

Identification of Organic Compounds

OUTLINE

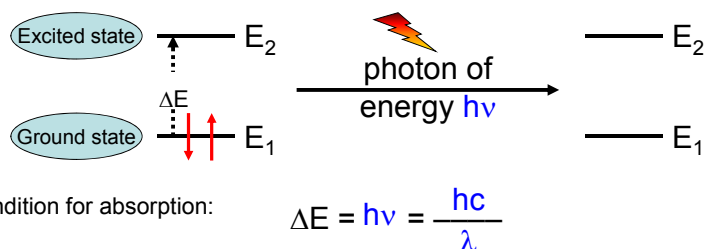
- Mass spectrometry
- Absorption spectroscopy
 - Infrared spectroscopy
 - Ultraviolet and visible spectroscopy
- NMR spectroscopy

spectral data

molecular structure

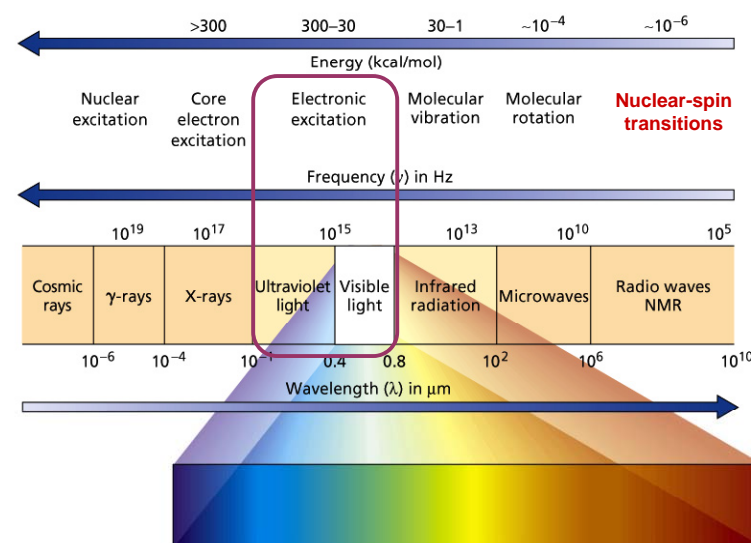
Absorption Spectroscopy

Molecules absorb energy in the form of *electromagnetic radiation* when the energy difference between two states, ΔE , is perfectly matched to the energy of the radiation



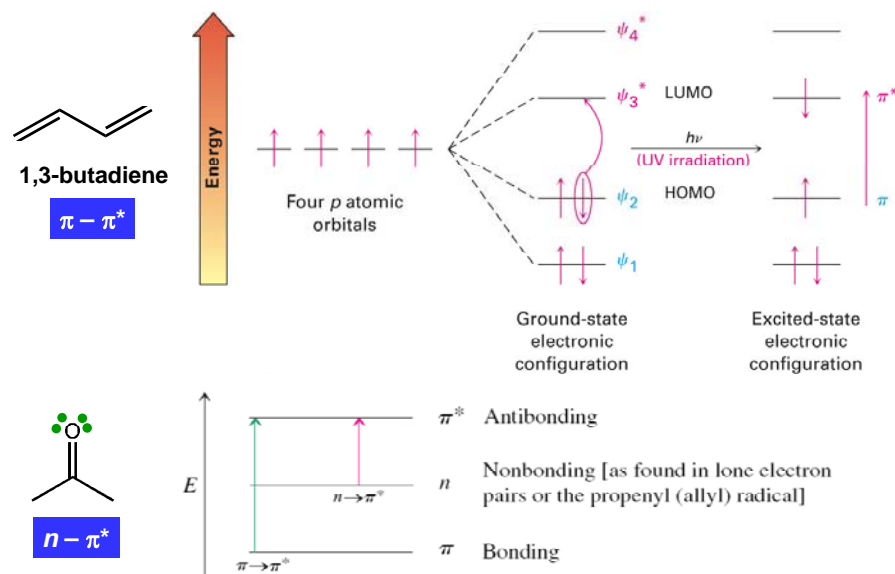
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Electronic Spectra



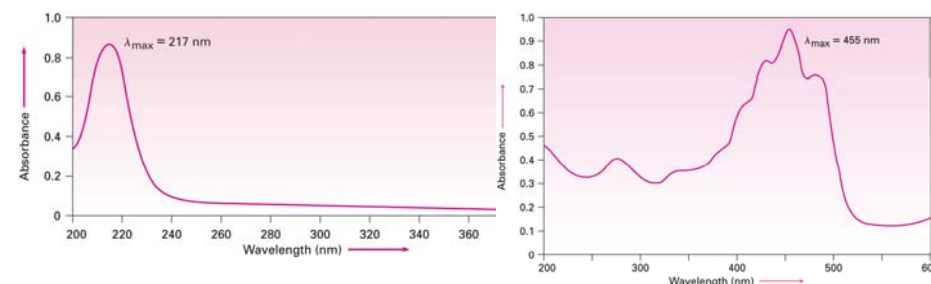
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Ultraviolet and Visible (UV-vis) Spectroscopy

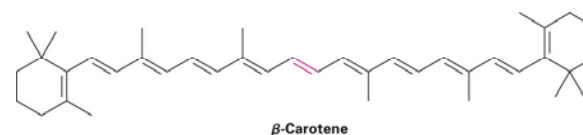


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UV-vis Spectra Reveal Extent of Conjugation



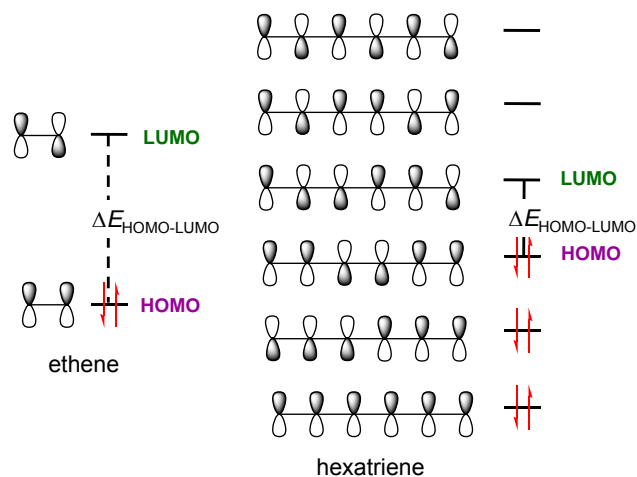
- Ethene $\lambda_{\text{max}} = 171 \text{ nm}$
- 1,4-Pentadiene (unconjugated) $\lambda_{\text{max}} = 178 \text{ nm}$
- 1,3-Butadiene (conjugated) $\lambda_{\text{max}} = 217 \text{ nm}$



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Molecular Orbital and UV-vis Absorption

Recall MO theory:



Extended conjugation system corresponds to small $\Delta E_{\text{HOMO-LUMO}}$, and hence long λ_{max} in the UV-vis absorption spectrum.

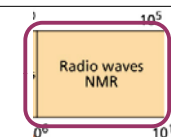
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NMR Spectroscopy

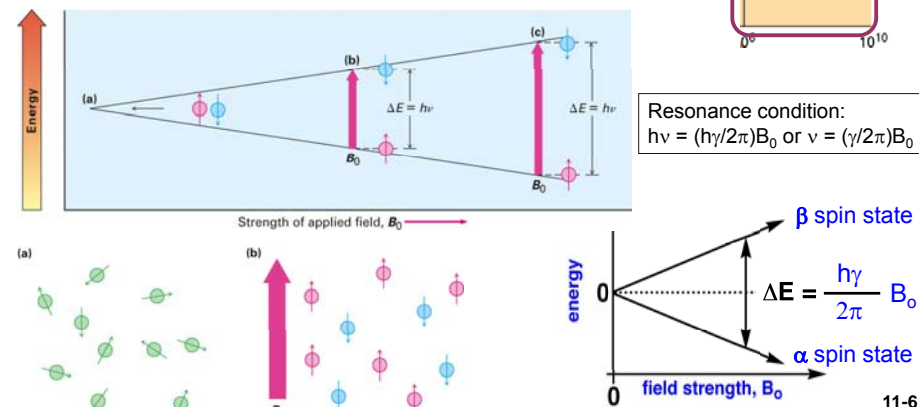
In a magnetic field, nuclei with nuclear spin quantum number $\neq 0$, align parallel or antiparallel to the applied field. The energy difference between these spin states is equivalent to radio frequency, and is directly proportional to B_0 , the magnitude of the magnetic field, and a characteristic of the nuclei known as the gyromagnetic ratio, γ .

Important active nuclei

^1H ^{13}C ^{15}N ^{19}F ^{31}P

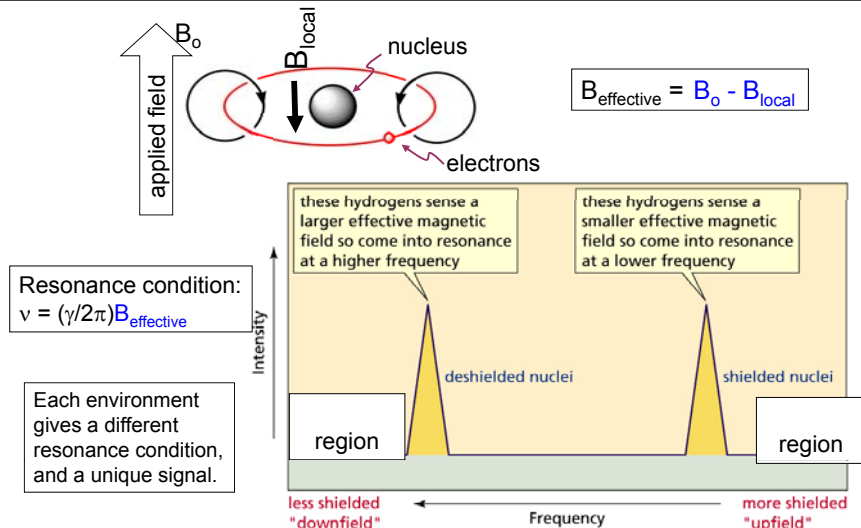


Resonance condition:
 $h\nu = (h\gamma/2\pi)B_0$ or $\nu = (\gamma/2\pi)B_0$



Effective Magnetic Field

Variations in the distribution of electrons around a nucleus (due to different chemical bonds and connected atoms) affect the effective magnetic field that the nucleus experiences.



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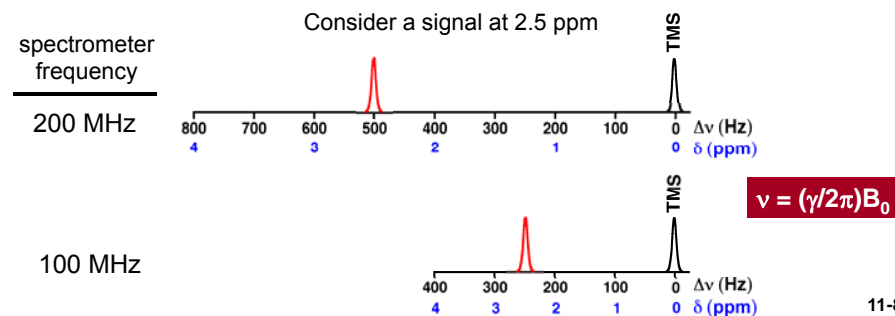
Standardizing Resonance Positions

Resonance positions are always referenced to a standard. For ^1H NMR, the standard is tetramethylsilane (TMS). The position of TMS is defined as the zero point. The scale is converted from frequency to a ppm scale.

$$\delta = \frac{\text{chemical shift (ppm)}}{\text{MHz operating frequency of spectrometer}} = \frac{\text{Hz downfield from TMS}}{\text{MHz operating frequency of spectrometer}}$$

Most proton (^1H) signals fall in the range 0 - 12 ppm

Positions are the same regardless of field strength (B_0)



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Analysis of NMR Spectra

The goal:

- To correlate a spectrum to its expected product
- To elucidate an unknown structure from spectra

Step I

Identify the number of resonance signals.

Each set of **chemically equivalent** protons (i.e., protons in the same environment) gives rise to a unique chemical shift.

Step II

Signal areas.

The area under the signal is proportional to the **number of hydrogens** giving rise to that signal.

Step III

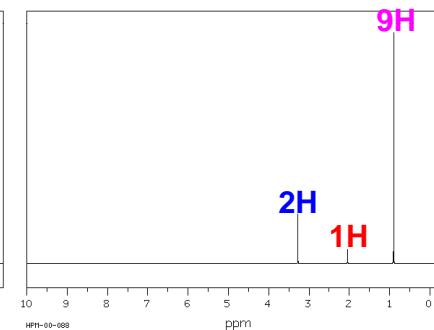
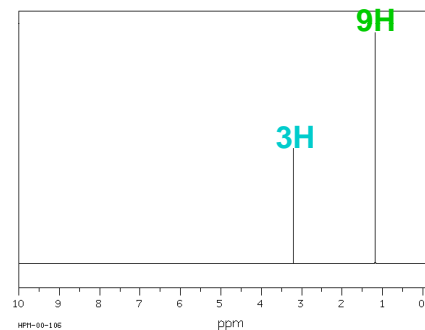
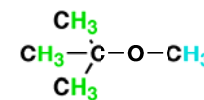
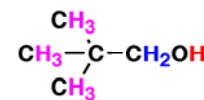
Position of ^1H NMR signals.

The **chemical shifts** of proton resonances are indicative of the **functional group** to which they are attached.

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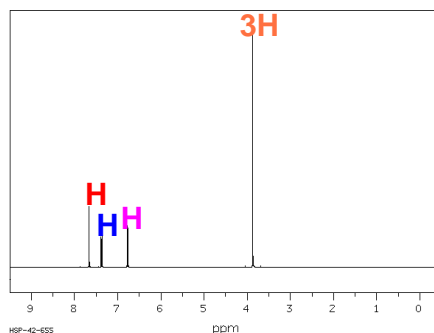
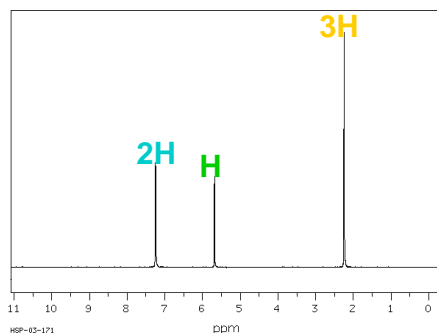
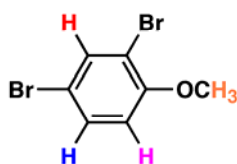
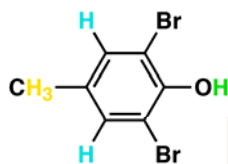
Chemical Shift Equivalency - Example #1

Match the ^1H NMR spectra to the structures



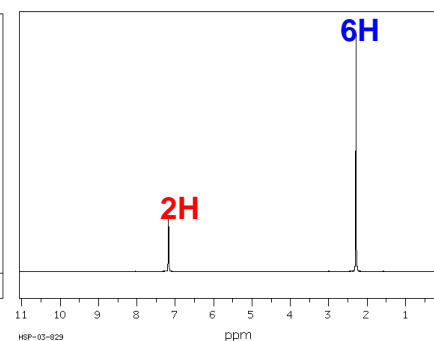
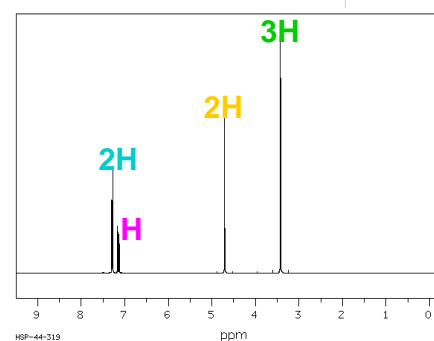
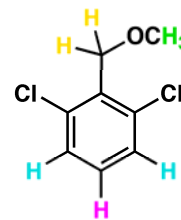
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Chemical Shift Equivalency - Example #2



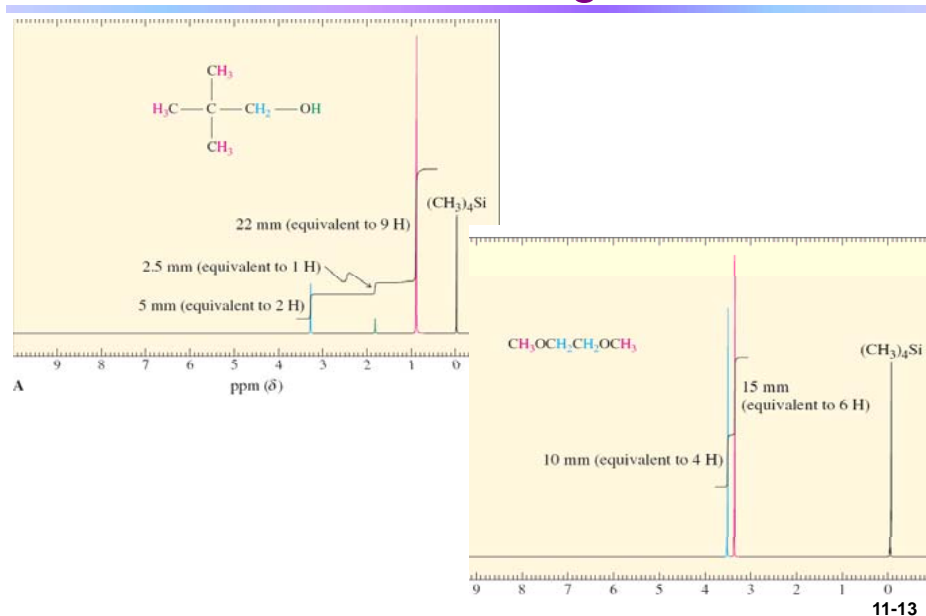
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Chemical Shift Equivalency - Example #3



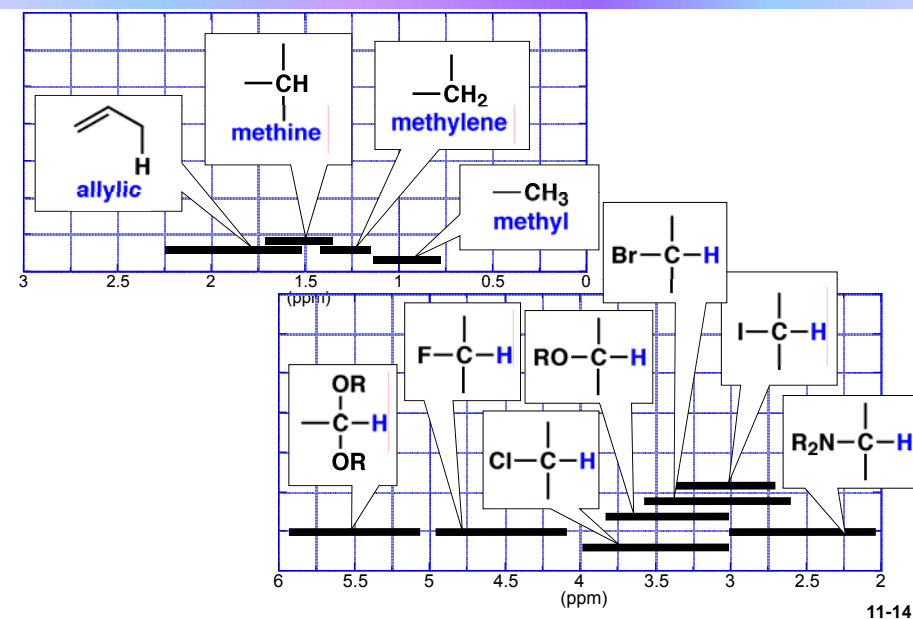
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Resonance Integration



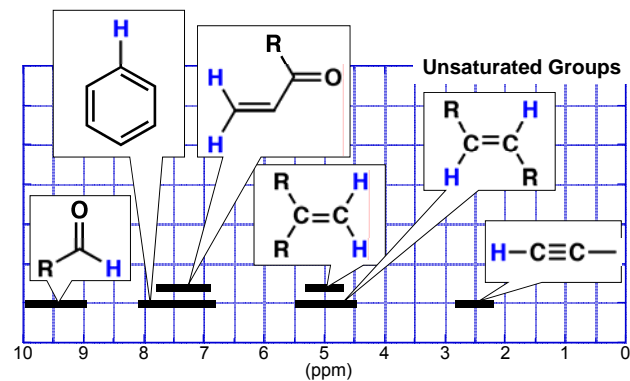
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Chemical Shifts of Alkanes



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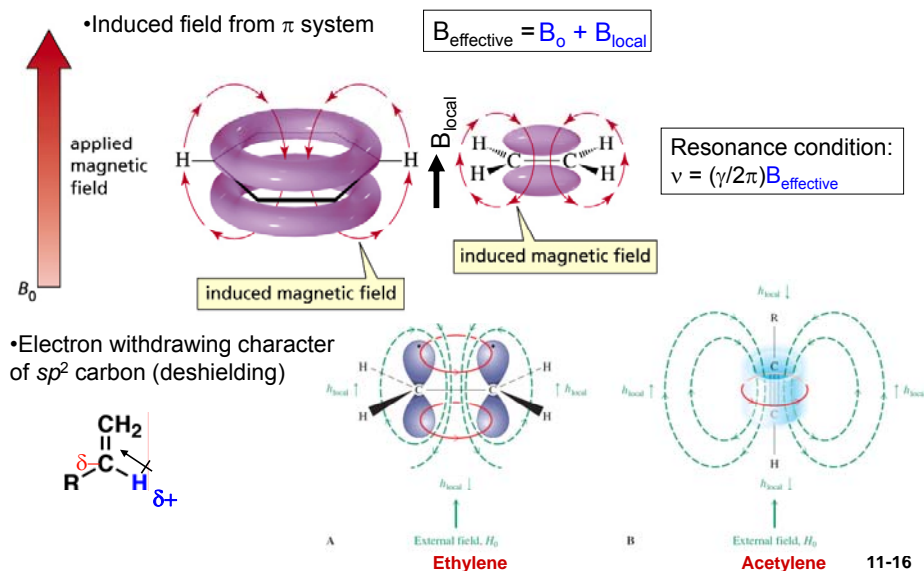
Chemical Shifts of Unsaturated Groups



Electron withdrawing groups reduce electron density at neighboring hydrogens, which decreases the ability of nearby electrons to shield the nucleus, causing chemical shifts to appear in the _____ region.

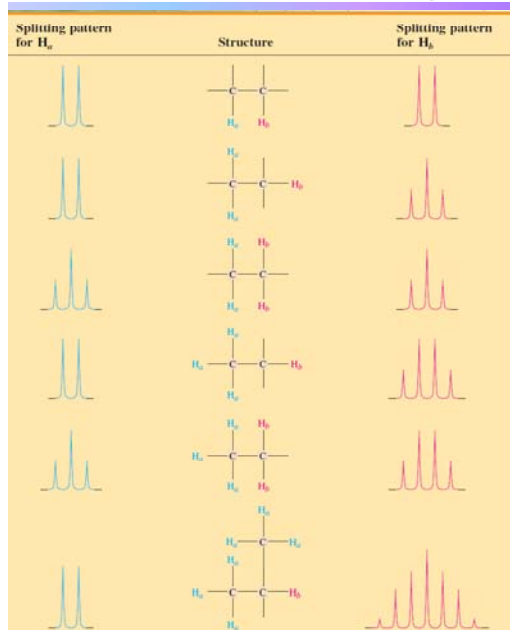
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Hydrogen Attached to C=C Bonds and Terminal Alkyne



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Splitting of Signals



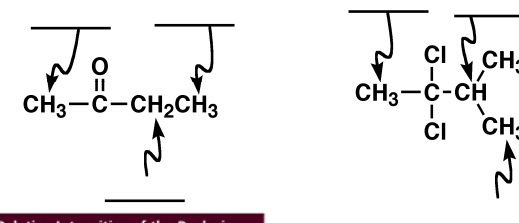
structure	signal of H_a	signal multiplicity
$\begin{array}{c} H_a \\ \\ -C-C- \\ \\ H_b \end{array}$		singlet
$\begin{array}{c} H_a & H_b \\ & \\ -C-C- \\ & \\ H_b & H_a \end{array}$		doublet
$\begin{array}{c} H_a & H_b \\ & \\ -C-C-H_b \\ & \\ H_b & H_a \end{array}$		triplet
$\begin{array}{c} H_a & H_b \\ & \\ -C-C-H_b \\ & \\ H_b & H_b \end{array}$		quartet

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Predicting Multiplicity

The number of peaks in a multiplet follows the $n+1$ rule where "n" is the number of adjacent protons.

Give the multiplicities of the indicated protons



Intensities of Multiplets

TABLE 13.2 Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

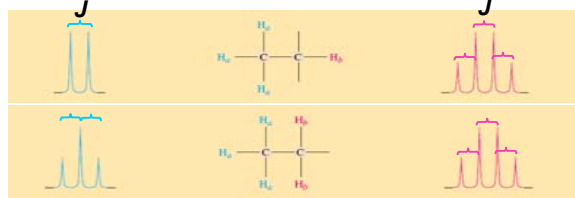
Number of equivalent protons causing splitting	Multiplicity of the signal	Relative peak intensities
0	singlet (s)	1
1	doublet (d)	1:1
2	triplet (t)	1:2:1
3	quartet (q)	1:3:3:1
4	quintet (quin)	1:4:6:4:1
5	sextet (sex)	1:5:10:10:5:1
6	septet (sept)	1:6:15:20:15:6:1

Pattern follows the mathematical mnemonic known as Pascal's triangle

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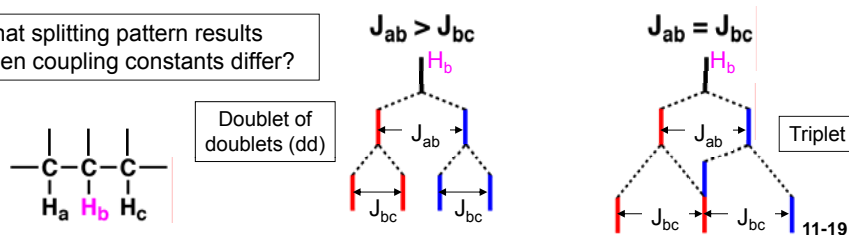
Strength of Spin-Spin Coupling

The strength of spin-spin coupling interaction is known as J , the coupling constant with units of Hz



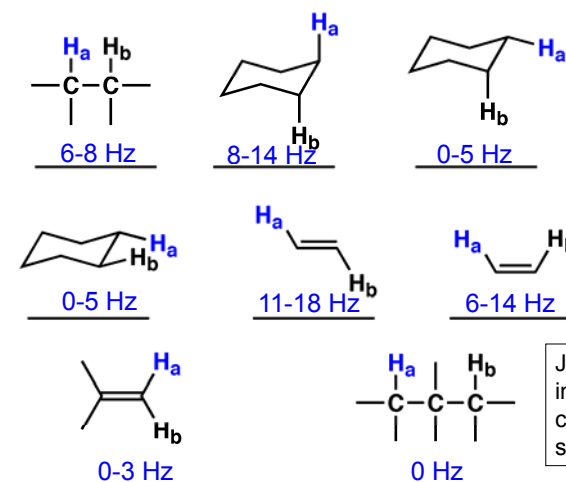
The coupling constants are reciprocal: $J_{AB} = J_{BA}$

What splitting pattern results when coupling constants differ?



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Representative J Values for Organic Compounds

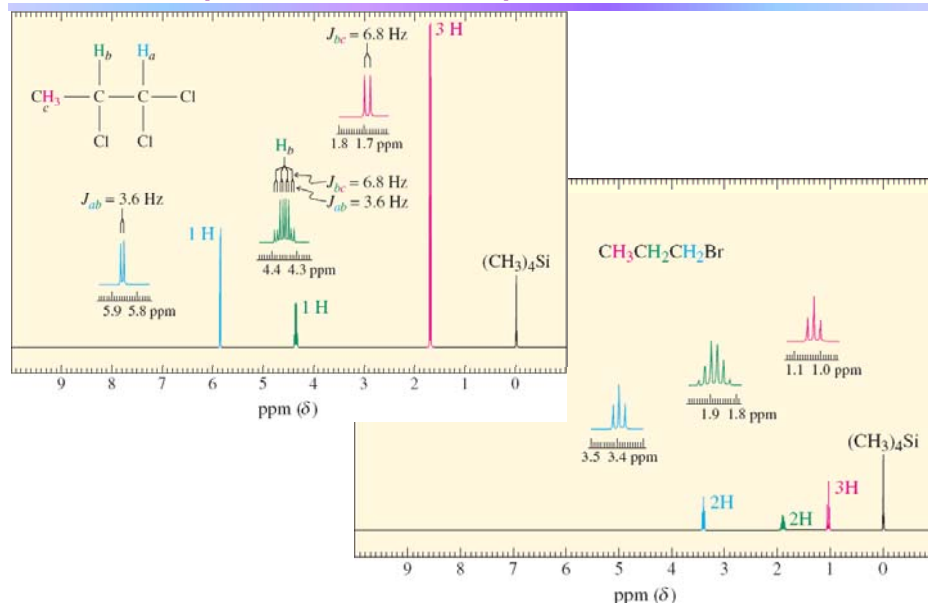


J values provide information about conformation and stereochemistry

Coupling between protons on adjacent carbons is known as vicinal coupling. Coupling between protons on the same carbon is known as geminal coupling.

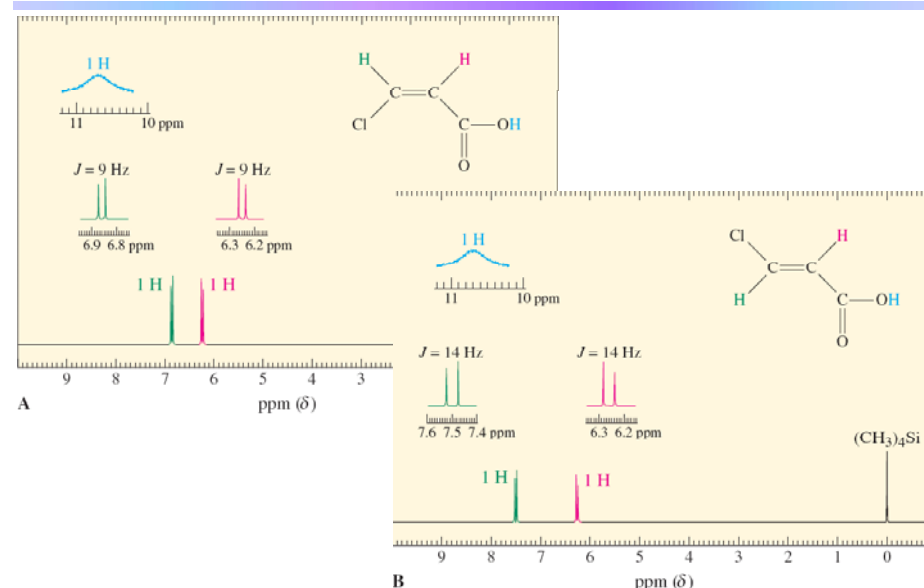
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Examples of NMR Spectra of Alkanes



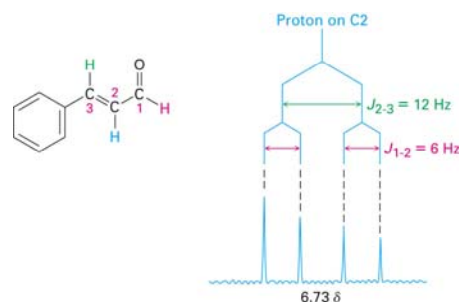
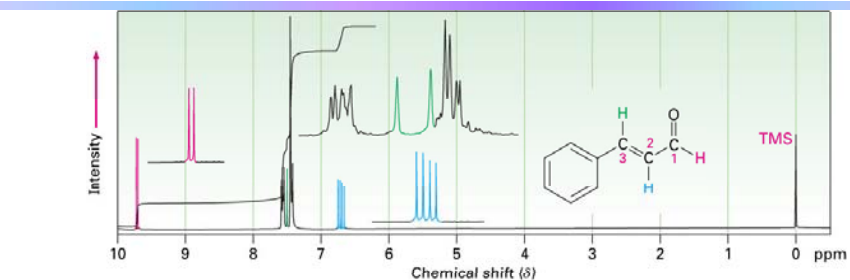
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Examples of NMR Spectra of Alkenes



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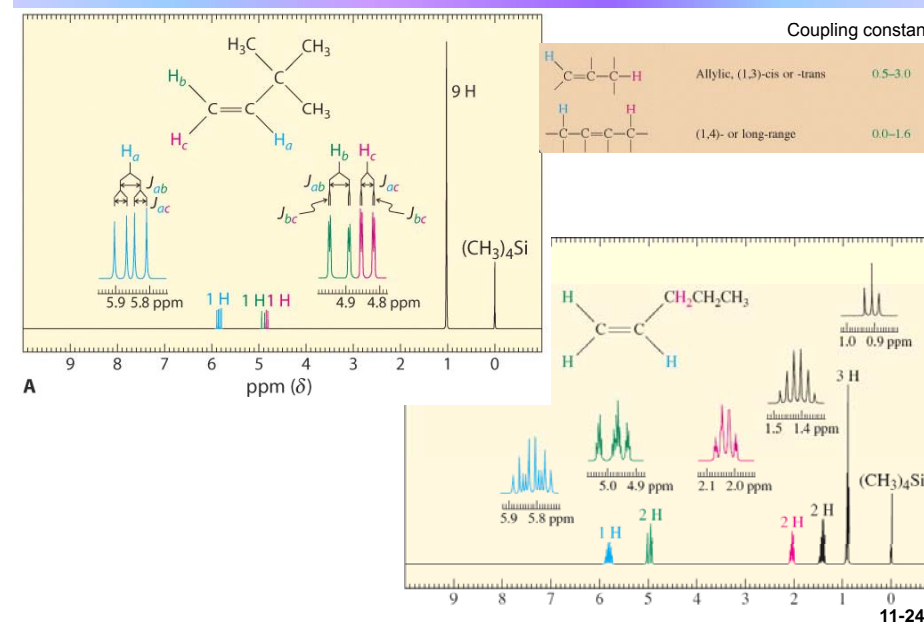
Examples of NMR Spectra of Alkenes



- The **number of signals** indicates the number of sets of equivalent hydrogen.
- The **chemical shift** of the signals indicates the type of hydrogen in each set.
- The **integration** of the signal tells the relative number of protons in each set.
- The **multiplicity (splitting)** of the signal tells the number of protons bonded to adjacent carbons.
- The **coupling constant** identifies which protons are coupled to one another.

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Examples of NMR Spectra of Alkenes

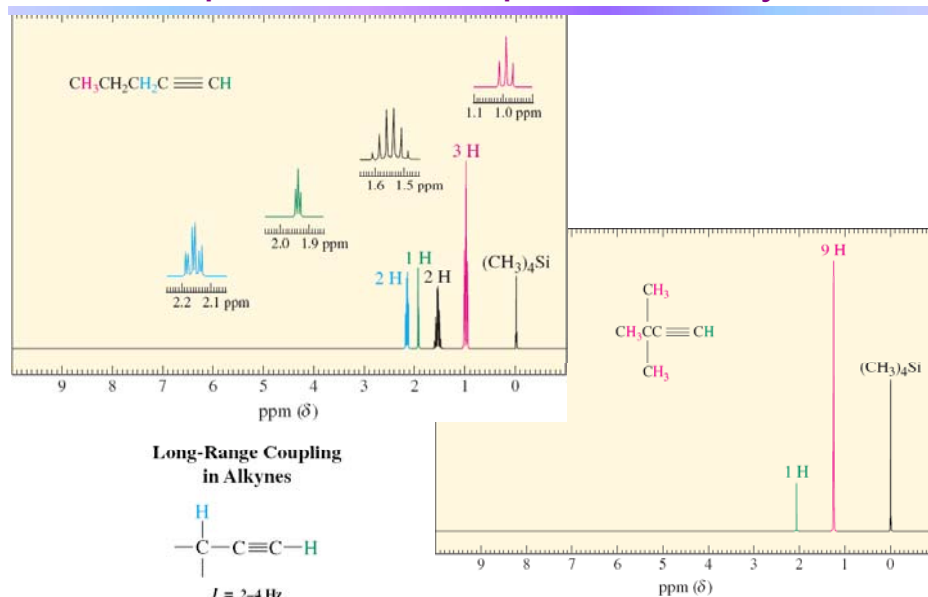


Coupling constant

$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	Allylic, (1,3)-cis or -trans	0.5-3.0
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	(1,4)- or long-range	0.0-1.6

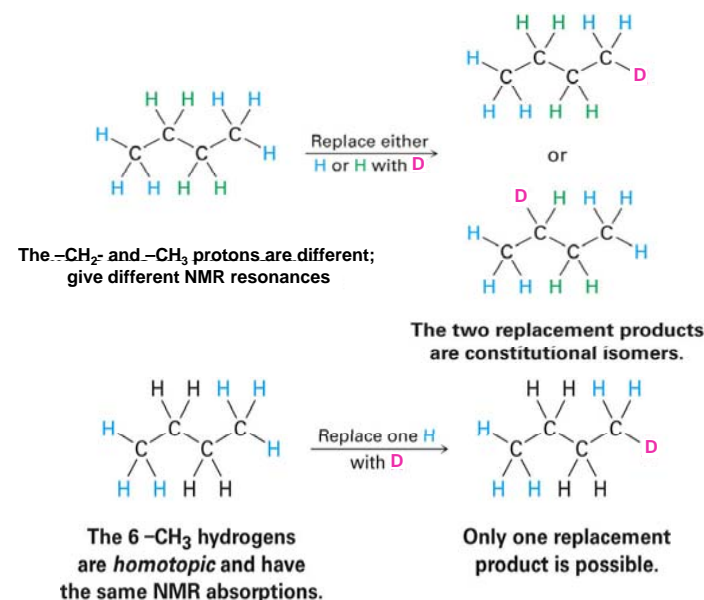
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Examples of NMR Spectra of Alkynes



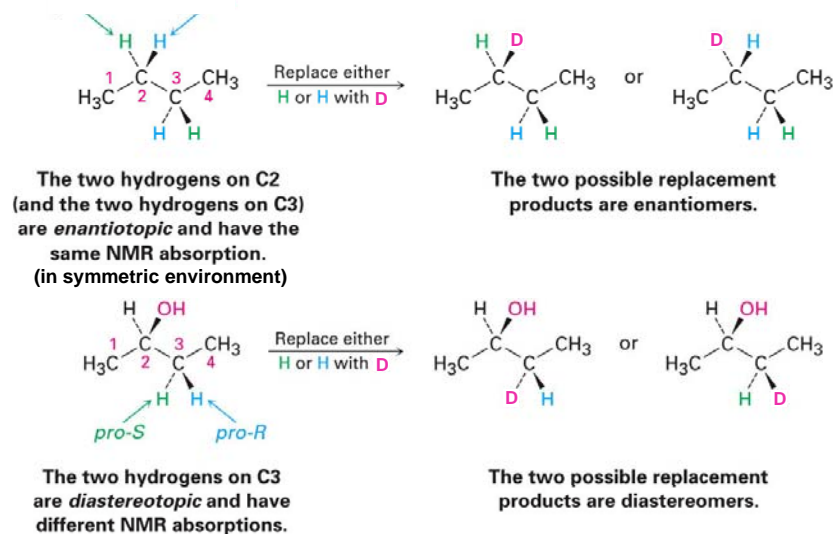
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Proton Equivalence



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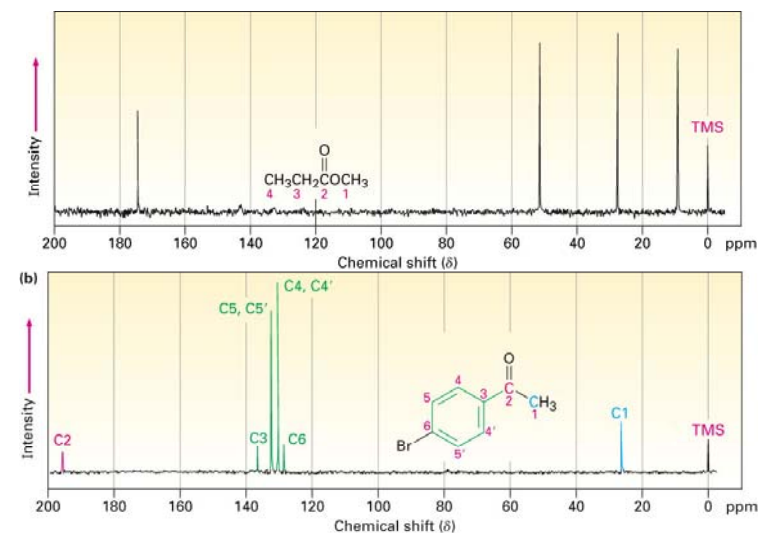
Proton Equivalence



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^{13}C NMR Spectroscopy

^{13}C NMR spectrum gives information on how many different sets of carbons there are in the molecule.



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Index of Hydrogen Deficiency (IHD) i.e., Degree of Unsaturation (Ω)

Calculating the number of **rings** and **pi bonds** based on the molecular formula

- Determine the number of Hs required for the molecule to be saturated:

for Saturated alkanes: C_nH_{2n+2}

for molecules containing heteroatoms: $H_{\text{sat}} = 2n_C + 2 - n_x + n_N$

- Each pi bond or ring lowers the hydrogen count by 2:

Degree of Unsaturation (Ω) = $(H_{\text{sat}} - H_{\text{actual}}) / 2$

