

## Predicting spin-spin coupling patterns in NMR spectra

1. Each chemically different magnetic nucleus or set of nuclei will give rise to a peak or multiplet in an NMR spectrum. The multiplet will be symmetrical about its centre. e.g. in  $\text{PF}_5$ , the  $^{31}\text{P}$  nucleus will give rise to a multiplet and the equivalent (under thermal conditions)  $^{19}\text{F}$  nuclei will give rise to a second multiplet.

2. Coupling of a magnetic nucleus A to N equivalent nuclei with spin I will split the signal from A into a multiplet consisting of  $2NI + 1$  peaks. A few examples:

i) Coupling to a single  $^1\text{H}$  nucleus will split the signal into  $2 \times 1 \times \frac{1}{2} + 1 = 2$  peaks.

ii) Coupling to 3 equivalent  $^1\text{H}$  nuclei (e.g. the protons in a methyl group) will give a multiplet consisting of  $2 \times 3 \times \frac{1}{2} + 1 = 4$  peaks.

iii) Coupling to 2 equivalent deuterium ( $^2\text{H}$ ) nuclei ( $I=1$ ) will split the signal into  $2 \times 2 \times 1 + 1 = 5$  peaks.

3. The relative peak intensities for multiplet peaks arising from spin-spin coupling of a nucleus to N equivalent nuclei can be determined using Pascal's triangle:

i) Coupling to spin- $\frac{1}{2}$  nuclei.

1	
1 1	coupling to first nucleus (N=1, doublet)
1 2 1	coupling to second nucleus (N=2, triplet)
1 3 3 1	coupling to third nucleus (N=3, quartet)
1 4 6 4 1	coupling to fourth nucleus (N=4, quintet)
1 5 10 10 5 1	coupling to fifth nucleus (N=5, sextet)
	etc

ii) Coupling to spin-1 nuclei

1	
1 1 1	coupling to first nucleus (N=1, triplet)
1 2 3 2 1	coupling to second nucleus (N=2, quintet)
1 3 6 7 6 3 1	coupling to third nucleus (N=3, septet)
1 4 10 16 19 16 10 4 1	coupling to fourth nucleus (N=4, nonet)
	etc

4. To work out the multiplet pattern for the signal from a given type of nucleus, splittings from spin-spin coupling with surrounding nuclei must be applied consecutively.

e.g. Proton NMR of  $\text{CH}_2\text{FCH}_2\text{CH}_3$

The  $\text{CH}_2\text{F}$  protons will be coupled to the F nucleus (spin- $\frac{1}{2}$ ) through 2 bonds, and to the  $\text{CH}_2$  protons through three bonds. Four bond couplings to the  $\text{CH}_3$  protons can be ignored. Each of these  $\text{CH}_2\text{F}$  protons is spin-spin coupled to the other proton in the group, but this does not lead to a further splitting because the two protons have the same chemical shift. The F nucleus will split the signal into a doublet. The two equivalent  $\text{CH}_2$  protons will then

split *each line* of the doublet into a triplet ( $2 \times 2 \times \frac{1}{2} + 1 = 3$ ). The  $\text{CH}_2\text{F}$  protons therefore give rise to a doublet of triplets in the spectrum.

The  $\text{CH}_2$  protons will be coupled to the  $\text{CH}_2\text{F}$  protons, the F nucleus, and the  $\text{CH}_3$  protons. The peak will be split into 4 by the  $\text{CH}_3$  protons ( $2 \times 3 \times \frac{1}{2} + 1 = 4$ ); each of these four peaks will be split into two by the F nucleus, giving 8 peaks; and each of these 8 peaks will be split into three through coupling to the  $\text{CH}_2\text{F}$  protons: there will be  $4 \times 2 \times 3 = 24$  peaks in total (note that there is no splitting due to coupling between the  $\text{CH}_2$  protons because these have the same chemical shift).

Finally, the  $\text{CH}_3$  protons will give rise to a triplet through spin-spin coupling to the  $\text{CH}_2$  protons.

The relative peak intensities can be determined using successive applications of Pascal's triangle, as described above.

5. In general, spin-spin couplings are only observed between nuclei with spin- $\frac{1}{2}$  or spin-1. Nuclei with  $I > \frac{1}{2}$  (e.g. Cl, Br) have nuclear electric quadrupole moments in addition to magnetic dipole moments. The reason that couplings involving these nuclei are often not observed is that quadrupole interactions with molecular electric field gradients provide a fast relaxation pathway, which means that other nuclei only ever 'see' these quadrupolar nuclei in their ground spin state (i.e. the nuclei are effectively *decoupled*). To understand the factors that determine whether or not coupling will be observed to such nuclei requires a little bit of theory about quadrupole interactions. The Hamiltonian matrix element for this interaction is  $\langle I | \mathbf{Q} | I \rangle$ , where  $I$  is the nuclear spin quantum number and  $\mathbf{Q}$  is the quadrupole coupling operator, given by

$$\mathbf{Q} = \frac{e Q}{2I(2I-1)} \mathbf{V}$$

where  $e$  is the electronic charge,  $Q$  is the nuclear quadrupole moment, and  $\mathbf{V}$  is the electric field gradient at the nucleus of spin  $I$ . From this expression, we can see that the nuclear quadrupole interaction, and therefore the rate of quadrupolar relaxation, depends on both the nuclear quadrupole moment and the electric field gradient at the nucleus. If the quadrupole moment is small, which is true for nuclei such as deuterium ( $^2\text{H}$ ) and  $^{14}\text{N}$ , both of which have spin 1, then coupling to the nucleus will often be observed. Even in nuclei with larger quadrupole moments, coupling is sometimes seen if the electric field gradient  $\mathbf{V}$  at the nucleus is small. The field gradient reflects the anisotropy of the molecular electric field at the position of the nucleus, so if the nucleus is in a highly symmetric environment, the electric field gradient can be small enough so that upper spin states survive long enough to couple to other magnetic nuclei in the molecule. This is the case for the  $^{11}\text{B}$  nucleus in molecules such as  $\text{BH}_4^-$  and  $\text{BF}_3$ . The boron is positioned at the centre of the molecule and experiences a fairly symmetrical field, with small field gradients at the nucleus. It also has a fairly small nuclear quadrupole moment, and coupling to  $^{11}\text{B}$  is usually observed in this type of molecule. In contrast, nuclei such as Cl and Br, both having spin  $3/2$  (in either of the two naturally occurring isotopes for each nucleus), are almost never involved in spin-spin coupling. These atoms are bound to just one other atom in a molecule; they are therefore found on the periphery of molecules, where the molecular fields are highly anisotropic and field gradients are large.