

NMR Definitions

(Terms in *italics* are defined elsewhere in the list).

Absolute Value:

Spectral display produced by taking the square root of the sum of the squares of the *real and imaginary parts* of the spectrum. Peaks are much broader than in the *absorption mode*, and are positive only.

Absorption Mode:

Customary mode of displaying NMR spectra, in which peaks have nominally *Lorentzian* shapes.

Acquisition Time:

Duration of the *digitization* of a *free induction decay (FID)*.

Aliasing (Foldback):

Production of false peaks, originating from outside the *spectral window*, due to a *digitization rate* less than twice the *Nyquist frequency*.

α and β Spin States:

The two possible states of a spin 1/2 nucleus in a magnetic field. By convention, if the *magnetogyric ratio* is positive, the α state will have lower energy (m_z aligned with B_0).

Analog-to-Digital Converter:

Hardware component that translates a voltage from the detector into a binary number, commonly 16 bits long.

Antiphase:

Term used to describe spin vectors that point 180° with respect to each other. Also refers to the opposite directions (positive/negative) of spectral peaks produced by antiphase spins.

Apodization:

Multiplication of the digitized *FID* before transformation by a mathematical function to improve *signal/noise ratio* or *spectral resolution*, but not both simultaneously.

Artifacts:

Unwanted components of the spectrum, for example, false peaks, bursts of noise, caused by imperfections in the *pulse sequence* or spectrometer system.

Attached Proton Test (APT):

Pulse sequence that yields a 1-D spectrum in which peaks corresponding to carbons with an odd number attached protons appear opposite in sense (*antiphase*) to those with an even number.

B_0 :

Static magnetic field about whose direction the *nuclear magnetic moment precesses*. Magnitude expressed in tesla or as the nominal proton precession frequency (e.g., 7T or 300 MHz).

B_0 Inhomogeneity:

Spatial non-uniformity in B_0 . Contributes to T_2^* and causes line broadening.

B₁:

The radio-frequency magnetic field that is applied to the nuclei. Causes *precession* of the *nuclear magnetic moments* about an axis normal to B₀.

Boltzmann Distribution:

Distribution of nuclear spins among their possible energy levels at thermal equilibrium. For a positive *magnetogyric ratio*, produces population excess (*polarization*) in the direction of B₀.

Broad Band Decoupling:

Irradiation of a group of nuclei with a wide distribution of *chemical shifts* by a radio-frequency field *modulated* in frequency and/or phase so as to effectively spread its *spin decoupling* effect evenly over all the nuclei. Often used to remove all ¹H-¹³C splittings from a ¹³C spectrum.

Chemical Shift:

Variation of the effective value of B₀ experienced by nuclei because of their different electromagnetic environments in the molecule. Usually reported in parts per million of applied field or frequency relative to a resonance in a reference compound (eg., TMS).

Clipping:

Overloading of the *receiver* and/or *analog-digital converter*, producing spurious and misshapen peaks in the transformed spectrum.

Continuous Wave (CW):

Method of observing an NMR spectrum where B₁ is applied continuously and either the magnitude of B₀ or the radio frequency is varied to bring the nuclei successively into resonance.

Contour Plot:

The most common mode of display of a 2-D spectrum; the axes are in frequency-related units (*chemical shift* or *coupling constant*) with peaks shown by concentric groups of lines of constant intensity (contours).

Correlation Spectroscopy:

Multi-dimensional method in which peaks appear at the coordinates of two nuclei related by a mutual interaction (*J-coupling*, *NOE*, or chemical exchange).

Correlation Time(τ_c):

Parameter related to the mean time during which a molecule maintains its spatial geometry. For an internuclear vector, τ_c is approximately equal to the average time for it to rotate through an angle of one radian.

COSY (H-H Correlation Spectroscopy):

Correlation spectroscopy that identifies pairs of protons that are spin coupled to each other, usually through 3 chemical bonds.

Coupling Constant:

see *spin coupling constant*

Cross Peaks:

Off-diagonal peaks in a 2-D spectrum that appear at the coordinates (usually chemical shifts) of the correlated nuclei.

Dead Time:

Very short delay just before the start of data acquisition. Allows the *transmitter* gate to close and the *receiver* gate to open.

Detectable Magnetization:

Magnetization precessing in the *xy* plane and capable of inducing a signal in the *receiver* coil. Requires that the nuclei be involved in a single-quantum coherence.

Detection Period:

Final segment of a *pulse sequence*. Consists of the acquisition of the FID. Called the t_2 domain in a 2-D experiment.

Diagonal peaks:

Peaks appearing on or very near to the main diagonal of a homonuclear 2-D spectrum. Their *projection* on the axes is the 1-D spectrum. They yield no correlation information and may overlap nearby *cross peaks*.

Diamagnetism:

Magnetic behavior of a substance that has no unpaired electrons. When placed in a magnetic field the induced magnetic field opposes the applied field.

Digital Resolution:

Frequency interval between data points in a transformed spectrum. Determines how well the peaks are described by the data points. Can be improved by *zero filling* before transformation.

Digitization:

Process of converting a voltage into its corresponding binary number for digital processing.

Digitization Rate:

Number of *analog/digital conversions* per second during data acquisition. Must be at least twice the highest signal frequency (*Nyquist* criterion).

Dipolar Mechanism:

Direct through-space interaction of two *nuclear magnetic moment* vectors. Principal mechanism of *spin-lattice relaxation* of spin 1/2 nuclei in *diamagnetic* liquids.

Dispersion Mode:

Lorentzian lineshape produced by a *phase-sensitive detector* 90° out of phase with one giving a pure *absorption mode* line. Bipolar in shape with very long tails; not integrable and highly undesirable in a spectrum.

Dynamic Range:

The ratio of the largest to the smallest signal observable in a *digitized* spectrum. Determined by either the number of bits in the output of the *analog-digital converter* or the length of the computer storage word.

Equilibration (Relaxation) Delay:

Period of time between repetition of single- or *multiple-pulse experiment* to allow nuclei to regain z axis magnetization by *spin-lattice relaxation*.

Ernst Angle:

In a *single-pulse experiment*, *tip angle* giving the best *signal/noise ratio* for a given combination of *spin-lattice relaxation* time and repetition rate.

Evolution Period:

Second segment of a pulse sequence. Consists of a delay time (sometimes including a *refocusing* pulse) during which the nuclei *precess* under the influence of *chemical shift* and/or *spin coupling*. In a 2-D experiment the length of the delay is *incremented* successively for each stored FID thus producing the t_1 *time domain*.

Exponential Multiplication:

Apodization with a decreasing exponential function to enhance the *signal/noise ratio* at the expense of added line broadening in the transformed spectrum.

f_1 :

Axis of a 2-D spectrum., Results from *Fourier transformation* of the t_1 domain signal.

f_2 :

Axis of a 2-D spectrum. Results from *Fourier transformation* of the *digitized FID's* (t_2 domain).

Field-Frequency Locking:

Stabilization of the magnitude of B_0 by maintaining the frequency of a resonance in the sample (usually ^2H in the solvent) equal to a fixed reference frequency.

Fourier Transformation:

Mathematical operation for interconverting data between the *time domain* and the equivalent *frequency spectrum*.

Free Induction Delay (FID):

Decaying, oscillatory *time-domain* wave-form generated by nuclei that are subjected to an rf pulse and are then allowed to *precess* "freely" in the absence of rf fields.

Frequency Domain:

Condition where the independent variable of all functions is frequency, for example, the display of a *frequency spectrum*.

Frequency Spectrum:

Plot of signal amplitude versus frequency. Result of *Fourier transformation* of a *time domain* signal.

Gated Decoupling:

Application of *spin decoupling* only during selected time periods in a pulse NMR experiment. Used to eliminate either ^1H - ^{13}C *spin coupling* or the *nuclear Overhauser effect* from a 1-D ^{13}C spectrum. Also essential in many *pulse sequences* (e.g., APT, J-spectroscopy).

Heteronuclear Correlation Spectroscopy (HETCOR):

Correlation spectroscopy in which different types of nuclei are related by their mutual *spin coupling*. Commonly used to detect directly bonded ^1H - ^{13}C atoms.

Increment:

Short fixed-time interval repeatedly added to t_1 in a 2-D experiment.

Inversion-Recovery:

Pulse sequence used to determine *spin-lattice relaxation times*.

Isochromat:

Group of nuclei that *precess* at exactly the same frequency. Often refers to nuclei located in a microscopic region of homogeneous B_0 field strength.

J-Coupling:

See *Spin Coupling*

J-Spectroscopy:

2-D method in which *chemical shift* is plotted along the f_2 axis, with *J-coupling* along f_1 . Appropriate sections parallel to f_1 display the coupling pattern of each nucleus to nuclei of the same (homonuclear) or different (heteronuclear) type.

Laboratory Frame:

Cartesian coordinate (x,y,z) stationary with respect to the observer.

Larmor Frequency:

The frequency of *precession* of a nucleus about the direction of B_0 ; equal to $\gamma B_0/2\pi$

Lorentzian:

Normal line shape of an NMR peak. Linewidth determined by T_2 ($LW = 1/\pi T_2$). Can be displayed in either *absorption* or *dispersion mode*.

Magnetic Quantum Number (m_I):

Number which specifies the energy of a nucleus in the B_0 field ($E = -m_I \gamma \hbar B_0/2\pi$; γ = magnetogyric ratio). m_I takes values of $-I, -I+1, \dots, +I$ ($\pm 1/2$ for an $I = 1/2$ nucleus). The two states correspond to alignment of the z-component of the *nuclear magnetic moment* with or opposed to B_0 .

Magnetization:

Existence of nuclear *polarization* for an ensemble of nuclei in a magnetic field.

Magnetization Vector(M):

Resultant of the individual *magnetic moment vectors* for an ensemble of a particular type of nucleus. At equilibrium M points in the direction of B_0 (positive γ).

Magnetogyric Ratio (γ):

Inherent property of a nucleus; can be either positive (e.g. ^1H , ^{13}C) or negative (^{15}N , ^{29}Si). For particular values of B_0 and the *magnetic quantum number*, g determines the energy level of the nucleus.

Mixing Period:

Third part of a *pulse sequence* for *correlation spectroscopy*. Consists of one or more pulses and sometimes delay times.

Modulation:

Variation in the amplitude and/or phase of an oscillatory signal with the amplitude of another function, for example, AM or FM modulation of a broadcast rf by a voice or modulation of a nuclear *precession* frequency by a *spin coupling* interaction.

Multiple-Pulse Experiment:

Experiment in which more than one pulse is applied to the nuclei before acquisition of the *FID*.

Nonselective Pulse:

Radio frequency pulse with a wide frequency bandwidth (short, high-power pulse) that excites all nuclei of a given type (e.g., all protons in a sample).

Nuclear Magnetic Moment: (m)

Physical consequence of a nucleus having both charge and angular momentums (i.e., non-zero spin). The observed magnetic moment is the projection of m on the B_0 axis, m_z , with magnitude given by $m_I \hbar \gamma / 2\pi$ ($m_I =$ magnetic quantum number, $\gamma =$ magnetogyric ratio). In the classical description the magnetic moment vectors precess about the B_0 axis.

Nuclear Overhauser Effect (NOE):

Change in intensity of the resonance of one nucleus when the *polarization* of another nucleus is not at equilibrium. The two nuclei must relax each other by the *dipolar mechanism*. Can be used for signal enhancement in ^{13}C NMR by *nonselective proton* irradiation or to determine spatial proximity of two nuclei (usually protons) by *selective irradiation* of one nucleus and observation of any changes in the intensity of other resonances.

Nuclear Overhauser Effect Correlation Spectroscopy (NOESY):

2-D method that correlates pairs of nuclei that are related by the *nuclear Overhauser effect*.

Nyquist Frequency:

Highest frequency that can be characterized by sampling at a given rate. Equal to one-half of the *digitization rate*.

One-Dimensional (1-D) NMR:

Experiment producing a spectrum with only one frequency axis.

Paramagnetism:

Magnetic behavior of a substance containing unpaired electrons. When placed in a magnetic field the induced magnetic field is parallel to the applied field.

Phase Correction (Phasing):

Linear combination of the *real and imaginary parts* of a 1-D spectrum to produce peaks with pure *absorption mode* shape. Performed either automatically by software or interactively by the operator.

Phase Cycling:

Repetition of a *pulse sequence* changing only the phases of the pulse(s) and the *phase-sensitive detector* reference; the *FID's* are then added. Used to suppress undesirable signal components (e.g., zero-

frequency glitch) and/or to produce the desired effect of a pulse sequence (e.g., multiple quantum filtration).

Phase-Sensitive Detector:

Detector whose output is the product of the input signal and a periodic reference signal. Output depends on the amplitude of the input signal and its phase relative to the reference.

Polarization:

Excess of *nuclear magnetic moment* vectors (m_z) aligned with or opposed to B_0 . At equilibrium the magnitude of the population excess is determined by the values of the *magnetogyric ratio*, B_0 , and temperature (*Boltzmann distribution*).

Precession:

Classical description of the behavior of *nuclear magnetic moments*, in which the vectors rotate about the B_0 axis at their *Larmor frequencies*.

Preparation Period:

First segment of a *pulse sequence*. Consists of an *equilibration delay* followed by one or more pulses (often a single 90° pulse) to put the spin system into the state needed for the *evolution period*.

Presaturation:

Suppression of a signal from an interfering nucleus (e.g. a solvent peak) by *selective irradiation* to *saturate* it prior to application of a *nonselective pulse* to the system as a whole.

Projection:

One dimensional spectrum produced when one of the axes of a 2-D spectrum is collapsed.

Pulse Fourier Transform NMR:

Use of an rf pulse to rotate the *magnetization vectors* of all the nuclei to be observed. The *time-domain* signal (the *FID*) is subsequently *digitized* and converted into the *frequency spectrum* by *Fourier transformation*.

Pulse Sequence:

Train of pulses, with various durations and application axes, separated by delays and ending in acquisition of the *FID*. Designed to achieve a certain result in the spectrum.

Pulse Width:

Time duration of the rf pulse. Determines the *tip angle* of the *magnetization vector* for a given radio frequency intensity. Inversely related to the effective bandwidth of the pulse.

Quadrature Detection:

Detection method that discriminates between peaks equally spaced above and below the *spectrometer frequency* (placed at the center of the *spectral window*). Uses two *phase-sensitive detectors* with reference phases offset by 90° .

Quadrature Images:

Ghost peaks resulting from imbalances between the two channels of a *quadrature detection system*. Appear as weak signals symmetrically located on the opposite side of the *spectrometer frequency* from true peaks. Eliminated by the CYCLOPS phase cycle, but often present on one scan.

Real and Imaginary Parts:

Two equally sized blocks of frequency data produced by *Fourier transformation* of the *time domain* signal; usually only the real frequency data is displayed.

Receiver:

Coil of wire (often the same one used by the *transmitter*) and associated electronics that amplify the rf signal produced by nuclei *precessing* in the xy plane.

Refocusing:

Spin vectors returning into phase after previously losing their coherent rotation in the xy plane. Usually achieved by means of the *spin-echo pulse sequence*.

Relaxation Reagent:

Paramagnetic species added to the sample to promote more rapid *spin-lattice relaxation* and enable a faster pulse repetition rate.

Rotating Frame:

Coordinate axes x' and y' that rotate about the z axis at the *spectrometer frequency*.

Saturation:

Partial or complete equalization of the populations of the energy levels of an ensemble of nuclei. Occurs when the rate of input of energy from the applied rf field exceeds the rate of energy dissipation by *spin-lattice relaxation*. Can occur if rf is applied continuously (see *spin decoupling*) or when pulse repetition rate is too rapid.

Selective Decoupling:

Spin decoupling by irradiation of a single multiplet with low-power rf. Used to identify coupled proton pairs in a 1-D proton spectrum.

Selective Irradiation (Selective Excitation):

Application of rf to a single frequency. Often used to excite a nucleus to only one of the possible combinations of spin states of the nuclei coupled to it.

Selective Pulse:

Radio frequency (rf) pulse with a narrow frequency bandwidth (long, low-power pulse) to excite nuclei in a limited *chemical shift* range.

Signal Averaging:

Repetition of an experiment n times to achieve an increase in *signal/noise ratio* of $n^{1/2}$ (multiplex advantage).

Signal/Noise Ratio:

Ratio of peak signal intensity to the root-mean-square noise level. Effectively determines the minimum signal that can be detected.

Sine-Bell

Apodization function in the form of the first half-cycle of a sine function. Used for resolution enhancement in 2-D spectra displayed in the *absolute value mode*.

Single-Pulse Experiment:

Simplest type of FT-NMR experiment. Only one rf pulse is issued for each repetition of the experiment.

Solvent Suppression:

Reduction of an intense signal from the solvent by some means (e.g. a *selective pulse* or *presaturation*) before *digitization* to avoid *dynamic range* problems.

Spectral Resolution:

Instrumental performance parameter that determines minimum peak separation that can be distinguished. Usually specified in terms of peak width at half-height called $LW_{1/2}$ or LW .

Spectral Window:

The observed spectral region in the frequency domain, centered on the *spectrometer frequency* and having a width equal to the *digitization rate*. Peaks occurring in this window appear at their correct positions, without aliasing.

Spectrometer Frequency:

Center frequency of band produced by the rf pulse generator. Same as the frequency that is electronically subtracted from the detector signal prior to digitization. Also the center of the spectral window.

Spectrum Width:

Width of the *frequency spectrum*, equal to spectral window.

Spin (I):

Number associated with the quantization of the nuclear angular momentum. **I** must be zero or an integer if the mass number (total number of protons and neutrons) is even, or half-integral (1/2, 3/2, etc.) if the mass number is odd.

Spin Coupling (J-Coupling):

Effect of the spin state of one nucleus on the energy of another nucleus; responsible for peak splitting. Spin coupling is transmitted through intervening bonding electrons, in contrast to the *dipolar mechanism*.

Spin Coupling Constant:

Measure of the *J-coupling* interaction between two nuclei. Coupling constants are expressed in hertz, can be positive or negative and are independent of B_0

Spin Decoupling:

Irradiation of a nucleus to induce rapid transitions between its energy levels. Removes the effects of *spin coupling* to another nucleus. (See *broad band*, *selective*, *gated*, decoupling).

Spin Echo:

Peak signal produced when divergent spin vectors are *refocused* in the xy plane by the $(\tau-180^\circ-\tau)$ pulse sequence. Used to eliminate effects of B_0 *inhomogeneities* and *chemical shift* precession.

Spin-Lattice Relaxation Time (T_1):

Time constant for the return of the *magnetization vector*, M , to its full (equilibrium) length along the z axis, after the spin system has been disturbed from equilibrium by an applied rf field.

Spin-Spin Relaxation Time (T_2):

Time constant for the loss of magnetization in the xy plane in the absence of B_0 *inhomogeneities*. Includes T_1 relaxation plus chemical and spin exchange, etc.

Stacked Plot:

Presentation mode of a 2-D NMR spectrum in which an f_1 spectrum is plotted horizontally for each of a series of f_2 values, or vice versa.

Symmetrization:

Method of removing *artifacts* from 2-D *contour plots* that are symmetrical about the diagonal (H-H *COSY*) or the f_1 axis (*J-spectra*). Spots equidistant from midline are compared and replaced either with their average value or lower value of the two.

 t_1 :

Time domain arising from the regular *increments* of the delay period in a 2-D experiment. Time during which the *FID* is acquired in a 2-D experiment.

 t_1 Noise:

Streaks of spurious signals in a 2-D spectrum parallel to the f_1 axis at the f_2 of a strong (e.g., solvent) resonance. Not reduced by *signal averaging*.

 T_2^* :

Time constant for loss of magnetization in the xy plane. Includes losses due to B_0 *inhomogeneities* as well as *spin-spin relaxation*.

Three-Dimensional NMR:

Three-frequency-domain analog of *two-dimensional NMR*. Requires data collection as a function of three time domains.

Time Domain:

Condition where the independent variable of all functions is time (e.g., in the display of an *FID*).

Tip Angle (α):

Angle through which the *magnetization vector* is rotated by the B_1 field in *pulse NMR*.

Transmitter:

Coil of wire (often the same as used by the *receiver*) and associated electronics that apply radio frequency energy to the NMR sample.

Two-Dimensional (2-D) NMR:

Spectral method in which data are collected in two *time domains*: acquisition of the *FID* (t_2) and a successively *incremented* delay (t_1). The resulting data matrix is subjected to two successive FT's to produce a spectrum with two frequency axes, usually either *chemical shift/chemical shift (correlation spectroscopy)* or *chemical shift/J-coupling (J-spectroscopy)*.

Zero Filling:

Addition of zeros to the *FID* to adjust the size of the data set to a power of two. Commonly used to improve the *digital resolution* of the transformed spectrum (e.g., in the t_1 domain of 2-D NMR).

Zero-frequency Glitch:

Sharp signal at the *spectrometer frequency*. Caused by dc offsets in the two channels of the *quadrature detection* system. Can be eliminated by the *CYCLOPS phase cycle*; also alleviated by baseline correction (bc) of the FIDs.