3.15 Nuclear Magnetic Resonance Spectroscopy, NMR

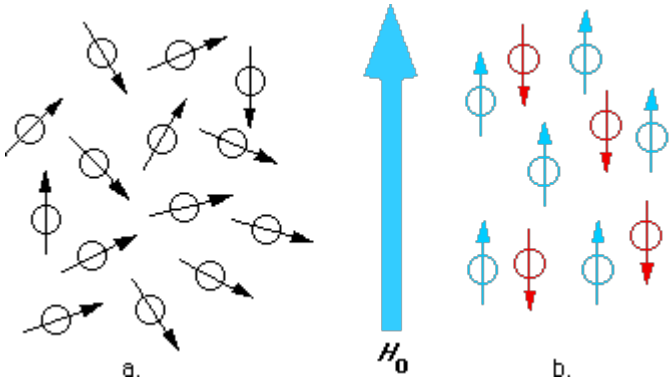
What is Nuclear Magnetic Resonance - NMR

- Developed by chemists and physicists together it works by the interaction of magnetic properties of certain nuclei and their chemical environment.
- This technique only works with atoms with an odd number of nucleons (protons and neutrons).
- This gives us 2 types of NMR: ^{1}H NMR (or proton NMR) and ^{13}C NMR.

Nuclear spin

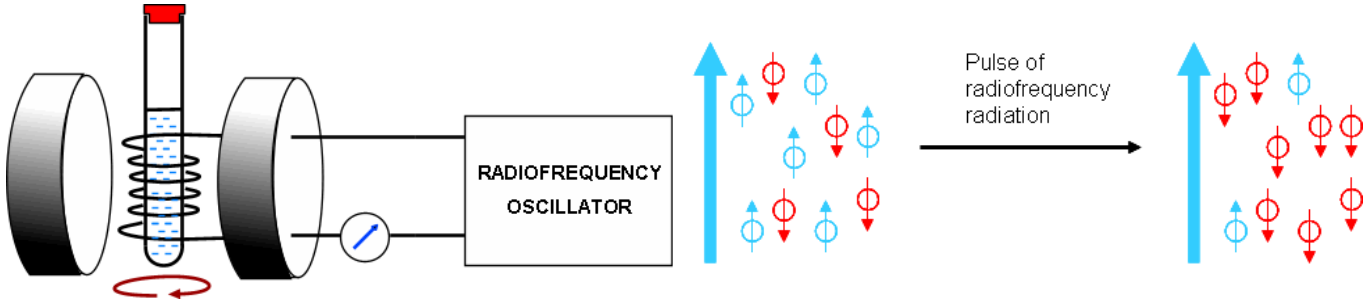
- All nucleons spin, and pair up just as electrons do.
- With an odd number of nucleons there will be one nucleon that is not paired.
- A spinning nucleus such as hydrogen behaves as a spinning charge and generates a magnetic field.
- For example - $^{1}_{1}H$ and $^{13}_{6}C$ possess spin whereas $^{12}_{6}C$ does not.
- It can be likened to a bar magnet:

- When this is placed in an external magnetic field it will align with or against the field.
- The nuclei which align parallel are at a lower energy than those aligned anti parallel:



Resonance:

- When they are subjected to a pulse of radiofrequency radiation, some nuclei flip from parallel to anti parallel:



- This promotes the nuclei from low energy spin (parallel) to high energy spin (antiparallel) thus absorbing energy - **excitation**.
- The frequency required to make this happen is specific to the difference in energy between the 'parallel' and 'antiparallel'
- The excited nuclei will at some point drop back to its low energy state (parallel) **emitting the same amount of energy** (that is specific for that nuclei)
- As electrons surround the nuclei, the energy needed to flip the nuclei depend on the **environment** they find themselves.
- This pulse oscillates so the nuclei continually flip or resonate back and forth, **absorbing and emitting energy.**
- The resonance is recorded as a trace.
- By looking at the field strength at which the nuclei absorb energy while resonating, we can work out the structure of a molecule

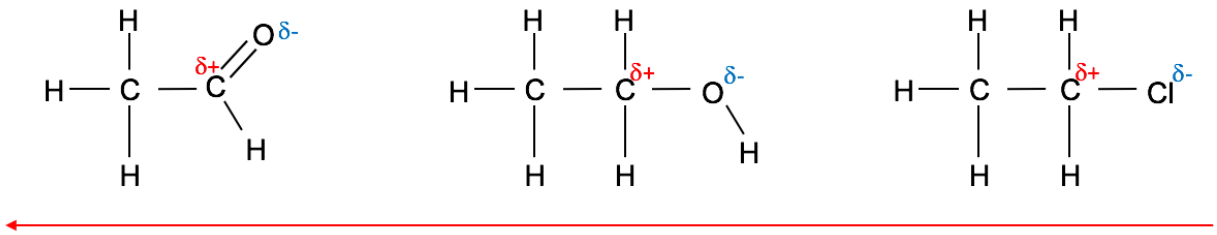
Environment - Nuclear shielding:

- The magnetic field felt by a nucleus depends on:

1) Strength of the externally applied magnetic field

2) Environment: Surrounding electrons and nearby atoms affect nuclear shielding

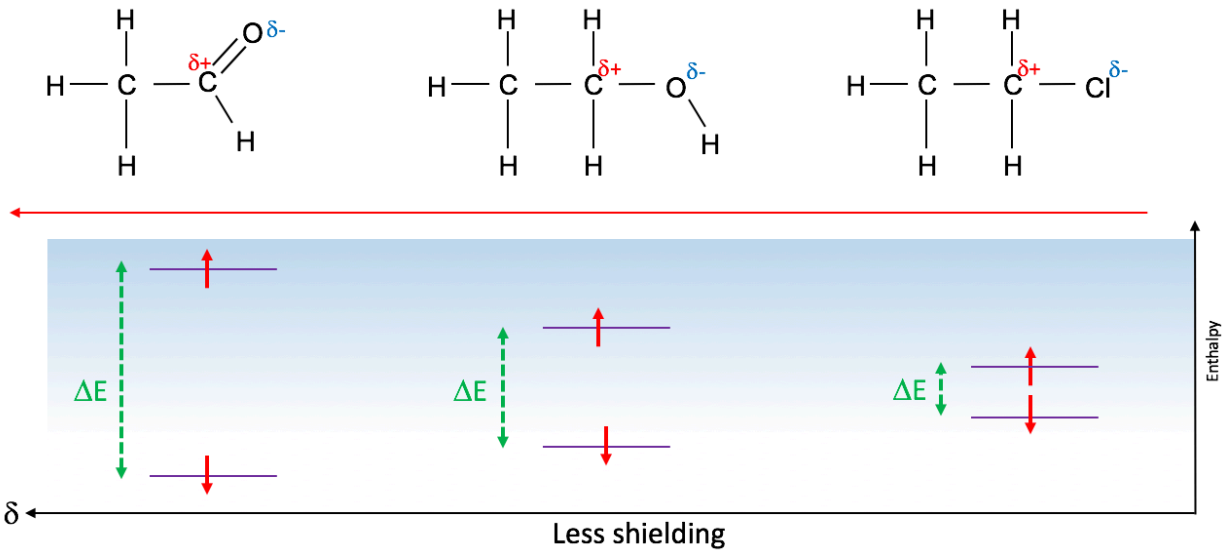
- The electrons in an atom also produce tiny magnetic fields which '**shield**' the nucleus from the applied magnetic field.
- This is called **nuclear shielding** and the extent depends upon nearby atoms or groups of atoms:



More electronegative element pull a pair electrons away from the δ+ carbon
More electronegative element in a double bond pulls 2 pairs of electrons away from the δ+ carbon

Less shielded δ+ carbon

Chemical shift: Environment / Nuclear shielding

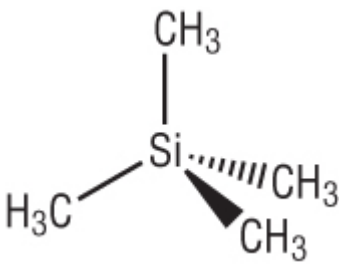


Less shielding
Therefore nucleus is held more strongly by the external magnetic field
Therefore the frequency to resonate increases
Chemical shift increases, δ

- With **less shielding** from the external magnetic field, the (magnetic) nuclei is more **strongly held**.
- A **higher frequency** is required to resonate the nuclei (as it held strongly).
- This frequency is called **chemical shift, δ.**
- The **chemical shift** (frequency) tells us the **environment** we find that nuclei.

The scale:

- The scale is measured against a reference signal, **TMS = 0** chemical shift is measured from this.
- **TMS** is **T**etra**m**ethyl**s**ilane:

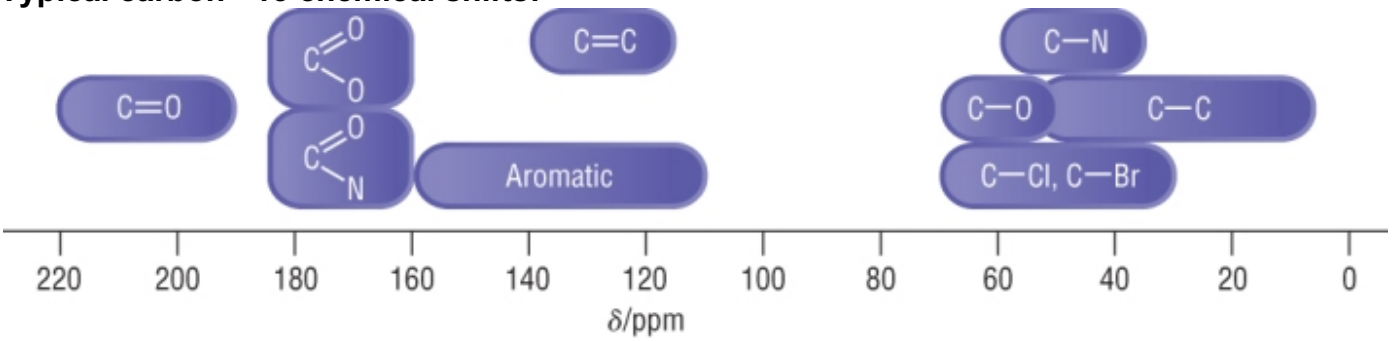


- This molecule has 12 equivalent H's / 4 equivalent C's giving rise to a single peak.
- This peak is assigned the value = 0
- All peaks of a sample under study are related to it and reported in ppm, parts per million (x 10^{-6})

Carbon - 13 NMR spectroscopy

- **99%** of any sample of carbon - ^{12}**C**
- **1%** of any sample of carbon - ^{13}**C**
- This 1% has an uneven number of nucleons, this means it will have a magnetic spin and be detected using NMR

Typical carbon - 13 chemical shifts:

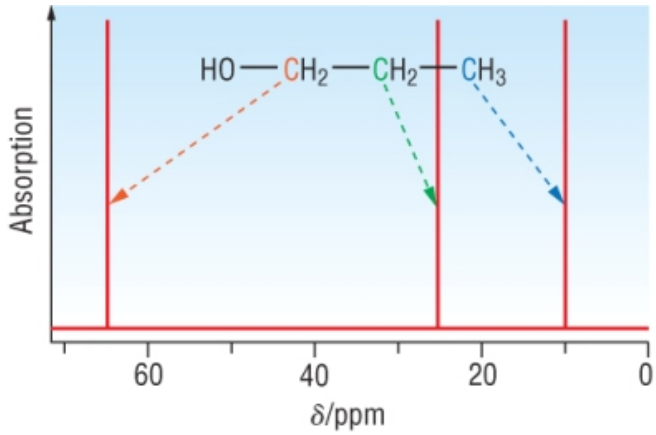


- The chemical shift indicates the environments the 'carbons' are in.
- An electronegative element causes a significant shift as carbon - 13 is sensitive to nuclear shielding.
- The scale ranges 0 - 230, this means that each carbon is likely to have its own separate signal.
- Values will vary with different solvents.

Interpreting ^{13}C NMR:

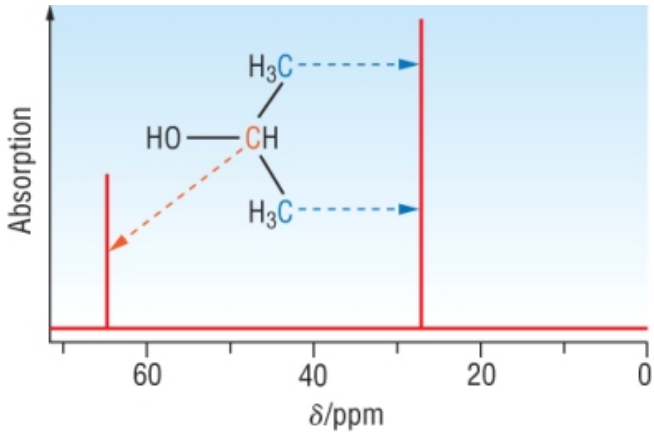
- 2 things can be obtained from ^{13}C NMR is:

1) The number of different carbons – number of peaks
2) The carbon environment – chemical shift



Propan - 1 - ol:

- 3 peaks indicating 3 different carbon environments
- A peak at ~ 64ppm: C - O (nearest the electronegative element O)
- A peak at ~ 27ppm: C - C
- A peak at ~ 10ppm: C - C (furthest from the electronegative O)

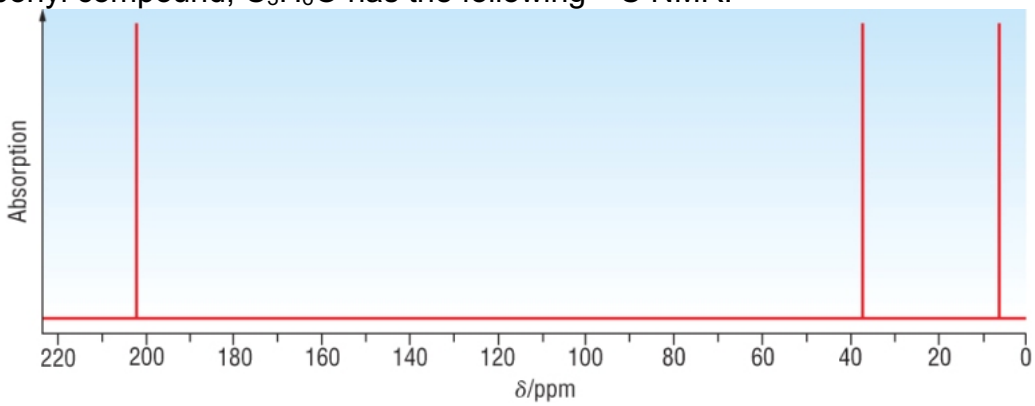


Propan - 2 - ol:

- 2 peaks indicating 2 different carbon environments
- A peak at ~ 64ppm: C - O (nearest the electronegative element O)
- A peak at ~ 27ppm: C - C (furthest from the electronegative O)

Questions:

1) A carbonyl compound, C_3H_6O has the following ^{13}C NMR:

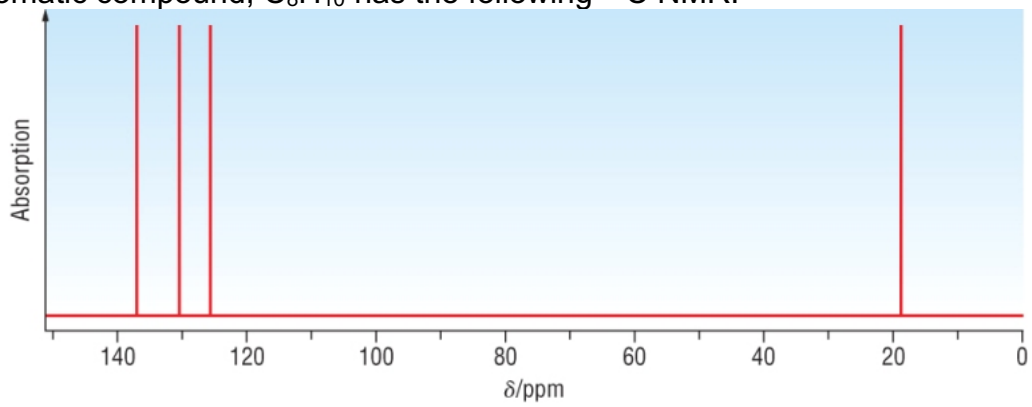


a) Draw the possible isomers of this carbonyl compound:

b) Number the carbons in the **same environment** from the carbonyl carbon outwards.

c) Identify which of your isomers is responsible for the ^{13}C NMR above. Justify your answer.

2) An aromatic compound, C_8H_{10} has the following ^{13}C NMR:



a) Draw the possible isomers of this aromatic compound:

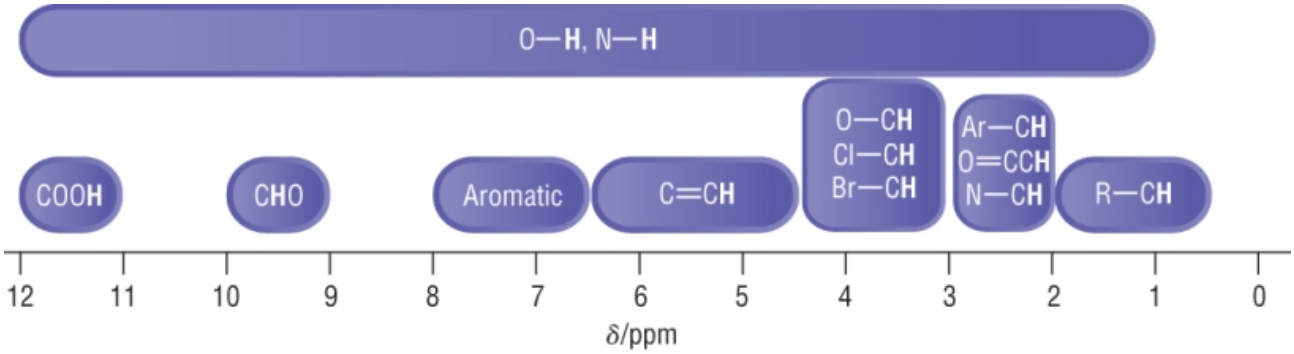
b) Number the carbons in the **same environment** from the line of symmetry inwards.

c) Identify which of your isomers is responsible for the ^{13}C NMR above. Justify your answer.

Proton NMR spectroscopy

- Is based around the ^{1}**H** which is a single proton.
- Proton NMR is done in the same way as ^{13}C NMR and gives all the same information as ^{13}C NMR but for protons.
- In addition:
  - Relative ratio of all the protons
  - Adjacent protons (later)

Typical chemical shifts:



- The scale is narrower which means some signals will overlap.
- Actual chemical shifts can vary depending on environments.
- The scale should be used as a rule of thumb.

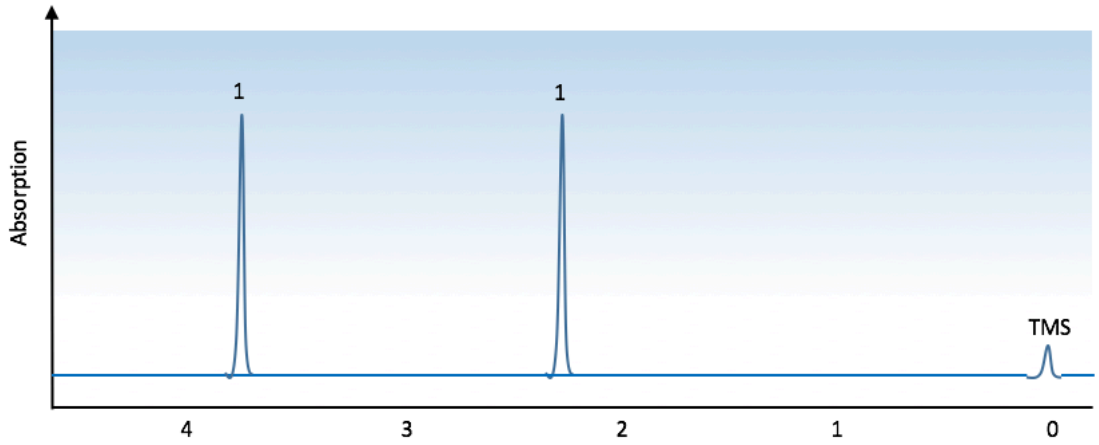
Integration traces:

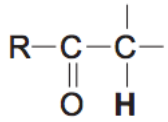
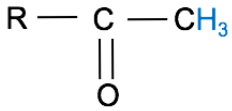
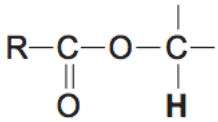
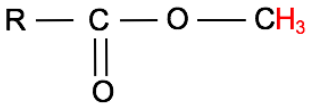
- The area under the peak is proportional to the **relative number of protons**.
- On the NMR spectrum, the spectrometer measures this and is recorded as an **integration trace** or a **number**.
- The integration line is above the peak and can be measured for **relative abundances**.

The solvent

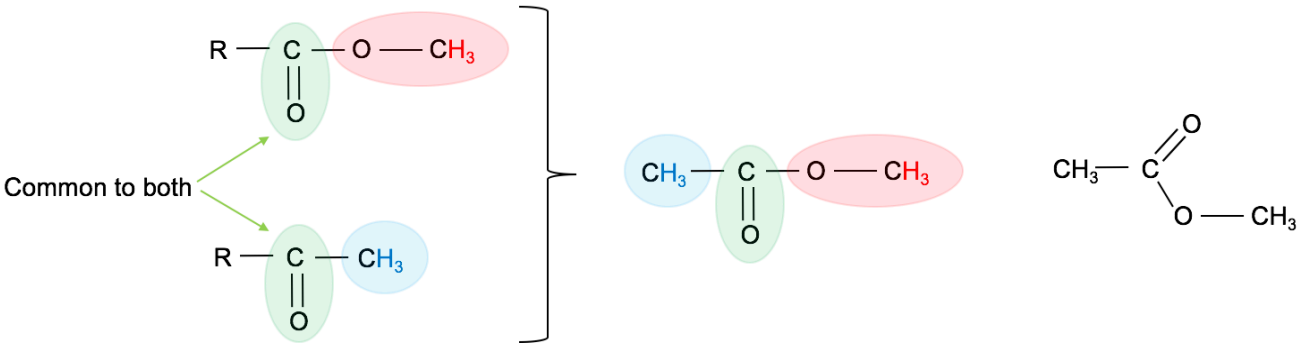
- The solvent used needs to be proton free so as not to produce any peaks that might obscure any peaks from the molecule.
- It needs to be volatile so it can be evaporated off afterwards.
- CCl_4, $CDCl_3$, C_6D_6 are the common solvents where D it deuterium, ^{2}H.

Example: This is the proton NMR for $C_3H_6O_2$



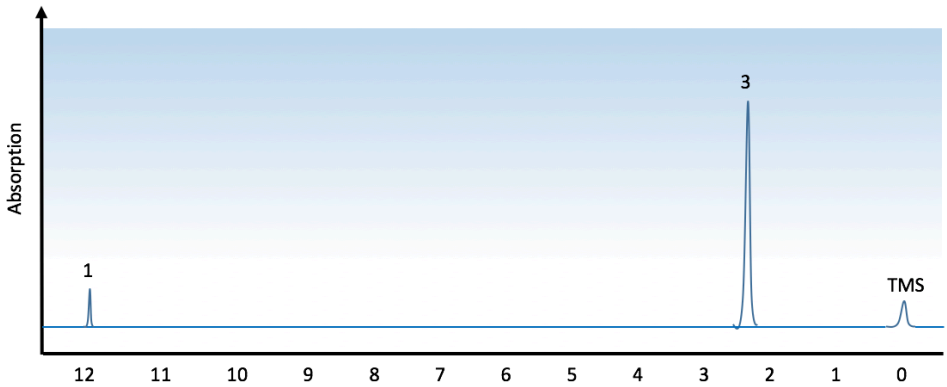
Chemical shift, δ	Environment	Integration	Interpretation
2.1		1 (3 H's)	
3.7		1 (3 H's)	

- 2 equally sized peaks indicating 2 different proton environments
- This means that there are 2 areas of 3 protons.
- Put the pieces together: Methyl ethanoate:



Questions:

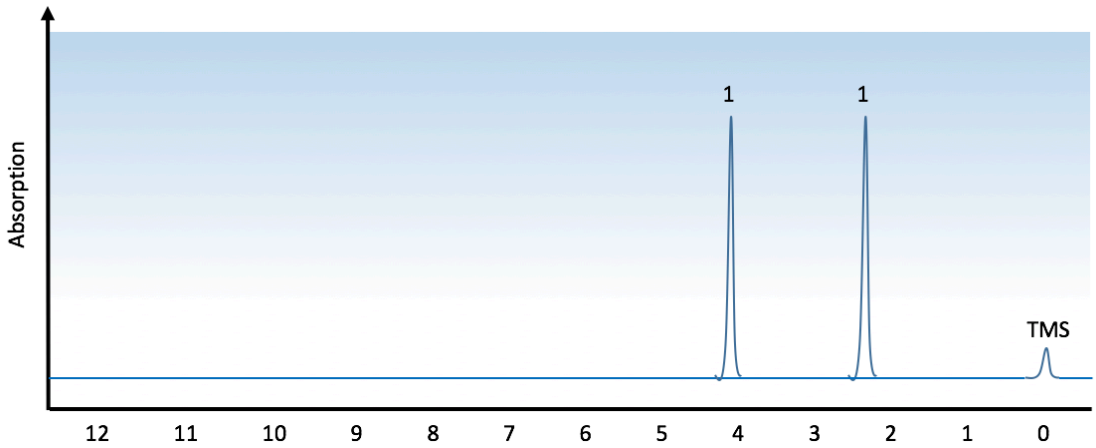
1) The spectrum below is of a molecule with a molecular formula, $C_2H_4O_2$. Identify the molecule by completing the table below:



Chemical shift, δ	Environment	Integration	Interpretation

Displayed structure:

2) The spectrum below is of a molecule with a molecular formula, $C_3H_6O_2$. Identify the molecule by completing the table below:



Chemical shift, δ	Environment	Integration	Interpretation

Displayed structure:

Spin - spin coupling in proton NMR spectra

- Splitting patterns are worked out by considering the effect that adjacent, chemically different hydrogen's have on another signal in a given environment.
- The spin of the proton producing the signal is affected by each of the two forms of the adjacent hydrogen's (parallel and anti parallel).
- One orientation enhances its field and the other diminishes it.
- We can work this out by calculating the various possible combinations of alignment of adjacent protons.

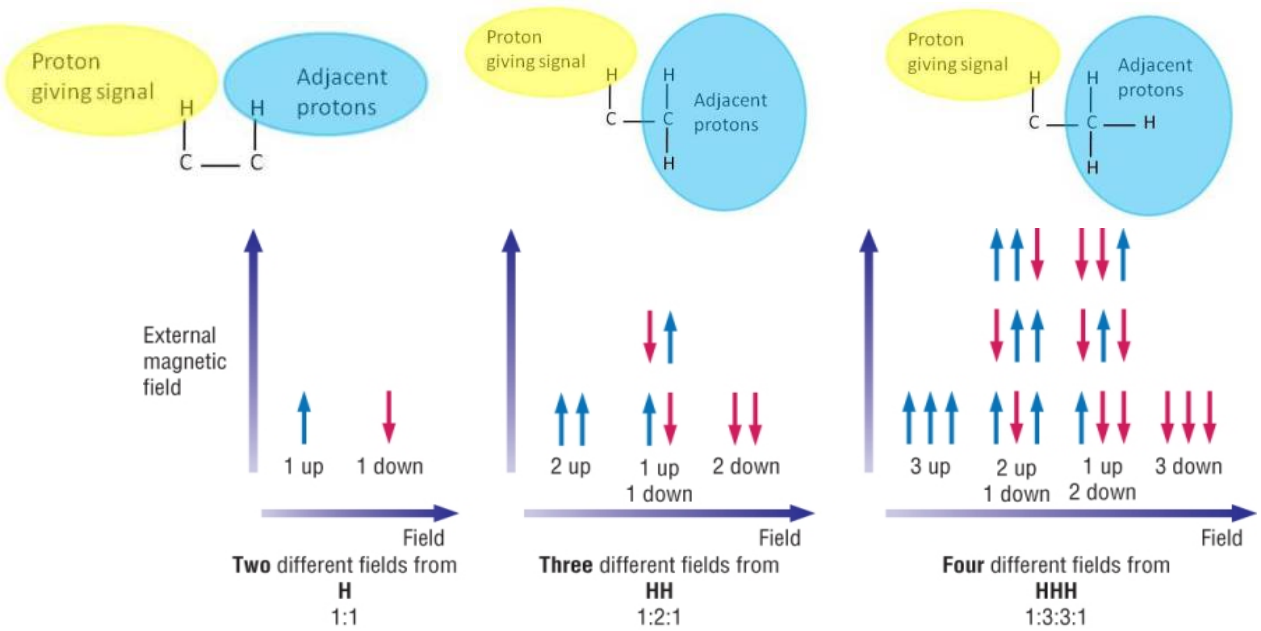
Theory:

- The proton gives a signal by its magnetic field from its spin.
- Its signal is influenced by adjacent protons (on neighbouring carbons).
- Each proton will either spin in the same direction or the opposing direction.
- This means that each adjacent proton either enhances the magnetic field or diminishes it.
- There are 2 possibilities of equal chance per adjacent proton - enhancing or diminishing the magnetic field.
- This **splits** the signal given by the proton

Analogy:

- Like an opinion. If nobody influenced you, your opinion would be the same.
- If another person had a view on the topic, they would either agree or disagree with you.
- Their ideas would either enhance what you thought or diminish it.
- There would be 2 possibilities of equal chance per person agreeing or disagreeing with you:

1 adjacent proton | **2 adjacent protons** | **3 adjacent protons**



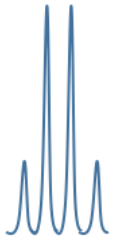
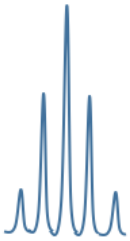
- The adjacent proton spins in the same or opposing direction.
- **Agree, A**
- **Disagree, D**

- Each of the 2 adjacent protons spins in the same or opposing direction.
- **A - A**
- **A - D x 2**
- **D - D**

- Each of the 2 adjacent protons spins in the same or opposing direction.
- **A - A - A**
- **A - A - D x 3**
- **D - D - A x 3**
- **D - D - D**

2 fields of equal intensity | **3 fields with an intensity of 1:2:1** | **4 fields with an intensity of 1:3:3:1**

Splitting patterns: The n + 1 rule:

n + 1 rule: Number of peaks = Number of different H's on adjacent atoms + 1				
0 Neighbouring H	**1 Peaks**	**Singlet**	**1:1**	
1 Neighbouring H	**2 Peaks**	**Doublet**	**1:1**	
2 Neighbouring H	**3 Peaks**	**Triplet**	**1:2:1**	
3 Neighbouring H	**4 Peaks**	**Quartet**	**1:3:3:1**	
4 Neighbouring H	**5 Peaks**	**Multiplet of 5 peaks (Quintet)**	**1:4:6:4:1**	

NOTE: Pascal's triangles

- Just a note of interest. The signal peaks show the patterns described by Pascal's triangles:

1

1 1

1 2 1

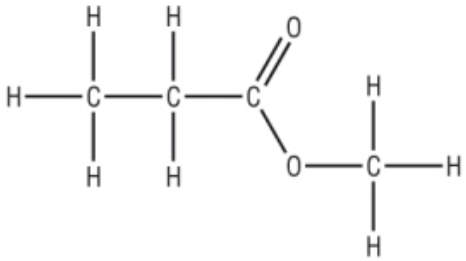
1 3 3 1

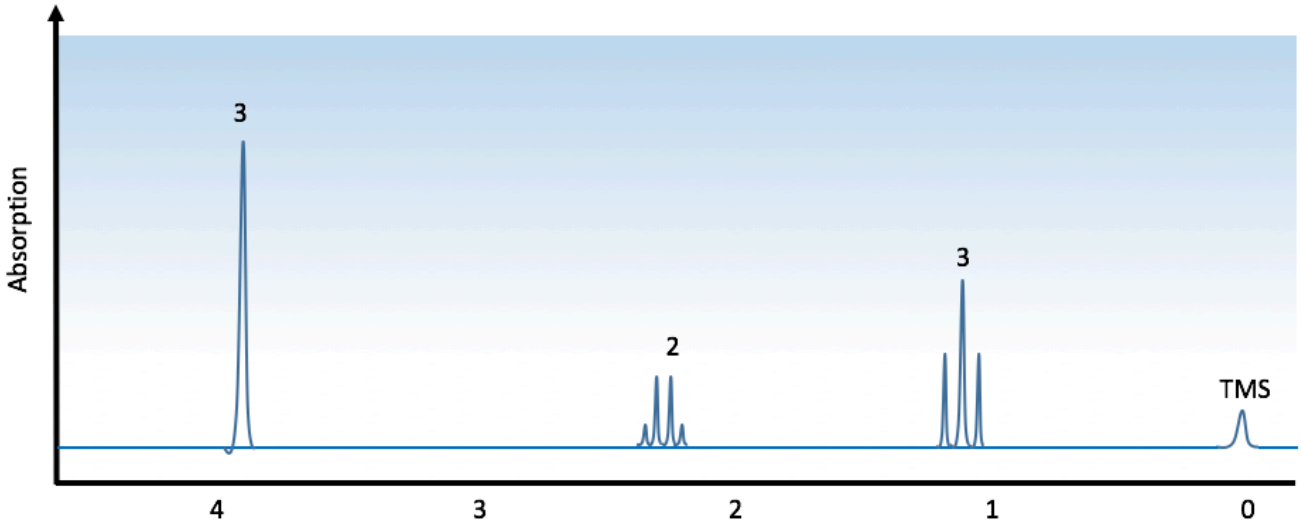
1 4 6 4 1

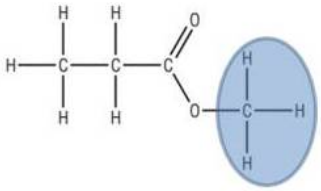
NOTE: O – H and N – H protons are unaffected by adjacent protons and are not split.
**** Singlets only**

The proton NMR spectrum of methyl propanoate:

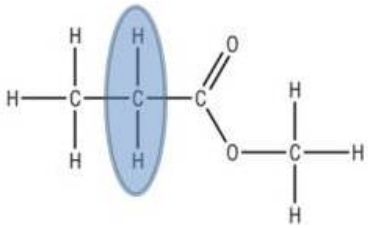
- There are 3 areas of protons - this will give 3 areas of signal:



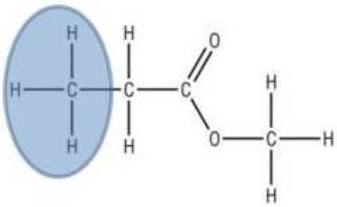




- These protons are adjacent to = 0 protons
- n+1 = 1 peak
- Singlet

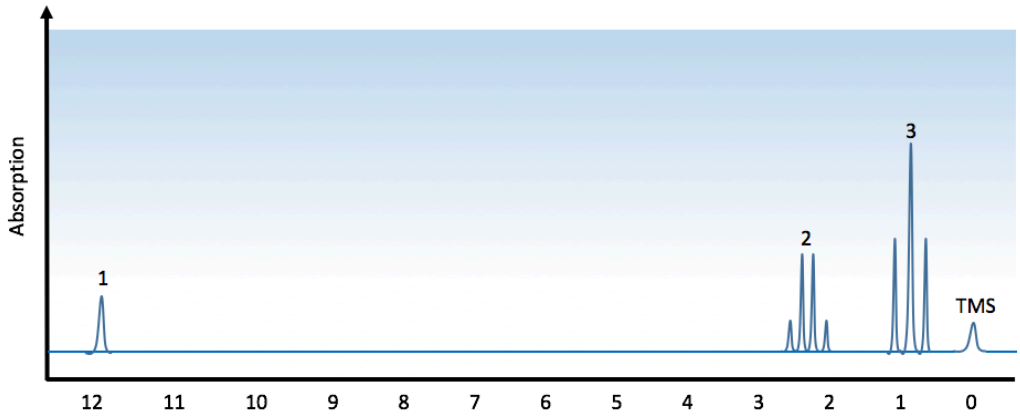


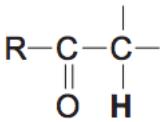
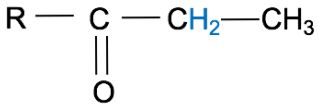
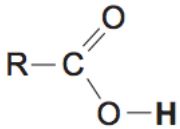
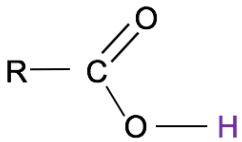
- These protons are adjacent to = 3 protons
- n+1 = 4 peaks
- Quartet



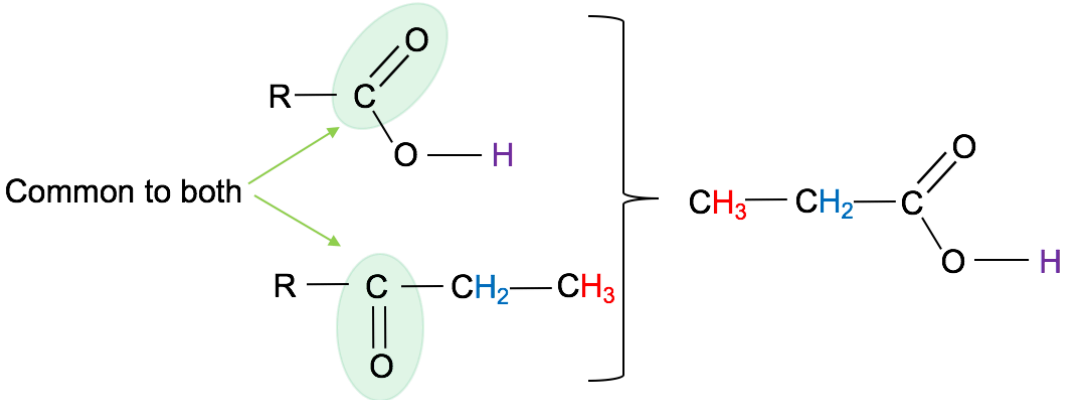
- These protons are adjacent to = 2 protons
- n+1 = 3 peaks
- Triplet

Example: Use the NMR below to identify the organic molecule:



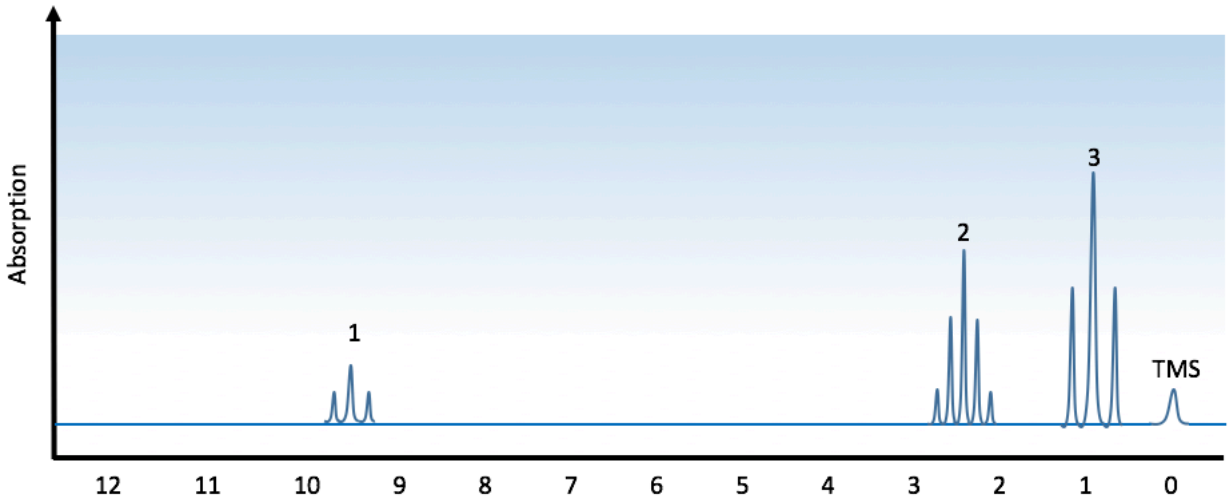
Chemical shift, δ	Environment	Integration	Splitting pattern	Interpretation
0.9	RCH_3	3	Triplet (adj to 2H's)	$—CH_2\ CH_3$
2.1		2	Quartet (adj to 3H's)	
11.9		1	Singlet	

- Put the pieces together:



Questions:

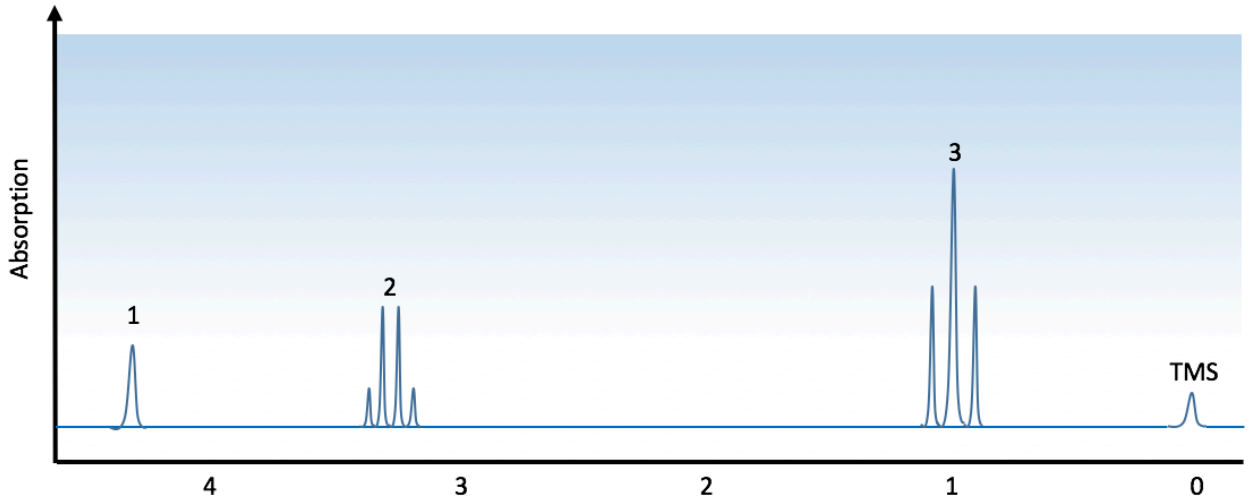
1) Identify the molecule by completing the table below:



Chemical shift, δ	Environment	Integration	Splitting pattern	Interpretation

Displayed structure:

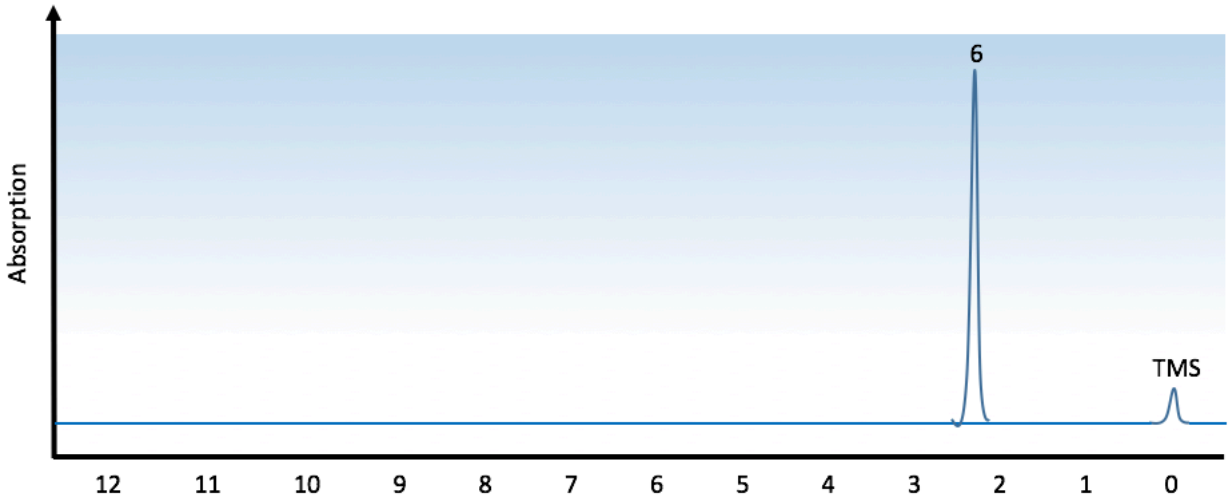
2) Identify the molecule by completing the table below:



Chemical shift, δ	Environment	Integration	Splitting pattern	Interpretation

Displayed structure:

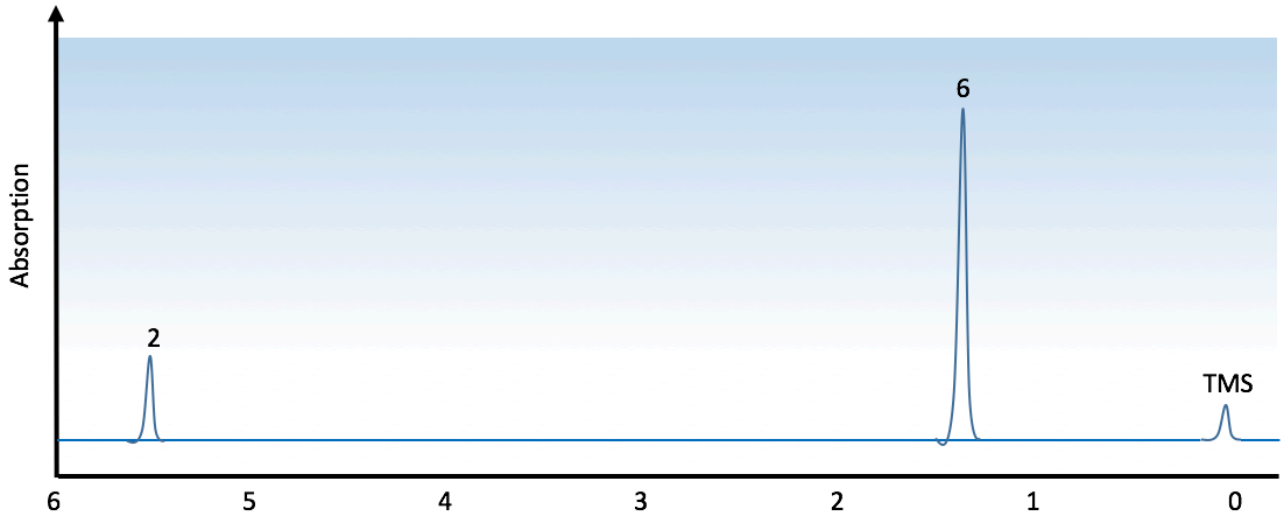
3) Identify the molecule by completing the table below:



Chemical shift, δ	Environment	Integration	Splitting pattern	Interpretation

Displayed structure:

4) Identify the molecule by completing the table below:



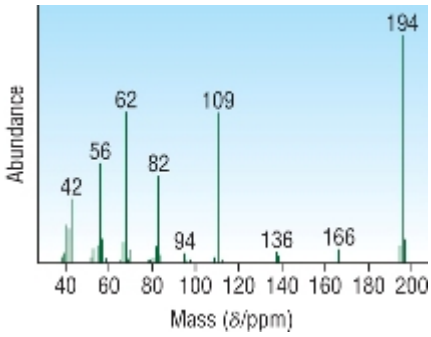
Chemical shift, δ	Environment	Integration	Splitting pattern	Interpretation

Displayed structure:

Combined techniques:

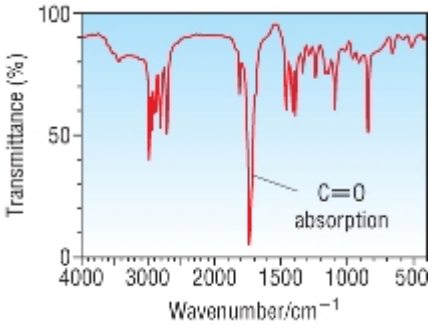
- A single spectroscopic technique tells you 'bits' of information on the structure of a molecule or compound.
- Combining the techniques give you lots of 'bits' of information that can be used to determine the actual structure of the molecule or compound:

Mass Spectroscopy:



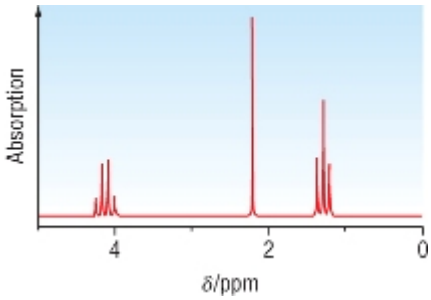
- Chemical analysis provides the empirical formula of the compound.
- Mass spectroscopy gives the Mr and hence the molecular formula.
- Fragmentation patterns give clues about the carbon skeleton.

IR spectroscopy:



- IR spectroscopy gives information about functional groups presemt in the molecule:
- O - H
- C = O
- C - O
- However many functional groups can have these bonds present

NMR spectroscopy:



Carbon - 13 NMR:

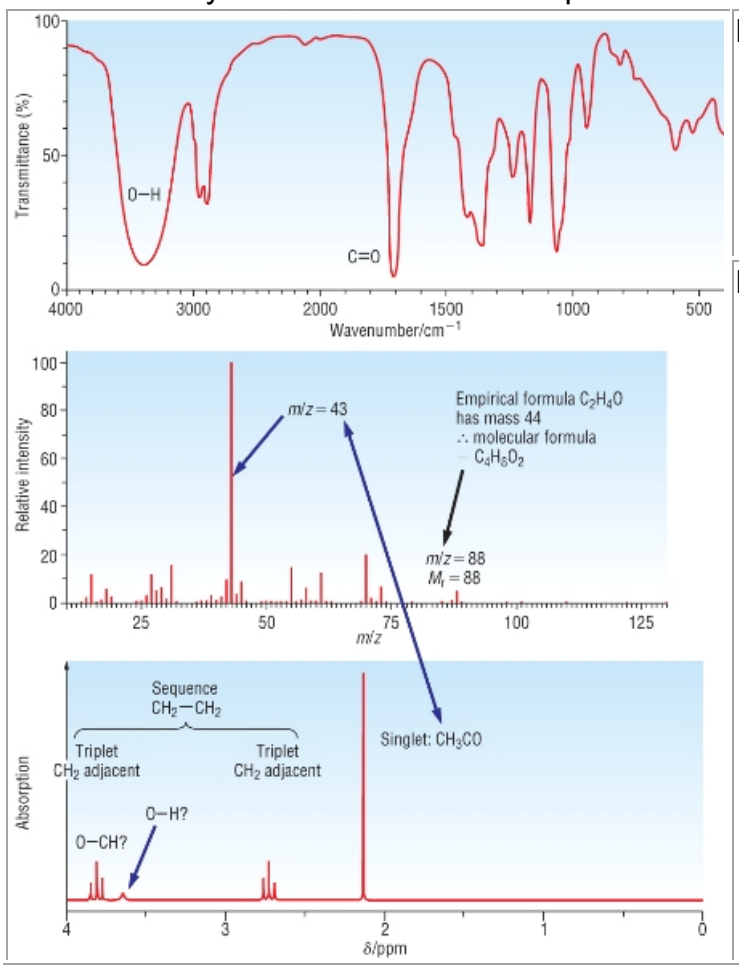
- Gives information about the numbers and types of carbon environments.

Proton NMR:

- Gives information about the numbers and types of protons.
- It also tells you the environments the protons are in.

Worked example:

Chemical analysis has identified the empirical formula as C_2H_4O (Mr = 44)

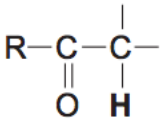
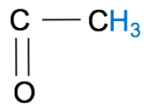
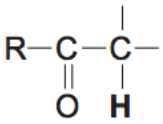
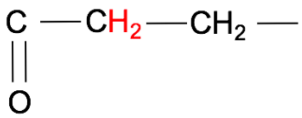
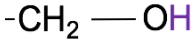
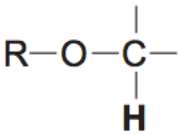


IR spectra:

- **O - H present**
- **C = O present**

Mass Spectra:

- **Molecule has a mass, Mr = 88**
- **Molecular formula = $C_4H_8O_2$**

Chemical shift, δ	Environment	Integration	Splitting pattern	Interpretation
2.1		3	Singlet (adj to 0H's)	
2.7		2	Triplet (adj to 2H's)	
3.6	**ROH**	1	Singlet	
3.9		2	Triplet (adj to 2H's)