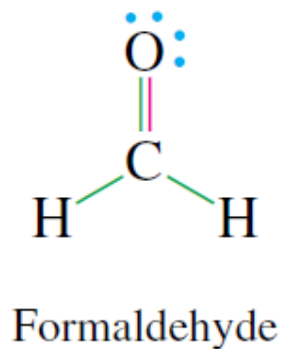
Formaldehyde

MOLECULAR ORBITAL ENERGY LEVELS FOR FORMALDEHYDE, CH₂O.

Matter

High
energy

Low
energy

Energy

Sigma antibonding

Pi antibonding

Nonbonding

Pi bonding

Sigma bonding
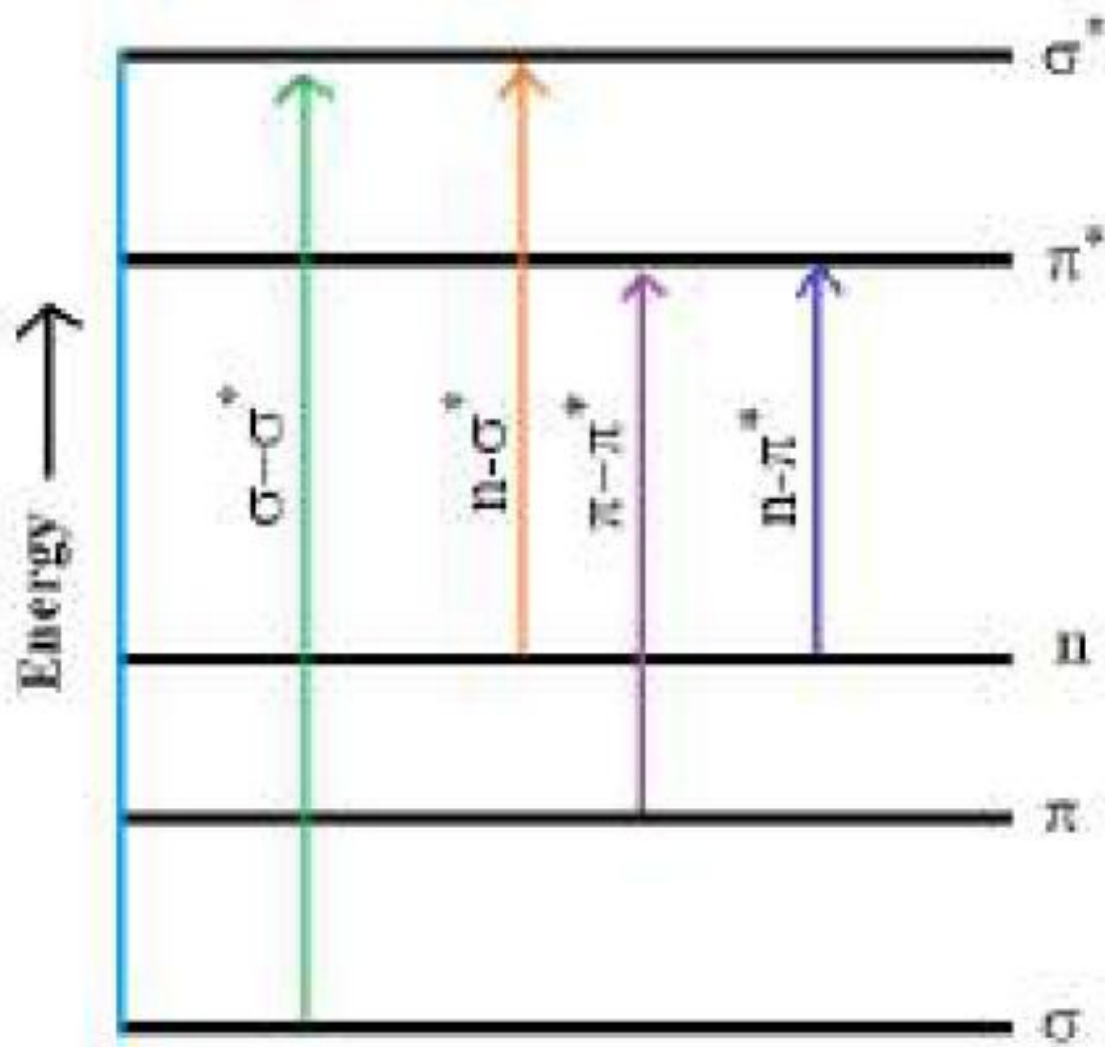
Matter

$$n\text{-}\pi^* < \pi\text{-}\pi^* < n\text{-}\sigma^* < \sigma\text{-}\sigma^*$$

Energy

Interaction between Radiation and Matter
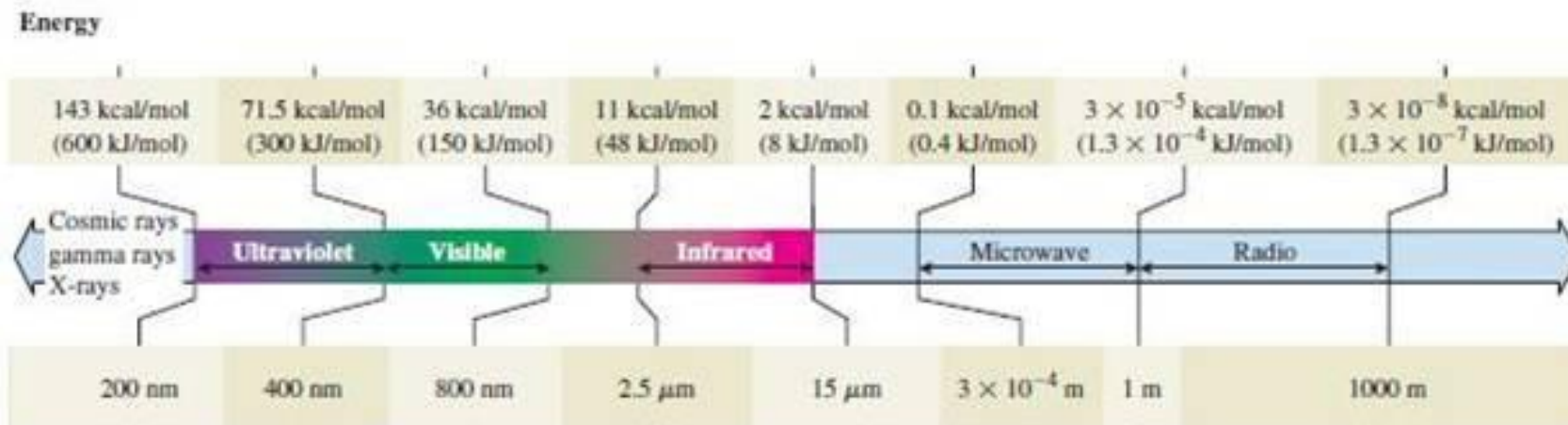
RADIATION
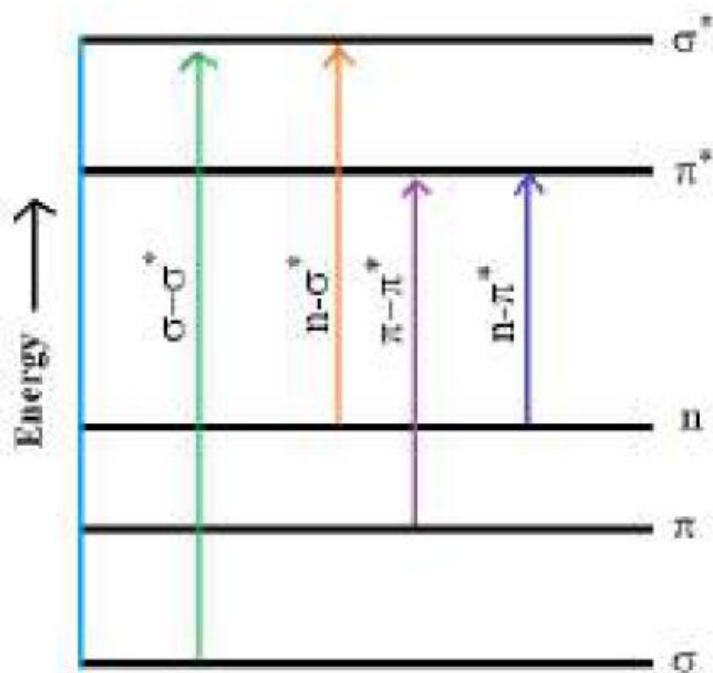
MATTER
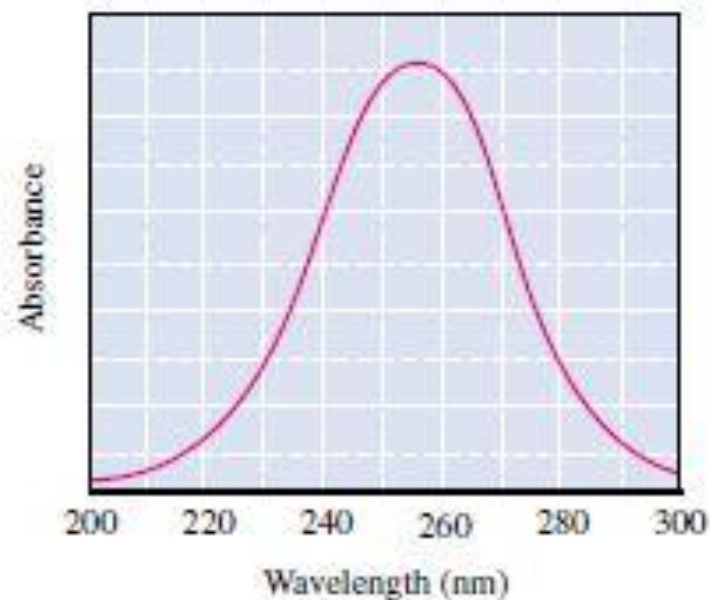
SPECTRUM

Simplified schematic diagram of an absorption spectrophotometer
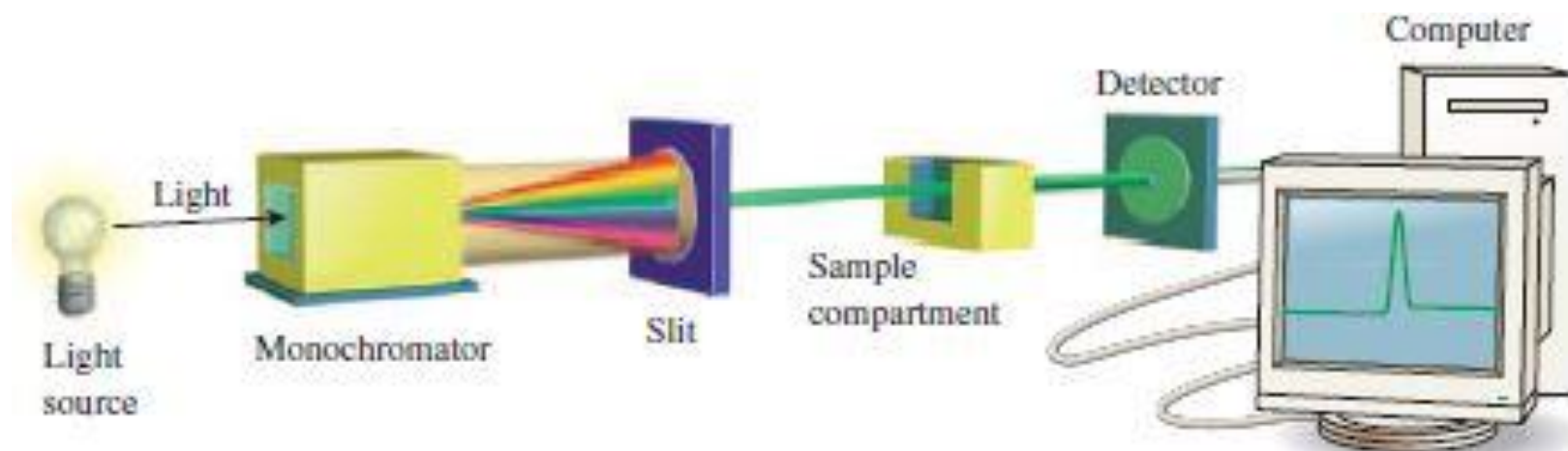
Lambert-Beer's Law for UV-Visible Spectroscopy
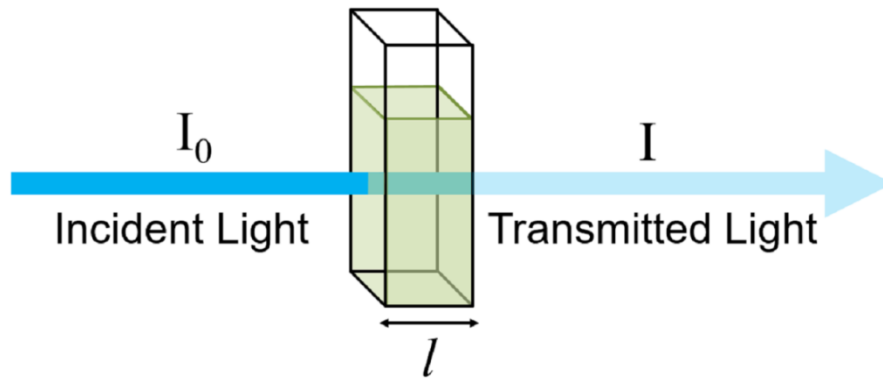
Lambert Law : It states that when a monochromatic beam of light passes through a solution, rate of decrease of intensity with respect to the thickness of the medium is directly proportional to the intensity of incident light.

$$- dI/dl = kI$$

Beer Law : It states that when a monochromatic beam of light passes through a solution, rate of decrease of intensity with respect to the thickness of the medium is directly proportional to the incident light and concentration of the solution.

Lambert-Beer Law:

$$- dI/dl = k' IC$$

Lambert-Beer Law :

-dI/dl   =   k′ IC

$-dI/I$ = k' C dl

After integration (Io to I   and   l = 0 to l = l)

$-\text{Log } I / I_o$ = $k'/2.303$ C l

$\text{Log } I_o / I$ = ϵ C l

$$A = \epsilon\ C\ l$$

A = Absorbance
ϵ = Molar extinction coefficient
C = Concentration
l = path length

Types of electronic Transition:

1. **σ – σ* :**   Electron gets excited from **sigma bonding molecular orbital** to **sigma anti-bonding molecular orbital**. It is high energy process. Absorption will occur at lower wavelength.

Generally such transitions do not absorb in the region 200-400 nm.

Examples: methane ethane etc. absorb below 200 nm

Types of electronic Transition:

2. n – σ* : Electron gets excited from **non-bonding molecular orbital** to **sigma anti-bonding molecular orbital**. These transitions require less energy than σ – σ* transitions.

Such transitions generally take place in saturated compounds having at least one hetero atom.

Examples: Halide, alcohol, ether etc

H_2O λ_{max} = 167 nm , CH_3OH λ_{max} = 174 nm

CH_3Cl λ_{max} = 175 nm, CH_3I λ_{max} = 258 nm

Types of electronic Transition:

3. $\pi - \pi^*$: Electron gets excited from **pi-bonding molecular orbital** to **pi-antibonding molecular orbital**.

Such transitions occur in unsaturated compounds such as alkene, alkyne etc.

Examples: ethene, 1,3-butadiene

For unconjugated system λ_{max} = 170 - 190 nm

For conjugated system λ_{max} = 215 - 250 nm

Types of electronic Transition:

4. n – π* **:** Electron gets excited from **non-bonding molecular orbital** to **pi-antibonding molecular orbital**.

Such transitions occur in unsaturated compounds such as aldehyde, ketones, acid, ester etc.

Examples: For acetone

$$H_3C \diagdown \atop H_3C \diagup C = O \quad , \text{ two peaks}$$

λ   =   190 nm

λ   =   275 nm

λmax = 195 nm
π ⟶ π* transition

:O:
C
H₃C   CH₃
acetone

λmax = 274 nm
n ⟶ π* transition

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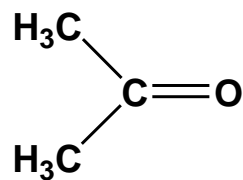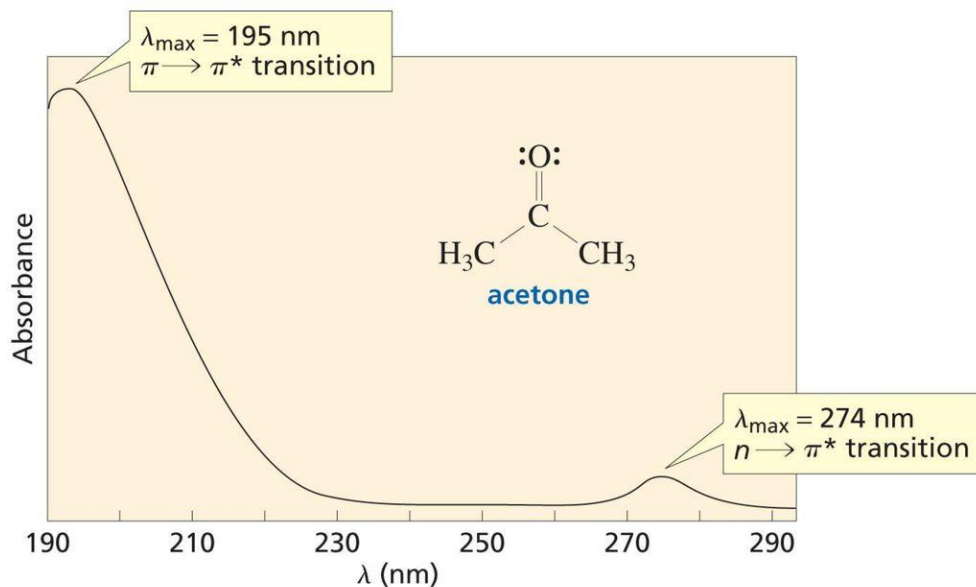
Selection Rules

1. Spin selection rule: $\Delta S = 0$

allowed transitions: singlet $\rightarrow$ singlet or   triplet $\rightarrow$ triplet
forbidden transitions: singlet $\rightarrow$ triplet   or   triplet $\rightarrow$ singlet

Changes in spin multiplicity are forbidden

ground singlet state   excited singlet state   excited triplet state
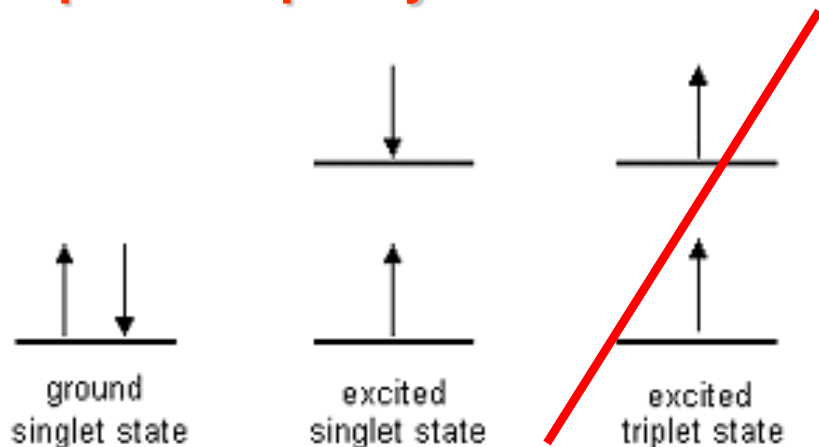
2. Laporte (orbital) selection rule: $\Delta l = \pm 1$

allowed transitions: s $\rightarrow$ p or p $\rightarrow$ d

forbidden transitions: s $\rightarrow$ s or p $\rightarrow$ p

❶ In the skin of animals, 7-dehydrocholesterol is converted to pre-cholecalciferol by the action of sunlight. This electrocyclic reaction must occur in a conrotatory fashion to avoid forming a trans double bond in one of the rings. Because three electron pairs are involved, this reaction is photochemically allowed.

7-Dehydrocholesterol

❶ $h\nu$

Pre-cholecalciferol

❷ Δ
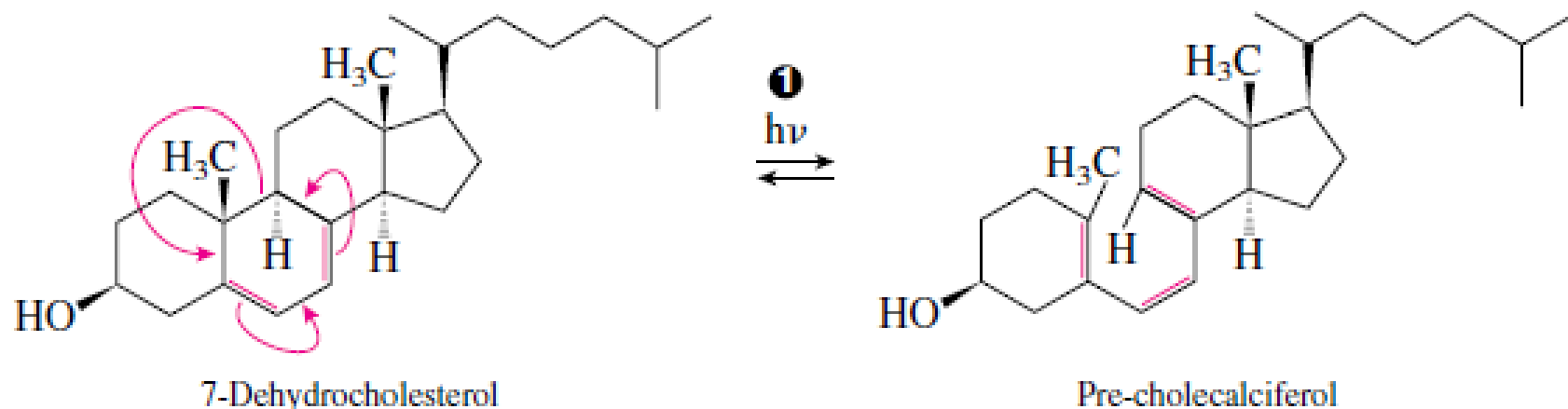
❷ The second step is a [1,7] sigmatropic rearrangement and has been shown to occur thermally. Because it involves four electron pairs, to be thermally allowed it must occur with an unusual geometry, where the hydrogen migrates from the top of the pi system on one end to the bottom of the pi system on the other.

Cholecalciferol
(vitamin D_3)

Ergosterol

1) hν

2) Δ

Calciferol
(vitamin D₂)
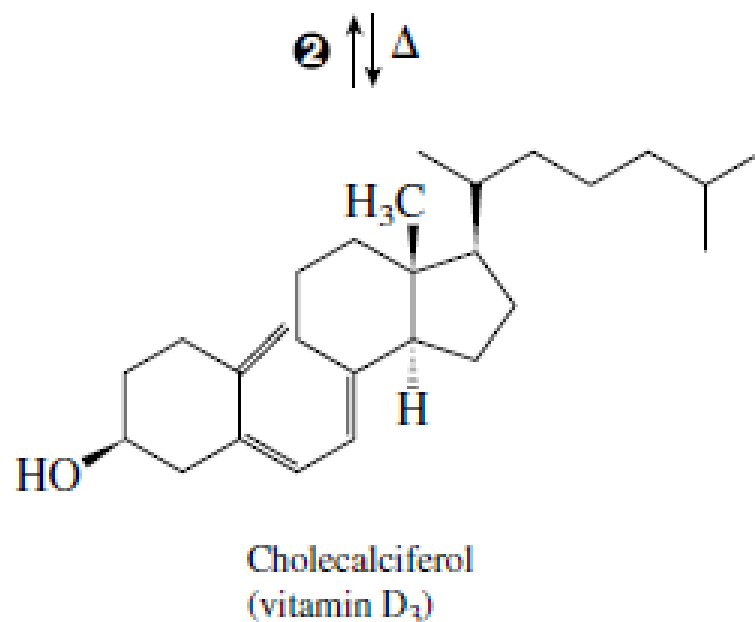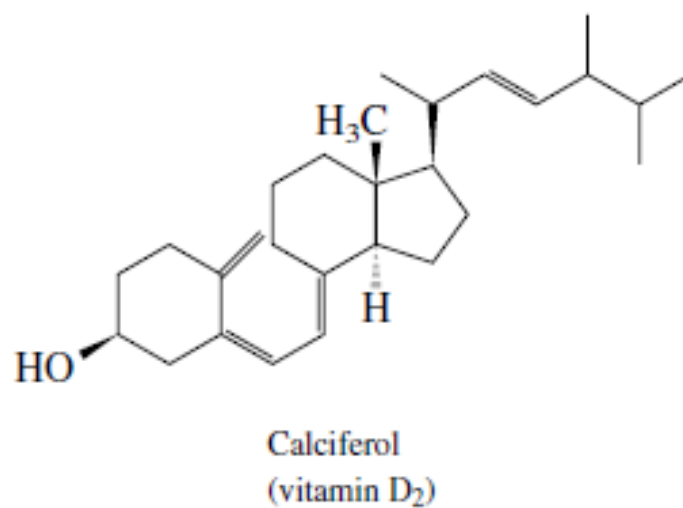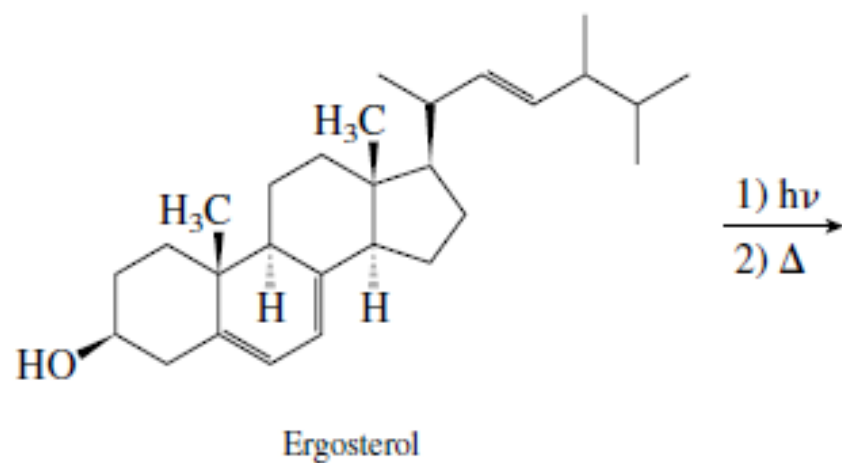
Chromophore:

A functional group that absorbs in UV-visible region i.e. 200-800 nm.

e.g. >C=O, -NO$_2$, N=N , C=C etc.
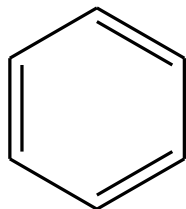
λ_{max} = **255 nm**

Auxochromes

A functional group that enhances the absorbing properties of chromophore,
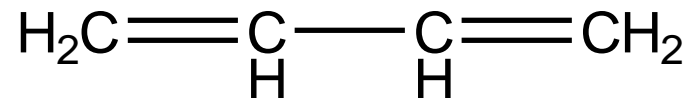
e.g. –OR, -NH$_2$, -NR$_2$ etc

NH$_2$
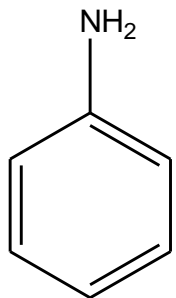
λ_{max} = **280 nm**

a) Effect of conjugation on λ_{max}

$$H_2C = CH_2$$

$$\lambda_{max} = 190 \text{ nm}$$

$$H_2C = \underset{H}{C} - \underset{H}{C} = CH_2$$
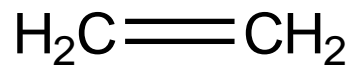
$$\lambda_{max} = 217 \text{ nm}$$
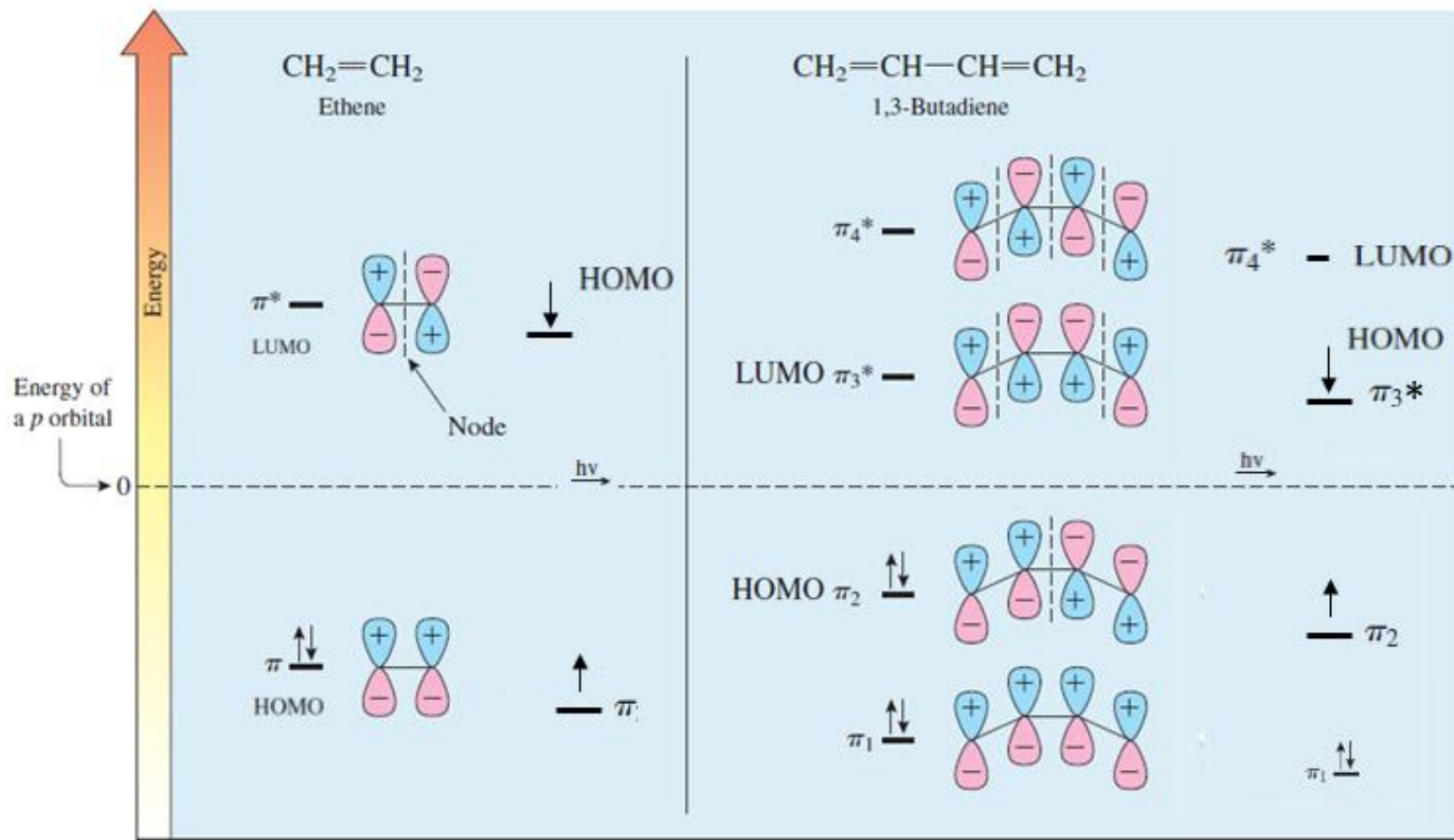
ENERGIES AND NODAL PROPERTIES FOR THE PI MOS OF ETHENE AND 1,3-BUTADIENE.

The energy gap between HOMO to LUMO decreases due to conjugation. Therefore, transition in 1,3-butadiene occur at higher wavelength as compared to ethene. The λ_{max} value is at about 217 nm, a significant difference from the value of 190 nm in ethene.

Shifts and Effects
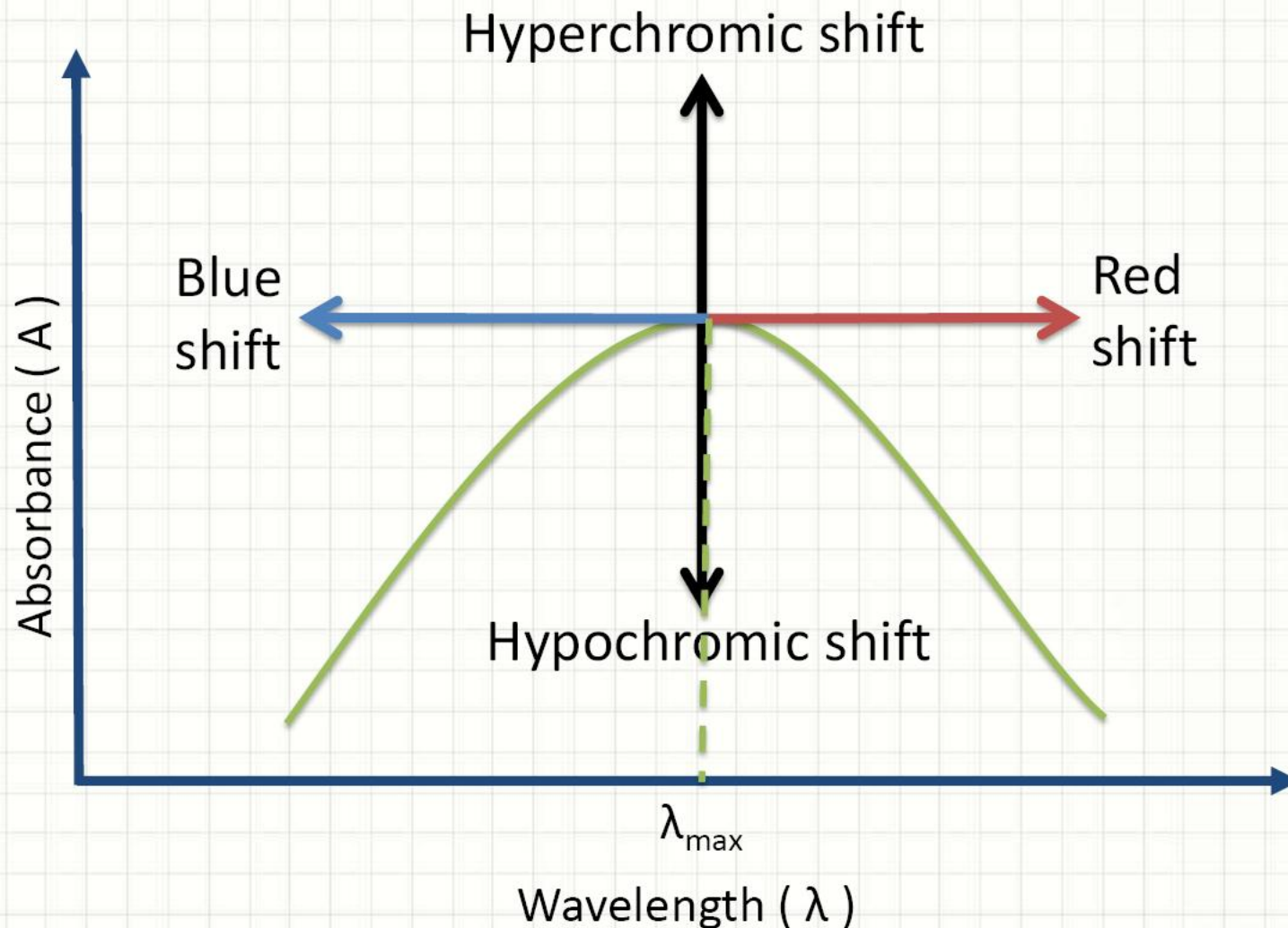
Which of the isomers of pentadiene a) or b) will show the longest wavelength of the UV absorption

a) CH2=CH-CH=CH-CH3

b) CH2=CH-CH2-CH=CH2
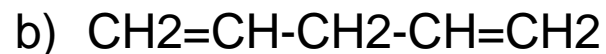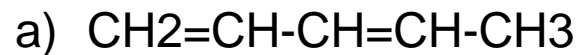
Isomer a), Since conjugated dienes have longer wavelength of absorption than nonconjugated

The following are pairs of isomers, and one member of each pair absorbs ultraviolet/visible light at longer wavelength than the other: In each case state whether it is first or second member

a) 1,3-hexadiene and 1,4-hexadiene

b) 1,2-dihydronaphthalene and 1,4-dihydronaphthalene

a) 1,3-hexadiene

b) 1,2-dihydronaphthalene

Given that extending a chromophore involves additional conjugation or the involvement of non bonding electrons, which of the following as a substituent in benzene will substantially increase the maximum wavelength of absorption in the electronic spectrum

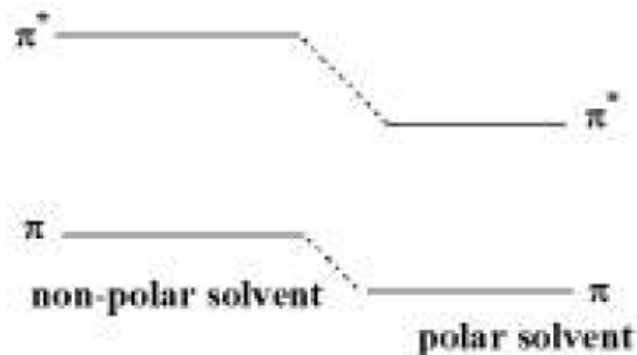a) –CH=CH2   b) –OH   c) –N=N-Me   d) –NO2   e) –CH3

All except e)
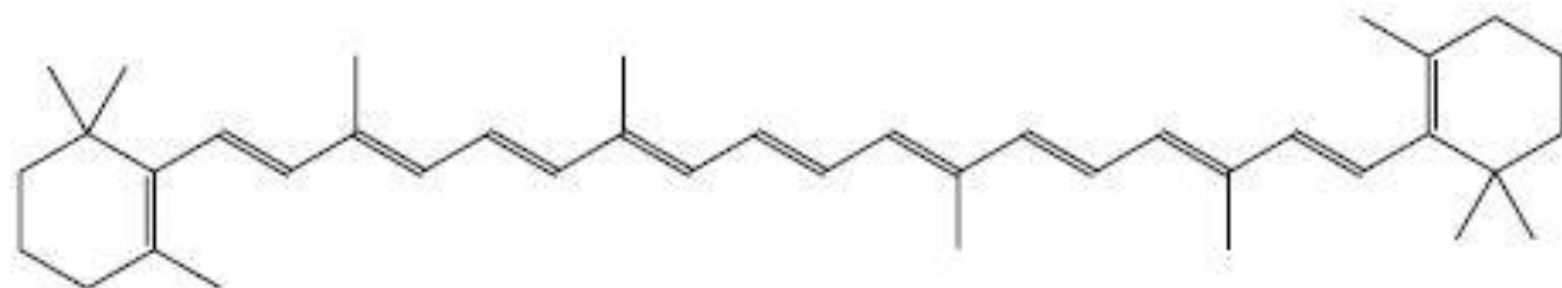
β-Carotene $\lambda_{max} = 452$ nm

b) Effect of solvent:

In polar solvent, $\pi - \pi^*$ transitions shift towards longer wavelength (Red shift), because dipole interactions with polar solvent molecules lower the energy of excited state (π^*) than that of the ground state $(\pi^*$ orbital's are stabilized by hydrogen bonding with polar solvent).

Whereas in polar solvent, $n - \pi^*$ transitions shift towards lower wavelength (Blue shift), because dipole interactions with polar solvent molecules lower the energy of ground state (n) than that of the excited state $(n$ orbital's are stabilized by hydrogen bonding with polar solvent).
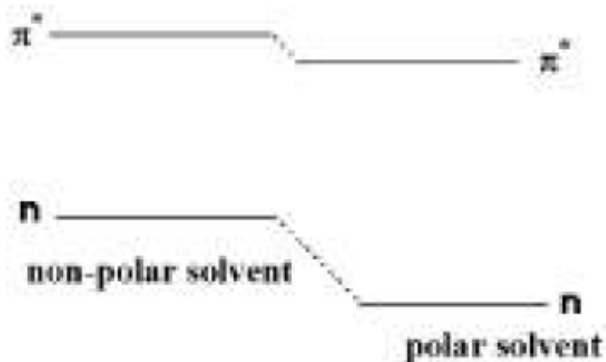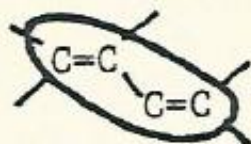
Woodward rules to calculate λ_{max} in the case of Dienes
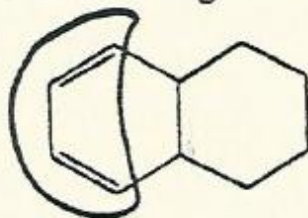
A. Definition of Terms and Illustrations.

Acyclic diene: Two double bonds in conjugation which are not part of a ring system.

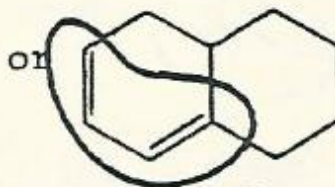e.g.

Homoannular diene: Two double bonds in conjugation both of which are in one ring of a fused six-membered ring system.
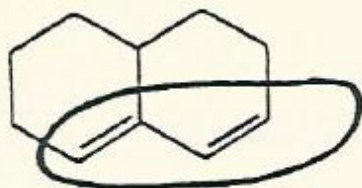
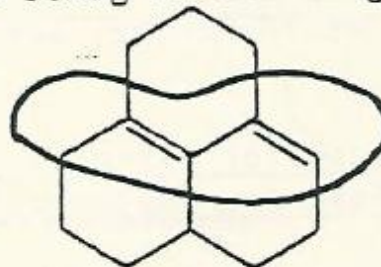e.g.   or

Heteroannular diene: Two double bonds in conjugation in a fused six-membered ring structure, one double bond being in one ring, the other double bond in another ring.
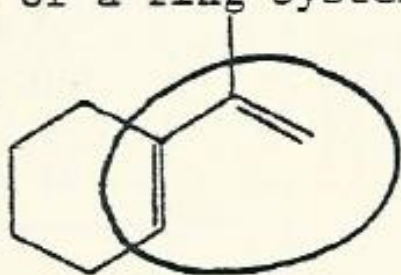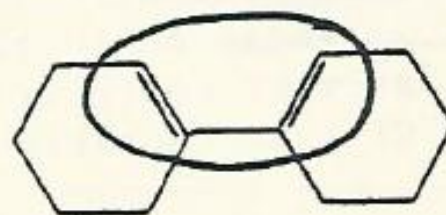
e.g.   or

Semicyclic diene: Two double bonds in conjugation, one of which is part of a ring system, while the other is outside the ring system.
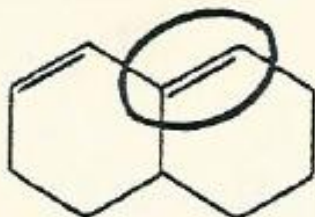
e.g.

Exocyclic Double Bond: Any carbon-carbon double bond in which one carbon of the double bond is part of one ring which does not contain that double bond.
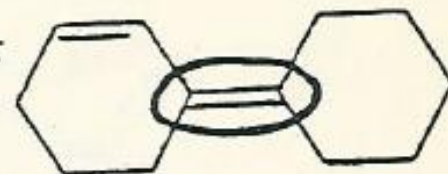
e.g.

B. <u>Numerical Statement of Rules.</u> **All values of λ are in nm (nanometer)**

1. Heteroannular, acyclic, and semicyclic dienes

      <u>Base for parent system - heteroannular</u>   <u>214</u>
      <u>Base for parent system - acyclic or semicyclic</u>   <u>217</u>
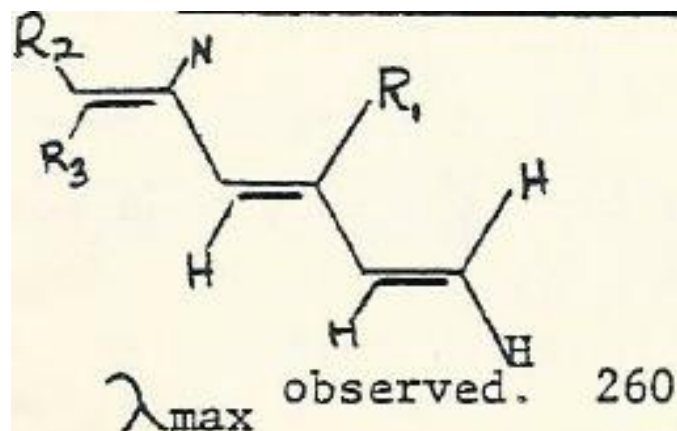
Additive Effects:

    a. each alkyl substituent   5
    b. each exocyclic double bond   5
    c. extended conjugation per double bond   30
    d. solvent correction if necessary   --
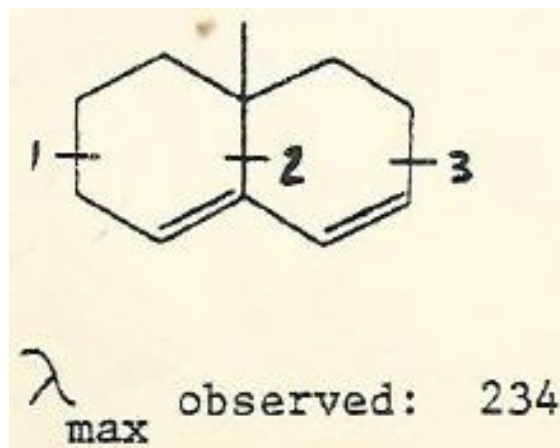   e. Cl or Br substituent   17

                              TOTAL

Examples

Acyclic System (or semicyclic)

λmax observed. 260

Calculated

Base	=	217
3 Alkyl	=	15
extended conj.	=	30
		262

Heteroannular System

λmax observed: 234

Calculated

Base	=	214
3 alkyl	=	15
1 exo-double bond	=	5
		234

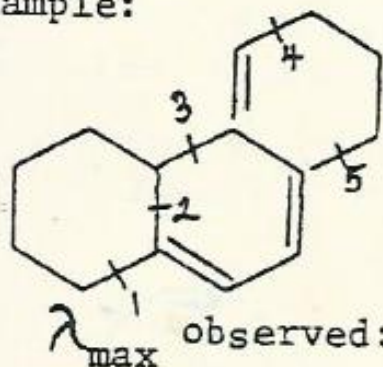2. Homoannular dienes

   Base for Parent System   253

Additive Effects:

   a. Each alkyl substituent   5
   b. Each exocyclic double bond   5
   c. Extended conjugation/per double bond   30
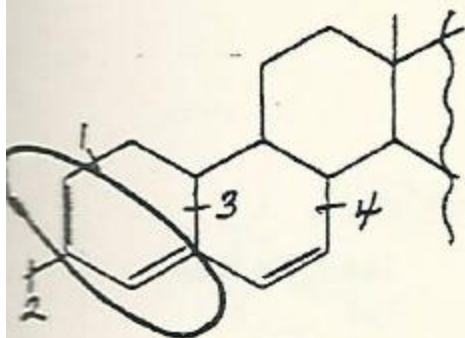   d. Solvent Correction if necessary   ---
   e. Clor Br stubstituent   17

Example:

λ_{max} observed: 323

Calculated

Base	= 253
5 alkyl	= 25
extended conj.	= 30
3 exo-double bond	= 15

323

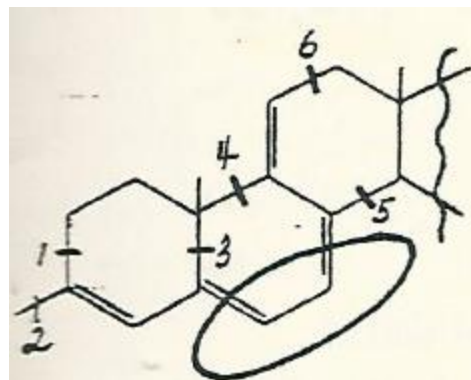observed

306

calculated

253 – Base-Homo
20 – 4 alkyl
5 – 1 exo-DB
30 – 1 conj. DB
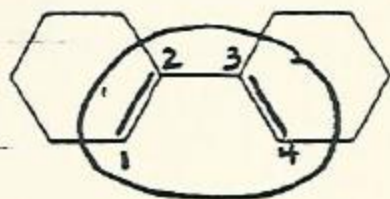
308

observed

355

calculated

253 – Base-Homo
30 – 6 alkyl
15 – 3 exo-DB
60 – 2 conj. DB
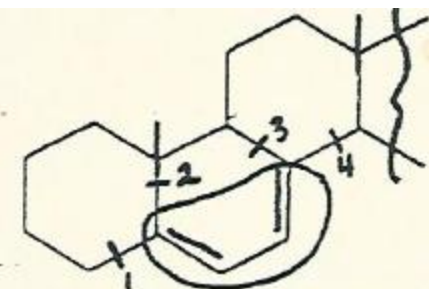
358

observed

236

calculated

217 - Base-Acyclic
 20 - 4 alkyl
237

observed

282

calculated

253 - Base-Homo
 20 - 4 alkyl
 10 - 2 exo-DB
283

Table 15.1   Relationship between Color Absorbed and Color Observed

Wavelength Absorbed (nm)	Color Absorbed	Color Observed
400	Violet	Yellow-green
425	Blue-violet	Yellow
450	Blue	Orange
490	Blue-green	Red
510	Green	Purple
530	Yellow-green	Violet
550	Yellow	Blue-violet
590	Orange	Blue
640	Red	Blue-green
730	Purple	Green

THANK YOU