M.Sc. Semester-III
Core Course - 7 (CC-7)
Application of Spectroscopy

III. Nuclear Magnetic Resonance Spectroscopy

L4: Spin-Spin Coupling, The n+1 Rule and Pascal's Triangle

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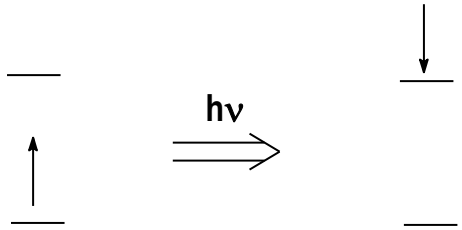
Theory of NMR

- The small energy difference between the two alignments of magnetic spin corresponds to the energy of radio waves according to Einstein's equation $E=h\nu$.



- Application of just the right radiofrequency (ν) causes the nucleus to "flip" to the higher energy spin state
- Not all nuclei require the same amount of energy for the quantized spin 'flip' to take place.
- The exact amount of energy required depends on the chemical identity (H, C, or other element) and the chemical environment of the particular nucleus.

Spin-spin splitting (Coupling)

- Proton NMR spectra are not typically as simple as CMR (^{13}C NMR) spectra, which usually give a single peak for each different carbon atom in the structure.
- Proton NMR spectra are often much more complex.
- Because of its nuclear spin, each proton exerts a slight effect on the localized magnetic field experienced by its neighboring proton(s).
- The spin state ($\uparrow$ or $\downarrow$) of any one proton is independent of any other proton.
- The energies of protons of different spin states are so nearly equal that there is close to a 50:50 chance for each proton to be up (or down).

Spin-spin splitting (Coupling)

- The spin states of the neighboring protons (those on the adjacent carbon) exert a small influence on the magnetic field, and therefore on the chemical shift of a given proton.
- The result is that proton signals in the NMR spectrum are typically split into multiplets. This phenomenon is called coupling; the consequence is signal splitting.
- The type of multiplet (doublet, triplet, quartet, etc.) depends on the number of protons on the next carbon.

The n+1 rule

- The multiplicity of a proton or a group of protons is given by the n+1 rule, where n = the number of protons on the adjacent (adjoining) carbon atom (or atoms)

n	n+1	multiplet name (abbrev)		intensity pattern
0	1	singlet	(s)	1
1	2	doublet	(d)	1 : 1
2	3	triplet	(t)	1 : 2 : 1
3	4	quartet	(q)	1 : 3 : 3 : 1
4	5	quintet/pentet	-	1 : 4 : 6 : 4 : 1
5	6	sextet	-	1 : 5 : 10 : 10 : 5 : 1
6	7	septet/heptet	-	1 : 6 : 15 : 20 : 15 : 6 : 1

Pascal's Triangle

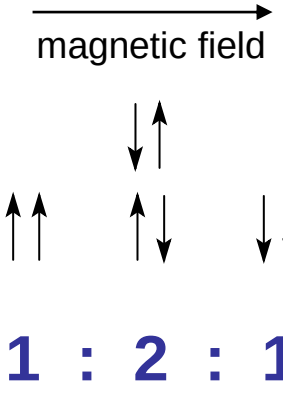
Spin-spin Coupling in Chloroethane

- Consider the ethyl group in chloroethane CH_3CH_2Cl.
- The **methyl protons** experience a magnetic field that is somewhat influenced by the chlorine on the adjacent carbon, but is also affected slightly by the nuclear spin states of the adjacent methylene (CH_2) protons.
- The two CH_2 protons can have the following possible combination of spins:

  two spin up (1 way)

  one up and one down (2)

  two spin down (1)



1 : 2 : 1

- This results in a **1:2:1 triplet** for the methyl group

Spin-spin Coupling in Chloroethane

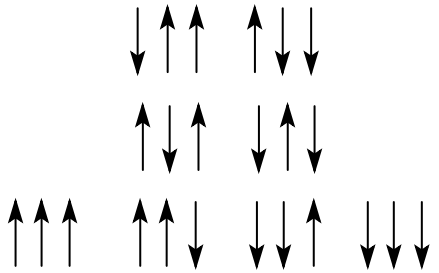
- The magnetic field experienced by the CH_2 protons in chloroethane (CH_3CH_2Cl) is mainly influenced by the electronegative chlorine.
- However, it is slightly perturbed by the spin states of the three methyl (CH_3) protons on the adjoining carbon
- They have four possible combinations of spins:

Three spin up (1 way)

Two up and one down (3)

Two down and one up (3)

Three spin down (1)

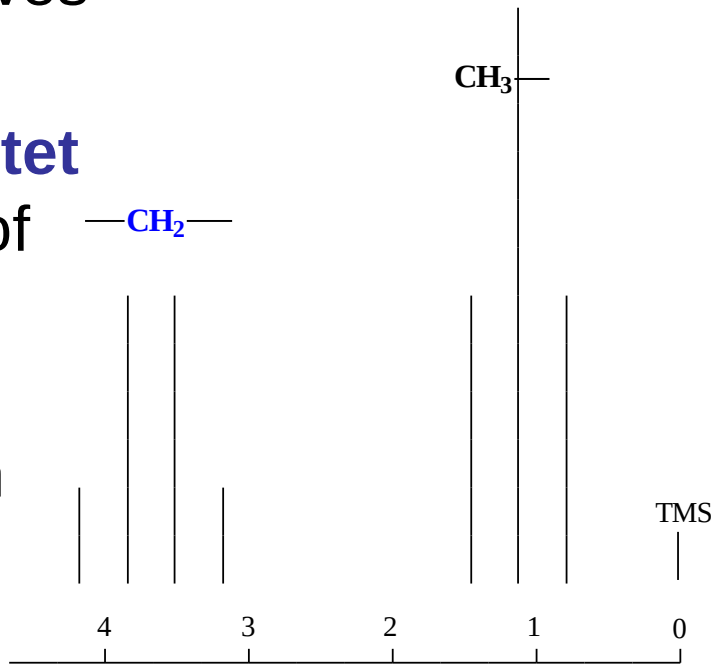


1 : 3 : 3 : 1

- As a result, the $\underline{CH_2 \text{ group}}$ appears as a **1:3:3:1 quartet**.

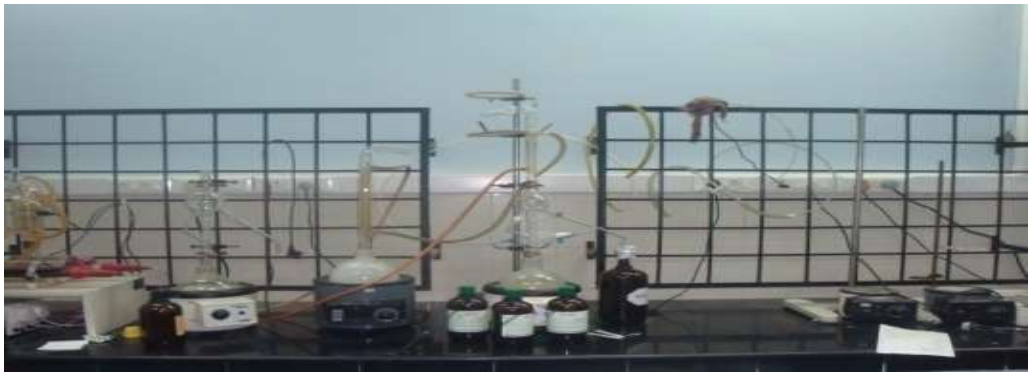
PMR Spectrum of Chloroethane

- Putting the multiplets together gives the predicted spectrum.
- The pattern of a **downfield quartet** and an **upfield triplet** is typical of the presence of an ethyl group in the molecular structure.
- Note that the triplet is larger than the quartet. That is because there are 3 protons giving rise to the triplet, and only 2 protons giving rise to the quartet.
- The integrated signal areas are in a 3:2 ratio.



CH_3CH_2Cl

Thank You



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