Physical Chemistry - Magnetic Shielding, Chemical Shift, Nuclear Coupling, Multiplet splitting, limitations of continuous pulse NMR and Pulse NMR

Magnetic Shielding

- The exact resonance frequency of a nucleus is a function of the static magnetic field seen by the nucleus - small changes make measurable change in resonance frequency.
- Such small changes occur as a result of local magnetic fields produced by nearby circulation e- - resonance frequency of a nucleus is changed slightly by local arrangement of e- in the molecule (the 'environment' of a particular nucleus).
- Addition of magnetic field produced by electrons ςB is proportional to and opposite to applied field: $\varsigma B = -\sigma B$: where σ is shielding constant (usually positive, but can be negative) and B is magnetic field at nucleus (discussed in previous notes).

The total local field is:

$B_{loc} = B + \varsigma B = (1 - \sigma) B$

and resonance frequency, which depends on local magnetic field, becomes:

$$\nu = \frac{\gamma}{2\pi} = (1 - \sigma) B$$

Chemical Shift

- Because the shielding varies with position in a molecule, the same nuclei e.g. 1H in different parts of the molecule will all resonate at slightly different frequencies. Shifted from an agreed 'standard' frequency νo. The difference $\nu - \nu o$ depends on the standard frequency (or value of B).

However, $\varsigma = \frac{\nu - \nu o}{\nu o}$ x 106 (ppm)

- Represents a chemical shift that is independent of field, and so will apply to the same nucleus in a molecule in any NMR machine.
- If $\varsigma > 0$ resonance frequency is higher than standard and nucleus is said to be deshielded.
- Thus we can use NMR spectroscopy to identify protons and other nuclei in a sample in different chemical environments or different parts of a molecule, to obtain quantitative information to help identify.

1) Must use a solvent free of nucleus of interest e.g. D2O
2) Proton standard is commonly tetramethylsilane (TMS) - 12 protons in identical environments.

Nuclear Coupling

- There is an interaction between nuclei in a molecule, which affects energy levels of all other nuclei. However, in liquid samples the effect is negatively small at distances greater than 2 bonds.
- Without detailing eneergy considerations, we can generalise the fact that:

A group of P equivalent nuclei split a neighbouring group into P+1 lines, with intensities given by the Pth line of Pascal's triangle.

Multiplet splitting

P = 1 1 1
P = 2 1 2 1
P = 3 1 3 3 1
P = 4 1 4 6 4 1

- This provides structural information, helping to assign spectural lines to particular proton groups
- The observed spacing pf the multiplet lines is called coupling constant, J. It is independent of the field or measurement frequency and so is quoted in Hz, not ppm.