Course : SC202 (Chemistry)
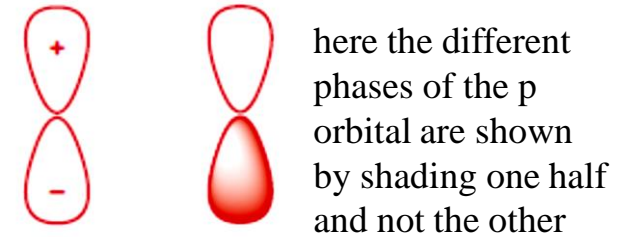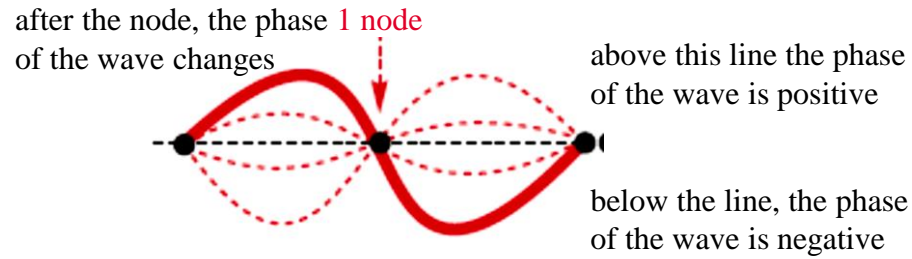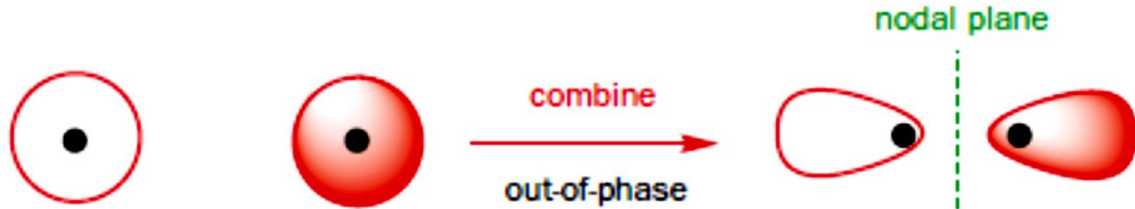# Dr. Sangita Talukdar
Lecture-2

The phase of an orbital

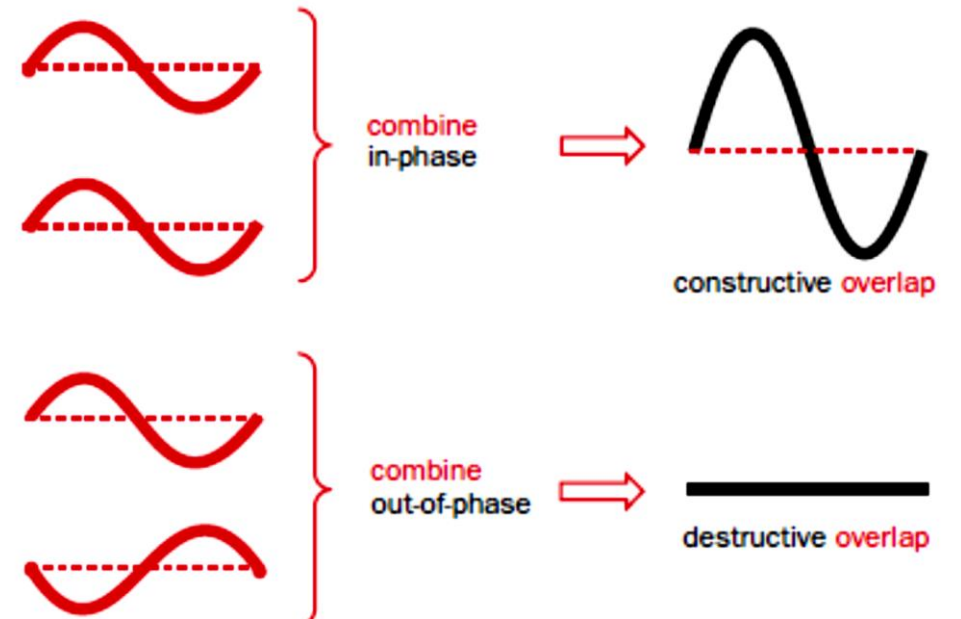after the node, the phase 1 node
of the wave changes

above this line the phase
of the wave is positive

below the line, the phase
of the wave is negative

here the different
phases of the p
orbital are shown
by shading one half
and not the other
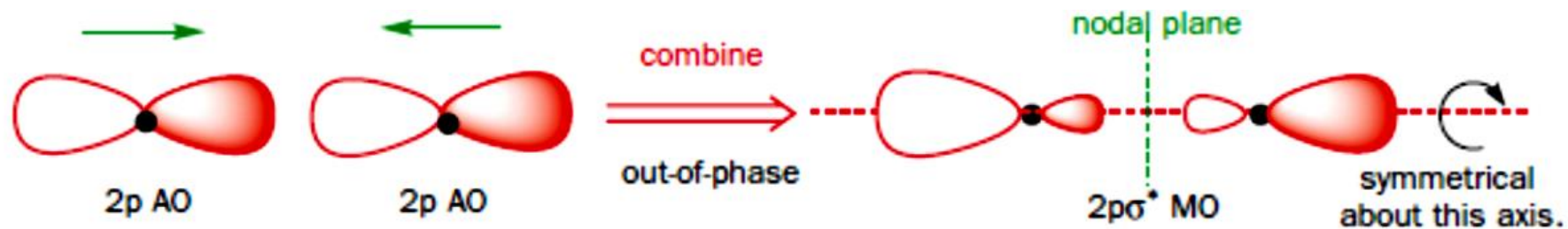
Molecular orbitals

combine
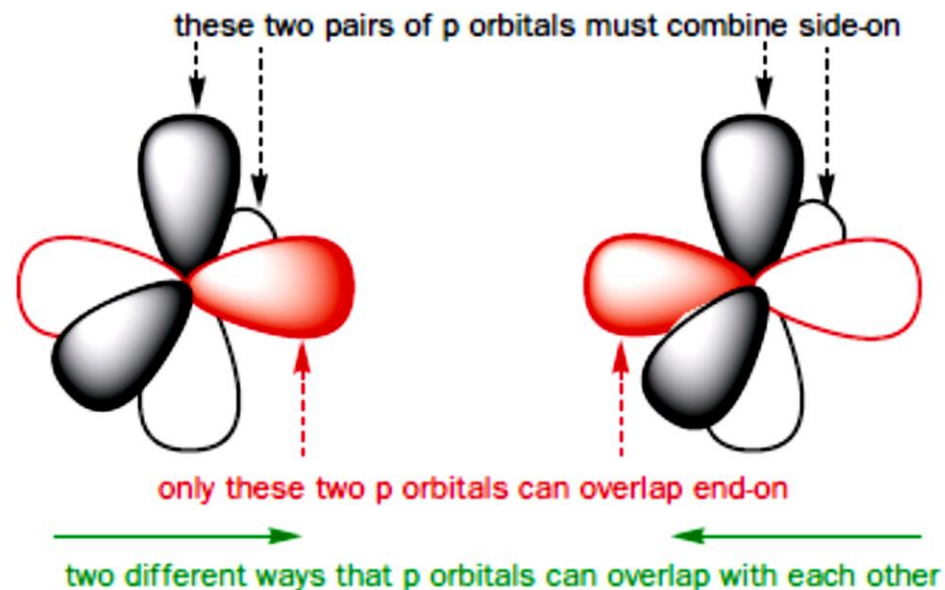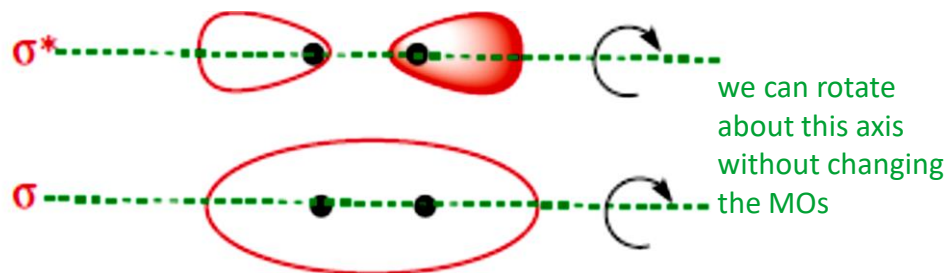out-of-phase

nodal plane

the two 1s orbitals combining out-of-phase to give an **antibonding orbital**
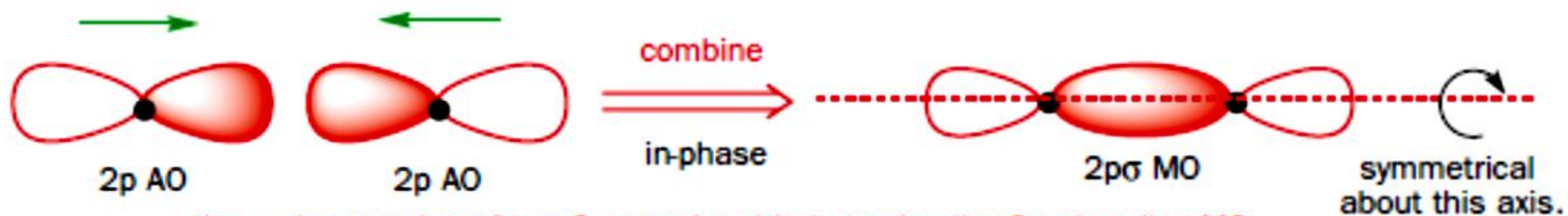
combine
in-phase

the two 1s orbitals combining in-phase to give a **bonding orbital**

combine
in-phase

constructive overlap

combine
out-of-phase

destructive overlap

Molecular orbitals

σ*

σ

we can rotate
about this axis
without changing
the MOs

these two pairs of p orbitals must combine side-on

only these two p orbitals can overlap end-on

two different ways that p orbitals can overlap with each other

combine

out-of-phase

2p AO   2p AO

nodal plane

$2p\sigma^*$ MO

symmetrical
about this axis.

the end-on overlap of two 2p atomic orbitals to give the $2p\sigma^*$ antibonding MO

combine

in-phase

2p AO   2p AO

$2p\sigma$ MO

symmetrical
about this axis.

the end-on overlap of two 2p atomic orbitals to give the $2p\sigma$ bonding MO

3

Molecular orbitals
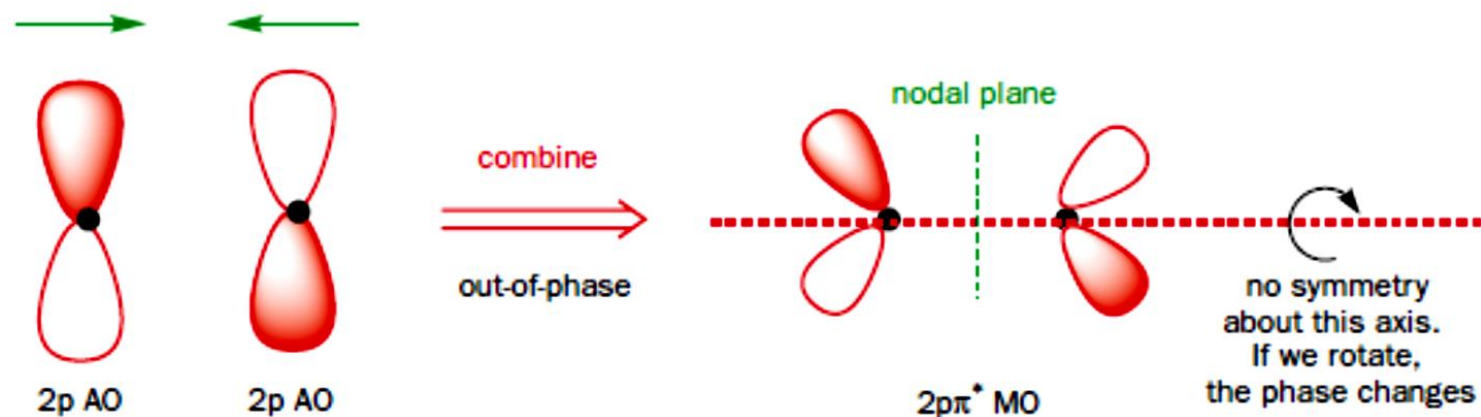

the side-on overlap of two 2p atomic orbitals to give the 2pπ* antibonding MO

the side-on overlap of two 2p atomic orbitals to give the 2pπ bonding MO

Molecular orbitals resulting from the combination of atomic orbitals

increasing energy of orbitals

$2p\sigma^*$

$2 \times 2p\pi^*$

$3 \times 2p$ $3 \times 2p$

$2 \times 2p\pi$

$2p\sigma$

$2s\sigma^*$

$2s$ $2s$

$2s\sigma$

the $1s\sigma$ and $1s\sigma^*$ MOs are much lower in energy than the other MOs

$1s\sigma^*$

$1s$ $1s$

atomic orbitals
on atom A

$1s\sigma$

atomic orbitals
on atom B

molecular orbitals resulting from the combination of atomic orbitals
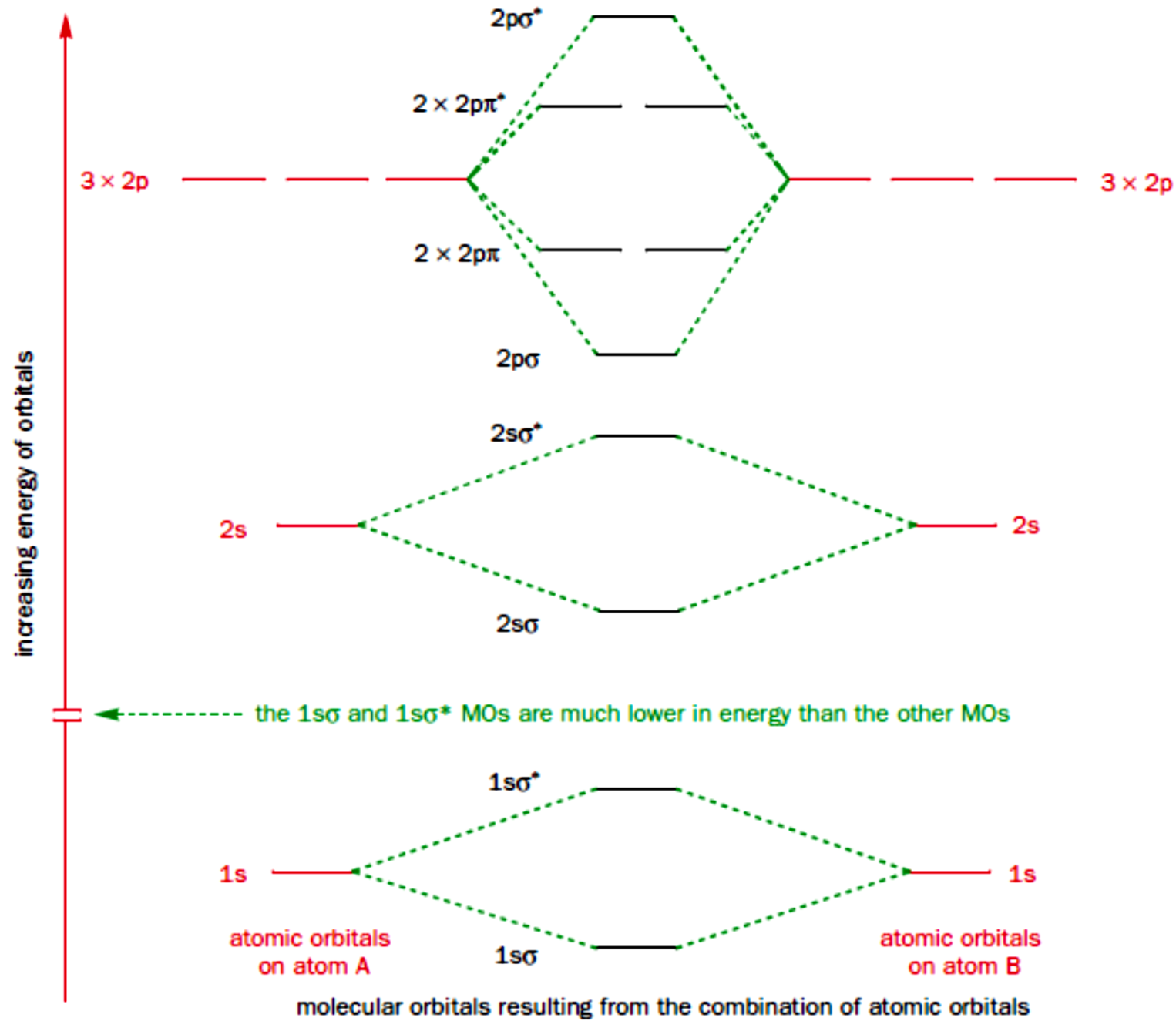
Delocalization and Conjugation

σ bonds shown in green

a single p orbital
different phases shown
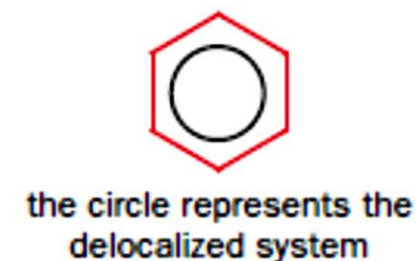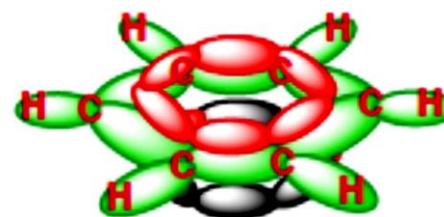in red and black

combining different pairs of p orbitals puts
the double bonds in different positions
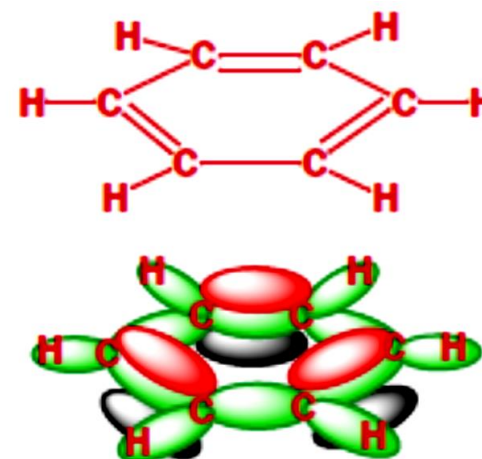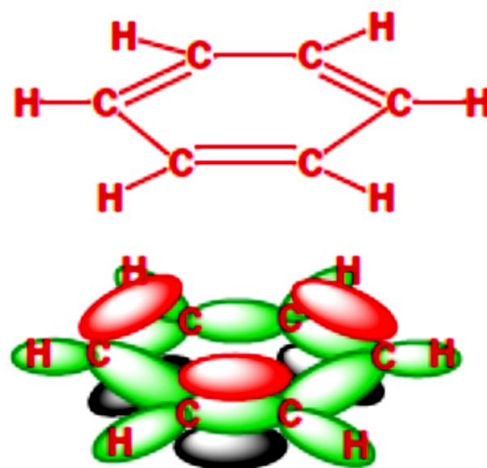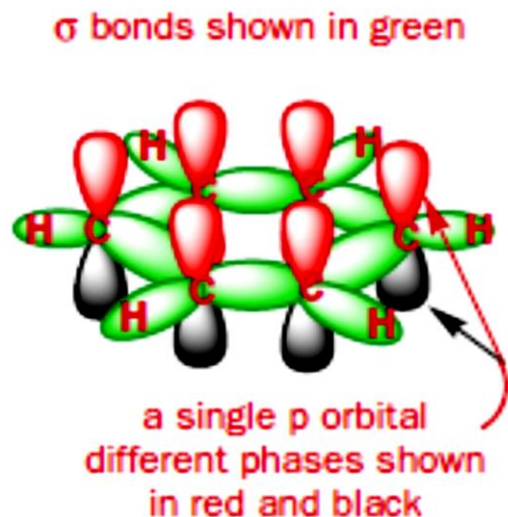
π electrons in benzene as **delocalized**, that is, no longer localized in specific double bonds between two particular carbon atoms but spread out, or delocalized, over all six atoms in the ring.

the circle represents the
delocalized system

When two double bonds are separated by just one single bond, the two double bonds are said to be **conjugated**. Conjugated double bonds have different properties from isolated double bonds, both physically and chemically.
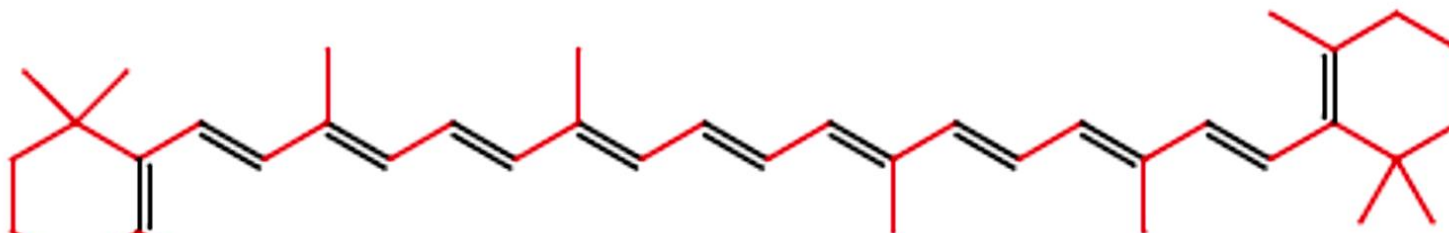
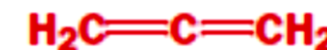β-carotene – all eleven double bonds are conjugated
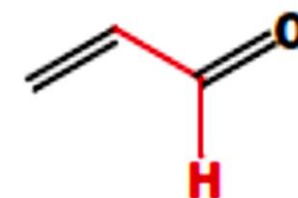
Propenal

these four double bonds are not conjugated – they are all separated by two single bonds

$H_2C{=}C{=}CH_2$
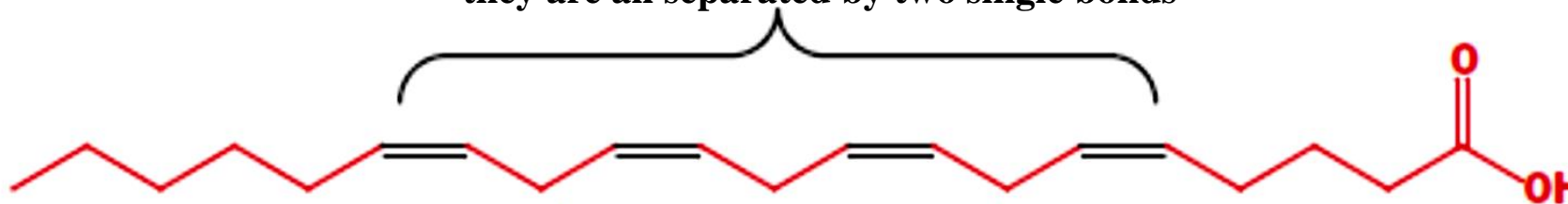
Conjugation focuses on the sequence of alternating double and single bonds while **delocalization** focuses on the molecular orbitals covering the whole system.
Electrons are *delocalized* over the whole of a *conjugated* system.

Theory of electronic transitions
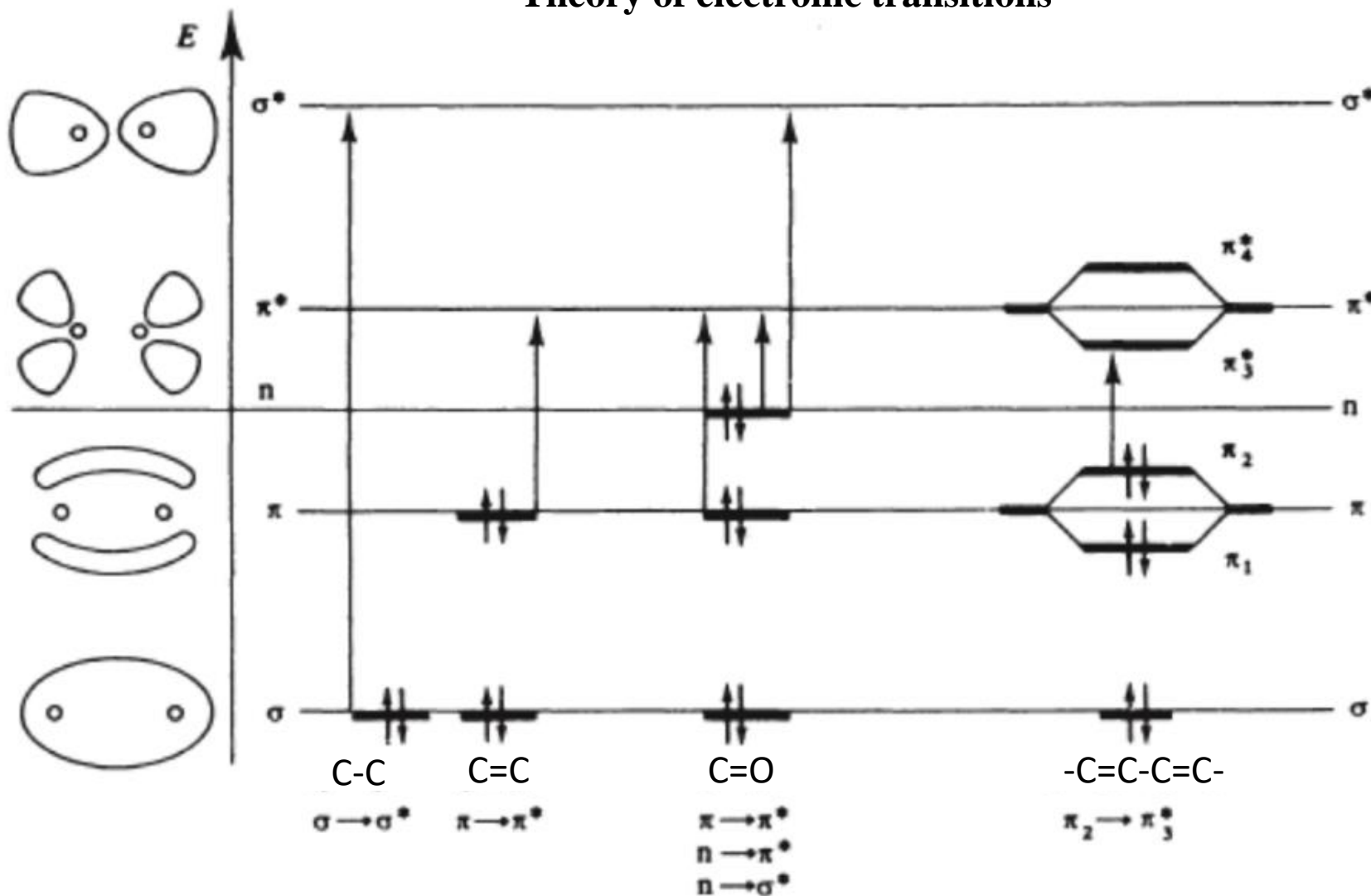
$$E = hv = hc/\lambda$$

Conjugated dienes show absorption at much longer wavelength than do isolated alkene groups

NUCLEAR MAGNETIC RESONANCE (NMR)

- Nuclear magnetic resonance (NMR) spectroscopy: a spectroscopic technique that gives us information about the number and types of atoms in a molecule, for example, about the number and types of

  - hydrogen atoms using ^{1}H-NMR spectroscopy
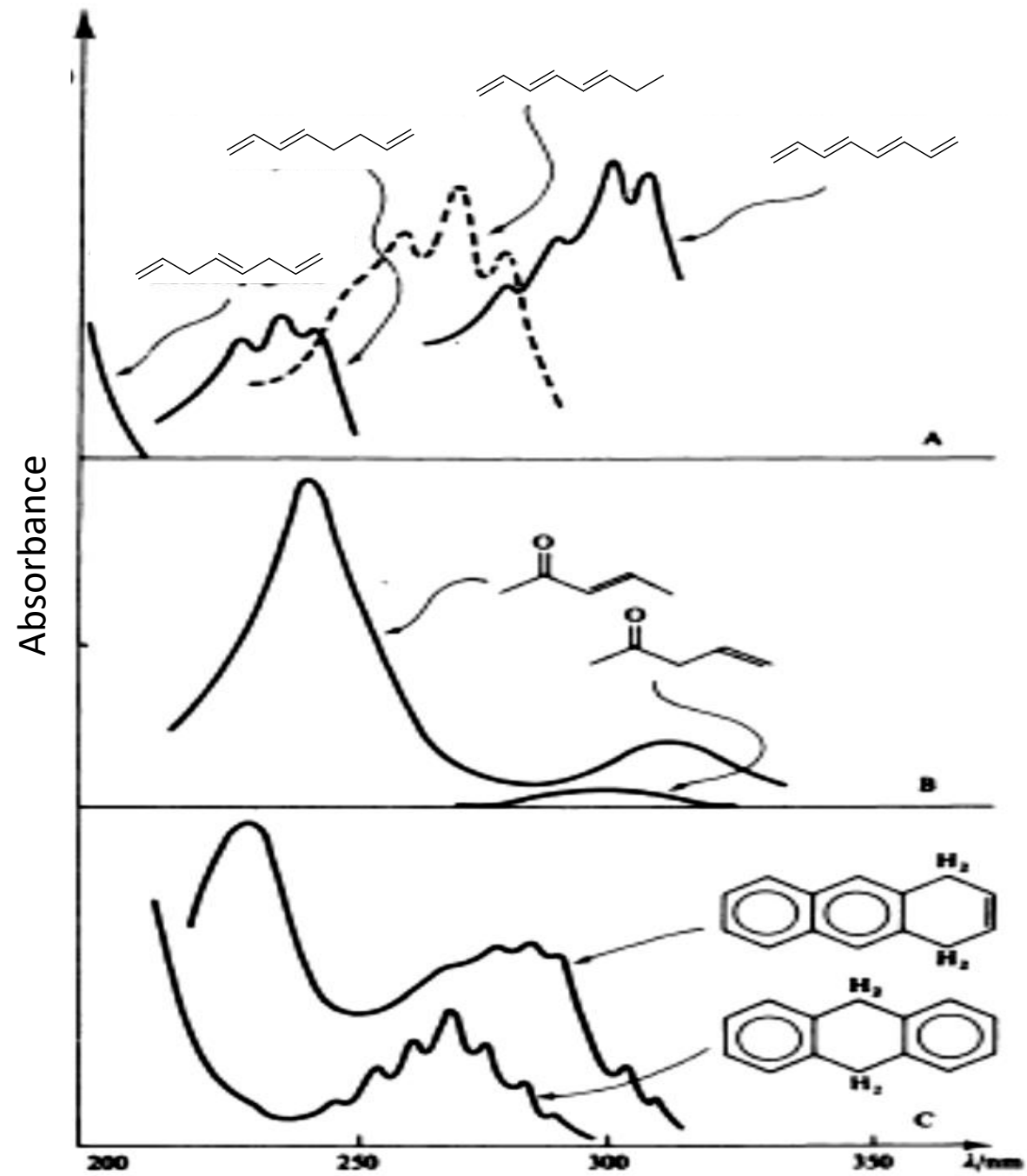 - carbon atoms using ^{13}C-NMR spectroscopy
  - phosphorus atoms using ^{31}P-NMR spectroscopy

- An electron has a spin quantum number of 1/2 with allowed values of +1/2 and -1/2

  - this spinning charge creates an associated magnetic field

  - in effect, an electron behaves as if it is a tiny bar magnet and has what is called a magnetic moment

- The same effect holds for certain atomic nuclei

  - any atomic nucleus that has an odd mass number, an odd atomic number, or both also has a spin and a resulting nuclear magnetic moment.

  - the allowed nuclear spin states are determined by the spin quantum number, I, of the nucleus

  - a nucleus with spin quantum number I has **2I + 1** spin states; if I = 1/2, there are two allowed spin states
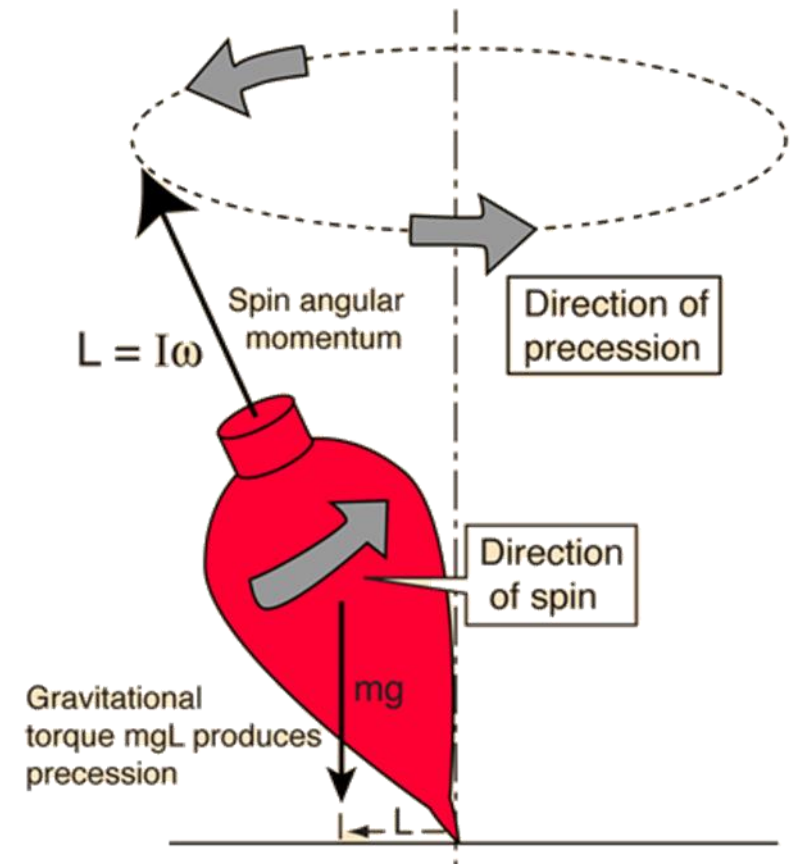
Principles of Nuclear Magnetic Resonance

- When nuclei with a spin quantum number of 1/2 are placed in an applied field, a small majority of nuclear spins are aligned with the applied field in the lower energy state
- the nucleus begins to precess and traces out a cone-shaped surface, in much the same way a spinning top or gyroscope traces out a cone-shaped surface as it precesses in the earth's gravitational field
- we express the rate of precession as a frequency in hertz

$$\nu = \frac{\gamma B_0}{2\pi}$$

where B_0 = strength of the applied external field experienced by the proton,

γ = magnetogyric ratio, being the ratio between the nuclear magnetic moment, μ, and the nuclear angular momentum, I: γ is also called the gyromagnetic ratio.

Spin angular momentum

$L = I\omega$

Direction of precession

Direction of spin

Gravitational torque mgL produces precession

mg

$|\leftarrow L \rightarrow|$

Nuclear Spins in B_0
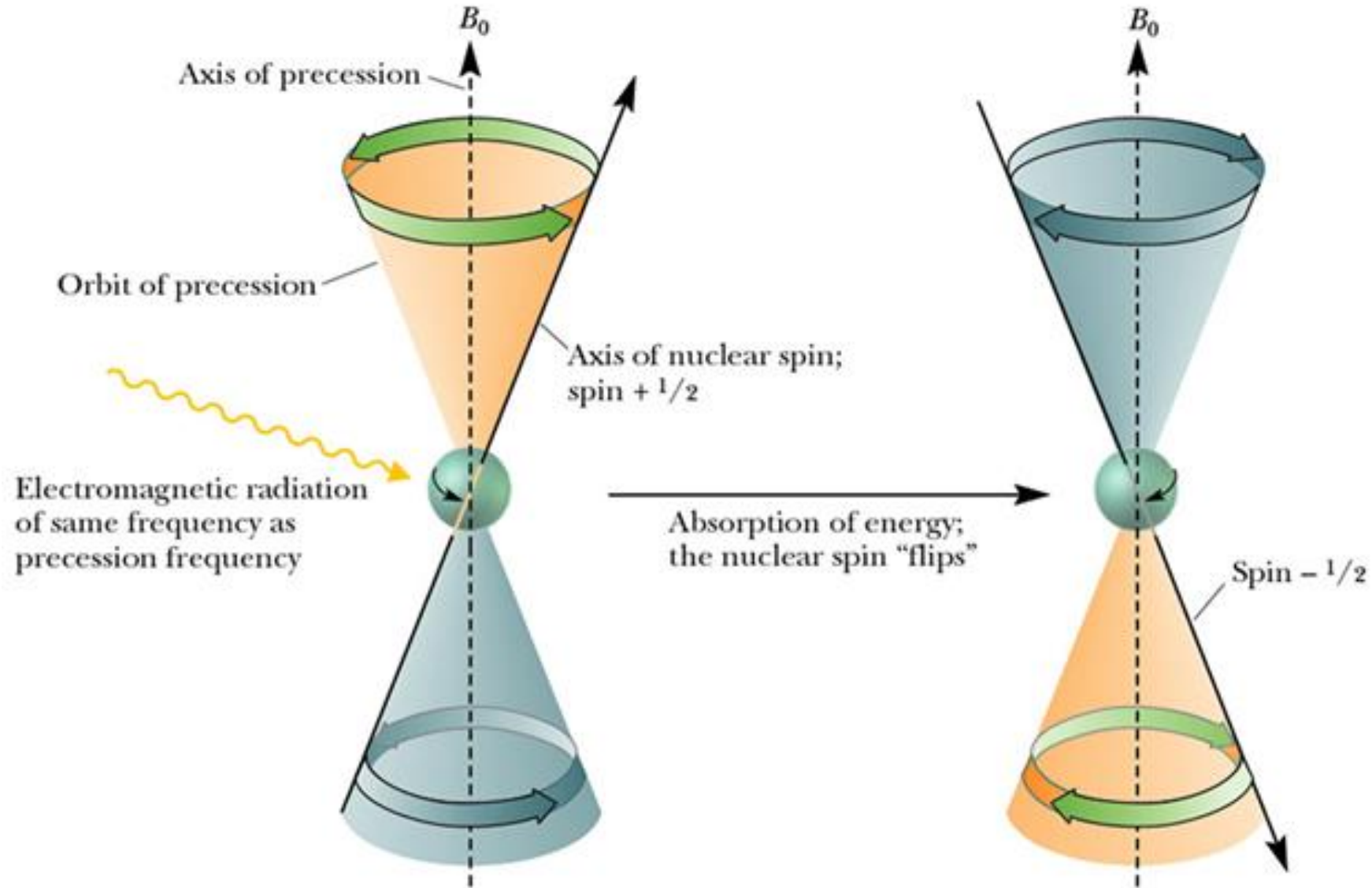
- for ^1H and ^{13}C, only two orientations are allowed
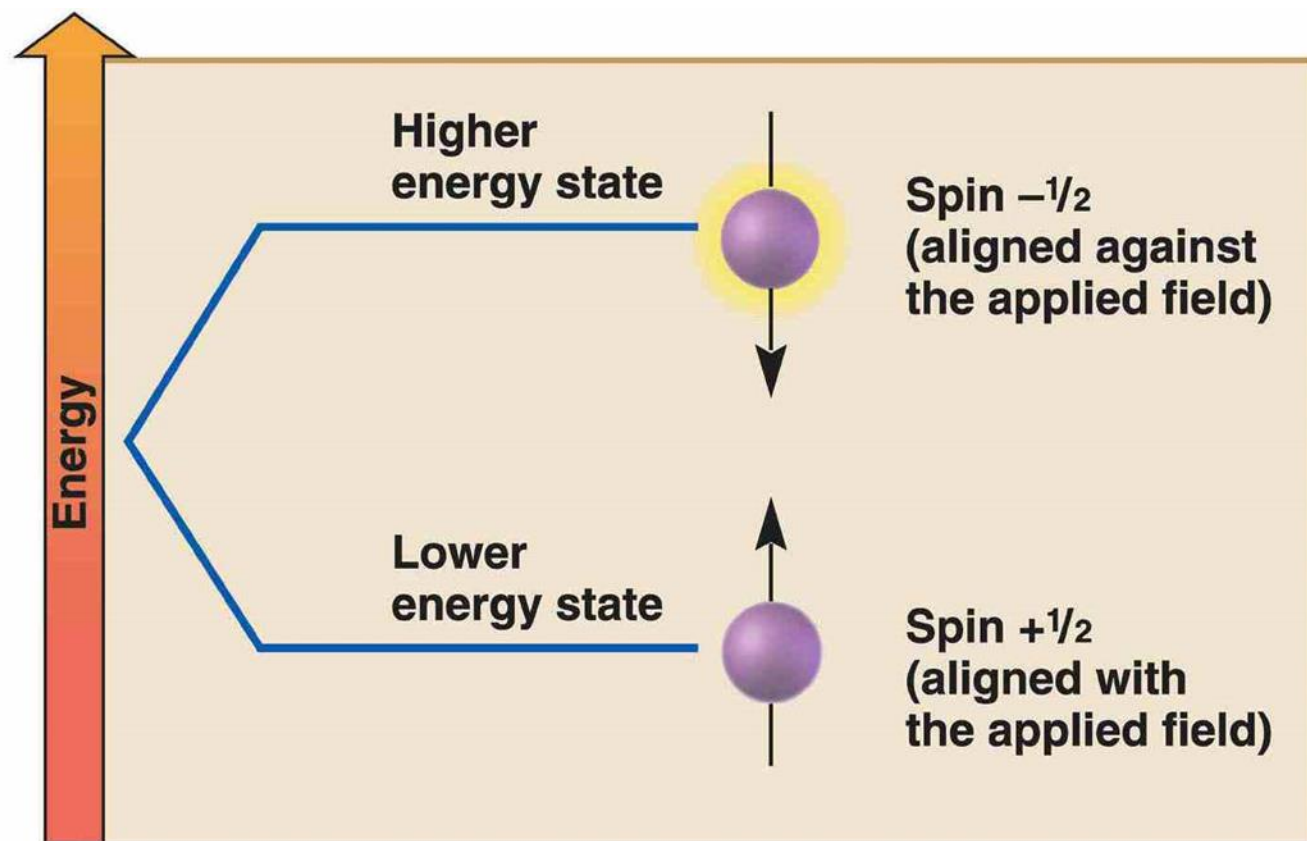
■ If the precessing nucleus is irradiated with electromagnetic radiation of the same frequency as the rate of precession,
- the two frequencies couple,
- energy is absorbed, and
- the nuclear spin is flipped from spin state +1/2 (with the applied field) to -1/2 (against the applied field)

Origin of Nuclear Magnetic Resonance

Nuclear Magnetic Resonance

- **Resonance:** in NMR spectroscopy, resonance is the absorption of electromagnetic radiation by a precessing nucleus and the resulting "flip" of its nuclear spin from a lower energy state to a higher energy state
- The instrument used to detect this coupling of precession frequency and electromagnetic radiation records it as a signal
  - **signal:** a recording in an NMR spectrum of a nuclear magnetic resonance
  - signals are measured relative to the signal of the reference compound tetramethylsilane (TMS)

$$
\begin{array}{c}
CH_3 \\
| \\
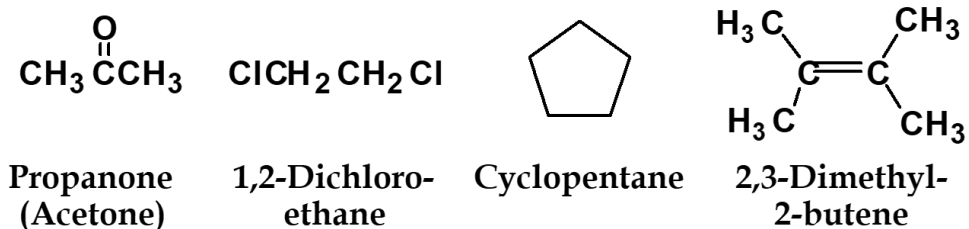H_3C-Si-CH_3 \\
| \\
CH_3
\end{array}
$$
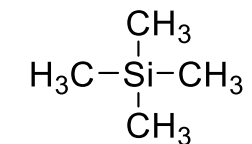
Tetramethylsilane (TMS)

  - for a ^{1}H-NMR spectrum, signals are reported by their shift from the 12 H signal in TMS

  - for a ^{13}C-NMR spectrum, signals are reported by their shift from the 4 C signal in TMS

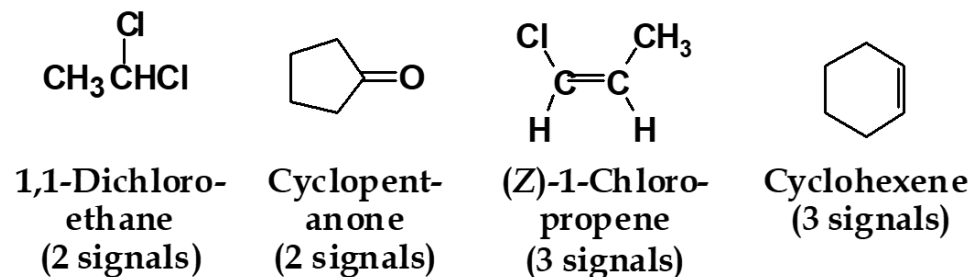 - **Chemical shift (δ):** the shift in ppm of an NMR signal from the signal of TMS

NMR Spectrometer
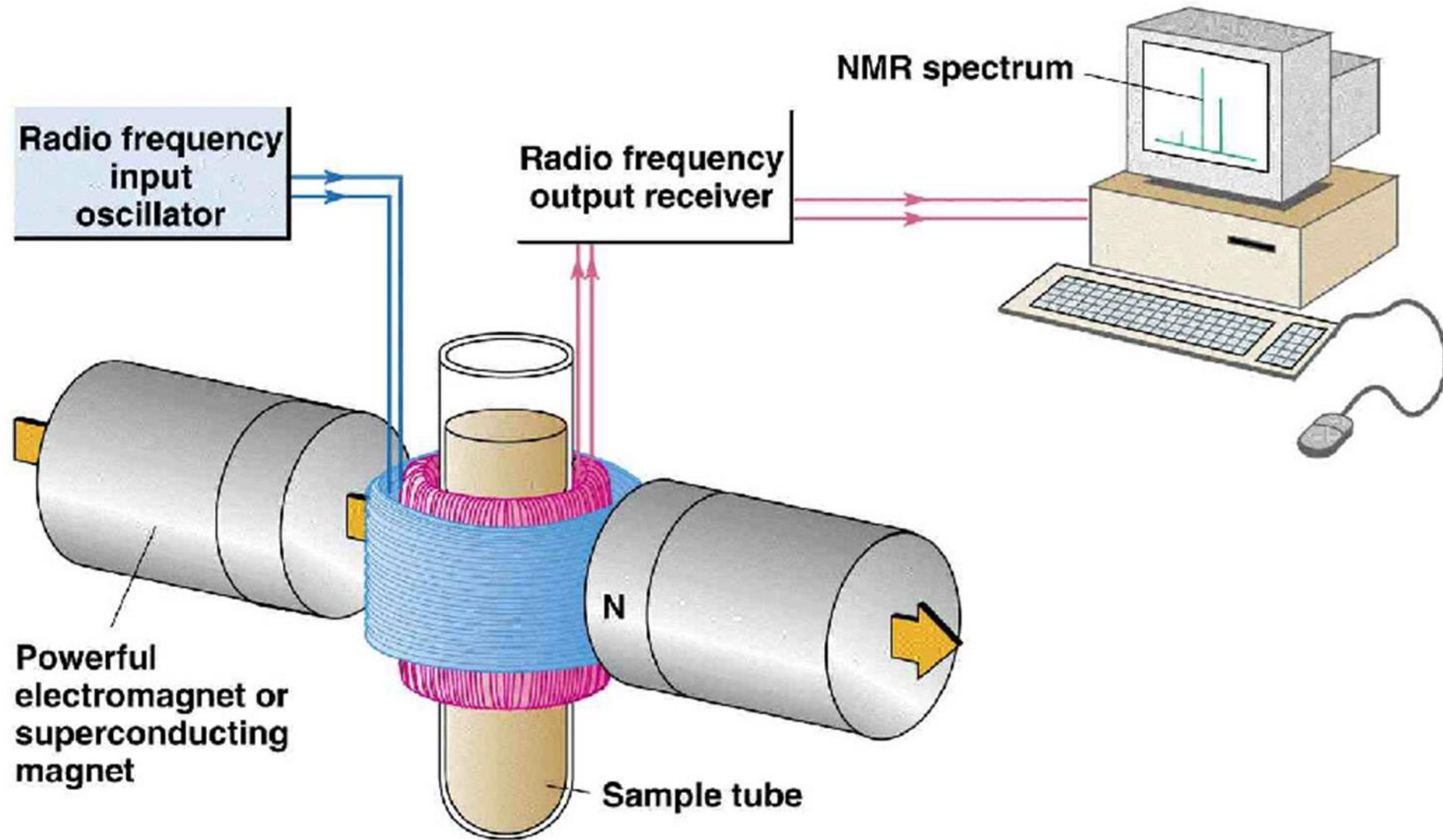
- Essentials of an NMR spectrometer are a powerful magnet, a radio-frequency generator, and a radio-frequency detector
- The sample is dissolved in a solvent, most commonly $CDCl_3$ or D_2O, and placed in a sample tube which is then suspended in the magnetic field and set spinning
- Using a Fourier transform NMR (FT-NMR) spectrometer, a spectrum can be recorded in about 2 seconds
- **Equivalent hydrogens:** have the same chemical environment

    a molecule with 1 set of equivalent hydrogens gives 1 NMR signal

$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \quad ClCH_2CH_2Cl$$

Propanone (Acetone) **1,2-Dichloro-ethane** **Cyclopentane** **2,3-Dimethyl-2-butene**

- a molecule with 2 or more sets of equivalent hydrogens gives a different NMR signal for each set

$$CH_3\overset{\overset{Cl}{|}}{C}HCl$$

1,1-Dichloro-ethane (2 signals) **Cyclopent-anone (2 signals)** **(Z)-1-Chloro-propene (3 signals)** **Cyclohexene (3 signals)**

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Downfield: the shift of an NMR signal to the left on the chart paper
Upfield: the shift of an NMR signal to the right on the chart paper

$$CH_3COCH_3$$

Chemical Shift (δ)

$$CH_3COCCH_3$$
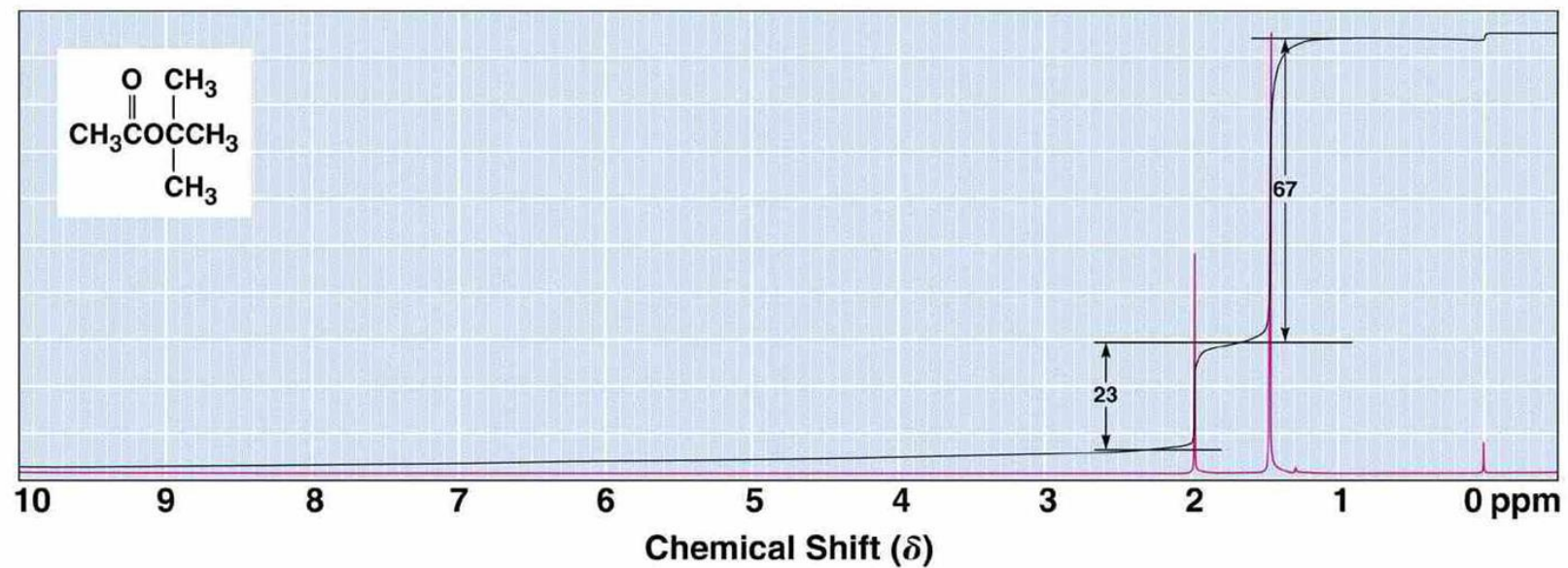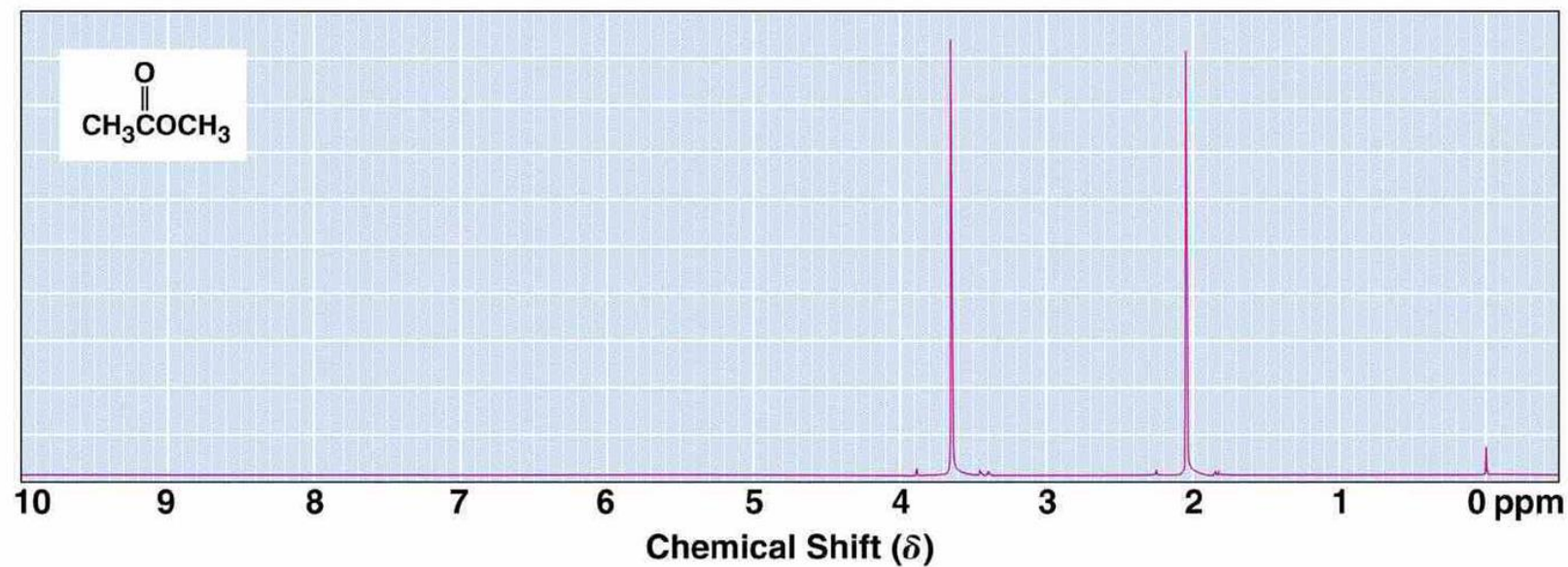
Chemical Shift (δ)

Chemical Shifts ^{1}H-NMR

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
$(CH_3)_4Si$	0 (by definition)	$RCOCH_3$ (C=O)	3.7-3.9
RCH_3	0.8-1.0		
RCH_2R	1.2-1.4	$RCOCH_2R$ (C=O)	4.1-4.7
R_3CH	1.4-1.7	RCH_2I	3.1-3.3
$R_2C=CRCHR_2$	1.6-2.6	RCH_2Br	3.4-3.6
$RC{\equiv}CH$	2.0-3.0	RCH_2Cl	3.6-3.8
$ArCH_3$	2.2-2.5	RCH_2F	4.4-4.5
$ArCH_2R$	2.3-2.8	$ArOH$	4.5-4.7
ROH	0.5-6.0	$R_2C=CH_2$	4.6-5.0
RCH_2OH	3.4-4.0	$R_2C=CHR$	5.0-5.7
RCH_2OR	3.3-4.0	ArH	6.5-8.5
R_2NH	0.5-5.0	RCH (C=O)	9.5-10.1
$RCCH_3$ (C=O)	2.1-2.3	$RCOH$ (C=O)	10-13
$RCCH_2R$ (C=O)	2.2-2.6		

1. A local radio station transmits (a) at approximately 95 MHz on its VHF transmitter and (b) at 810 kHz on medium wave.
Calculate the wavelengths of these transmissions.

Ans: c= 3 x 10^8 ms$^{-1,}$ and λ = c/v. Thus, wavelength corresponding to (a) 95 MHz, or 95 x 10^6 s^{-1} is 3.158 m. (b) 810 kHz is 370 m.

2. For ultraviolet light of wavelength 200 nm, calculate (a) the frequency of this light, (b) the amount of energy absorbed by one molecule when it interacts with this light, and (c) the corresponding amount of energy absorbed by one mole of substance.

Ans : (a) v = 1.5 x 10^{15} s^{-1} (b) E = hv = (6.6 x 10^{-34} Js) x (1.5 x 10^{15} s^{-1}) = 9.9 x 10^{-19} J, (c) To the amount of energy absorbed by one mole of substance , we must multiply by the Avogadro constant N_A (= 6.02 X 10^{23} mol^{-1}), giving approximately 6 x 10^5 J mol^{-1}

3. An αβ-unsaturated ketone of relative molecular mass 110 has an absorption band with λ_{max} at 215 nm and ε 10,000. A solution of this ketone showed absorbance A = 2.0 with a 1 cm cell. Calculate the concentration of the ketone in this solution, expressed in grams per liter, gl^{-1} .

Ans: Using the formula: A = εcl , c = 2 x 10^{-4} mol/l. We know that the relative molecular mass is 110, so the concentration can be expressed as 2 X 110 X 10^{-4} or 2.2 x 10^{-2} g l^{-l} .

4. (a) Calculate the absorbance, A, for a solution showing 50 per cent transmittance, T. (b) Calculate the transmittance, T, for a solution showing absorbance, A, of 1.0.

Ans: (a) Since $A = \log(I/T)$ and $T = 50$ per cent or 0.50, then $A = \log(I/0.50) = \log 2 = 0.3010$. (b) Since $A = \log(Io/I) = 1.0$, we must find the antilog of 1.0, which is 10.00. T is the reciprocal of this = 0.1, which expressed as a percentage = 10%.

5. How could infrared spectroscopy be used to distinguish the members of the following pairs? (a) natural rubber (cis-polyisoprene) and butyl rubber (polyisobutene) (b) cis and trans isomers of 3-hexane (c) 1- hexyne and 3-hexyne?

Ans: (a) Natural rubber contains an alkene group; butyl rubber does not. The presence of a weak/medium band for C=C *str* will identify the former with reasonable certainty.
(b) The out -of-plane C- H *def* bands for cis and *trans* alkenes appear, respectively, near 970 and 700 cm^{-1} (c) l-Hexyne is a terminal alkyne and shows both the C=C *str* and alkyne
C-H *str* bands. 3-Hexyne shows neither of these bands.