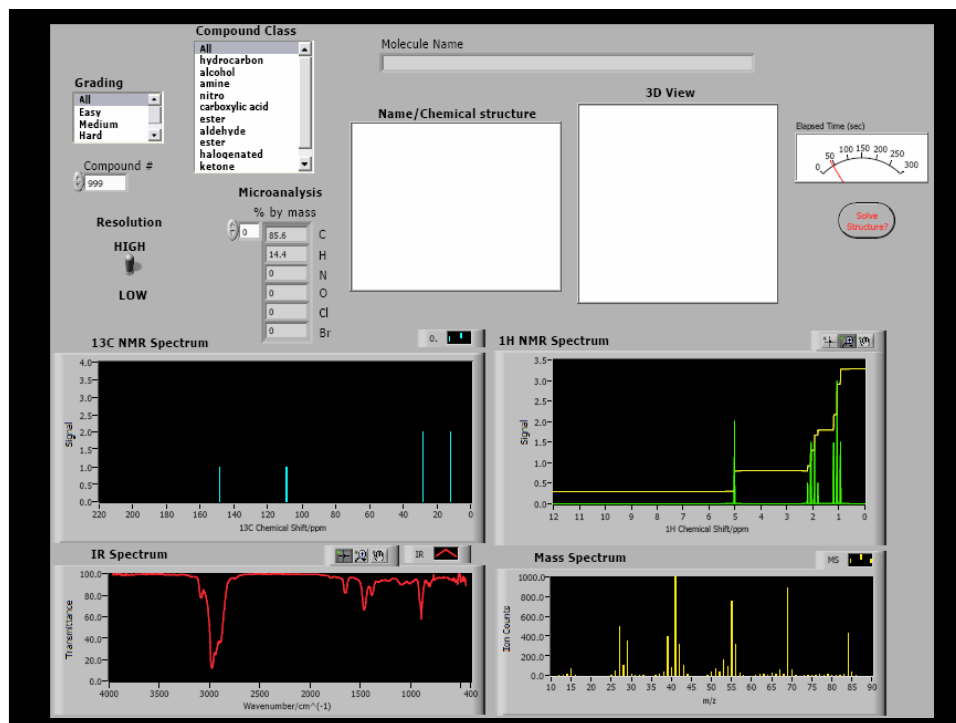


Chemical Detectives

A Problem-Solving Spectral and
Structural Database = a Fun and
Engaging Way to Teach Spectroscopy

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Uses of Chemical Detectives program:

- Aids with nomenclature
- Can choose different classes, difficulty levels
- Initial spectral recognition based on known compounds
- Finding unknown structures based on integrated spectral analysis

Microanalysis

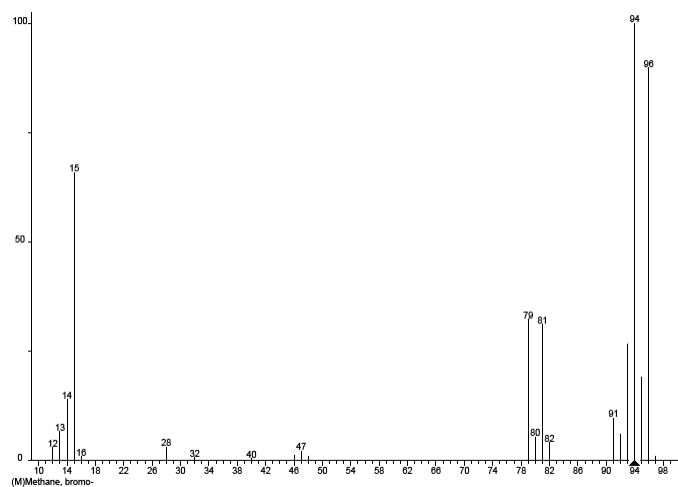
- Percentage by mass of each atom in molecule

	<u>C</u>	<u>H</u>	<u>O</u>
% mass	54.5	9.2	36.3
Atom ratio	$54.5/12.01$ $= 4.54$ $4.54/2.27$ $= 1.98$	$9.2/1.008$ $= 9.13$ $9.13/2.27$ $= 4.02$	$36.3/16.00$ $= 2.27$ $2.27/2.27$ $= 1.00$
Empirical formula	C_2H_4O		
Molecular formulas	C_2H_4O	$C_4H_8O_2$	$C_6H_{12}O_3$

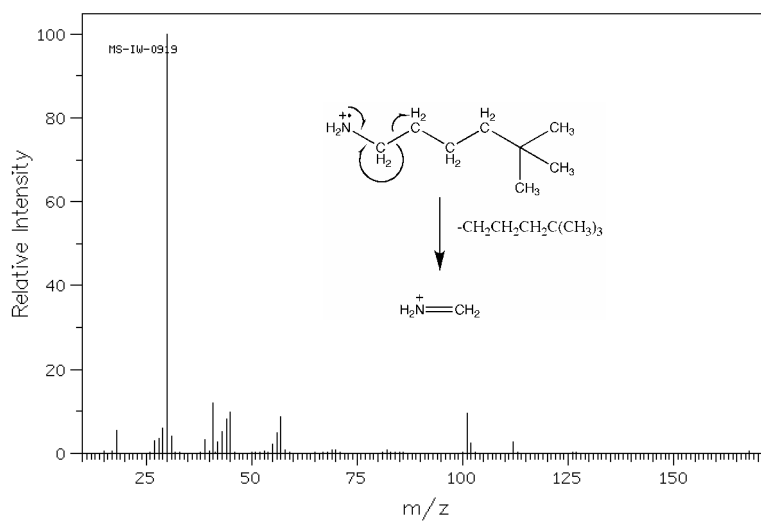
Mass Spectrometry

- Electron-impact (EI) mass spectrum
- Positive ions are separated based on their mass-to-charge (m/z) ratio
- One electron is removed as a result of impact
- Molecular ion (M^+) – an odd-electron ion – at an even m/z if an even # of nitrogens
- Fragment ions are indicative of structure, isotope peaks can also be very useful (think halogens !)
- Double bond equivalents : $C_xH_yN_zO_n = x - y/2 + z/2 + 1$
(rings + double bonds)

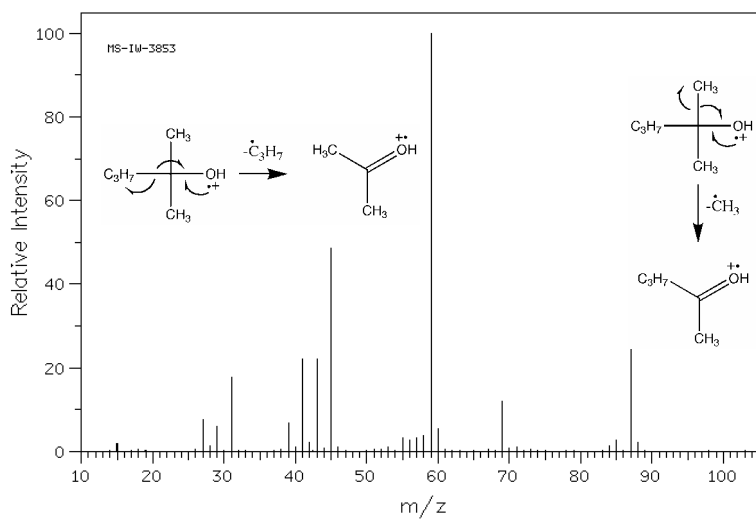
Methyl bromide - MS



α -cleavage



α -cleavage

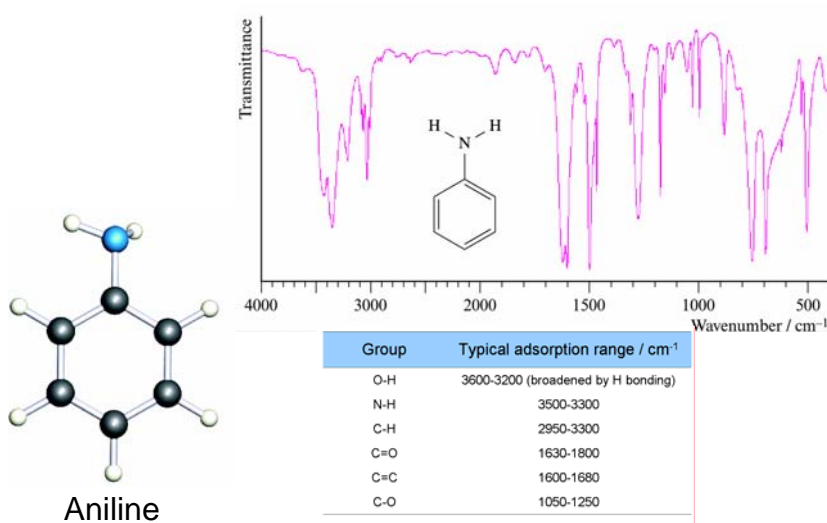


Infrared Spectroscopy

- Reveals presence of molecular **functional groups** by the vibrations of their bonds
- Peaks beyond 'fingerprint' region important ($> 1500 \text{ cm}^{-1}$)
- Presence/absence of peaks can both be useful !!

- O-H bond: $3200 - 3500 \text{ cm}^{-1}$ Strong and broad
- N-H bond: $3100 - 3500 \text{ cm}^{-1}$ Medium
- C-H bond: $2850 - 3100 \text{ cm}^{-1}$ Medium to strong
- C=O bond: $1630 - 1800 \text{ cm}^{-1}$ Strong
- C=C bond: $1600 - 1680 \text{ cm}^{-1}$ Weak

IR Spectroscopy



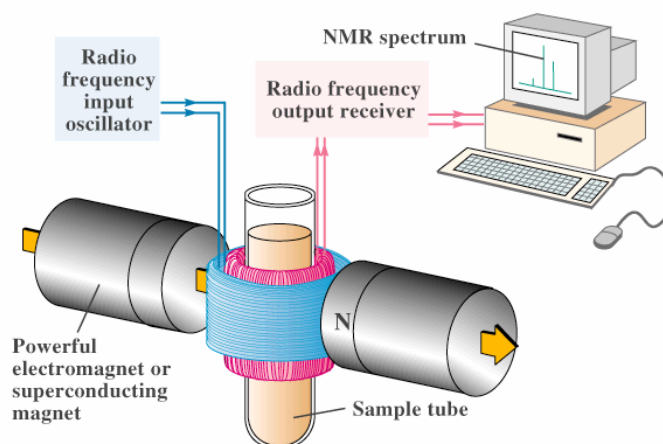
NMR Spectroscopy

Nuclei : resonance frequencies,
isotope abundances

Nucleus	Resonance frequency / MHz	Natural abundance / %
^1H	100	≈ 99.9
^{19}F	94.0	100
^{31}P	40.48	100
^{119}Sn	37.29	8.6
^{13}C	25.00	1.1
^{195}Pt	21.46	33.8
^{29}Si	19.87	4.7
^{107}Ag	4.05	51.8
^{103}Rh	3.19	100

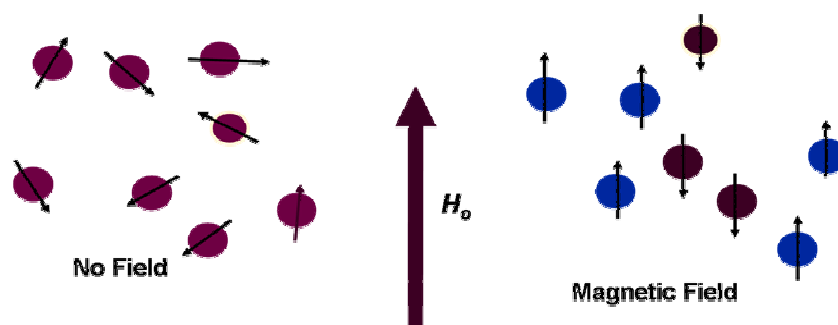
Not all nuclei are NMR active

NMR Spectroscopy



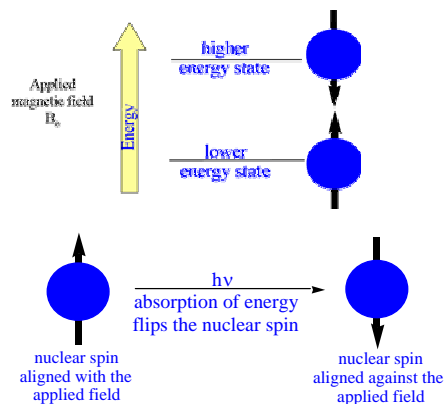
Nuclear Spins in a Magnetic Field

- A spinning charge creates an associated magnetic field.
- If a nucleus of ^1H is placed in a strong external magnetic field (B_0 Tesla, $1\text{T} = 10^4$ Gauss), its magnetic moment will line up with field.
- The moment can be parallel or anti-parallel to the field.



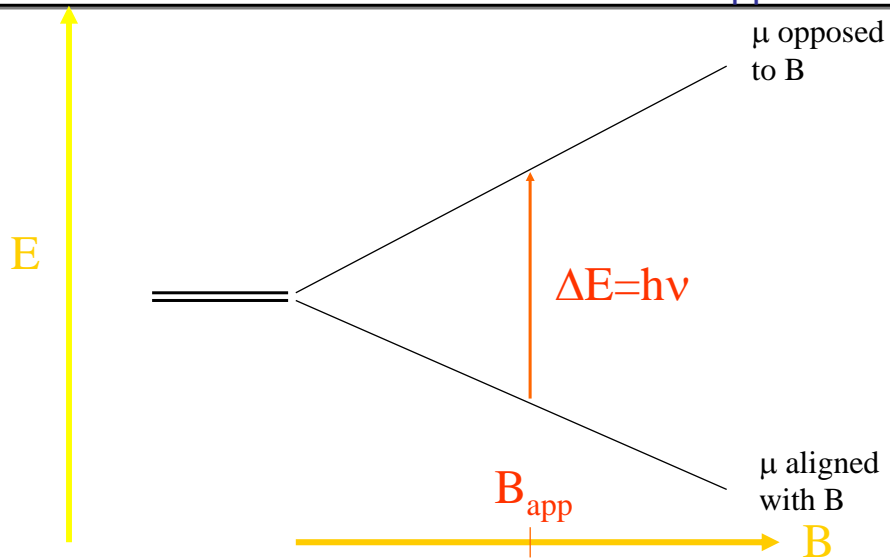
Nuclear Spins in a Magnetic Field

- For ^1H and ^{13}C , only two orientations are allowed.

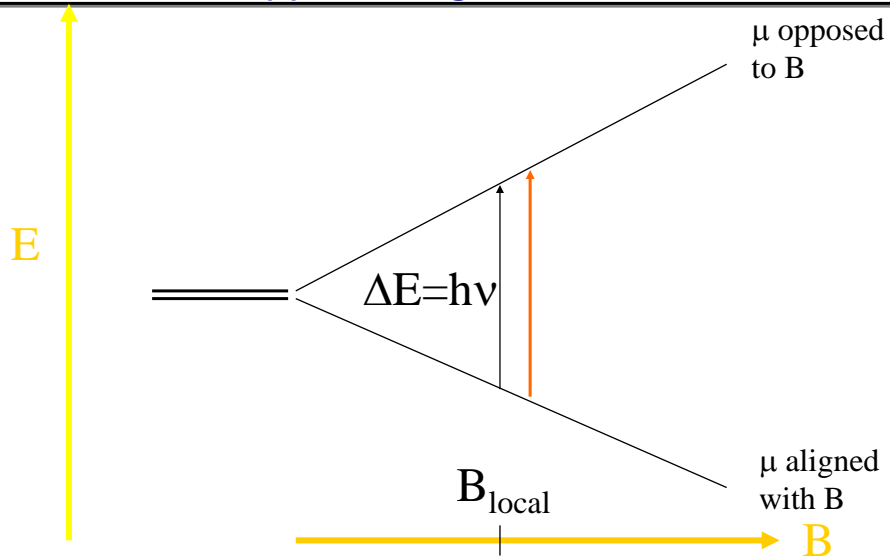


- Absorption of *radio-frequency* radiation of the appropriate energy flips the nuclear spin

Frequency depends on B_{app}



Local vs. Applied Magnetic Field



^1H NMR Spectroscopy

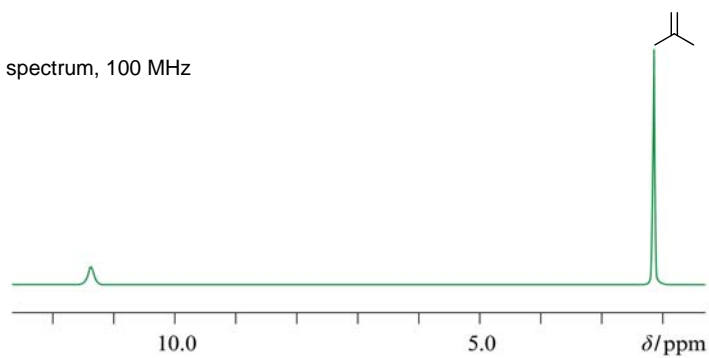
- Three characteristics of the spectrum aid in identifying structure
 - **Chemical shift** – depends on environment (shielding/deshielding)
 - **Integration** – the number of equivalent protons determines the area under peak
 - **Splitting pattern** - identifies number of adjacent protons (more in a moment....)

Chemical Shifts (^1H NMR)

R-CH_3	0.7-1.6	R-(C=O)-H	8.0-10.0
$\text{R-CH}_2\text{-R}$	1.2-1.4	R-(C=O)-OH	11.0-12.0
R_3CH	1.6-2.9	R-CH=CH-R	4.5-6.0
$(\text{C=O})\text{-CH}_2\text{-R}$	2.0-2.9	-CH=CH-CH_3	1.7
R-OH	1.0-5.5	$\text{-CH=CH-CH}_2\text{-R}$	2.3
$\text{-O-CH}_2\text{-R}$	3.3-4.3	R-NH_2	0.5-6.5
$\text{R-CH}_2\text{-Cl}$	3.0-4.0	Aromatic C-H	6.0-9.0

^1H Chemical Environments

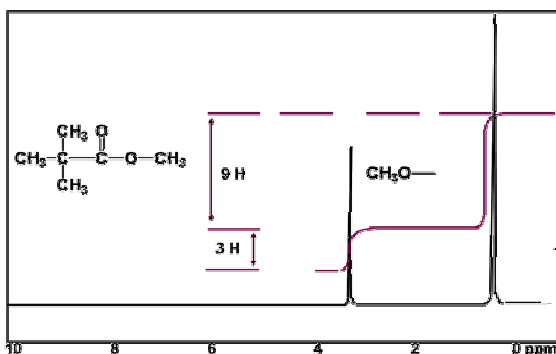
^1H NMR spectrum, 100 MHz



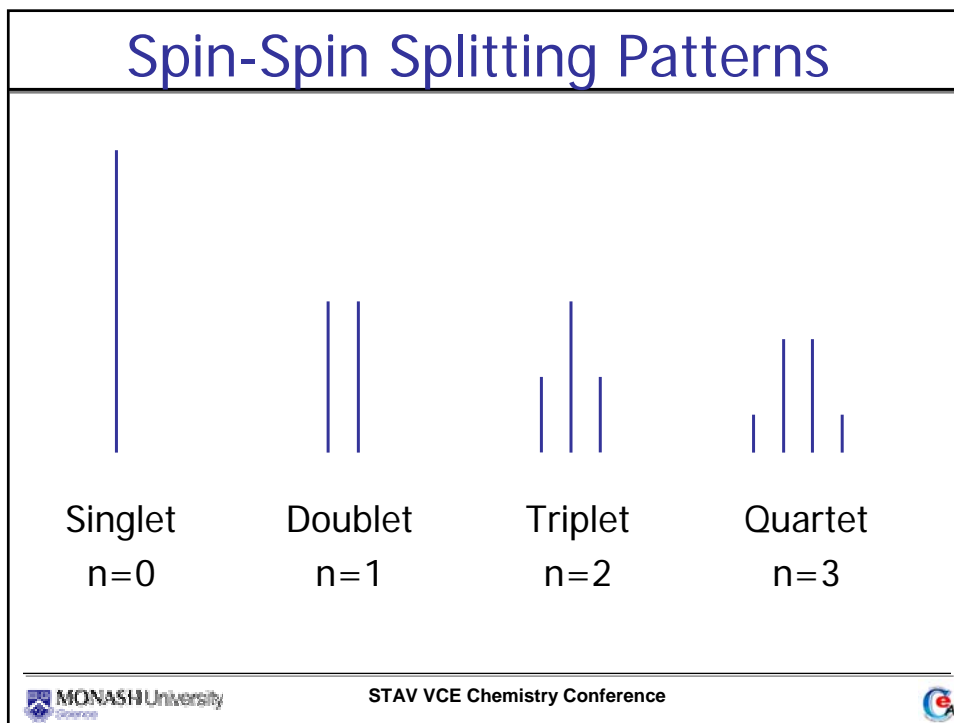
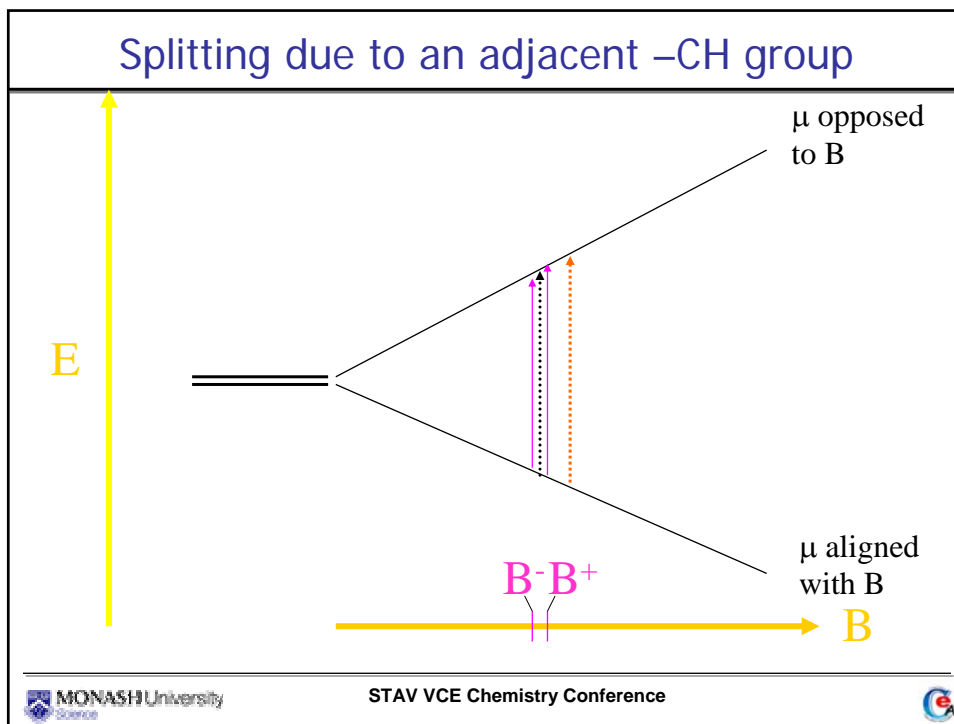
OH and NH_2 protons can give broad signals due to exchange processes

^1H NMR Spectra: Integration

- Integration : the area under an NMR peak is proportional to the number of equivalent hydrogens in an environment.



Integration is the proton count.



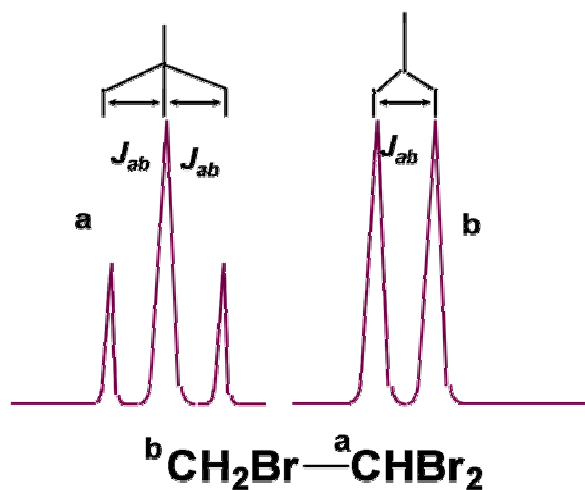
Multiplet Splittings and Pascal's Triangle

of adj. H

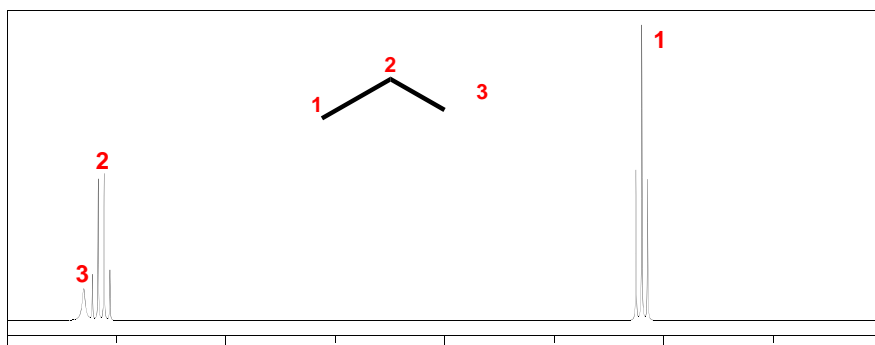
0	Singlet									1						
1	Doublet								1	1						
2	Triplet								1	2	1					
3	Quartet								1	3	3	1				
4	Quintet								1	4	6	4	1			
5	Sextet								1	5	10	10	5	1		
6	Septet								1	6	15	20	15	6	1	
7	Octet								1	7	21	35	35	21	7	1

Gives the relative integration of the multiplet signals.

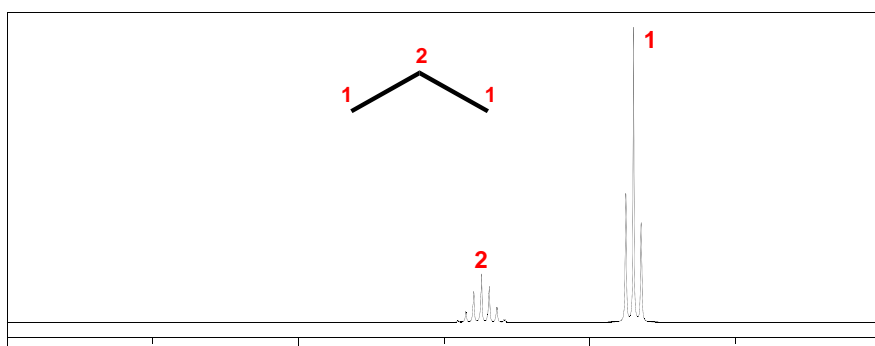
Spin-spin coupling



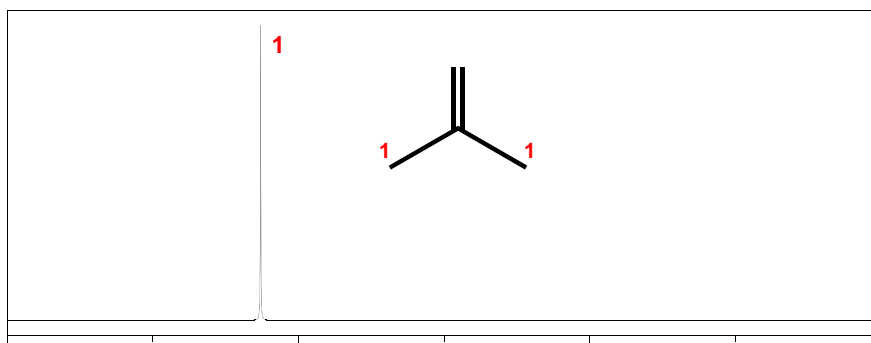
^1H NMR Spectroscopy



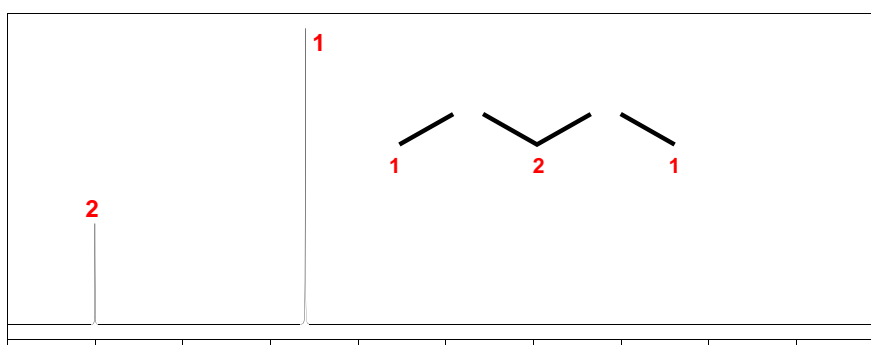
^1H NMR Spectroscopy



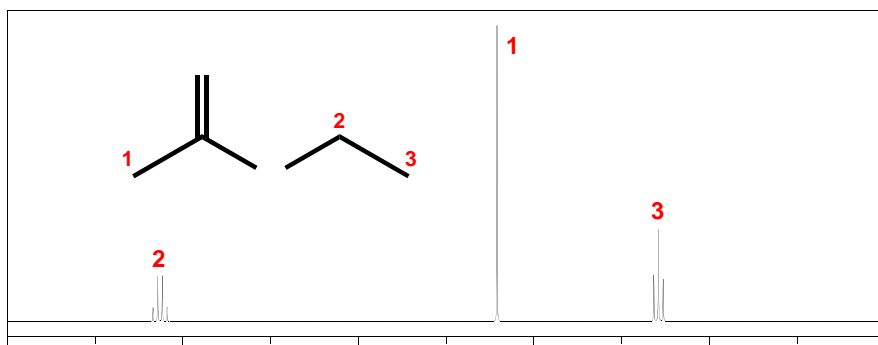
^1H NMR Spectroscopy



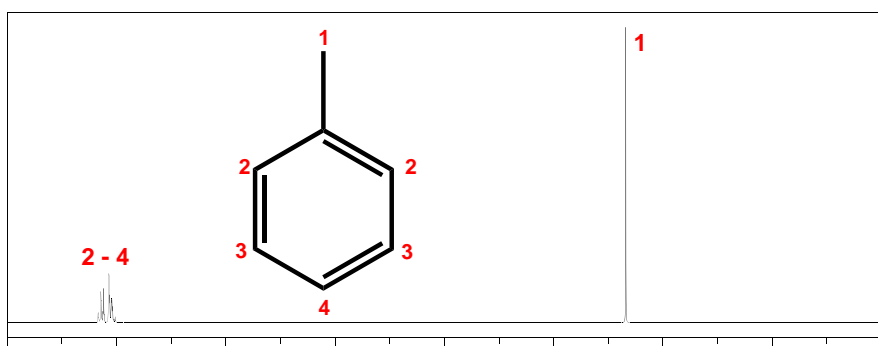
^1H NMR Spectroscopy



^1H NMR Spectroscopy



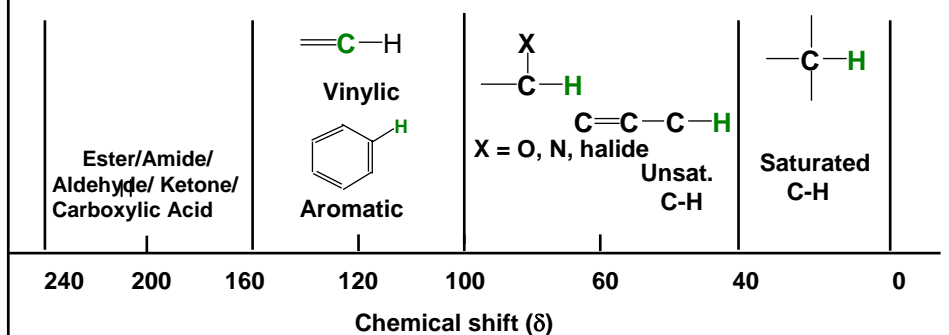
^1H NMR Spectroscopy



^{13}C NMR Spectroscopy

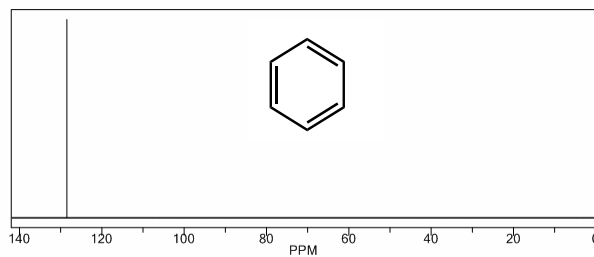
- Distinct peak for each C environment ($^{13}\text{C} = 1.1\%$)
- Chemical shifts: 0-200 ppm vs 0-12 ppm for ^1H
- δ depends on hybridization of C and electronegativity of attached groups
- Peak areas are not indicative (a quirk of the instrumentation in pulsed FT-NMR)
- Spin-spin coupling is not important : ^{13}C - ^{13}C is unlikely due to low ^{13}C abundance and ^{13}C - ^1H coupling is removed by a technique known as "broadband decoupling"

^{13}C NMR Spectra : Chemical Environments



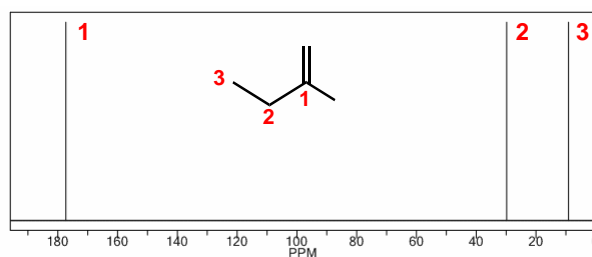
Chemical shift related to the B_L which is determined by the hybridization of the carbon centre and the groups attached.

^{13}C NMR Spectroscopy



Aromatic C - H

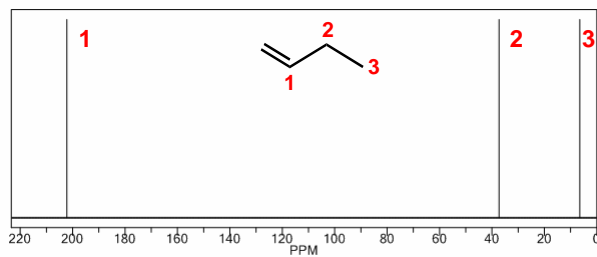
^{13}C NMR Spectroscopy



Carboxylic acid C (Quaternary C)

Aliphatic C

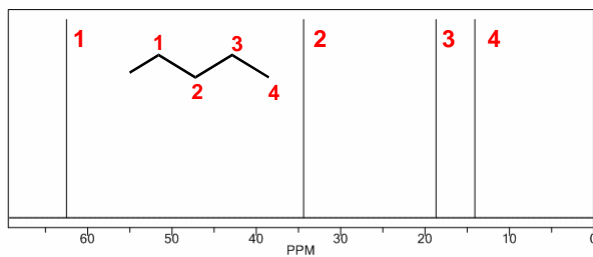
^{13}C NMR Spectroscopy



Aldehyde C

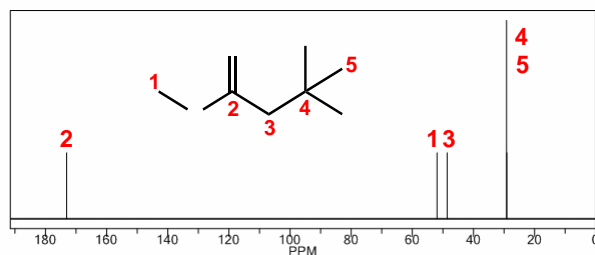
Aliphatic C

^{13}C NMR Spectroscopy



Aliphatic C

^{13}C NMR Spectroscopy

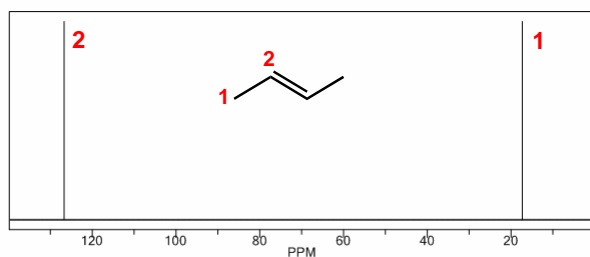


Carbonyl C (quaternary C)

Aliphatic C

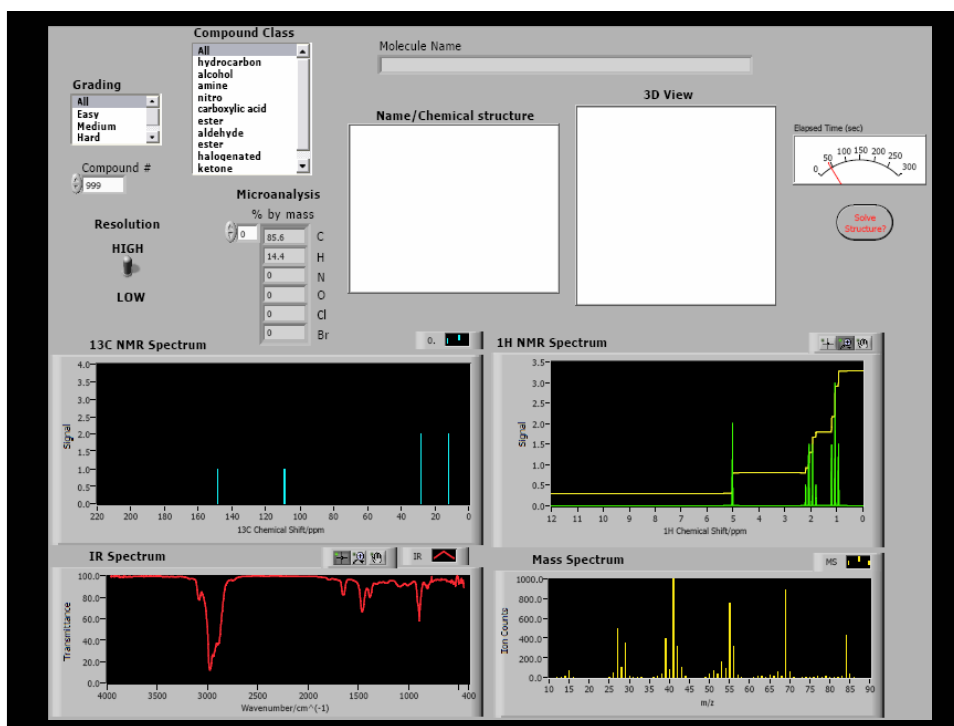
Quaternary C

^{13}C NMR Spectroscopy



Alkene C

Alkane C



Packages / Applications

Use

<i>NIST WebBook</i>	Source of IR & MS spectra
<i>ChemDraw</i>	Computing NMR, 2D structures
<i>Microsoft Word, Notebook</i>	Reformatting data
<i>IGOR</i>	JCAMP: Reformatting files
<i>Spartan</i>	3D Structures
<i>Adobe Photoshop</i>	Image processing
<i>LabVIEW</i>	Building and presenting "Chemical Detectives"