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Standard Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy[1]

This standard is issued under the fixed designation E386; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This standard contains definitions of basic terms, conventions, and recommended practices for data presentation in the area of high-resolution NMR spectroscopy. Some of the basic definitions apply to wide-line NMR or to NMR of metals, but in general it is not intended to cover these latter areas of NMR in this standard. This version does not include definitions pertaining to double resonance nor to rotating frame experiments.

2. Terminology Nomenclature and Basic Definitions

2.1 *nuclear magnetic resonance (NMR) spectroscopy*—that form of spectroscopy concerned with radio-frequency-induced transitions between magnetic energy levels of atomic nuclei.

2.2 *NMR apparatus; NMR equipment*—an instrument comprising a magnet, radio-frequency oscillator, sample holder, and a detector that is capable of producing an electrical signal suitable for display on a recorder or an oscilloscope, or which is suitable for input to a computer.

2.3 *high-resolution NMR spectrometer*— an NMR apparatus that is capable of producing, for a given isotope, line widths that are less than the majority of the chemical shifts and coupling constants for that isotope.

NOTE 1—By this definition, a given spectrometer may be classed as a high-resolution instrument for isotopes with large chemical shifts, but may not be classed as a high-resolution instrument for isotopes with smaller chemical shifts.

2.4 *basic NMR frequency,* ν_o—the frequency, measured in hertz (Hz), of the oscillating magnetic field applied to induce transitions between nuclear magnetic energy levels. The static magnetic field at which the system operates is called H_o (Note 1) and its recommended unit of measurement is the tesla (T) (1 T = 10^4 gauss).

2.4.1 The foregoing quantities are approximately connected by the following relation:

$$\nu_o = \frac{\gamma}{2\pi} H_o \quad (1)$$

where γ = the magnetogyric ratio, a constant for a given nuclide (Note 2). The amplitude of the magnetic component of the radio-frequency field is called H_1. Recommended units are millitesla and microtesla.

NOTE 2—This quantity is normally referred to as B by physicists. The usage of H to refer to magnetic field strength in chemical applications is so widely accepted that there appears to be no point in attempting to reach a totally consistent nomenclature now.

NOTE 3—This expression is correct only for bare nuclei and will be only approximately true for nuclei in chemical compounds, since the field at the nucleus is in general different from the static magnetic field. The discrepancy amounts to a few parts in 10^6 for protons, but may be of magnitude 1×10^{-3} for the heaviest nuclei.

2.5 *NMR absorption line*—a single transition or a set of degenerate transitions is referred to as a line.

2.6 *NMR absorption band; NMR band*— a region of the spectrum in which a detectable signal exists and passes through one or more maxima.

2.7 *reference compound (NMR)*—a selected material to whose signal the spectrum of a sample may be referred for the measurement of chemical shift (see 2.9).

2.7.1 *internal reference (NMR)*—a reference compound that is dissolved in the same phase as the sample.

2.7.2 *external reference (NMR)*—a reference compound that is not dissolved in the same phase as the sample.

2.8 *lock signal*—the NMR signal used to control the field-frequency ratio of the spectrometer. It may or may not be the same as the reference signal.

2.8.1 *internal lock*—a lock signal which is obtained from a material that is physically within the confines of the sample tube, whether or not the material is in the same phase as the sample (an annulus for the purpose of this definition is considered to be within the sample tube).

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Chromatography and is the direct responsibility of Subcommittee E13.15 on Analytical Data.

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2.8.2 *external lock*—a lock signal which is obtained from a material that is physically outside the sample tube. The material supplying the lock signal is usually built into the probe.

NOTE 4—An external lock, if also used as a reference, is necessarily an external reference. An internal lock, if used as a reference, may be either an internal or an external reference, depending upon the experimental configuration.

2.8.3 *homonuclear lock*—a lock signal which is obtained from the same nuclide that is being observed.

2.8.4 *heteronuclear lock*—a lock signal which is obtained from a different nuclide than the one being observed.

2.9 *chemical shift,* δ—the defining equation for δ is the following:

$$\delta = \frac{\Delta\nu}{\nu_R} \times 10^6 \quad (2)$$

where ν_R is the frequency with which the reference substance is in resonance at the magnetic field used in the experiment and $\Delta\nu$ is the frequency of the subject line minus the frequency of the reference line at constant field. The sign of $\Delta\nu$ is to be chosen such that shifts to the high frequency side of the reference shall be positive.

2.9.1 If the experiment is done at constant frequency (field sweep) the defining equation becomes

$$\delta = \frac{\Delta\nu}{\nu_R} \times \left(1 - \frac{\Delta\nu}{\nu_R}\right) \times 10 \quad (3)$$

2.9.2 In case the experiment is done by observation of a modulation sideband, the audio upper or lower sideband frequency must be added to or subtracted from the radio frequency.

2.10 *spinning sidebands*—bands, paired symmetrically about a principal band, arising from spinning of the sample in a field (dc or rf) that is inhomogeneous at the sample position. Spinning sidebands occur at frequencies separated from the principal band by integral multiples of the spinning rate. The intensities of bands which are equally spaced above and below the principal band are not necessarily equal.

2.11 *satellites*—additional bands spaced nearly symmetrically about a principal band, arising from the presence of an isotope of non-zero spin which is coupled to the nucleus being observed. An isotope shift is normally observed which causes the center of the satellites to be chemically shifted from the principal band. The intensity of the satellite signal increases with the abundance of the isotope responsible.

2.12 *NMR line width*—the full width, expressed in hertz (Hz), of an observed NMR line at one-half maximum height (FWHM).

2.13 *spin-spin coupling constant (NMR), J*—a measure, expressed in hertz (Hz), of the indirect spin-spin interaction of different magnetic nuclei in a given molecule.

NOTE 5—The notation ${}^{n}J_{AB}$ is used to represent a coupling over *n* bonds between nuclei *A* and *B*. When it is necessary to specify a particular isotope, a modified notation may be used, such as, ${}^{3}J\,({}^{15}NH)$.

3. Types of High-Resolution NMR Spectroscopy

3.1 *sequential excitation NMR; continuous wave (CW) NMR*—a form of high-resolution NMR in which nuclei of different field/frequency ratio at resonance are successively excited by sweeping the magnetic field or the radio frequency.

3.1.1 *rapid scan Fourier transform NMR; correlation spectroscopy* —a form of sequential excitation NMR in which the response of a spin system to a rapid passage excitation is obtained and is converted to a slow-passage spectrum by mathematical correlation with a reference line, or by suitable mathematical procedures including Fourier transformations.

3.2 *broad-band excitation NMR*—a form of high-resolution NMR in which nuclei of the same isotope but possibly different chemical shifts are excited simultaneously rather than sequentially.

3.2.1 *pulse Fourier transform NMR*—a form of broad-band excitation NMR in which the sample is irradiated with one or more pulse sequences of radio-frequency power spaced at uniform time intervals, and the averaged free induction decay following the pulse sequences is converted to a frequency domain spectrum by a Fourier transformation.

3.2.1.1 *pulse Fourier difference NMR*—a form of pulse Fourier transform NMR in which the difference frequencies between the sample signals and a strong reference signal are extracted from the sample response prior to Fourier transformation.

3.2.1.2 *synthesized excitation Fourier NMR*— a form of pulse Fourier NMR in which a desired frequency spectrum for the exciting signal is Fourier synthesized and used to modulate the exciting radio frequency.

3.2.2 *stochastic excitation NMR*—a form of broad band excitation NMR in which the nuclei are excited by a range of frequencies produced by random or pseudorandom noise modulation of the carrier, and the frequency spectrum is obtained by Fourier transforming the correlation function between the input and output signals.

3.2.3 *Hadamard transform NMR*—a form of broad band excitation NMR in which the phase of the excitation signal is switched according to a binary pseudorandom sequence, and the correlation of the input and output signals by a Hadamard matrix yields an interference pattern which is then Fourier-transformed.

4. Operational Definitions

4.1 *Definitions Applying to Sequential Excitation (CW) NMR*:

4.1.1 *field sweeping (NMR)*—systematically varying the magnetic field strength, at constant applied radio-frequency field, to bring NMR transitions of different energies successively into resonance, thereby making available an NMR spectrum consisting of signal intensity versus magnetic field strength.

4.1.2 *frequency sweeping (NMR)*—systematically varying the frequency of the applied radio frequency field (or of a modulation sideband, see 4.1.4), at constant magnetic field strength, to bring NMR transitions of different energies successively into resonance, thereby making available an NMR spectrum consisting of signal intensity versus applied radio frequency.

4.1.3 *sweep rate*—the rate, in hertz (Hz) per second at which the applied radio frequency is varied to produce an NMR spectrum. In the case of field sweep, the actual sweep

rate in microtesla per second is customarily converted to the equivalent in hertz per second, using the following equation:

$$\frac{\Delta\nu}{\Delta t} = \frac{\gamma}{2\pi} \cdot \frac{\Delta H}{\Delta t} \tag{4}$$

4.1.4 *modulation sidebands*—bands introduced into the NMR spectrum by, for example, modulation of the resonance signals. This may be accomplished by modulation of the static magnetic field, or by either amplitude modulation or frequency modulation of the basic radio frequency.

4.1.5 *NMR spectral resolution*—the width of a single line in the spectrum which is known to be sharp, such as, TMS or benzene (^{1}H). This definition includes sample factors as well as instrumental factors.

4.1.6 *NMR integral (analog)*—a quantitative measure of the relative intensities of NMR signals, defined by the areas of the spectral lines and usually displayed as a step function in which the heights of the steps are proportional to the areas (intensities) of the resonances.

4.2 *Definitions Applying to Multifrequency Excitation (Pulse) NMR*:

4.2.1 *pulse (v)*—to apply for a specified period of time a perturbation (for example, a radio frequency field) whose amplitude envelope is nominally rectangular.

4.2.2 *pulse (n)*—a perturbation applied as described above.

4.2.3 *pulse width*—the duration of a pulse.

4.2.4 *pulse flip angle*—the angle (in degrees or radians) through which the magnetization is rotated by a pulse (such as a 90-deg pulse or $\pi/2$ pulse).

4.2.5 *pulse amplitude*—the radio frequency field, H_1, in tesla.

NOTE 6—This may be specified indirectly, as described in 8.3.2.

4.2.6 *pulse phase*—the phase of the radio frequency field as measured relative to chosen axes in the rotating coordinate system.[2]

NOTE 7—The phase may be designated by a subscript, such as, $90°_x$ or $(\pi/2)_x$.

4.2.7 *free induction decay (FID)*—the time response signal following application of an r-f pulse.

4.2.8 *homogeneity spoiling pulse; homo-spoil pulse; inhomogenizing pulse*—a deliberately introduced temporary deterioration of the homogeneity of the magnetic field *H*.

4.2.9 *filter bandwidth; filter passband*— the frequency range, in hertz, transmitted with less than 3 dB (50 %) attenuation in power by a low-pass filter.

NOTE 8—On some commercial instruments, filter bandwidth is defined in a slightly different manner.

NOTE 9—Other parameters, such as rate of roll-off, width of passband, or width and rejection of center frequency in case of a notch filter, may be required to define filter characteristics adequately.

4.2.10 *data acquisition rate; sampling rate; digitizing rate*—the number of data points recorded per second.

4.2.11 *dwell time*—the time between the beginning of sampling of one data point and the beginning of sampling of the next successive point in the FID.

4.2.11.1 *aperture time*—the time interval during which the sample-and-hold device is receptive to signal information. In most applications of pulse NMR, the aperture time is a small fraction of the dwell time.

NOTE 10—*Sampling Time* has been used with both of the above meanings. Since the use of this term may be ambiguous, it is to be discouraged.

4.2.12 *detection method*—a specification of the method of detection.

4.2.12.1 *single-phase detection*—a method of operation in which a single phase-sensitive detector is used to extract signal information from a FID.

4.2.12.2 *quadrature detection*—a method of operation in which dual phase-sensitive detection is used to extract a pair of FID's which differ in phase by 90°.

4.2.13 *spectral width*—the frequency range represented without foldover. (Spectral width is equal to one half the data acquisition rate in the case of single-phase detection; but is equal to the full data acquisition rate if quadrature detection is used.)

4.2.14 *foldover; foldback*—the appearance of spurious lines in the spectrum arising from either *(a)* limitations in data acquisition rate or *(b)* the inability of the spectrometer detector to distinguish frequencies above the carrier frequency from those below it.

NOTE 11—These two meanings of *foldover* are in common use. Type *(a)* is often termed "aliasing." Type *(b)* foldover is obviated by the use of quadrature detection.

4.2.15 *data acquisition time*—the period of time during which data are acquired and digitized; equal numerically to the product of the dwell time and the number of data points acquired.

4.2.16 *computer-limited spectral resolution*—the spectral width divided by the number of data points.

Note—This will be a measure of the observed line width only when it is much greater than the spectral resolution defined in 4.1.5.

4.2.17 *pulse sequence*—a set of defined pulses and time spacings between these pulses.

NOTE 12—There may be more than one way of expressing a sequence, for example, a series $(90°, \tau)_n$ may be one sequence of *n* pulses or *n* sequences each of the form $(90°, \tau)$.

4.2.18 *pulse interval*—the time between two pulses of a sequence.

4.2.19 *waiting time*—the time between the end of data acquisition after the last pulse of a sequence and the initiation of a new sequence.

NOTE 13—To ensure equilibrium at the beginning of the first sequence, the software in some NMR systems places the waiting time prior to the initiation of the first pulse of the sequence.

4.2.20 *acquisition delay time*—the time between the end of a pulse and the beginning of data acquisition.

4.2.21 *sequence delay time; recovery interval*—the time between the last pulse of a pulse sequence and the beginning of the succeeding (identical) pulse sequence. It is the time

[2] For a discussion of the rotating coordinate system, see Abragam, "Principles of Nuclear Magnetism," Oxford, 1961, pp. 19ff.

allowed for the nuclear spin system to recover its magnetization, and it is equal to the sum of the acquisition delay time, data acquisition time, and the waiting time.

4.2.22 *sequence repetition time*—the period of time between the beginning of a pulse sequence and the beginning of the succeeding (identical) pulse sequence.

4.2.23 *pulse repetition time*—the period of time between one r-f pulse and the succeeding (identical) pulse; used instead of *sequence repetition time* when the "sequence" consists of a single pulse.

4.2.24 *inversion-recovery sequence*—a sequence that inverts the nuclear magnetization and monitors its recovery, such as (180°,τ , 90°), where τ is the pulse interval.

4.2.25 *saturation-recovery sequence*—a sequence that saturates the nuclear magnetization and monitors its recovery, such as the sequence (90°, homogeneity-spoiling pulse, τ, 90°, *T*, homogeneity-spoiling pulse) or the sequence $(90°)_n$, τ, 90°, *T,* where $(90°)_n$ represents a rapid burst of 90° pulses.

4.2.26 *progressive saturation sequence*— the sequence 90°, $(\tau, 90°)_n$, where *n* may be a large number, and data acquisition normally occurs after each pulse (except possibly the first three or four pulses).

4.2.27 *spin-echo sequence*—the sequence 90°, τ, 180°

4.2.28 *Carr-Purcell (CP) sequence*—the sequence 90°, τ, 180°, $(2\tau, 180°)_n$, where *n* can be a large number.

4.2.29 *Carr-Purcell time*—the pulse interval 2τ between successive 180° pulses in the Carr-Purcell sequence.

4.2.30 *Meiboom-Gill sequence; CPMG sequence*—the sequence $90°_x$, τ, $180°_y$, $(2\tau, 180°_y)_n$.

4.2.31 *spin-locking sequence*—the sequence $90°_x$, $(SL)_y$, where SL denotes a "long" pulse (often measured in milliseconds or seconds, rather than microseconds) and *H* (lock) >> *H* (local).

4.2.32 *zero filling*—supplementing the number of data points in the time response signal with trailing zeroes before Fourier transformation.

4.2.33 *partially relaxed Fourier transform (PRFT) NMR*—a set of multiline FT spectra obtained from an inversion-recovery sequence and designed to provide information on spin-lattice relaxation times.

4.2.34 *NMR integral (digital)*—the integrals (see 4.1.6) of pulse-Fourier transform spectra or of digitized CW spectra, obtained by summing the amplitudes of the digital data points that define the envelope of each NMR band. The results of these summations are usually displayed either as a normalized total number of digital counts for each band, or as a step function (running total of digital counts) superimposed on the spectrum.

5. NMR Conventions

5.1 The dimensionless scale used for chemical shifts for any nucleus shall be termed the δ scale. The correct usage is δ = 5.00 or δ 5.00. Alternative forms, such as δ = 5.00 ppm or shift = 5.00 δ shall not be used.

5.2 The unit used for line positions should be hertz.

5.3 The dimensionless and frequency scales should have a common origin.

5.4 The standard sweep direction should be from high to low radio frequency (low to high applied magnetic field).

5.5 The standard orientation of spectra should be with low radio frequency (high field) to the right.

5.6 Absorption mode peaks should point up.

6. Referencing Procedures and Substances

6.1 *General*:

6.1.1 Whenever possible, in the case of proton and carbon-13 spectra, the chemical shift scale should be tied to an *internal* reference.

6.1.2 In case an external reference is used, either a coaxial tube or a capillary tube is generally adequate.

6.1.3 For nuclei other than protons or ^{13} C, for which generally agreed-upon reference substances do not yet exist, it is particularly important to report the reference material and referencing procedure fully, including separations in hertz and the spectrometer radio frequency when it is known.

6.2 *NMR Reference Substances for Proton Spectra*:

6.2.1 The primary internal reference for proton spectra in nonaqueous solution shall be tetramethylsilane (TMS). A concentration of 1 % or less is preferred.

6.2.2 The position of the tetramethylsilane resonance is defined as exactly zero.

6.2.3 The recommended internal reference for proton spectra in aqueous solutions is the sodium salt of 2,2,3,3-tetradeutero-4,4-dimethyl-4-silapentanoic acid (TSP-d_4). Its chemical shift is assigned the value zero.

6.2.4 The numbers on the dimensionless (shift) scale to high frequency (low field) of TMS shall be regarded as positive.

6.3 *NMR Reference Substances for Nuclei Other than Protons*:

6.3.1 For all nuclei the numbers on the dimensionless (shift) scale to high frequency (low field) from the reference substance shall be positive. In the interim, until this proposal has been fully adopted, the sign convention used should be explicitly given.

NOTE 14—The existing literature on NMR contains examples of both the sign convention given above and its opposite. It seems desirable to adopt a uniform convention for all nuclei, and the convention recommended herein is already widely used in both proton and ^{13}C NMR. The recommended convention will result in assigning the most positive numerical value to the transition of highest energy.

6.3.2 The primary internal reference for ^{13}C spectra of nonaqueous solutions shall be tetramethylsilane (TMS). For aqueous solutions, secondary standards such as dioxane have been found satisfactory. When such standards are used the line positions and chemical shifts should be reported with reference to TMS, and the conversion factor should be stated explicitly.

6.3.3 The primary external reference for boron spectra (^{10}B and ^{11}B) shall be boron trifluoride-diethyletherate $[(C_2H_5)_2O{:}BF_3]$.

6.3.4 The primary external reference for ^{31}P spectra shall be phosphorus trioxide (P_4O_6).

6.3.5 Specific recommendations for nuclei other than those mentioned above are not offered here. The following guidelines should be used: If previous work on the nucleus under study exists, any earlier reference should be used unless there are compelling reasons to choose a new reference. A reference substance should have a sharp line spectrum if possible. A singlet spectrum is preferred. A reference substance should be