

Glossary

Note – This glossary is by no means exhaustive but it hopefully contains most of the more important terms you will come across in a typical ‘NMR environment.’ Some of the entries may not even have featured in the text itself. Whilst every effort has been made to make the entries scientifically valid, please note that it is sometimes difficult to condense a highly complex topic into a pithy three-line explanation, so some of the definitions are sketchy to say the least!

Acquisition Process of collection of NMR data.

Adiabatic pulse A type of pulse employing a frequency sweep during the pulse. This type of pulse is particularly efficient for *broadband decoupling* over large sweep widths.

Aliased signals Signals that fall outside the *spectral window* (i.e., those that fail to meet the *Nyquist condition*). Such signals still appear in the spectrum but at the wrong frequency because they become ‘folded’ back into the spectrum and are characterised by being out of phase with respect to the other signals.

Anisotropy Non-uniform distribution of electrons about a group which can lead to non-uniform localised magnetic fields within a molecule. The phenomenon leads to unexpected chemical shifts – particularly in ^1H NMR – in molecules where steric constraints are present.

Apodization The use of various mathematical functions which when applied to an FID, yield improvements in the resultant spectrum. These include *exponential multiplication* and *Gaussian multiplication*.

Bloch-Siegert shift A shift in resonant frequency of a signal which is in close proximity to a secondary applied r.f. The effect forces signals away from the applied r.f. and is only ever noticeable in homonuclear decoupling experiments where the applied r.f. and the observed signal can be very close.

Boltzmann Distribution The ratio of nuclei which exist in the *ground state* to those in the *excited state* for a sample introduced into a magnetic field - prior to any r.f. pulsing. This varies with probe temperature but primarily with magnet field strength.

Broadband decoupling Decoupling applied across a wide range of frequencies, e.g., the decoupling of all proton signals during the acquisition of 1-D ^{13}C spectra.

CAMELSPIN Cross-relaxation appropriate for *minimolecules emulated by locked spins*. Now known as *ROESY*.

Chemical shift Position of resonance in an NMR spectrum for any signal relative to a reference standard.

Chiral centre An atom in a molecule (usually but not exclusively carbon) which is bound to four different atoms or groups such that the mirror image of the whole molecule is not super-imposable on the molecule itself. A chiral centre in a molecule implies the possibility of the isolation of two distinct forms of the compound which are known as *enantiomers*.

Chirality Properties conferred by the presence of one or more *chiral centres*.

- Composite pulses** Use of a series of pulses of varying duration and phase in place of a single pulse. Such systems, when used in the pulse sequences of many modern NMR techniques, give improved performance as they are more tolerant to r.f. inhomogeneity.
- Configuraton** The arrangement of atoms and bonds in a molecule. The configuration of a molecule can be changed by breaking and re-forming bonds to yield different *regioisomer*.
- Conformation** The shape a molecule adopts by the rotation and deformation (but *not* the breaking and re-forming) of its bonds.
- Continuous Wave (CW)** Technology used initially in the acquisition of NMR data. The radiofrequency or the magnetic field was swept and nuclei of different *chemical shift* were brought to resonance sequentially.
- COSY** Correlative spectroscopy. Homonuclear (normally ^1H) 2-D spectroscopic technique which relates nuclei to each other by spin coupling.
- Coupling** The interaction between nuclei in close proximity which results in splitting of the observed signals due to the alignment of the neighbouring nuclei with respect to the magnetic field. Also referred to as *spin coupling*.
- Coupling constant** The separation between lines of a coupled signal measured in Hz.
- CPMG pulse sequence** Carr-Purcell-Meiboom-Gill pulse sequence. A pulse sequence used for removing broad signals from a spectrum by multiple defocusing and refocusing pulses.
- Cryoprobe** Probe offering greatly enhanced sensitivity by the reduction of thermal electronic noise achieved by maintaining probe electronics at or near liquid helium temperature.
- Cryoshims** Rough (*superconducting*) shim coils that are built into superconducting magnets and adjusted at installation of the instrument.
- Decoupling** The *saturation* of a particular signal or signals in order to remove spin coupling from those signals. Also referred to as *spin decoupling*.
- DEPT** Distortionless enhancement by polarization transfer. A useful one-dimensional technique which differentiates methyl and methine carbons from methylene and quaternary carbons.
- Diastereoisomers** *Stereoisomers* that are not *enantiomers*. Diastereoisomers are compounds that always contain at least two centres of chirality.
- Diastereotopic proton/group** A proton (or group) which if replaced by another hypothetical group (not already found in the molecule), would yield a pair of diastereoisomers.
- Enantiomer** A single form of an optically active compound. Optically active compounds usually (but not exclusively) contain one or more chiral centres. Enantiomers are defined by their ability to rotate the plane of beam of polarised light one way or the other and these are referred to as either 'D' or 'L', or alternatively '+' or '-', depending on whether the polarised light is rotated to the right (*Dextro*) or the left (*Levo*).
- Enantiotopic proton/group** A proton (or group) which if replaced by another hypothetical group (not already found in the molecule), would yield a pair of *enantiomers*.
- Epimers** Diastereoisomers related to each other by the inversion of only one of their *chiral centres*.
- Epimerization** Process of inter-conversion of one *epimer* to the other. The process is usually base-mediated as abstraction of a proton is often the first step in the process.
- Excited state.** Condition where nuclei in a magnetic field have their own magnetic fields aligned so as to oppose the external magnet, i.e., N-N-S-S. Also known as the high-energy state.
- Exponential multiplication** The application of a mathematical function to an *FID* which has the effect of smoothing the peak shape. Signal/noise may be improved at the expense of resolution.

- First-order spin systems** Not very specific term used to describe spin systems where the difference in *chemical shift* between coupled signals is very large in comparison to the size of the *coupling*. In reality, there is no such thing as a completely first-order system as the chemical shift difference is never infinite. See *Non-first order spin system*.
- Folded signals** See aliased signals.
- Fourier Transformation.** Mathematical process of converting the interference *free induction decay* into a spectrum.
- Free Induction Decay (FID)** Interference pattern of decaying cosine waves collected by Fourier Transform spectrometers, stored digitally prior to *Fourier Transformation*.
- Gated decoupling** A method of *decoupling* in which the decoupling is switched on prior to acquisition and turned off during it.
- Gradient field** A linear magnetic field gradient, deliberately imposed on a sample in, for example, the z-axis in order to defocus the magnetisation. This allows other refocusing gradient pulses to be used to selectively observe desired transitions. Only possible with appropriate hardware. Gradient fields improve the quality of many 2-D techniques and where used, replace the need for *phase cycling*.
- Gradient pulse** The application of a *gradient field* for a discrete period of time. Also referred to as *Pulsed field gradients (PFGs)*.
- Gaussian multiplication** The application of a mathematical function to an *FID* to improve resolution (sharpen lines) at the expense of signal/noise.
- GOESY** Gradient Overhauser effect spectroscopy. An early version of a 1-D *NOESY* making use of gradients.
- Gradient shimming** A system of *shimming* based on mapping the magnetic field inhomogeneity using field gradients and calculating the required shim coil adjustments required to achieve homogeneity.
- Ground state** Condition where nuclei in a magnetic field have their own magnetic fields aligned *with* that of the external magnet, i.e., N-S-N-S. Also known as the low-energy state.
- Gyromagnetic ratio** A measure of how strong the response of a nucleus is. The higher the value, the more inherently sensitive will be the nucleus. ^1H has the highest value. Also known as *Magnetogyric ratio*.
- Hard pulse** A pulse which is equally effective over the whole chemical shift range. See *Soft pulse*.
- HETCOR** *Heteronuclear correlation*. Early method of acquiring one-bond ^1H - ^{13}C data. Not nearly as sensitive as *HMQC* and *HSQC* methods which have largely superseded it.
- HMBC** *Heteronuclear multiple bond correlation*. A proton-detected, two-dimensional technique that correlates protons to carbons that are two and three bonds distant. Essentially, it is an *HMQC* that is tuned to detect smaller couplings of around 10 Hz.
- HMQC** *Heteronuclear multiple quantum coherence*. A proton-detected, 2-D technique that correlates protons to the carbons they are directly attached to.
- HOHAHA** *Homonuclear Hartmann Hahn* spectroscopy. See *TOCSY*.
- HSQC** *Heteronuclear single quantum coherence*. As for *HMQC* but with improved resolution in the carbon dimension.
- INADEQUATE** Incredible *natural abundance double quantum transfer experiment*. Two-dimensional technique showing ^{13}C - ^{13}C coupling. It should be the 'holy grail' of NMR methods but is in fact of very limited use due to extreme insensitivity.
- Indirect detection** Method for the observation of an insensitive nucleus (e.g., ^{13}C) by the transfer of magnetisation from an abundant nucleus (e.g., ^1H). This method of detection offers great improvements in the sensitivity of proton-carbon correlated techniques.

- Inverse geometry** Term used to describe the construction of a probe that has the ^1H receiver coils as close to the sample as possible and the X nucleus coils outside these ^1H coils. Such probes tend to give excellent sensitivity for ^1H spectra at the expense of X nucleus sensitivity in 1-D techniques. They offer a lot of compensation in terms of sensitivity of *indirectly detected* experiments.
- J-resolved spectroscopy** Two-dimensional techniques, both homo- and heteronuclear, that aims to simplify interpretation by separating chemical shift and coupling into the two dimensions. Unfortunately prone to artifacts in closely coupled systems.
- Laboratory frame model** A means of visualising the processes taking place in an NMR experiment by observing these processes at a distance, i.e., with a static coordinate system. See *Rotating frame model*.
- Larmor frequency** The exact frequency at which nuclear magnetic resonance occurs. At this frequency, the exciting frequency matches that of the precession of the axis of the spin of the nucleus about the applied magnetic field.
- Larmor precession** The motion describing the rotation of the axis of the spin of a nucleus in a magnetic field.
- Linear prediction** Method of enhancing resolution by artificially extending the *FID* using predicted values based on existing data from the *FID*.
- Longitudinal relaxation (T_1)** Recovery of magnetisation along the 'z' axis. The energy lost manifests itself as an infinitesimal rise in temperature of the solution. This used to be called *spin-lattice relaxation*, a term which originated from solid-state NMR.
- Magic Angle Spinning (MAS)** $54^\circ 44'$ (from the vertical). Spinning a sample at this, the so-called 'magic angle' gives the best possible line shape as the broadening effects of chemical shift anisotropy and dipolar interactions are both minimised at this angle. Used in the study of molecules tethered to solid supports.
- Meso compound** A symmetrical compound containing two *chiral centres* configured so that the *chirality* of one of the centres is equal and opposite to the other. Such internal compensation means that these compounds have no overall effect on polarised light (e.g., meso tartaric acid).
- Normal geometry** Term used to describe the construction of a conventional dual/multi channel probe. Since the X nucleus is a far less sensitive nucleus than ^1H , a 'normal geometry' probe has the X nucleus receiver coils as close to the sample as possible to minimise signal loss and the ^1H receiver coils outside the X nucleus coils (i.e., further from the sample). This design of probe is thus optimised for X nucleus sensitivity at the expense of some ^1H sensitivity.
- NOE** Nuclear Overhauser effect/nuclear Overhauser enhancement. Enhancement of the intensity of a signal via augmented relaxation of the nucleus to other nearby nuclei that are undergoing saturation. See also:
- NOE** Nuclear Overhauser experiment. Experiment designed to capitalise on the above. Such experiments (and related techniques, e.g., *NOESY*, etc.) are extremely useful for solving stereochemical problems by spatially relating groups or atoms to each other.
- NOESY** Nuclear Overhauser effect spectroscopy. Two-dimensional technique that correlates nuclei to each other if there is any *NOE* between them.
- Non-first-order pattern** Splitting pattern where the difference in chemical shift between coupled signals is comparable to the size of the coupling between them. These are characterised by heavy distortions of expected peak intensities and even the generation of extra unexpected lines.
- Nyquist condition** Sampling of all signals within an *FID* such that each is sampled at least twice per wavelength.

- Phase** The representation of an NMR signal with respect to the distribution of its intensity. We aim to produce a pure absorption spectrum (one where all the signal intensity is positive).
- Phase cycling** The process of repeating a pulse sequence with identical acquisition parameters but with varying r.f. phase. This allows real NMR signals to add coherently whilst artifacts and unwanted NMR transitions cancel.
- Phasing** The process of correcting the *phase* of a spectrum (either manually or under automation).
- Probe** Region of the spectrometer where the sample is held during the acquisition of a spectrum. It contains the transmitter and receiver coils and gradient coils (if fitted).
- Pulse** A short burst of radio frequency used to bring about some nuclear spin transition.
- Pulsed field gradients** (PFGs) See *Gradient pulse*.
- Quadrature detection** Preferred system of signal detection using two detection channels with reference signals offset by 90°.
- Quadrupolar nuclei** Those nuclei, which because of their *spin quantum number* (which is always >1/2), have asymmetric charge distribution and thus possess an electric quadrupole as well as a magnetic dipole. This feature of the nucleus provides an extremely efficient relaxation mechanism for the nuclei themselves and for their close neighbors. This can give rise to broader than expected signals.
- Quadrupolar relaxation** Rapid relaxation experienced by *quadrupolar nuclei*.
- Racemate** A 50/50 mixture of *enantiomers*.
- Regiochemistry** The chemistry of a molecule discussed in terms of the positional arrangement of its groups.
- Regioisomers** Isomeric compounds related to each other by the juxtaposition of functional groups.
- Relaxation** The process of nuclei losing absorbed energy after excitation. See *longitudinal relaxation* and *transverse relaxation*.
- Relaxation time** Time taken for *relaxation* to occur.
- ROESY** Rotating-frame Overhauser effect spectroscopy. A variation (one and two dimensional) on the nuclear Overhauser experiment (*NOE*). The techniques have the advantage of being applicable for all sizes of molecule. See *Laboratory frame model*.
- Rotating frame model** A means of visualising the processes taking place in an NMR experiment by observing these processes as if you were riding on a disc describing the movement of the bulk magnetisation vector.
- Saturation** Irradiation of nuclei such that the slight excess of such nuclei naturally found in the *ground state* when a sample is introduced into a magnet, is equalized.
- Shim coils** Coils built into NMR magnets designed to improve the homogeneity of the magnetic field experienced by the sample. Two types of shims are used: *cryoshims* and room temperature shims. Normal shimming involves the use of the room temperature shims.
- Shimming** The process of adjusting current flowing through the room temperature *shim coils* in order to achieve optimal magnetic field homogeneity prior to the *acquisition* of NMR data. The process may be performed manually or under automation.
- Soft pulse** Pulse designed to bring about irradiation of only a selected region of a spectrum. See *Hard pulse*.
- Solvent suppression** Suppression of a dominant and unwanted signal (usually a solvent) either directly by saturation or by use of a more subtle method such as the *WATERGATE* sequence.
- Spectral Window** The range of frequencies observable in an NMR experiment.
- Spin coupling** See *Coupling*.

Spin decoupling See *Decoupling* and *Broadband decoupling*.

Spin quantum number Number indicating the number of allowed orientations of a particular nucleus in a magnetic field. For example, ^1H has an I value of $1/2$, allowing for two possible orientations, whereas ^{14}N has an I of 1, allowing three possible orientations.

Spin-lattice relaxation See *Longitudinal relaxation*.

Spin-spin relaxation See *Transverse relaxation*.

Stereochemistry The chemistry of a molecule discussed in terms of its 3-D shape.

Stereoisomers Diastereoisomers related to each other by the inversion of any number of chiral centres.

Superconduction Conduction of electric current with zero resistance. This phenomenon occurs at liquid helium temperature and has made possible the construction of the very high powered magnets that we see in today's spectrometers.

TOCSY Total correlation spectroscopy. One and two-dimensional techniques that are analogous to *COSY* but which differ in that it shows couplings within specific spin systems.

Transverse relaxation (T_2) Relaxation by transfer of energy from one spin to another (as opposed to loss to the external environment as in *longitudinal relaxation*). This used to be referred to as *spin-spin relaxation*.

WATERGATE Water suppression through gradient tailored excitation.

Zero filling Cosmetic improvement of a spectrum achieved by padding out the *FID* with zeros.