Designation: E2977 – 15

Standard Practice for Measuring and Reporting Performance of Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) Spectrometers for Liquid Samples[1]

This standard is issued under the fixed designation E2977; 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 practice covers procedures for measuring and reporting the performance of Fourier-transform nuclear magnetic resonance spectrometers (FT-NMRs) using liquid samples.

1.2 This practice is not directly applicable to FT-NMR spectrometers outfitted to measure gaseous, anisotropically structured liquid, semi-solid, or solid samples; those set up to work with flowing sample streams; or those used to make hyperpolarization measurements.

1.3 This practice was expressly developed for FT-NMR spectrometers operating with proton resonance frequencies between 200 and 1200 MHz.

1.4 This practice is not directly applicable to continuous wave (scanning) NMR spectrometers.

1.5 This practice is not directly applicable to instruments using single-sideband detection.

1.6 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E131 Terminology Relating to Molecular Spectroscopy

E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy

2.2 *ISO Standard:*[3]

ISO Guide 31 Reference Materials—Contents of Certificates and Labels

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E131, Practice E386, and Refs (**1-4**).[4] Chemical shifts are usually given in the dimensionless quantity, δ, commonly expressed in parts per million. For a given nucleus, the chemical shift scale is relative and is commonly pegged to the resonance of an agreed upon reference material as described by Eq 1.

$$\delta_{sample} = (\nu_{sample} - \nu_{reference}) \div \nu_{reference} \quad (1)$$

3.1.1 Frequencies are given in Hertz. Because the numerator is very small compared with the denominator, it is usually convenient to express δ in parts per million.

3.1.2 As the location of a resonance is determined in part by the ratio of the magnetic field to the radio frequency at which it is observed, chemical shifts and spectral regions are often designated as lower frequency (increased shielding) or higher frequency (decreased shielding) relative to a reference point. Defined in this manner, chemical shifts are independent of either the magnetic field or the radio frequency used. Coupling constants, which are independent of the magnetic field or radio frequency used, are expressed in Hertz.

3.1.3 *nuclear magnetic resonance (NMR) tube camber, n*—maximum total deflection of any part of the outer wall of the tube held at the ends and rotated 360°; a measure of the bow in the tube.

3.1.4 *NMR tube concentricity, n*—maximum variation in wall thickness of the tube; a measure of how centered the tube inside diameter is relative to the tube outer diameter.

[1] This test method is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.15 on Analytical Data.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] The boldface numbers in parentheses refer to the list of references at the end of this standard.

4. Significance and Use

4.1 This practice permits an analyst to compare the performance of an NMR spectrometer for a particular test on any given day with the instrument's prior performance for that test. The practice can also provide sufficient quantitative performance information for problem diagnosis and solving. If complete information about how a test is carried out is supplied and sufficient replicates are collected to substantiate statistical relevance, the tests in this practice can be used to establish the setting and meeting of relevant performance specifications. This practice is not necessarily meant for the comparison of different instruments with each other, even if the instruments are of the same type and model. This practice is not meant for the comparison of the performance of different instruments operated under conditions differing from those specified for a particular test.

5. Test Samples

5.1 In general, the test samples called for in this practice are commercially available materials made explicitly for the testing of NMR spectrometer performance. The particular samples chosen are those that have been widely accepted by the NMR community of users and vendors for these purposes. However, in certain instances, especially with higher field instruments, the commonly accepted samples may exhibit characteristics that render them less than ideal for such uses.

5.2 Each sample shall be uniquely identifiable, and a certificate containing information about the sample shall be available (ISO Guide 31). In addition to the information required elsewhere in this practice, the certificate shall list the manufacturer of the sample, the date of manufacture, the name of the sample, and a reference number (for example, sample serial or lot number) (see Fig. 1).

5.3 *Sample Tubes*—Although sample tubes with sizes ranging from about 1- to 25-mm outside diameter (OD) are used in modern NMR spectrometers, the 5-mm OD tube remains the most common size. To avoid detailing test procedures for all possible tube sizes, this practice specifies tests for use with 5-mm OD sample tubes. Users requiring sample tubes of differing size should scale the quantities, dimensions, and volumes given here to the requirements of their spectrometers taking into account any specific recommendations of the instrument's manufacturer.

5.3.1 The inside diameter of the sample container shall be stated along with tolerances from the manufacturer.

5.3.2 The quality of the tube in terms of its concentricity and camber shall be stated. The concentricity and camber of the tube should be smaller than 0.025 mm and 0.013 mm, respectively.

5.4 *Analytes, Solvents, and Chemical Shift Standards*—Analyte concentration is defined as a volume percentage (v/v) at 25°C, that is, the volume of the analyte divided by the total volume of the solution.

5.4.1 Unless otherwise specified, the chemical purity of each component for standard samples used to test sensitivity shall be ≥99.5 weight % and the purity of each component for all other standard samples shall be ≥99 weight %. The resonances of impurities observed in the spectrum of the standard sample should not interfere with the resonances of interest in the standard sample. This usually means that the impurity peaks shall not appear within the region of the satellite peaks, particularly for resolution standard samples. However, samples with higher water content may still be usable so long as the water signal does not interfere with the spectral test. Water content may be determined by Karl Fischer titration or by ^{1}H NMR spectroscopy (protic water only). The purity of the analyte(s) shall be stated.

5.4.2 Except as noted, the sample solvent should be deuterated to provide a field/frequency lock for the spectrometer, of the highest purity commonly obtainable, and have an atom-percent deuteration of at least 99 %. The solvent's purity and level of deuteration shall be stated.

5.4.3 When used, chemical shift standards should be of the highest purity commonly available and added to the sample to achieve a concentration approximately one tenth that of the analyte. The purity and concentration of the chemical shift standard shall be stated.

5.5 *Sample Preparation*—Either a m/m method or a v/v method may be used for sample preparation; however, care shall be taken to assure better than 1 % accuracy in the measurements. If a v/v method is used, the densities used for the liquid components shall be stated. Unless specified otherwise, any impurities in the final sample (including water) should be less than 10 mol % of the analyte concentration. The final analyte concentration and its uncertainty shall be stated.

5.5.1 The sample should be sealed under nitrogen or argon taking care that the final sample is near atmospheric pressure.

5.5.2 Each sample tube shall bear a label stating its content and reference identifier.

5.5.3 For long-term storage, samples should be maintained in the dark to prevent photolysis. Except as noted, samples may be stored at room temperature. For long-term storage, samples containing chloroform should be kept between −25 and 8°C unless the sample is known to have been deoxygenated.

6. Preliminary Experimental Procedures

6.1 To achieve consistent results, the following shall be completed before the performance measurement:

6.1.1 The sample temperature should be stabilized at approximately 25°C, controlled during the measurement (8.16), and specified in the report.

6.1.2 The magnetic field homogeneity shall be adjusted to the best achievable on the sample to be used (8.9 – 8.12).

6.1.3 The observe radio frequency (rf) circuitry shall be well-tuned and matched to the sample to be used. If decoupling is used, the decoupling rf circuitry shall be tuned and matched to the sample to be used.

6.1.4 The 90° pulse for the probe to be used should be measured and reported. If decoupling is used, parameters, such as peak power in Hertz, mean power level in Hertz, and the decoupling modulation pattern shall be measured and reported. The decoupling power is defined in Hertz as one divided by the duration of the decoupling channel 360° pulse in seconds at the power level being used for decoupling.

LD&D Laboratories

110 Maple St.

Quahog, RI 11959 USA

(401) 555-7734

Certificate of Analysis

NMR Performance Evaluation Standard

60 % (v/v) benzene-d_6 (C_6D_6) in *p*-dioxane

LD&D Part Number: ^{13}C-SNR1-5

Sample ID (tube label): 60 % C_6D_6 in *p*-dioxane; LD&D ^{13}C-SNR1-5; 11C1304

Date of Manufacture: 08/11/2011

Date of Qualification: 12/13/2011

Lot Number: 11C1304

Tube Parameters: borosilicate; 5.0 mm O.D.; 4.24 mm I.D.; 190 mm length; ≤0.025 mm concentricity; ≤0.013 mm camber

Constituent Purities (including water):

p-dioxane: 99.7 % pure by ^{1}H NMR

benzene-d_6: 99.6 % pure by GC; 99.6 atom % deuteration by ^{1}H NMR; 1.08 atom % ^{13}C by MS

Degassing: helium sparge of bulk sample prior to tube filling and sealing

Sealant Gas: nitrogen

Analyte Concentration: 60 % ± 0.08 % (v/v) benzene-d_6 by GC

Sample Filling Height: 50 mm ± 2.5 mm

Usage: determination of coupled ^{13}C NMR Sensitivity and ^{13}C NMR resolution and lineshape

Storage: keep in the dark between 10 °C and 30 °C

Stability: If handled and stored properly, this sample should be indefinitely useable. Sample stability may be monitored by appropriate quantitative NMR techniques.

FIG. 1 Example of a Certificate of Analysis for an NMR Test Sample

6.1.5 The T_1 relaxation time of the specific sample resonance of interest should be measured on each sample to assure that the equilibration period is adequate. As T_1 relaxation times are dependent on the specific resonance observed, sample concentration, sample temperature, magnetic field strength, and the concentration of certain impurities (most notably dissolved oxygen), basing the equilibration period on literature T_1 values is insufficient. Unless experimental conditions such as temperature or field strength are changed, the T_1 need only be determined once for a sealed sample.

6.1.6 For sensitivity tests in which the signal-to-noise ratio (S/N) is insufficient, signal averaging may be used. If multiple transients are collected, the resulting sensitivity value shall be adjusted as described in 7.2.

6.1.7 In cases in which the natural abundance of the measured isotope is low, it may be necessary to correct the S/N for the actual abundance of the measured isotope in the sample itself. Examples of this are S/N determinations for ^{13}C, ^{15}N, and ^{29}Si.

6.1.8 For both sensitivity and resolution tests, decoupling should not be used unless specified.

7. Reporting Results

7.1 *General Tests*—Results may be reported from determinations made by single procedures.

7.2 *Signal Averaging*—If signal averaging is used, the measured sensitivity value shall be adjusted by dividing by the square root of the number of transients.

7.3 *Tests for Establishing and Meeting Specifications*—Specification-level test results shall be reported as the average along with the standard deviation of the results from ten replications of the specified test made with no intervening adjustments. For specification results, actual analyte concentrations and their uncertainties and tube dimensions (specifically, either the internal diameter or the external diameter and wall thickness) shall be reported.

8. Specific Test Procedures

8.1 *^1H Sensitivity*—This practice describes the determination of the proton sensitivity of the NMR system.

8.1.1 *Sample*—The sample is 0.1 % (v/v) ethylbenzene in deuterochloroform (chloroform-*d*) containing 0.003 to 0.1 % (v/v) tetramethylsilane (TMS). The density of ethylbenzene is 0.86702 g/cm^3 at 20°C, 0.862 64 g/cm^3 at 25°C, and 0.858 28 g/cm^3 at 30°C (**5**). The density of chloroform-*d* is 1.5007 g/cm^3 at 20°C (**6**), 1.4999 g/cm^3 at 25°C, and 1.4906 g/cm^3 at 30°C (**7**). The density of TMS is 0.6386 g/cm^3 at 20°C, 0.6329 g/cm^3 at 25°C, and 0.6274 g/cm^3 at 30°C (**8**). The ethylbenzene shall be 99.95 % pure and free from chlorinated by-products, such as (2-chloroethyl)benzene (**9**) and (1-chloroethyl)benzene (in chloroform-*d*—5.12 and 1.88 ppm) (**10**), and care shall be taken to ensure that it has not reacted with air to produce oxygenated products (**11**), such as the hydroperoxide [chloroform-*d*—8 to 9 ppm (s, 1H), 5.05 ppm (q, 1H), 1.45 ppm (d, 3H)] (**12**), *sec*-phenethyl alcohol (**13**), acetophenone (**14**), and benzaldehyde (**15**). The total contribution from all impurities (excluding water) in the final sample shall be less than 1 mol % of the ethylbenzene concentration. The peak height of the signal from dissolved water in the sample shall be smaller than that of the methyl triplet. For very high-sensitivity systems, a more dilute sample may be used. Sensitivity shall then be converted to and clearly reported as "equivalent to 0.1 % (v/v) ethylbenzene at 25°C." The final concentration and its uncertainty shall be specified.

8.1.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.1.2.1 *Spectral Region*—The larger of 30-ppm or 11-kHz (for proton frequencies below 400 MHz) width centered on the methylene resonance of ethylbenzene.

8.1.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the ethylbenzene methylene resonance reduced by the acquisition time.

8.1.2.3 *Pulse Flip Angle*—90°.

8.1.2.4 *Data Acquisition Time*—4 to 8 s.

8.1.2.5 *Number of Transients*—One.

8.1.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.1.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.1.3 *Data Processing*—The following data processing parameters shall be used:

8.1.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (line broadening) = 1 Hz and t = time value for each acquired data point.

8.1.4 Zero fill to at least twice the size of the data table. Calculate the FT using sufficient data points to yield a digital resolution of ≤0.05 Hz per data point. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 2).

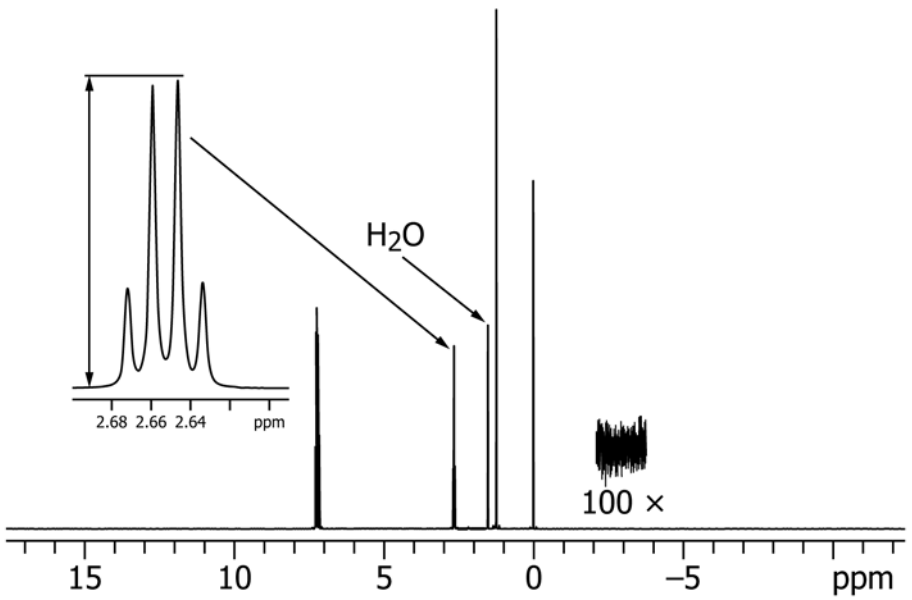

FIG. 2 600.1-MHz ^1H Sensitivity Test Spectrum of 0.1 % Ethylbenzene with Tetramethylsilane in Chloroform-*d*

8.1.5 No data smoothing or other types of data manipulation may be applied except as specified in 8.1.3.1.

8.1.6 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.1.6.1 Signal is defined as the amplitude of the tallest peak in the methylene resonance (2.65 ppm) of the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- (offset) and first-order (slope) baseline corrections should be applied to a region of 1 ppm around the signal.

8.1.6.2 Noise is defined as two times the root mean square (rms) noise in the region of 1 kHz starting at −2 ppm from the TMS signal and going to lower frequency where minimal interference from resonances of chemical impurities is found. Zero- and first-order baseline corrections should be applied to the 1-kHz noise region.

8.1.6.3 To calculate rms noise, use:

$$\text{rms noise} = \{[\Sigma\ (\text{amplitude})^2]/(N - 1)\}^{1/2} \quad (2)$$

(1) The amplitude of each point measured from the zero-intensity line in the selected 1-kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.1.6.4 The S/N is equal to: signal ÷ (2 × rms noise).

8.1.6.5 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.1.7 *Reporting Sensitivity*—The results of ^{1}H sensitivity measurements shall be reported as described in Section 7. If sample concentrations other than those in 8.1.1 are used, sensitivity results should be corrected for concentration and reported as "equivalent to 0.1 % (v/v) ethylbenzene."

8.2 *Decoupled ^{13}C Sensitivity*—This practice describes the determination of the decoupled carbon-13 sensitivity of the NMR system.

8.2.1 *Sample*—The sample is 10 % (v/v) ethylbenzene in chloroform-*d*. The densities and purities of the sample constituents are given in 8.1.1. The ethylbenzene shall be 99.95 % pure and free from chlorinated by-products, such as (2-chloroethyl)benzene (**16**) and (1-chloroethyl)benzene (**17**), and care shall be taken to ensure that it has not reacted with air to produce oxygenated products (**11**), such as the hydroperoxide (in chloroform-*d*—20.4, 84.0, 126.8, 128.5, 128.9, and 141.7 ppm) (**12**), *sec*-phenethyl alcohol (**18**), acetophenone (**19**), and benzaldehyde (**20**). The sample shall be prepared from ethylbenzene of known ^{13}C isotopic abundance near that of the natural mean abundance at positions 2 and 3 of the benzene ring. The ^{13}C abundance and the means of measuring this shall be reported on the certificate. The total contribution from all impurities in the final sample (including water) should be less than 10 mol % of the ethylbenzene concentration. The final concentration and its uncertainty shall be specified.

8.2.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.2.2.1 *Spectral Region*—A 200-ppm width with the transmitter frequency set to 100 ppm with chloroform-*d* referenced to approximately 77 ppm.

8.2.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the ethylbenzene C2 or C3 resonances reduced by the acquisition time.

8.2.2.3 *Pulse Flip Angle*—90°.

8.2.2.4 *Data Acquisition Time*—5 s.

8.2.2.5 *Number of Transients*—One.

8.2.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.2.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.2.2.8 *Decoupling Conditions*—Decoupling parameters such as peak power in Hertz, mean power levels in Hertz, and decoupling modulation pattern shall be specified. The parameters chosen should result in all the ethylbenzene peaks appearing as singlets with line widths less than 1 Hz. The decoupling frequency shall be centered at approximately 4.3 ppm relative to the proton signal of chloroform at 7.26 ppm. The same decoupling conditions shall be maintained during the acquisition and the relaxation delay.

8.2.3 *Data Processing*—The following data processing parameters shall be used:

8.2.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 0.3 Hz and t = time value for each acquired data point. Zero fill to at least double the size of the data table. Calculate the FT using sufficient data points to yield a digital resolution of ≤0.02 Hz per data point. If the instrument cannot achieve this resolution, the highest achievable resolution should be used. Apply phase corrections as needed to produce the pure absorption mode spectrum (see Fig. 3).

8.2.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.2.3.1.

8.2.5 *S/N Calculation*—The calculations for S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.2.5.1 Signal is defined as the amplitude of the tallest aromatic resonance of ethylbenzene (approximately 128 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of 10 ppm around the signal.

8.2.5.2 Noise is defined as two times the rms noise in the region between 80 and 120 ppm with the central peak of chloroform-*d* referenced at approximately 77 ppm. Zero- and first-order baseline corrections should be applied to the noise region.

8.2.5.3 Use Eq 2 to calculate rms noise.

8.2.5.4 The amplitude of each point measured from the zero-intensity line in the selected 40-ppm region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.2.5.5 The corrected S/N is equal to:

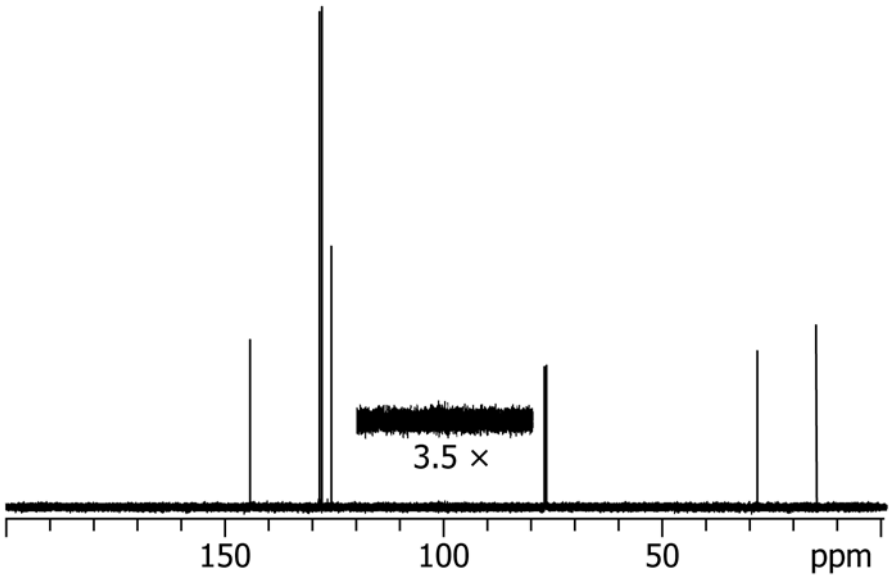

FIG. 3 125.8-MHz ^{1}H Decoupled ^{13}C Sensitivity Test Spectrum of 10 % Ethylbenzene in Chloroform-*d*

$$\text{signal} \div (2 \times \text{rms noise}) \times (1.105 \div \text{the measured } {}^{13}C \text{ abundance}) \quad (3)$$

NOTE 1—Corrected for the average natural abundance of ^{13}C (**21**).

8.2.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.2.6 *Reporting Sensitivity*—The results of the decoupled ^{13}C sensitivity measurements shall be reported as described in Section 7.

8.3 *Coupled ^{13}C Sensitivity*—This practice describes the determination of the coupled ^{13}C sensitivity of the NMR system.

8.3.1 *Sample*—The sample is 60 % (v/v) benzene-d_6 in *p*-dioxane (also known as 1,4-dioxane). The density of benzene-d_6 is 0.9494 g/cm^3 at 20°C, 0.9436 g/cm^3 at 25°C, and 0.9378 g/cm^3 at 30°C (**22**). The density of *p*-dioxane is 1.0336 g/cm^3 at 20°C, 1.0280 g/cm^3 at 25°C, and 1.0224 g/cm^3 at 30°C (**23**). The benzene-d_6 shall be at least 99 % deuterated. The *p*-dioxane shall be at least 99 % pure, and care shall be taken to ensure that it has not reacted with air to produce oxygenated products. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the *p*-dioxane concentration. The final concentration and its uncertainty shall be stated. For routine use (not for specification purposes), a relaxation agent, such as 0.2 % Cr(acac)$_3$, may be added to the sample to permit more rapid data acquisition, provided its use is reported.

8.3.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.3.2.1 *Spectral Region*—A 100-ppm width with the transmitter frequency set at 100 ± 10 ppm.

8.3.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the benzene-d_6 resonance reduced by the acquisition time.

8.3.2.3 *Pulse Flip Angle*—90°.

8.3.2.4 *Data Acquisition Time*—1 s.

8.3.2.5 *Number of Transients*—One.

8.3.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.3.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.3.2.8 No decoupling.

8.3.3 *Data Processing*—The following data processing parameters shall be used:

8.3.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 3.5 Hz and t = time value for each acquired data point.

8.3.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 4).

8.3.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.3.3.1, unless its use is specifically described in the resulting report.

8.3.5 *S/N Calculation*—The calculations for the S/N ratio are carried out on the real part of the pure phase absorption mode spectrum.

8.3.5.1 Signal is defined as the amplitude of the tallest benzene-d_6 resonance (approximately 128 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of 10 ppm around the signal.

8.3.5.2 Noise is defined as two times the rms noise in the region between 80 and 120 ppm. For spectrometers with proton frequencies less than 350 MHz, this will result in fewer than 1000 zero crossings within the noise region, which will reduce the precision of the noise measurement. Zero- and first-order baseline corrections should be applied to the noise region.

8.3.5.3 Use Eq 2 to calculate rms noise.

8.3.5.4 The amplitude of each point measured from the zero-intensity line in the selected 40-ppm region is squared.

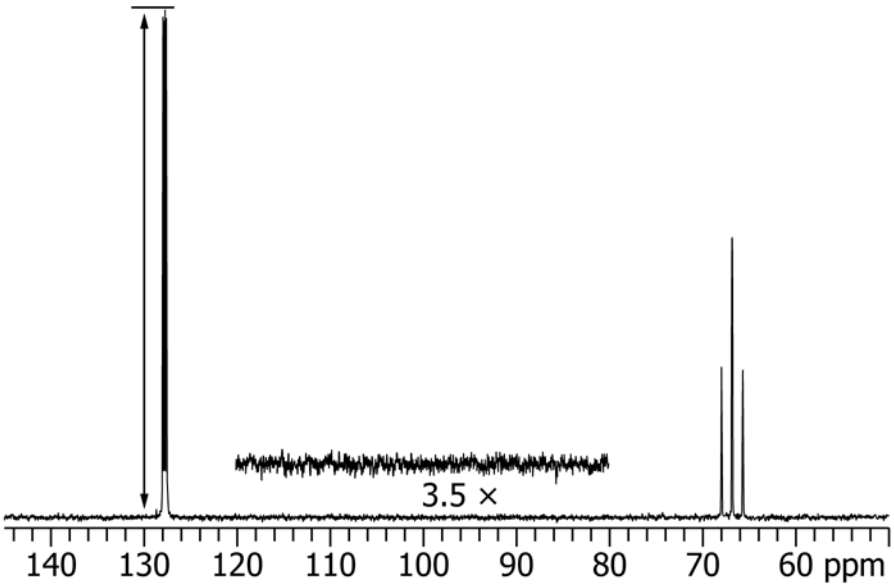

FIG. 4 125.8-MHz Coupled ^{13}C Sensitivity Test Spectrum of 60 % Benzene-d_6 and 40 % *p*-Dioxane

Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.3.5.5 The corrected S/N is equal to:

$$\text{signal} \div (2 \times \text{rms noise}) \times (1.105 \div \text{the measured } {}^{13}C \text{ abundance}) \quad (4)$$

NOTE 2—Corrected for the average natural abundance of ^{13}C (**21**).

8.3.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.3.6 *Reporting Sensitivity*—The results of the coupled ^{13}C sensitivity measurements shall be reported as described in Section 7.

8.4 *^{31}P Sensitivity*—This practice describes the determination of the ^{31}P sensitivity of the NMR system.

8.4.1 *Sample*—The sample is 0.0485 mol L^{-1} triphenylphosphate in acetone-d_6 or chloroform-*d*. The molecular mass of triphenylphosphate is 326.28 g. The triphenylphosphate shall be at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the triphenylphosphate concentration. The final concentration and its uncertainty shall be stated.

8.4.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.4.2.1 *Spectral Region*—A 40-kHz width with the transmitter frequency set to approximately the resonance of triphenylphosphate.

8.4.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the triphenylphosphate resonance reduced by the acquisition time.

8.4.2.3 *Pulse Flip Angle*—90°.

8.4.2.4 *Data Acquisition Time*—1 s.

8.4.2.5 *Number of Transients*—One.

8.4.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.4.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.4.2.8 No decoupling.

8.4.3 *Data Processing*—The following data processing parameters shall be used:

8.4.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 5 Hz and t = time value for each acquired data point.

8.4.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 5).

8.4.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.4.3.1.

8.4.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.4.5.1 Signal is defined as the amplitude of the triphenylphosphate resonance (approximately −18 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±5 kHz around the signal.

8.4.5.2 Noise is defined as two times the rms noise in the 5-kHz region starting from −5 to −10 kHz from the triphenylphosphate resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.4.5.3 Use Eq 2 to calculate rms noise.

8.4.5.4 The amplitude of each point measured from the zero-intensity line in the selected 5-kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.4.5.5 The S/N is equal to: signal ÷ (2 × rms noise).

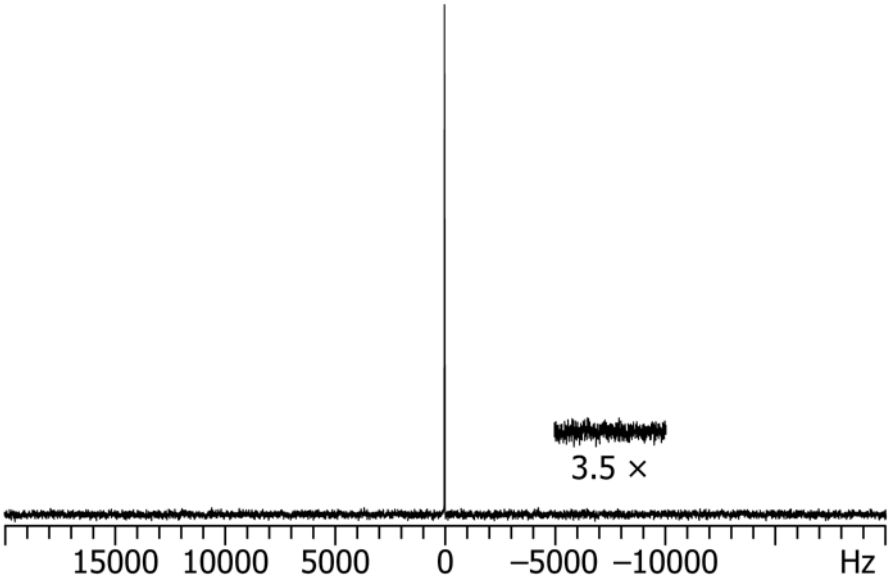

FIG. 5 202.5-MHz ^{31}P Sensitivity Test Spectrum of 0.0485 mol/L Triphenylphosphate in Acetone-d_6

8.4.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.4.6 *Reporting Sensitivity*—The results of the ^{31}P sensitivity measurements shall be reported as described in Section 7.

8.5 *^{19}F Sensitivity*—This practice describes the determination of the ^{19}F sensitivity of the NMR system.

8.5.1 *Sample*—The sample is 0.05 % (v/v) α,α,α-trifluorotoluene [also known as trifluorotoluene, benzotrifluoride, (trifluoromethyl) benzene, or phenylfluoroform] in benzene-d_6 or chloroform-*d*. The density of trifluorotoluene is 1.1884 g/cm^3 at 20°C, 1.1815 g/cm^3 at 25°C, and 1.1743 g/cm^3 at 30°C (**24**). The density of benzene-d_6 is given in 8.3.1. The density of chloroform-*d* is given in 8.1.1. The trifluorotoluene shall be at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the trifluorotoluene concentration. The final concentration and its uncertainty shall be stated.

8.5.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.5.2.1 *Spectral Region*—A 16-kHz width with the transmitter frequency set to approximately the resonance of trifluorotoluene.

8.5.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the trifluorotoluene resonance reduced by the acquisition time.

8.5.2.3 *Pulse Flip Angle*—90°.

8.5.2.4 *Data Acquisition Time*—At least 4 s.

8.5.2.5 *Number of Transients*—One.

8.5.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.5.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.5.2.8 No decoupling.

8.5.3 *Data Processing*—The following data processing parameters shall be used:

8.5.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB\cdot t\cdot\pi}$ where LB (also known as width) = 2 Hz and t = time value for each acquired data point.

8.5.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 6).

8.5.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.5.3.1.

8.5.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.5.5.1 Signal is defined as the amplitude of the trifluorotoluene resonance (approximately −63 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±2 kHz around the signal.

8.5.5.2 Noise is defined as two times the rms noise in the 2-kHz region from −2 to −4 kHz from the trifluorotoluene resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.5.5.3 Use Eq 2 to calculate rms noise.

8.5.5.4 The amplitude of each point measured from the zero-intensity line in the selected 2-kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.5.5.5 The S/N is equal to: signal ÷ (2 × rms noise).

8.5.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.5.6 *Reporting Sensitivity*—The results of the ^{19}F sensitivity measurements shall be reported as described in Section 7.

8.6 *^{29}Si Sensitivity*—This practice describes the determination of the ^{29}Si sensitivity of the NMR system.

8.6.1 *Sample*—The sample is 25 % (v/v) hexamethyldisiloxane in benzene-d_6. The density of hexamethyldisiloxane is 0.7636 g/cm^3 at 20°C, 0.7584 g/cm^3 at 25°C, and 0.7536 g/cm^3

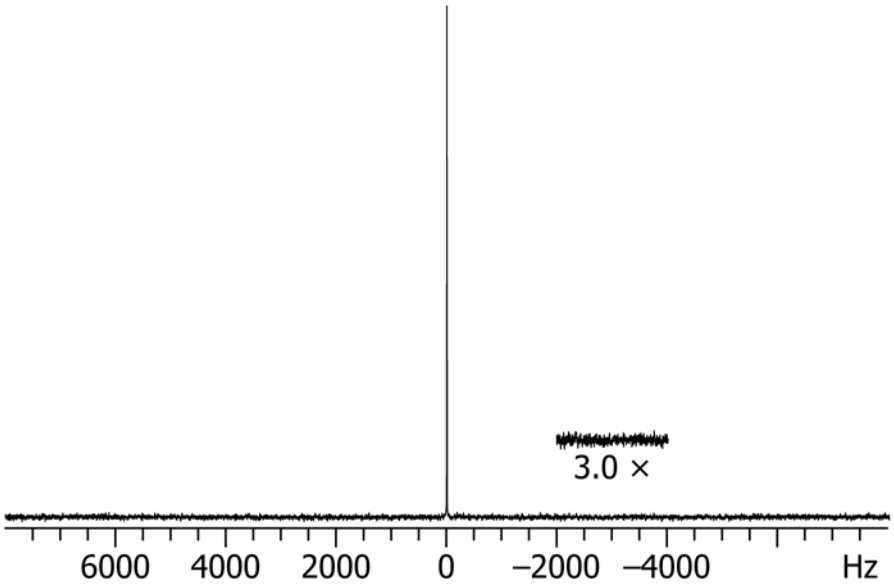

FIG. 6 470.6-MHz ^{19}F Sensitivity Test Spectrum of 0.05 % α,α,α-Trifluorotoluene in Chloroform-*d*

at 30°C (**25**). The density of benzene-d_6 is given in 8.3.1. The hexamethyldisiloxane shall be anhydrous and at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the hexamethyldisiloxane concentration. The final concentration and its uncertainty shall be stated.

8.6.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.6.2.1 *Spectral Region*—A 4-kHz width with the transmitter frequency set to approximately the resonance of hexamethyldisiloxane.

8.6.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the hexamethyldisiloxane resonance reduced by the acquisition time.

8.6.2.3 *Pulse Flip Angle*—90°.

8.6.2.4 *Data Acquisition Time*—At least 4 s.

8.6.2.5 *Number of Transients*—One.

8.6.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.6.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.6.2.8 *No Decoupling*—This test is run without decoupling to avoid issues resulting from the negative nuclear Overhauser enhancement (NOE) of ^{29}Si.

8.6.3 *Data Processing*—The following data processing parameters shall be used:

8.6.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB\cdot t\cdot\pi}$ where LB (also known as width) = 0.5 Hz and t = time value for each acquired data point.

8.6.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 7).

8.6.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.6.3.1.

8.6.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.6.5.1 Signal is defined as the amplitude of the hexamethyldisiloxane resonance (approximately 6 ppm) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±500 Hz around the signal.

8.6.5.2 Noise is defined as two times the rms noise in the 500-Hz region from −500 to −1000 Hz from the hexamethyldisiloxane resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.6.5.3 Use Eq 2 to calculate rms noise.

8.6.5.4 The amplitude of each point measured from the zero-intensity line in the selected 500-Hz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.6.5.5 The S/N is equal to:

$$\text{signal} \div (2 \times \text{rms noise}) \times (4.685 \div \text{the measured } ^{29}\text{Si abundance}) \quad (5)$$

NOTE 3—Corrected for the average natural abundance of ^{29}Si (**21**).

8.6.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.6.6 *Reporting Sensitivity*—The results of the ^{29}Si sensitivity measurements shall be reported as described in Section 7.

8.7 *^{15}N Sensitivity*—This practice describes the determination of the nitrogen-15 sensitivity of the NMR system.

8.7.1 *Sample*—The sample is 90 % (v/v) formamide in dimethyl sulfoxide-d_6. The density of formamide is 1.1334 g/cm^3 at 20°C, 1.1330 g/cm^3 at 25°C, and 1.1246 g/cm^3 at 30°C (**26, 27**). The density of dimethyl sulfoxide-d_6 is 1.195 g/cm^3 at 20°C (**7**), 1.190 g/cm^3 at 25°C (**28**), and 1.185 g/cm^3

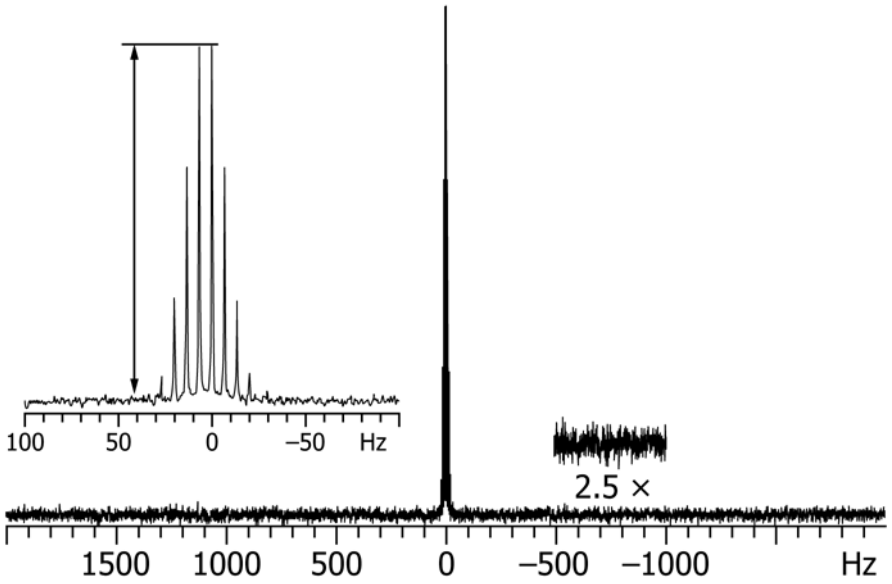

FIG. 7 119.2-MHz ^{29}Si Sensitivity Test Spectrum of 25 % Hexamethyldisiloxane in Benzene-d_6

at 30°C (**7**). The formamide shall be anhydrous and at least 99 % pure. The total contribution from all impurities in the final sample (excluding water) shall be less than 1 mol % of the formamide concentration. The final concentration and its uncertainty shall be stated.

8.7.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.7.2.1 *Spectral Region*—A 2.4-kHz width with the transmitter frequency set to approximately the resonance of formamide.

8.7.2.2 *Equilibration Delay*—At least seven times the T_1 relaxation time of the formamide resonance.

NOTE 4—This is seven rather than five times T_1 and not reduced by the acquisition time to allow sufficient time for the decay of the strongly negative nuclear Overhauser effect (NOE).

8.7.2.3 *Pulse Flip Angle*—90°.

8.7.2.4 *Data Acquisition Time*—6 s.

8.7.2.5 *Number of Transients*—At least one. (The low sensitivity of ^{15}N may mean that more than one transient is required to obtain an accurate result.)

8.7.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.7.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.7.2.8 *Decoupling Conditions*—Decoupling parameters such as peak power in Hertz, mean power levels in Hertz, and decoupling modulation pattern shall be specified. The parameters chosen should result in the signal appearing as a singlet with line widths less than 0.6 Hz after the application of apodization as described in 8.7.3.1. From the proton spectrum of the sample, determine the mean frequency of the amide signals and set the decoupling frequency to this value. The same decoupling conditions shall be maintained only during the acquisition. Because of the negative NOE of ^{15}N, no decoupling should be applied during the relaxation delay.

8.7.3 *Data Processing*—The following data processing parameters shall be used:

8.7.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 0.3 Hz and t = time value for each acquired data point.

8.7.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 8).

8.7.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.7.3.1.

8.7.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.7.5.1 Signal is defined as the amplitude of the formamide resonance (approximately 113 ppm relative to Ξ = 10.132 911 1 %) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of ±300 Hz around the signal.

8.7.5.2 Noise is defined as two times the rms noise in the 300-Hz region from −300 to −600 Hz from the formamide resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.7.5.3 Use Eq 2 to calculate rms noise.

8.7.5.4 The amplitude of each point measured from the zero-intensity line in the selected 300-Hz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.7.5.5 The corrected S/N is equal to:

$$\text{signal} \div (2 \times \text{rms noise}) \times (0.366 \div \text{the measured } ^{15}\text{N abundance}) \quad (6)$$

NOTE 5—Corrected for the average natural abundance of ^{15}N (**21**).

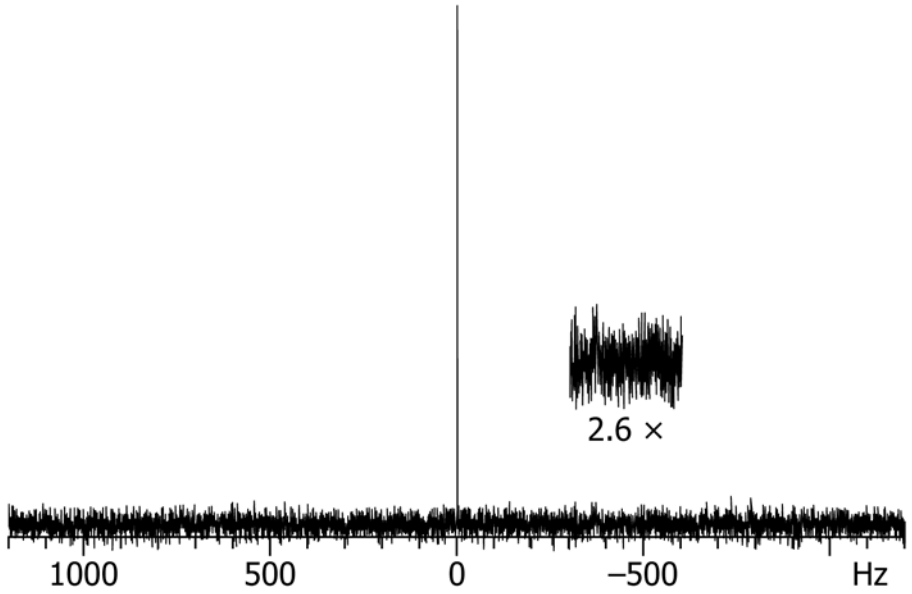

FIG. 8 50.7-MHz ^{15}N Sensitivity Test Spectrum of 90 % Formamide in Dimethyl sulfoxide-d_6

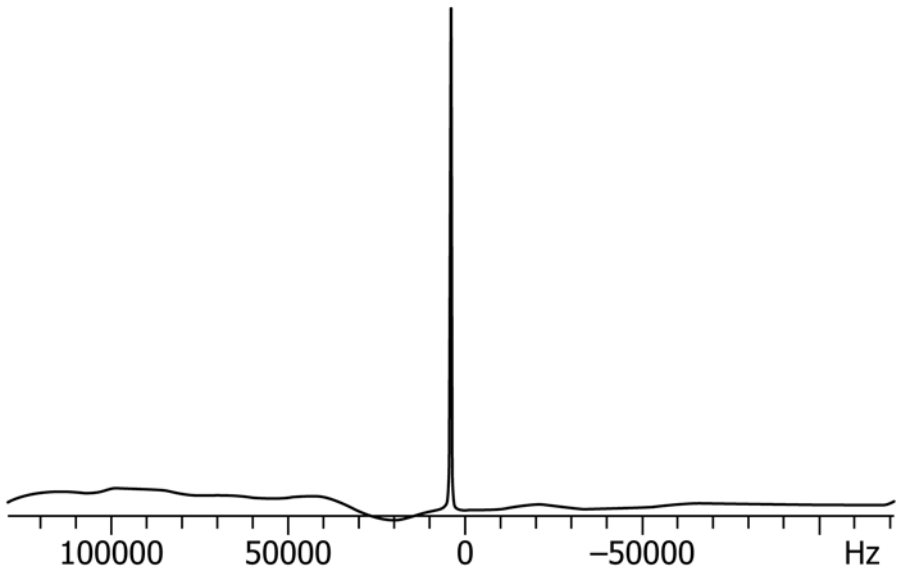

FIG. 9 36.1-MHz ^{14}N Sensitivity Test Spectrum of 90 % Formamide in Dimethyl Sulfoxide-d_6 without Acoustic Ringing Suppression

8.7.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.7.6 *Reporting Sensitivity*—The results of the ^{15}N sensitivity measurements shall be reported as described in Section 7.

8.8 *^{14}N Sensitivity*—This practice describes the determination of the nitrogen-14 sensitivity of the NMR system.

8.8.1 *Sample*—The sample is 90 % (v/v) formamide in dimethyl sulfoxide-d_6 and is described in 8.7.1.

8.8.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.8.2.1 *Spectral Region*—A 250-kHz width with the transmitter frequency set to approximately the resonance of formamide.

8.8.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the formamide resonance reduced by the acquisition time.

8.8.2.3 *Pulse Flip Angle*—90°.

8.8.2.4 *Data Acquisition Time*—30 ms.

8.8.2.5 The pre-acquisition delay to allow for dead time should be set so that the S/N without acoustic ringing suppression is maximized.

8.8.2.6 *Number of Transients*—Sixty-four. If acoustic ringing distortion is present, the test may be carried out with acoustic ringing suppression **(29, 30**, pp. 235-236). If acoustic ringing suppression is used (Fig. 9), the associated pulse sequence shall be specified.

8.8.2.7 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.8.2.8 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.8.2.9 No decoupling.

8.8.3 *Data Processing*—The following data processing parameters shall be used:

8.8.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 50 Hz and t = time value for each acquired data point.

8.8.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 10).

8.8.4 No data smoothing or other types of data manipulation may be applied except as specified in 8.8.3.1.

8.8.5 *S/N Calculation*—The calculations for the S/N are carried out on the real part of the pure phase absorption mode spectrum.

8.8.5.1 Signal is defined as the amplitude of the formamide resonance (approximately 114 ppm relative to Ξ = 7.22 356 1 %) in the spectrum measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region ±50 kHz around the signal.

8.8.5.2 Noise is defined as two times the rms noise in the 50-kHz region from −50 to −100 kHz from the formamide resonance. Zero- and first-order baseline corrections should be applied to the noise region.

8.8.5.3 Use Eq 2 to calculate rms noise.

8.8.5.4 The amplitude of each point measured from the zero-intensity line in the selected 50-kHz region is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.8.5.5 The measured S/N is equal to: signal ÷ (2 × rms noise).

8.8.5.6 As 64 transients are used, the measured S/N ratio is divided by 8 to yield an S/N ratio reported as the equivalent to that from a single-scan measurement.

8.8.5.7 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.8.6 *Reporting Sensitivity*—The results of the ^{14}N sensitivity measurements shall be reported as described in Section 7.

8.9 *Primary Proton Resolution and Line Shape*—This practice describes the measurement of the proton resolution and line shape of the NMR system. It is useful for spectrometers with proton resonances between 200 and 1200 MHz. As the measured resolution and line shape are critically dependent on the shimming of the spectrometer, it is not possible to separate unambiguously the instrument performance from operator performance.

8.9.1 *Sample*—The sample is 0.003 to 0.1 % (v/v) (depending on instrument sensitivity) TMS in chloroform-*d*. The TMS concentration is defined as a volume percentage (v/v) at 25°C. The densities of TMS and chloroform-*d* are given in 8.1.1. The concentration need not be precise. However, low-signal intensity will reduce the accuracy of the measurements, and a signal that is too intense will lead to line broadening from radiation damping (**30**, p. 75). The TMS should be at least 99.9 % pure, and the chloroform-*d* should be at least 99.8 % deuterated. For long-term storage, samples should be maintained in the dark at room temperature to prevent photolysis. Photolysis is indicated by peaks at 0.128, 2.768, 0.437, and 2.210 ppm.[5] If the spectrometer has sufficient sensitivity, the same sample used for the ^{1}H NMR sensitivity measurement—0.1 % (v/v) ethylbenzene in chloroform-*d* containing 0.01 % TMS—may be used for the TMS resolution and line shape standard.

8.9.2 *Data Acquisition*—The following data acquisition parameters shall be used:

[5] R. E. Hoffman, personal communication.

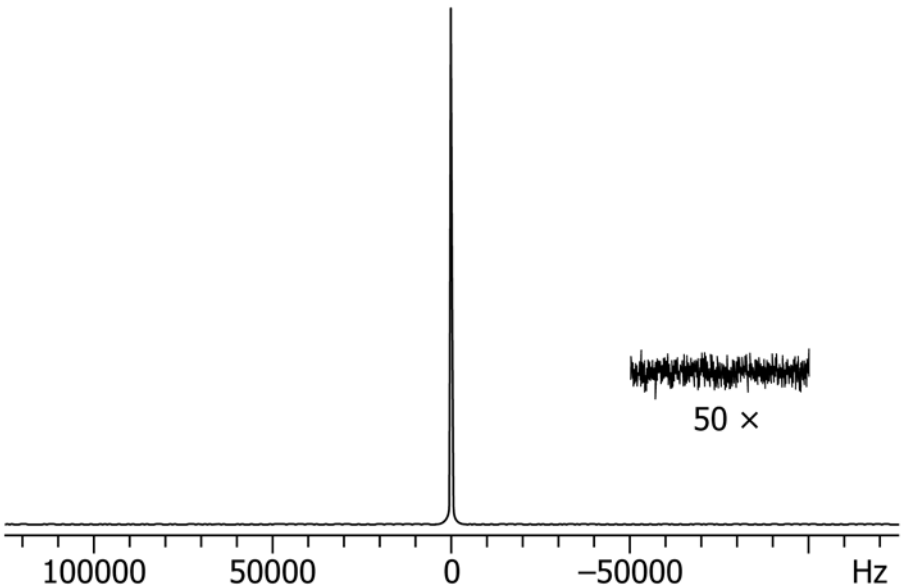

FIG. 10 36.1-MHz ^{14}N Sensitivity Test Spectrum of 90 % Formamide in Dimethyl Sulfoxide-d_6 with Acoustic Ringing Suppression

8.9.2.1 *Spectral Region*—A ≥500-Hz spectral width with the transmitter centered 50 ± 10 Hz off the resonance frequency of the TMS.

8.9.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the TMS resonance reduced by the acquisition time.

8.9.2.3 *Pulse Flip Angle*—90°.

8.9.2.4 *Data Acquisition Time*—At least 10 s to avoid truncation of the free induction decay causing spectral artifacts.

8.9.2.5 *Number of Transients*—One. However, multiple transients may be required, if necessary, and reported to average out baseline artifacts resulting from field modulation caused by any combination of physical vibration, lock instability, or Q-modulation when spinning (**30**, p. 301).

8.9.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.9.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified (Figs. 11 and 12).

8.9.2.8 No decoupling.

8.9.3 *Data Processing*—The following data processing parameters shall be used:

8.9.3.1 Do not apply an exponentially decaying function or any other apodization to the time domain data as is done in sensitivity measurements.

8.9.3.2 Calculate the FT using sufficient data points to yield a digital resolution of ≤0.01 Hz per data point. Apply phase corrections as needed to produce the pure absorption-mode spectrum.

8.9.3.3 Apply only zero- and first-order baseline corrections as needed.

8.9.4 No additional data smoothing or other types of data manipulation may be applied.

8.9.5 *Resolution and Line Shape Calculations*—The calculations for resolution and line shape are carried out on the real part of the pure phase absorption mode spectrum.

8.9.5.1 Resolution is defined as the width of the resonance in Hertz at one half the amplitude of the TMS resonance.

8.9.5.2 Line shape is defined as the width of the resonance at 0.55 and 0.11 % of the amplitude of the TMS resonance. Note that the TMS resonance will have ^{29}Si satellites ($^2J_{SiH}$ = 6.6 Hz) (intensity ≈ 2.34 %) and ^{13}C sidebands at ($^1J_{CH}$ = 118.2 Hz) (intensity ≈ 0.55 %) around the main peak. The peak heights do not reflect the isotopic abundance because they are affected by long-range couplings and differences in relaxation rates. At high resolutions, three-bond couplings ($^3J_{CH}$ = 2.1 Hz) may be observable, and at very high field strengths, a small signal caused by isotope shift from $(CH_3)_4{}^{30}$Si may be visible (Fig. 13).

8.9.6 *Reporting Proton Resolution and Line Shape*—Resolution and line shape measurement results shall be reported as described in Section 7.

8.10 *Secondary Proton Resolution and Line Shape*—This practice describes the measurement of the proton resolution and line shape of the NMR system. It is useful for spectrometers with ^{1}H resonances between 200 and 500 MHz. At higher field strengths, isotope effects caused by ^{35}Cl and ^{37}Cl begin to be resolvable making line shape measurements using this sample difficult. Accordingly, the procedure described in 8.9 should be used at higher field strengths.

8.10.1 *Sample*—The sample is 0.3 to 3 % (v/v) (depending on probe sensitivity) chloroform in acetone-d_6. The density of chloroform is 1.4885 g/cm^3 at 20°C, 1.4798 g/cm^3 at 25°C, and 1.4709 g/cm^3 at 30°C (**31**, **32**). The density of acetone-d_6 is 0.8749 g/cm^3 at 20°C (**33**), 0.8680 g/cm^3 at 25°C, and 0.8616 g/cm^3 at 30°C (**34**). The chloroform concentration is defined as a volume percentage (v/v) at 25°C. The chloroform concentration need not be precise. However, low-signal intensity will reduce the accuracy of the measurements, and a signal that is too intense will lead to line broadening from radiation damping (**30**, p. 75). The chloroform should be at least 99.9 % pure (0.5

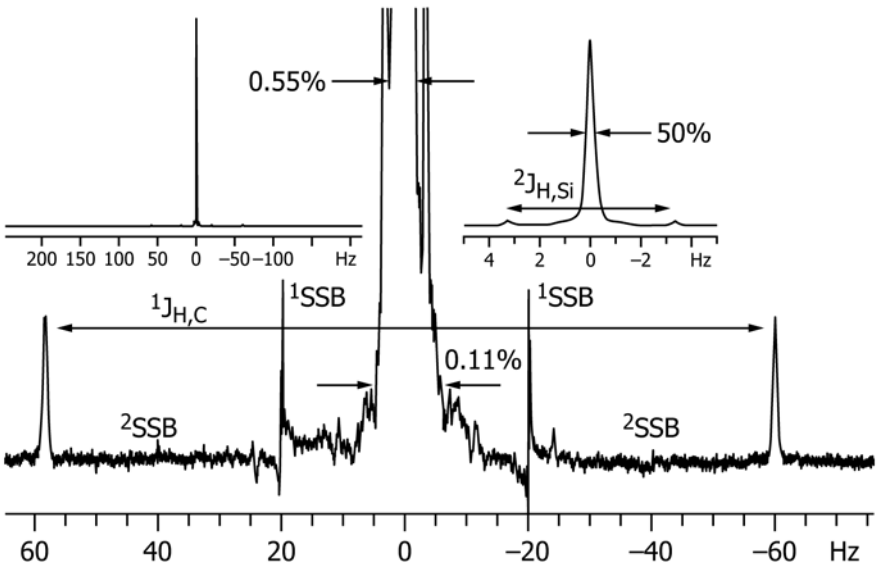

FIG. 11 500.2-MHz ^{1}H Line Shape Test Spectrum of 0.104 % Tetramethylsilane in Chloroform-*d* Spinning (^{1}SSB—First-Order Spinning Sideband; ^{2}SSB—Second-Order Spinning Sideband)

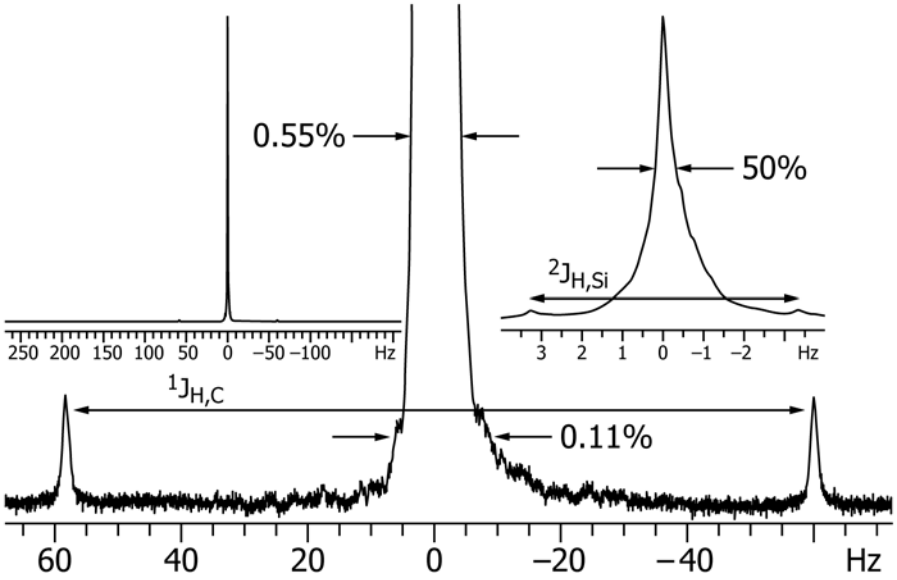

FIG. 12 500.2-MHz ^{1}H Line Shape Test Spectrum of 0.104 % Tetramethylsilane in Chloroform-*d* Nonspinning

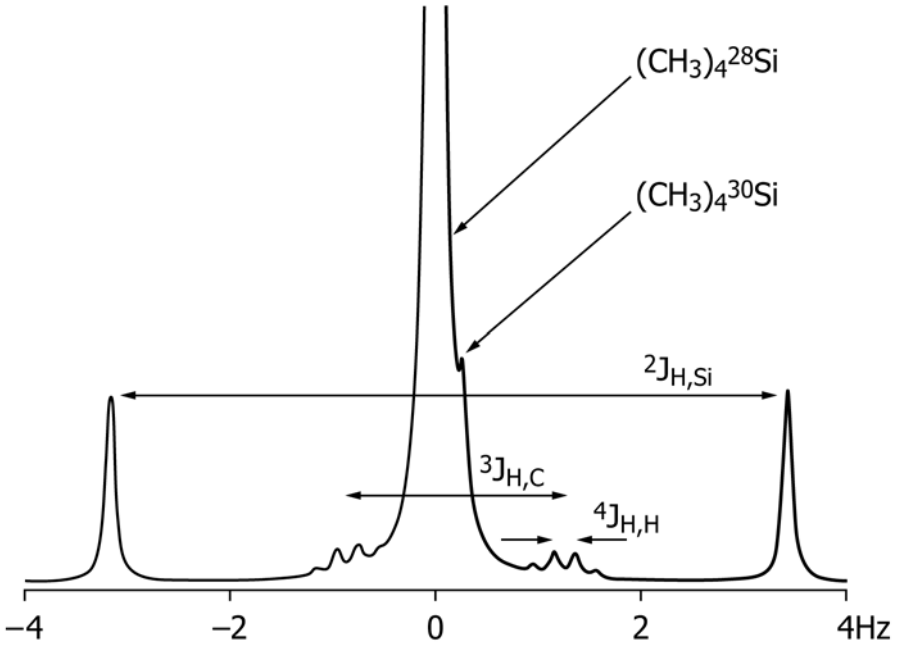

FIG. 13 Simulated 1500-MHz ^{1}H Spectrum of Tetramethylsilane Satellites

to 1.0 % ethanol may be added as a stabilizer), and the acetone-d_6 should be at least 99.9 % deuterated.

8.10.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.10.2.1 *Spectral Region*—A ≥500-Hz spectral width with the transmitter centered 50 ± 10 Hz from the resonance frequency of the chloroform.

8.10.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the chloroform resonance reduced by the acquisition time; insufficient equilibration delay may yield a poorer line shape.

8.10.2.3 *Pulse Flip Angle*—90°.

8.10.2.4 *Data Acquisition Time*—At least 10 s to avoid truncation of the free induction decay causing spectral artifacts.

8.10.2.5 *Number of Transients*—One. However, multiple transients may be required, if necessary, and reported to average out baseline artifacts resulting from field modulation caused by any combination of physical vibration, lock instability, or Q-modulation when spinning (**30**, p. 301).

8.10.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.10.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified (Figs. 14 and 15).

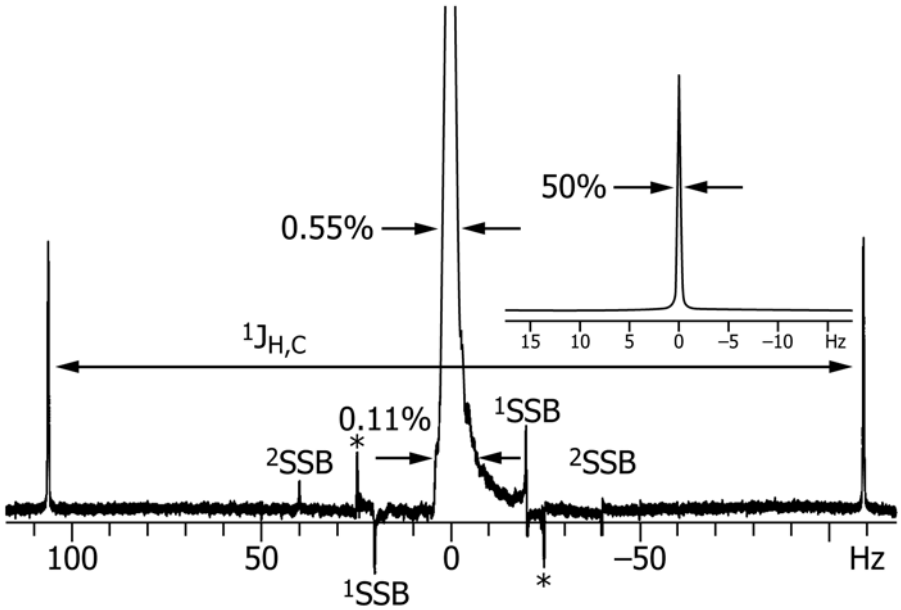

FIG. 14 500.2-MHz ^{1}H Line Shape Test Spectrum of 1 % Chloroform in Acetone-d_6 Spinning; * Indicates a Possible Vibration-Induced Artifact (^{1}SSB—First-Order Spinning Sideband; ^{2}SSB—Second-Order Spinning Sideband)

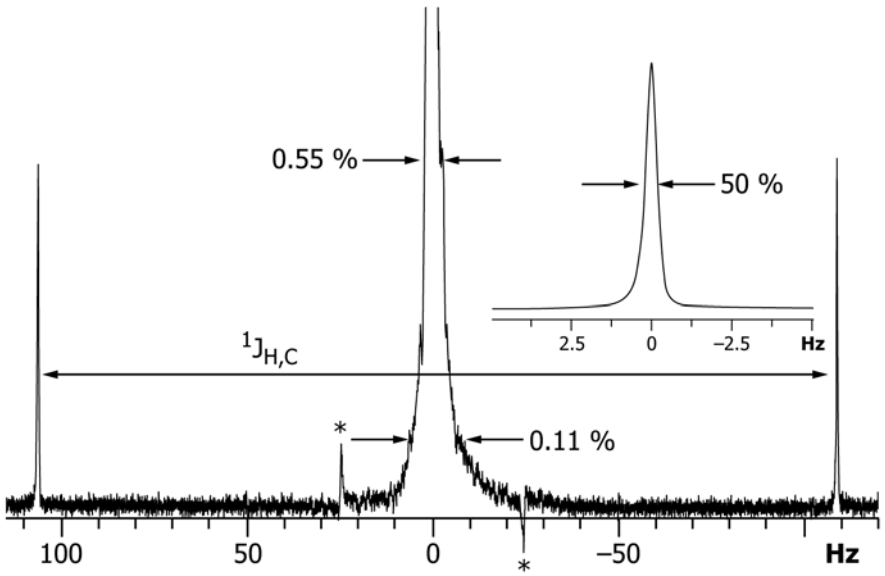

FIG. 15 500.2-MHz ^{1}H Line Shape Test Spectrum of 1 % Chloroform in Acetone-d_6 Nonspinning; * Indicates a Possible Vibration-Induced Artifact

8.10.2.8 No decoupling.

8.10.3 *Data Processing*—The following data processing parameters shall be used:

8.10.3.1 Do not apply an exponentially decaying function or any other apodization to the time domain data as is done in sensitivity measurements.

8.10.3.2 Calculate the FT using sufficient data points to yield a digital resolution of ≤0.01 Hz per data point. Apply phase corrections as needed to produce the pure absorption mode spectrum.

8.10.3.3 Apply only zero- and first-order baseline corrections as needed.

8.10.4 No additional data smoothing or other types of data manipulation may be applied.

8.10.5 *Resolution and Line Shape Calculations*—The calculations for resolution and line shape are carried out on the real part of the pure phase absorption mode spectrum.

8.10.5.1 Resolution is defined as the width of the resonance in Hertz at one half the amplitude of the chloroform resonance.

8.10.5.2 Line shape is defined as the width of the resonance at 0.55 and 0.11 % of the amplitude of the chloroform resonance. Note that the chloroform resonance will have ^{13}C sidebands ($^1J_{CH}$ = 215.2 Hz) (intensity ≈ 0.55 %) around the main peak. Determine the 0.55 % point from the height of the

main resonance, not from the heights of the ^{13}C satellites, which may be enhanced in amplitude relative to the main resonance if insufficient equilibration time is used.

8.10.6 *Reporting ^{1}H Resolution and Line Shape*—Resolution and line shape measurement results shall be reported as described in Section 7.

8.11 *Primary ^{13}C Resolution and Line Shape*—This practice describes the measurement of the ^{13}C resolution and line shape of the NMR system.

8.11.1 *Sample*—The sample is 60 % (v/v) benzene-d_6 in *p*-dioxane (also known as 1,4-dioxane). The sample parameters are given in 8.3.1. For routine use (not for specification purposes), a relaxation agent, such as 0.2 % $Cr(acac)_3$ may be added to the sample to permit more rapid data acquisition, provided its use is reported.

8.11.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.11.2.1 *Spectral Region*—Adequate spectral width to prevent any aliasing with the observe transmitter 50 ± 10 Hz from the ^{13}C resonance frequency of the *p*-dioxane.

8.11.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the *p*-dioxane resonance reduced by the acquisition time.

8.11.2.3 *Pulse Flip Angle*—90°.

8.11.2.4 *Data Acquisition Time*—Sufficient to avoid truncation of the free induction decay.

8.11.2.5 *Number of Transients*—One. However, multiple transients may be acquired, if necessary, and reported to average out baseline artifacts resulting from field modulation caused by any combination of physical vibration, lock instability, or Q-modulation when spinning (**30**, p. 301).

8.11.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.11.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.11.2.8 *Decoupling*—Continuous wave centered on the ^{1}H resonance of the *p*-dioxane resonance using the minimal rf field strength necessary to effect complete proton decoupling (excessive decoupling power shall be avoided as it will cause line broadening; however, because the decoupling field is small, it is important that it be accurately centered over the proton resonance signals).

8.11.3 *Data Processing*—The following data processing parameters shall be used:

8.11.3.1 Do not apply an exponentially decaying function or any other apodization to the time domain data as is done in sensitivity measurements.

8.11.3.2 Calculate the FT using sufficient data points to yield a digital resolution of ≤0.01 Hz per data point. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 16).

8.11.3.3 Apply only zero- and first-order baseline corrections as needed.

8.11.4 No additional data smoothing or other types of data manipulation may be applied.

8.11.5 *Resolution and Line Shape Calculations*—The calculations for resolution and line shape are carried out on the real part of the pure phase absorption mode spectrum.

8.11.5.1 Resolution is defined as the width of the resonance in Hertz at one half the amplitude of the *p*-dioxane resonance.

8.11.5.2 Line shape is defined as the width of the resonance at 0.55 and 0.11 % of the amplitude of the *p*-dioxane resonance.

8.11.6 *Reporting ^{13}C Resolution and Line Shape*—Resolution and line shape measurement results shall be reported as described in Section 7.

8.12 *Secondary ^{13}C Resolution and Line Shape*—This practice describes the measurement of the ^{13}C resolution and line shape of the NMR system.

8.12.1 *Sample*—The sample is 80 % (v/v) benzene in acetone-d_6. The benzene concentration need not be accurate.

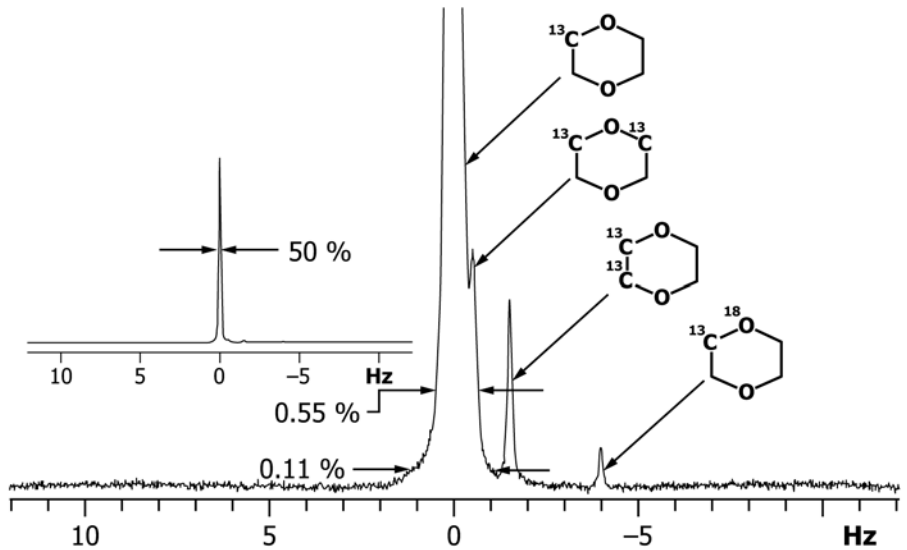

FIG. 16 201.2-MHz ^{13}C Line Shape Test Spectrum of 40 % *p*-Dioxane and 60 % Benzene-d_6 Showing Minor Dioxane Isotopomers

The density of benzene is 1.5011 g/cm^3 at 20°C, 1.4979 g/cm^3 at 25°C, and 1.4948 g/cm^3 at 30°C (**5**). The density of acetone-d_6 is given in 8.10.1. The benzene shall be at least 99 % pure, and care shall be taken to ensure that it has not reacted with air to produce oxygenated products.

8.12.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.12.2.1 *Spectral Region*—Adequate spectral width to prevent any line folding with the observe transmitter 50 ± 10 Hz from the ^{13}C resonance frequency of the benzene.

8.12.2.2 *Equilibration Delay*—At least five times the T_1 relaxation time of the benzene resonance reduced by the acquisition time.

8.12.2.3 *Pulse Flip Angle*—90°.

8.12.2.4 *Data Acquisition Time*—Sufficient to avoid truncation of the free induction decay.

8.12.2.5 *Number of Transients*—One. However, multiple transients may be acquired, if necessary, and reported to average out baseline artifacts resulting from field modulation caused by any combination of physical vibration, lock instability, or Q-modulation when spinning (**30**, p. 301).

8.12.2.6 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.12.2.7 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.12.2.8 *Decoupling*—Continuous wave centered on the ^{1}H resonance of benzene using a power level necessary to effect complete proton decoupling.

8.12.3 *Data Processing*—The following data processing parameters shall be used:

8.12.3.1 Do not apply an exponentially decaying function or any other apodization to the time domain data as is done in sensitivity measurements.

8.12.3.2 Calculate the FT using sufficient data points to yield a digital resolution of ≤0.01 Hz per data point. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 17).

8.12.3.3 Apply only zero- and first-order baseline corrections as needed.

8.12.4 No additional data smoothing or other types of data manipulation may be applied.

8.12.5 *Resolution and Line Shape Calculations*—The calculations for resolution and line shape are carried out on the real part of the pure phase absorption mode spectrum.

8.12.5.1 Resolution is defined as the width of the resonance in Hertz at one half the amplitude of the benzene resonance.

8.12.5.2 Line shape is defined as the width of the resonance at 0.55 and 0.11 % of the amplitude of the benzene resonance.

8.12.6 *Reporting ^{13}C Resolution and Line Shape*—Resolution and line shape measurement results shall be reported as described in Section 7.

8.13 *Water Suppression*—This practice describes the measurement of solvent signal suppression for an aqueous sample.

8.13.1 *Sample*—The sample is 2.0-mmol L^{-1} sucrose with 0.5-mmol L^{-1} sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS, also known as 3-(trimethylsilyl)-1-propanesuflonic acid sodium salt, or 4,4-dimethyl 4-silapentane sodium sulfonate) and ≈0.5-mmol L^{-1} sodium azide in 10 % D_2O/90 % H_2O. The sucrose shall be greater than 99.9 % pure, and the DSS purity should be greater than 97 %. The precise concentrations of sucrose and DSS shall be stated. The total contribution from all impurities in the final sample shall be less than 1 mol % of the sucrose concentration. The concentration of sodium azide, used to suppress bacterial growth, does not need to be precisely known, but should be less than 2 mmol L^{-1}. The percentage of D_2O, used for locking, also does not need to be exact but should be kept at or below 10 % (v/v) to minimize proton exchange in the sucrose.

8.13.2 *Data Acquisition*—This experiment consists of a weak selective pulse at the water resonance frequency followed

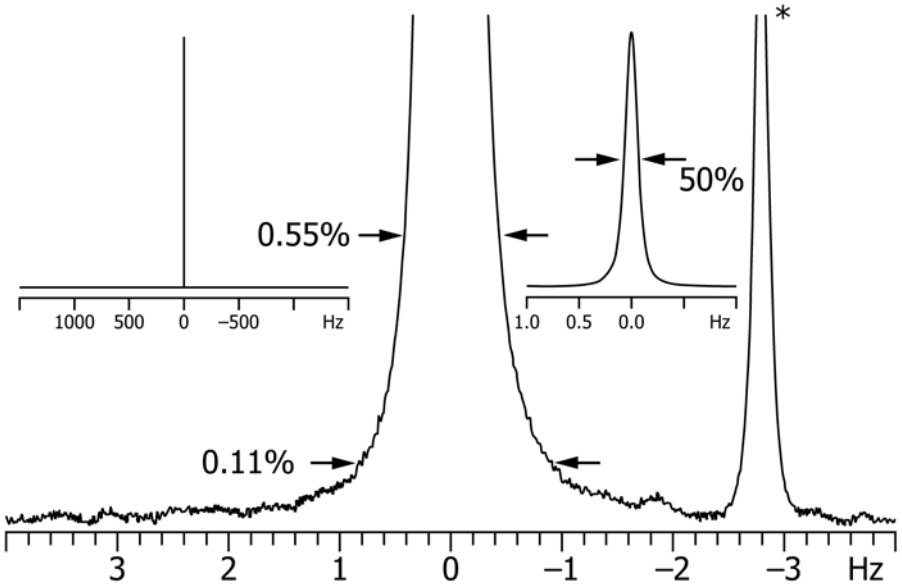

FIG. 17 150.9-MHz ^{13}C Line Shape Spectrum of 80 % Benzene in Acetone-d_6; * Indicates a Benzene Isotopomer with Two ^{13}C Atoms

by a short 90° pulse and data acquisition. The following data acquisition parameters shall be used:

8.13.2.1 *Spectral Region*—At least 10 ppm with the observe transmitter centered on the water resonance. The transmitter offset position should be optimized for the best water suppression.

8.13.2.2 *Equilibration Delay*—This delay occurs during the water-selective irradiation.

8.13.2.3 *Observe Pulse Flip Angle*—90°.

8.13.2.4 *Water-selective Irradiation*—At a transmitter power level corresponding to $\gamma B_1/2\pi \approx 25$ to 75 Hz where γ is the gyromagnetic ratio and B_1 is the magnetic field ($\gamma B_1/2\pi \approx 1/(4 \times \text{pw90})$, pw90 in seconds; for example, the power level required to produce a 2.5-ms 90° pulse generates a 100-Hz field).

8.13.2.5 *Data Acquisition Time*—1 s.

8.13.2.6 *Number of Transients*—Eight following four "dummy" (steady-state) transients.

8.13.2.7 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

8.13.2.8 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.13.2.9 No decoupling.

8.13.3 *Data Processing*—The following data processing parameters shall be used:

8.13.3.1 Do not apply an exponentially decaying function or any other apodization to the time domain data as is done in other sensitivity measurements.

8.13.3.2 Calculate the FT using sufficient data points to yield a digital resolution of ≤0.05 Hz per data point. Apply phase corrections as needed to produce the pure absorption mode spectrum (Fig. 18).

8.13.4 No data smoothing or other types of data manipulation may be applied.

8.13.5 *S/N Calculation*—The calculations for the S/N ratio are carried out on the real part of the pure phase absorption mode spectrum.

8.13.5.1 Signal is defined as the amplitude of the tallest peak in the doublet from the anomeric sucrose proton around 5.41 ppm measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of 1 ppm around the signal.

8.13.5.2 Noise is defined as two times the rms noise in the region between 5.6 and 7.0 ppm. Zero- and first-order baseline corrections should be applied to the noise region.

8.13.5.3 Use Eq 2 to calculate rms noise.

8.13.5.4 The amplitude of each point measured from the zero-intensity line in region between 5.6 and 7.0 ppm is squared. Sum all of these squared values. Divide the sum by one less than the number of data points in the region. Take the square root of the result.

8.13.5.5 The S/N is equal to: signal ÷ (2 × rms noise).

8.13.5.6 Any alteration of data points or use of alternative regions for the rms noise calculation constitutes noncompliance with this practice.

8.13.6 *Water Suppression*—Using the spectrum from 8.13.5, the width of the residual water signal should be measured at the full height of the sucrose anomeric proton signal (see Note 6). The symmetry of the base of residual water peak and the reference signal used should be noted.

NOTE 6—In variants of this test, the width of the residual water peak is measured at the full height or 50 % the height of the DSS signal. This practice is deprecated because the DSS signal may be unrelated to its expected concentration because of DSS adsorbing onto the tube wall.

8.13.7 *Resolution*—Using the spectrum from 8.13.5, the depth of the splitting of the doublet as a result of the sucrose anomeric proton at 5.41 ppm is measured from the larger peak of the doublet. Percentage resolution is expressed as % res = $100 \times (a - b)/a$ where a and b are defined as in Fig. 18.

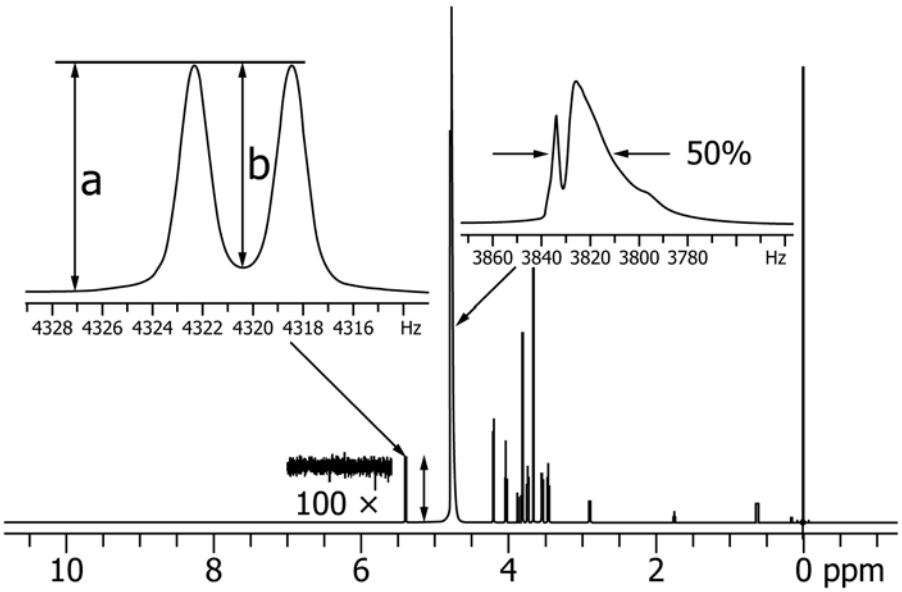

FIG. 18 800.2-MHz ^{1}H Water Suppression Test Spectrum of 0.002 mol/L Sucrose in 10 % D_2O and 90 % H_2O

8.13.8 *Reporting*—The results of the sensitivity measurements (8.13.5) shall be reported as described in Section 7. Report the width (in Hertz) of the residual water resonance at the height of the largest of the anomeric proton resonances (8.13.6). Report the percentage to which the sucrose anomeric doublet is resolved (8.13.7).

8.14 *Gradient Profile*—This practice describes the measurement of gradient strength.

8.14.1 *Sample*—The sample is ≈1 volume % H_2O, ≈0.1 mg/mL $GdCl_3$, and ≈0.1 weight % DSS in D_2O. Alternatively, the sample used for 8.13 (water suppression—sucrose plus DSS in 10 % D_2O/90 % H_2O) may be used. For a *Z*-gradient, the height of the sample in the tube shall be specified and should exceed the length of the probe's proton observe coil by at least 50 %, or an inert disk ("phantom") may be used to define the boundaries of the sample (**30**, pp. 89-91). This procedure is suitable for detecting changes in gradient performance but not for determining absolute calibration of the gradient strength unless a phantom is used. For *X*- or *Y*-gradients, the sample boundary is determined by the tube without a phantom.

8.14.2 *Data Acquisition*—The following data acquisition parameters shall be used:

8.14.2.1 Set up the necessary ^1H 1D pulse sequence with gradients as shown in Fig. 19.

8.14.2.2 Using a rectangular pulse profile, set the positive gradient strength to be about 10 % of maximum.

8.14.2.3 Set the transmitter power and the first ^1H pulse for a 90° pulse determined for the probe. Set the length of the second ^1H pulse to a 180° pulse.

8.14.2.4 Set up the following parameters for data acquisition:

(1) Spectral Width—At least 100 000 Hz.

(2) Acquisition Time (Acq)—3 ms.

(3) Pulse Delay—2 s.

(4) Gradient Duration (Acq/2)—1.5 ms; half the acquisition time.

(5) d2—Sufficient for ring down.

8.14.2.5 Repeat 8.14.2.1 – 8.14.2.4 using negative gradients in 8.14.2.2.

8.14.3 *Data Processing*—The following data processing steps shall be used:

8.14.3.1 Zero fill by at least a factor of two and calculate the FT in absolute value mode.

8.14.3.2 Apply only zero- and first-order baseline corrections as needed to produce a flat baseline on either side of the broad peak (Fig. 20).

8.14.3.3 Apodization using a –90 to +90° sine bell centered over the echo signal may be used to improve the S/N ratio.

8.14.4 *Gradient Profile Calculations and Reporting*—Determine the width of the peak at a consistent point between 15 and 50 % of the maximum peak height. As this is a relative measurement, the specific height at which the width is measured is not critical so long as a consistent height is used.

8.14.5 The gradient strength can be determined from the equation $G = 2\pi\Delta\nu/\gamma\Lambda$ where $\Delta\nu$ is the frequency separation in Hertz, γ is the ^1H gyromagnetic ratio (2.67×10^8 rad · T^{-1} · s^{-1}), and Λ is the length of the object in centimetres. The object length in this test is either the smaller of the length of the active region of the probe coil or the phantom length for *Z*-gradients. The inner diameter of the tube is used for *X*- or *Y*-gradients. For a 50-kHz peak width in a probe with 1.6-cm coil window: $G = 100 \times (2\pi \times 50\,000\ \text{Hz}) \div (2.67 \times 10^8\ \text{rad} \cdot T^{-1} \cdot s^{-1} \times 0.016\ \text{m}) = 7.34$ G/cm. Assuming that the gradient amplifier is linear over its entire range, the maximum gradient strength would be approximately ten times this value or 73.4 G/cm.

8.15 *Gradient Recovery Consistency*—This practice describes the measurement of gradient recovery consistency over time.

8.15.1 *Sample*—The sample is water, $GdCl_3$, and DSS in D_2O and is described in 8.14.1. For a *Z*-gradient, the height of the sample in the tube shall be specified and should exceed the length of the probe's proton observe coil by at least 50 % (**30**, pp. 89-91).

8.15.2 *Data Acquisition*—The following data acquisition parameters shall be used. Set up the necessary ^1H 1D pulse sequence with gradients as shown in Fig. 21.

8.15.2.1 Using a rectangular pulse profile, set the gradient strength to approximately half maximum and set the length to 1 ms.

8.15.2.2 Set the transmitter power and the ^1H pulse to the values of the 90° pulse determined for the probe.

8.15.2.3 Set up the following parameters for data acquisition:

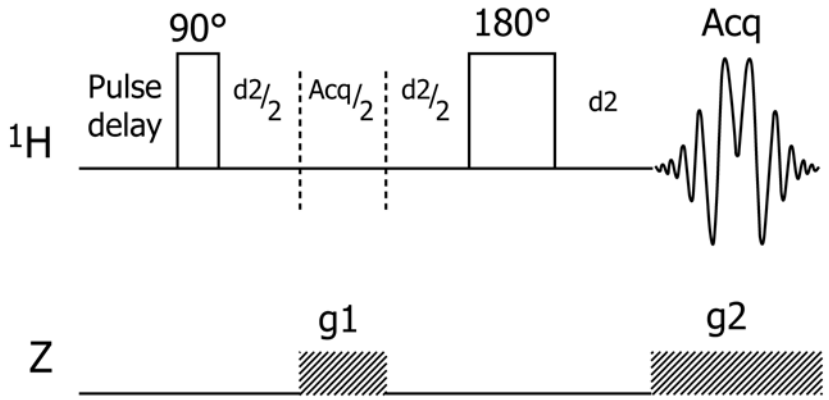

FIG. 19 Gradient Profile Pulse Sequence; Acq = Acquisition Time, d2 = Second Fixed Delay Time, Z = Gradient Channel, g1 = First Gradient Duration, and g2 = Second Gradient Duration (2 × g1)

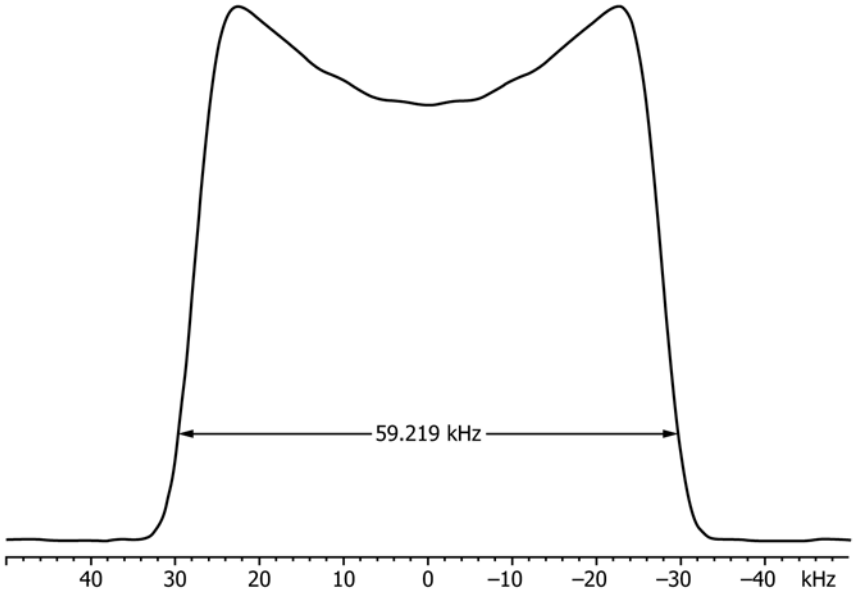

FIG. 20 399.8-MHz Pulsed Field Gradient Profile Spectrum; Width Measurement is at 20 % of the Maximum Height

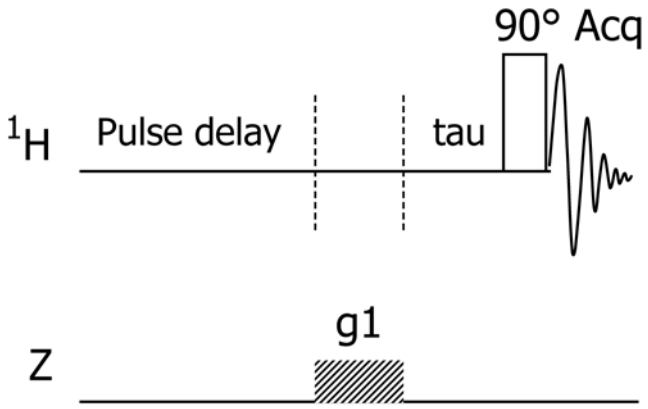

FIG. 21 Gradient Recovery Pulse Sequence; Acq = Acquisition Time, tau = Variable Recovery Delay Time, Z = Gradient Channel, and g1 = Gradient Duration

(1) Spectral Width—5000 Hz.

(2) Acquisition Time—2 s.

(3) Pulse Delay—2 s.

(4) g— ≈1 ms.

8.15.2.4 Set up a series of eight or more gradient recovery experiments with gradient recovery times (tau) spanning the appropriate recovery value specified by the manufacturer for the probe being tested (50 to 500 µs for gradient recovery is typical). A tau span from ≈20 to ≈500 % of the manufacturer's value should be used. Ensure that one of the tau values is the manufacturer's specified value for the probe and that the longest of the tau values is approximately 1 s.

8.15.2.5 Acquire the set of spectra.

8.15.3 *Data Processing*—The following data processing steps shall be used:

8.15.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 10 Hz and t = time value for each acquired data point.

8.15.3.2 Zero fill to at least twice the size of the data table. Calculate the FT.

8.15.3.3 Properly phase each spectrum and apply first-order baseline correction to produce a flat baseline on either side of the broad peak.

8.15.3.4 Adjust the vertical scale of each spectrum to the same value used for the spectrum with the 1-s tau delay (Fig. 22).

8.15.4 *Gradient Recovery Calculations and Reporting:*

8.15.4.1 Examine the series of spectra comparing the maximum intensity of the peak versus the tau value. A simultaneous display of all the spectra should show a smooth recovery pattern from the shortest to longest delay. The maximum intensity values should asymptotically approach the full gradient recovery value. Irregularities in the curve of the maximum intensity values indicate possible instrument malfunctions.

8.15.4.2 Determine the maximum peak intensity from the spectrum from the 1-s tau delay, I_1.

8.15.4.3 Without adjusting the vertical scale, determine the maximum peak intensity from spectrum at the tau delay specified by the probe manufacturer, I_m.

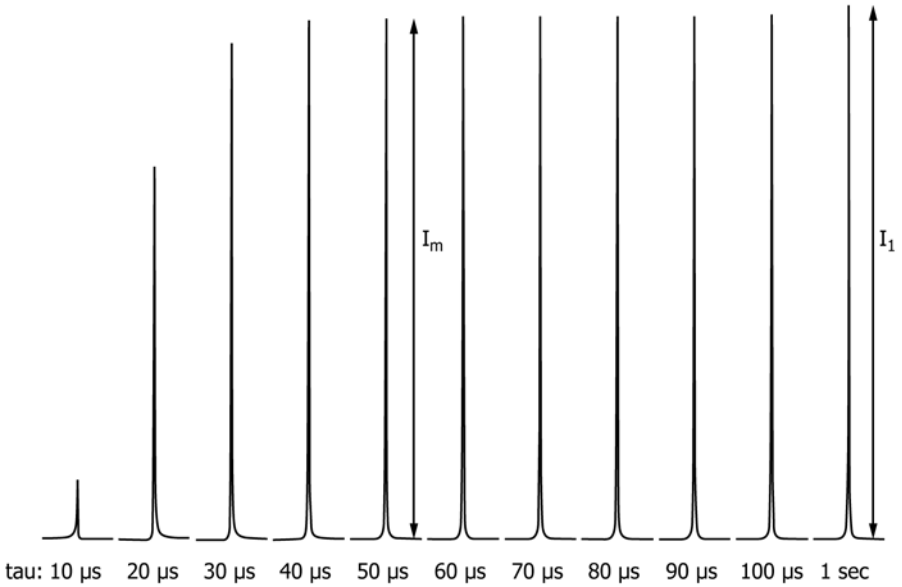

FIG. 22 399.8-MHz Gradient Recovery Spectra Set; I_m = Peak Height at the Probe Manufacturer's Specified Recovery Time, and I_1 = Peak Height at 1-s Recovery Time

8.15.4.4 The recovery ratio, I_m/I_1, should be compared with the manufacturer's specification and be consistent over time.

8.16 *Probe Temperature*—The purpose of this practice is to calibrate the probe temperature control. For best results, the measurements of analytical samples should be made as nearly as possible under the same conditions as the calibration measurements. Even so, the accuracy of the temperature measurements will be affected by differences in the following: the viscosity of the samples, heights of the sample column in the tube, wall thickness of the tube, variations in gas flow rate, and differences between the actual analytical temperature and the calibration temperatures. (Convection in the sample may become a greater issue at higher temperatures. Differences in the rf and gradient duty cycles combined with differences in dielectric constant between the analytical and calibration samples can result in temperature deviations.) The precision and accuracy of measurements on NMR thermometer test samples will only transfer to measurements on experimental samples if all of the above conditions are similar for both samples. Because of the physical properties of the sample materials, it is important to choose the sample appropriate to the temperature range being measured.

8.16.1 *Samples*—Three different samples may be used to cover differing conditions and temperature ranges. These samples are all very hygroscopic, and water content will affect the measurement accuracy.

8.16.1.1 *Sample 1*—Methanol optionally containing up to 3 % dimethyl sulfoxide-d_6 for locking (see Note 7). The dimethyl sulfoxide-d_6 should be at least 99 % atom D. Ensure that the dimethyl sulfoxide-d_6 does not freeze out at low temperatures (dimethyl sulfoxide-d_6 mp = 18°C). The methanol should be greater than 99 % pure. The measurement is made using the methyl and hydroxyl signals.

NOTE 7—Addition of 3 % dimethyl sulfoxide-d_6 has been shown not to affect the chemical shift difference significantly in Ref **35**.

8.16.1.2 *Sample 2*—Methanol-d_4 that should be 99 % pure and 99.96 % atom D. The measurement is made using the residual CD_2H and OH signals in the perdeuterated methanol. The relative line widths of these two signals are indicative of temperature homogeneity. With good temperature homogeneity, the line widths of the CD_2H and OH signals should be similar.

8.16.1.3 *Sample 3*—Ethylene glycol optionally containing up to 3 % dimethyl sulfoxide-d_6 for locking (see Note 7). The dimethyl sulfoxide-d_6 should be at least 99 % atom D. The ethylene glycol should be anhydrous and greater than 99 % pure. The measurement is made using the methylene and hydroxyl signals.

8.16.2 *Data Acquisition*—To achieve the best sensitivity results, the following shall be completed before the measurement:

8.16.2.1 The sample temperature shall be stabilized and controlled during the measurement. The flow of the regulated gas may have to be increased to achieve the desired temperature regulation. The height of the sample will affect the accuracy of temperature measurements because of thermal convection in the sample.

8.16.2.2 For methanol-d_4 and D_2O, the rf circuitry should be well tuned and matched to the sample to be used. For methanol and ethylene glycol, the probe shall be detuned until signal broadening from radiation damping is removed.

8.16.2.3 Use the following parameters:

(1) Spectral Region—Sufficient to observe the signals of interest (for example, 2 to 8 ppm).

(2) Pulse Flip Angle—Less than or equal to 90°.

(3) Data Acquisition Time—At least 4 s.

(4) Number of Transients—One.

(5) Receiver Gain—Optimized to take advantage of the full dynamic range of the receiver.

(6) Spinning Rate—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

8.16.3 *Data Processing*—The following data processing parameters shall be used:

8.16.3.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where LB (also known as width) = 3.0 Hz and t = time value for each acquired data point to remove any peak multiplicity and facilitate the determination of the peak centroids.

8.16.3.2 Zero fill to at least twice the size of the data table. Calculate the FT. Apply phase corrections as needed to produce the pure absorption mode spectrum. Apply zero- and first-order baseline corrections as needed (Figs. 23-25).

8.16.4 *Temperature Calculation:*

8.16.4.1 Measure the chemical shift of the highest point of the two specified signals. If the signal is a quartet (methanol hydroxyl signal at low temperature), then use the average chemical shift between the two inner peaks.

8.16.4.2 Insert the chemical shift difference (Δδ) into the appropriate equation given in 8.16.4.3, 8.16.4.4, or 8.16.4.5 to obtain the temperature (θ in Celsius).

8.16.4.3 *Calculation for Sample 1*—For methanol, the equation is $\theta = -21.85(\Delta\delta)^2 - 36.546\Delta\delta + 135.85$ over the range −95 to 57°C. This equation is given by Ref **36** (see Note 8) that refined previous methodology **(37-40)** and reported a fit to the equation of ±0.2°C.

NOTE 8—The Kelvin values versus Hertz at 60 MHz given in this reference have been converted to Celsius values versus parts per million herein.

8.16.4.4 *Calculation for Sample 2*—For methanol-d_4, the equation is $\theta = -16.7467(\Delta\delta)^2 - 52.513\Delta\delta + 145.9881$ over the range 7 to 54°C with an accuracy of 0.17°C **(41)** (see Note 9). Below this temperature range, the equation is $\theta = -24.436(\Delta\delta)^2 - 26.94\Delta\delta + 125.55$ in the range −88 to 7°C with a fit to the equation of ±0.69°C **(42)** (see Note 10). There is a discontinuity in this function at 7°C that is within experimental error. A continuous function covering the whole temperature range can be devised with a fit to the equation of ±0.7°C: $\theta = -22.885(\Delta\delta)^2 - 33.165\Delta\delta + 131.397$.[5]

NOTE 9—The Kelvin values given in this reference have been converted to Celsius herein.

NOTE 10—The Kelvin values versus Hertz at 200 MHz given in this reference have been converted to Celsius values versus parts per million herein.

8.16.4.5 *Calculation for Sample 3*—For ethylene glycol **(35)**, the equation is $\theta = -0.39(\Delta\delta)^2 - 100.91\Delta\delta + 192.62$ in the range 0 to 166°C. This is a fit to the equation of ±0.2°C below 143°C and ±0.5°C above this temperature. This equation is a combination of two previously published results **(36, 43)** that improves on previous methodology **(38, 44, 45)**.

8.16.5 *Reporting the Temperature:*

8.16.5.1 Measure the temperature as above three to ten times with no intervening adjustments to ensure that the temperature has reached thermal equilibrium and the results are reliable.

8.16.5.2 Report the average value of the chemical shift difference and the calculated temperature along with their standard deviations.

8.16.6 *Measurement Precision and Accuracy*—With the exception of Ref **41**, the body of literature concerning the temperature measurement procedures described above primarily states how well the experimental measurements fit the equations and how well temperature calculations agree with thermal measurements made using other temperature sensors (thermocouples, platinum resistance devices, and so forth). The information presented in this literature is not sufficient to determine the accuracy or uncertainty of these NMR thermometer measurements. The precision of such measurements, ascertained from repetitive determinations, can be used along with the statements about the goodness of the fit to the equation to address the quality of relative temperature determinations.

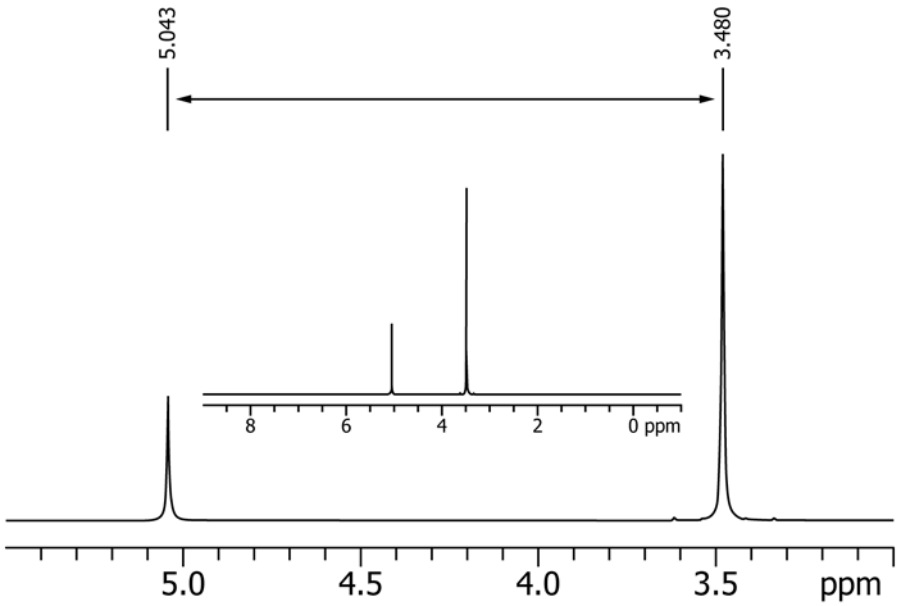

FIG. 23 NMR Thermometer—500.2-MHz ^{1}H Spectrum of Neat Methanol at 25.3°C

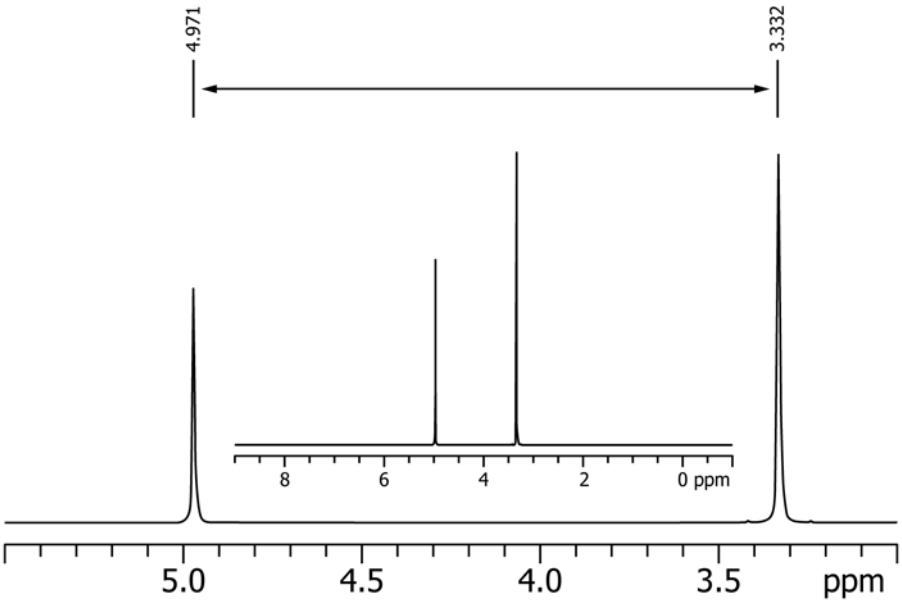

FIG. 24 NMR Thermometer—800.2-MHz ^{1}H Spectrum of the Residual Solvent Signals in Methanol-d_4 at 14.9°C

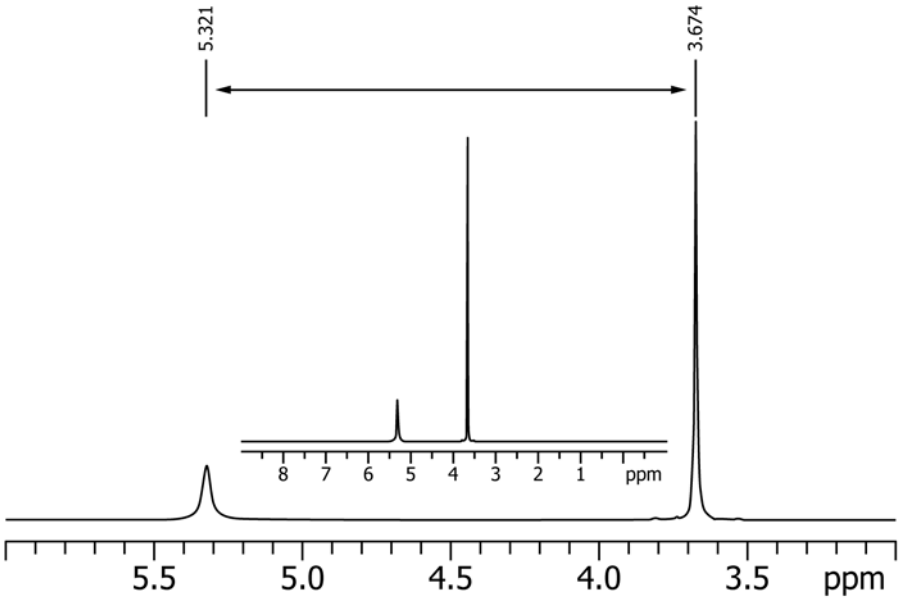

FIG. 25 NMR Thermometer—Unlocked 500.2-MHz ^{1}H Spectrum of Neat Ethylene Glycol at 25.4°C

However, without independent means for assessing uncertainty or accuracy, caution shall be used in applying NMR-thermometer-based temperatures in which absolute temperature values are required.

9. Keywords

9.1 Fourier transform NMR; FT-NMR; gradient test; line shape test; NMR spectrometer; NMR standard; NMR test sample; performance test; probe temperature measurement; resolution test; sensitivity test

APPENDIX

(Nonmandatory Information)

X1. GUIDELINES FOR X-NUCLEUS NMR SENSITIVITY STANDARDS

X1.1 *Purpose of these Guidelines*—This appendix proposes guidelines for developing physical standards and practices for determining NMR spectrometer sensitivity for nuclei not covered by existing ASTM International sensitivity physical standards and practices.

X1.1.1 While the prime purpose of these standards is to determine sensitivity, the results are inevitably affected by field homogeneity, temperature stability, and, if decoupling is used, decoupling efficiency. While some steps can be taken to minimize this, it is considered undesirable to take extreme steps to eliminate such effects when they also affect typical spectra of these nuclei. As such, inhomogeneity, temperature variation, and, if decoupling is used, decoupling efficiency may be considered intrinsic to the effective sensitivity.

X1.1.2 Sensitivity measurements should be acquired without decoupling wherever there is sufficient signal intensity (X1.2.6).

X1.1.3 For sensitivity tests in which the S/N ratio is insufficient, signal averaging may be used. If multiple transients are collected, the resulting sensitivity value shall be adjusted as described in X1.6.8.

X1.1.4 Where ASTM International standard practices exist for a given nucleus, those recommendations take precedence over these guidelines. Where no ASTM International standards exist for determining the sensitivity for a nucleus, the following examples may be helpful. However, the examples herein are only illustrative and are neither ASTM International recommendations nor requirements.

X1.2 *Choice of Sample and Solvent*—The test sample and solvent should be chosen to approach the following properties as is reasonably possible. For many nuclei, it will not be possible to reach, even within orders of magnitude, the ideal values for some parameters. A standard lacking ideal properties (see Note X1.1) may still be a valid, useful standard.

NOTE X1.1—For example, many nuclei, such as ^{127}I, cannot approach the ideal T_1. The ^{127}I T_1 of 1 mol L^{-1} KI in D_2O at 400 MHz is 137 µs.

X1.2.1 Where there is a choice, select test sample compounds that are least hazardous.

NOTE X1.2—For example, in the case of ^{199}Hg, $HgCl_2$ in D_2O, while very poisonous, is much less dangerous than neat $(CH_3)_2Hg$.

X1.2.2 *Temperature:*

X1.2.2.1 The sample should be liquid in the range 20 to 30°C in almost all cases.

NOTE X1.3—This is not possible for ^{235}U in which UF_6 is the only compound reported and is liquid under pressure above 65°C. For ^{83}Kr, ^{129}Xe, and ^{131}Xe, gaseous samples may be used, but care shall be taken to measure their pressure to within 1 % for sensitivity measurements.

X1.2.2.2 The temperature range within which the sample can safely be stored without breakage as a result of pressures exerted by phase changes or chemical reactions should be determined and stated.

X1.2.2.3 The sample shall be able to withstand temperatures between 5 and 60°C without breaking the tube.

X1.2.3 *Stability:*

X1.2.3.1 The materials used should be tested for stability to heat and light to estimate shelf life and light sensitivity.

X1.2.3.2 Shelf life should be five years or more in the dark plus 500 h if exposed to 1000 lux of ambient light.

X1.2.3.3 NMR signals arising from degradation products should be identified so that they can be used to determine the extent of decomposition.

X1.2.3.4 The sample should not react with (see Note X1.4) or diffuse through (see Note X1.5) glass.

NOTE X1.4—Where possible, do not use HF or other solutions that dissolve glass. For example, one could use $TiCl_4$ as a titanium standard instead of $(TiF_6)^{2-}$ in a concentrated HF solution. Where there is no choice, such as for ^{235}U-NMR, where only UF_6 is available, use alternate tube materials, such as polychlorotrifluorethylene (PCTFE).

NOTE X1.5—Do not use gaseous hydrogen, helium, or neon as they diffuse through glass; hydrogen and helium diffuse out in a matter of weeks and neon diffuses out over a period of years. For ^{3}He and ^{21}Ne, consider using $^{3}He@C_{60}$ and $^{21}Ne@C_{60}$, respectively, instead. Do not use helium or neon as the inert gas to provide pressure over the liquid.

X1.2.3.5 Where there is a background NMR signal from the NMR tube or probe material, either the background signal should be sufficiently far from the sample signal (see Note X1.6) or a different tube/probe material should be used (see Note X1.7).

NOTE X1.6—For ^{29}Si, the signal of $[(CH_3)_3Si]_2O$ is sufficiently far from the signal of glass to prevent overlap. The contribution of the glass signal in the recommended noise region under the recommended acquisition conditions for a standard NMR tube/probe is less than 10^{-7} of that of the sample signal.

NOTE X1.7—For ^{10}B and ^{11}B, the NMR tube should not contain boron. Quartz NMR tubes are commonly used for this purpose.

X1.2.3.6 The stability of the sample is usually a function of the partial pressure of oxygen in the sample. This partial pressure can be determined, when it significantly affects the spin-lattice relaxation time (T_1), by measuring the relaxation time of a signal in the sample under high vacuum at a known pressure such as atmospheric pressure and then for the sealed sample using Eq X1.1.

$$P(O_2) = \frac{P_0(O_2)\left(\frac{1}{T_1(meas)} - \frac{1}{T_1(P_0)}\right)}{\frac{1}{T_1(P_0)} - \frac{1}{T_1(vacuum)}} \quad \text{(X1.1)}$$

where:

$P(O_2)$ = partial pressure of oxygen in the sample being tested,

$P_0(O_2)$ = partial pressure of oxygen in the sample measured at a known pressure,

$T_1(P_0)$ = longitudinal relaxation time at the known pressure,
$T_1(meas)$ = longitudinal relaxation time of the sample being tested, and
$T_1(vacuum)$ = longitudinal relaxation time of the sample under vacuum.

X1.2.4 Where possible, and to reduce the number of standard samples, the sample should be selected to be multipurpose, containing several nuclei.

NOTE X1.8—For example, KCl in D_2O can be used as a sensitivity standard for seven nuclei: ^{2}H, ^{17}O, ^{35}Cl, ^{37}Cl, ^{39}K, ^{40}K, and ^{41}K.

X1.2.5 If possible, the concentration of the standard should be adjusted so that the measured sensitivity is between 100:1 and 10 000:1 for all probes in commonly available instruments (200 MHz and above). However, this may not be practical for all nuclei.

X1.2.6 Some nuclei require inordinately long experiment times or prohibitively expensive isotopic enrichment, or both, to achieve a reasonable sensitivity. In such cases, it may be preferable to use decoupling or to carry out the sensitivity test on another nucleus with a similar frequency.

NOTE X1.9—For example, it may be possible to use ^{103}Rh instead of ^{57}Fe or ^{41}K instead of ^{187}Os.

X1.2.7 The X-nucleus spectrum should contain a well-isolated singlet or multiplet and a large empty region for noise measurement.

X1.2.7.1 The line shape of the reference signal should be characterized including coupling constants. Isotopic impurities and their coupling constants and isotope shifts should be characterized.

NOTE X1.10—For example, 86 % v/v hexamethyldisiloxane in benzene-d_6: $\delta(^{29}Si)$ 6.514 ppm, $^{2}J_{H,Si}$ 6.71 Hz (Fig. X1.1), $^{4}J_{H,Si}$ 0.04 Hz, $^{1}J_{C,Si}$ 59.62 Hz, $^{3}J_{C,Si}$ 0.3 Hz, $^{1}\Delta Si(^{13/12}C)$ 0.0026 ppm, $^{2}\Delta Si(^{29/28}Si)$ –0.0024 ppm, and $^{2}\Delta Si(^{30/28}Si)$ –0.0061 ppm (Fig. X1.2). 90 % v/v formamide in dimethyl sulfoxide-d_6: $\delta(^{15}N)$ 113.016 ppm, $^{1}J_{N,HA}$ 90.45 Hz, $^{1}J_{N,HB}$ 87.85 Hz, $^{2}J_{N,H}$ 14.26 Hz (Fig. X1.3), $^{1}J_{N,C}$ 14.19 Hz (Fig. X1.4), and $^{1}\Delta^{15}N(^{13/12}C)$ –0.0474 ppm. The coupling constants that may be unresolvable for other isotopes of the same element such as ^{14}N can be estimated using their frequency ratio, for example,

$$^{1}J_{^{14}N,H_A} \approx {}^{1}J_{^{15}N,H_A} \frac{\Xi_{^{14}N}}{\Xi_{^{15}N}} = 90.45\ \text{Hz} \times \frac{7.223561\%}{10.1329111\%} = 64.48\ \text{Hz} \quad \text{(X1.2)}$$

X1.2.7.2 The chemical shift should be known to locate the signal easily, and its temperature dependence known to assess the degree of temperature stabilization necessary (see Note X1.11). The standard should be chosen so that the temperature dependence of its chemical shift is not atypically large for that nucleus.

NOTE X1.11—For example, for 86 % v/v hexamethyldisiloxane in benzene-d_6, the temperature dependence of the ^{29}Si chemical shift near 25°C is –0.0041 ppm K^{-1}, and for 90 % v/v formamide in dimethyl sulfoxide-d_6, the temperature dependence of the ^{15}N chemical shift near 25°C is –0.027 ppm K^{-1}.

X1.2.7.3 To determine the effective line width, all the signals that are not separated by a trough less than 1 % of the largest signal without the application of a weighting function should be grouped. Measure the width at half height of the tallest signal grouping and fit it to a combined Gaussian/Lorentzian (pseudo-Voigtian) function (see Note X1.12). If a combined function is used, the Gaussian proportion shall be specified. If another fitting function is used, for example, true Voigtian, it shall be specified.

NOTE X1.12—For example, for 86 % v/v hexamethyldisiloxane in benzene-d_6 (Fig. X1.1), the ^{29}Si multiplet structure is a decuplet of 93 % Lorentzian, 7 % Gaussian lines of width 0.20 Hz, and for 90 % v/v formamide in dimethyl sulfoxide-d_6 (Fig. X1.3), the ^{15}N multiplet structure is a double-double-doublet of Lorentzians in which the outer four signals are significantly taller than the center four signals as a result of relaxation effects (see Note X1.13). The line widths at 500 MHz of the outer signals are 0.18 Hz and those of the inner four signals are 0.26 Hz.

NOTE X1.13—For example, the ^{15}N multiplet of 90 % v/v formamide in dimethyl sulfoxide-d_6 (Fig. X1.3) is a double-double-doublet. The outer

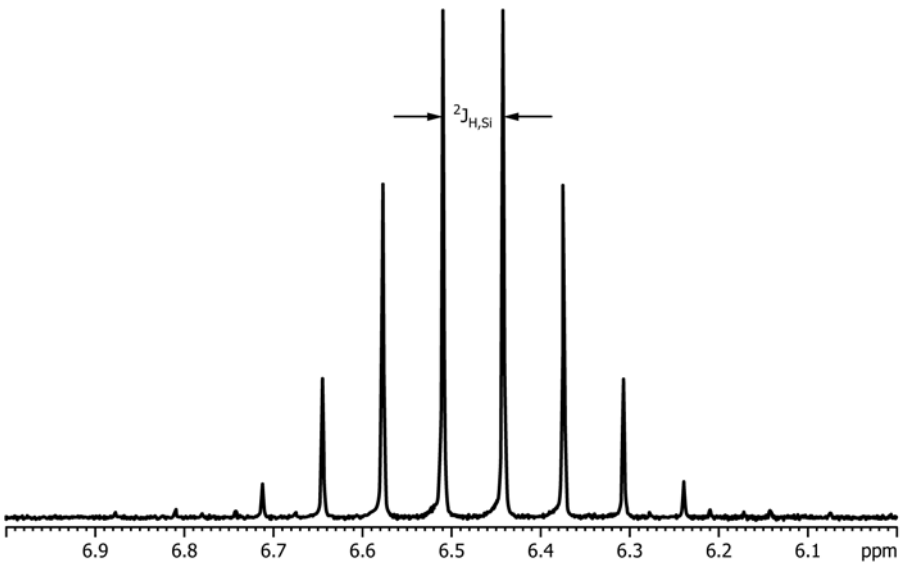

FIG. X1.1 Fully Coupled 99.4-MHz ^{29}Si Spectrum of 86 % Hexamethyldisiloxane in Benzene-d_6 Showing a Decuplet as a Result of Two-Bond ^{1}H to ^{29}Si Coupling and Slight Broadening of the Individual Signals Arising from Four-Bond Coupling; the Remaining Small Signals are a Result of ^{13}C Satellites

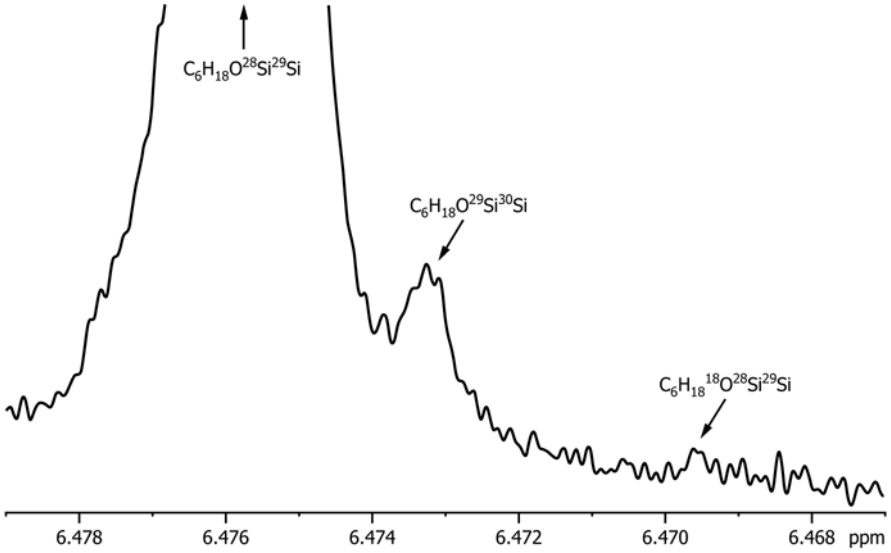

FIG. X1.2 Proton Decoupled 99.4-MHz ^{29}Si Spectrum of 86 % Hexamethyldisiloxane Showing Minor Isotopomers ($C_6H_{18}O^{29}Si_2$ is Too Close to the Main Signal to be Resolved)

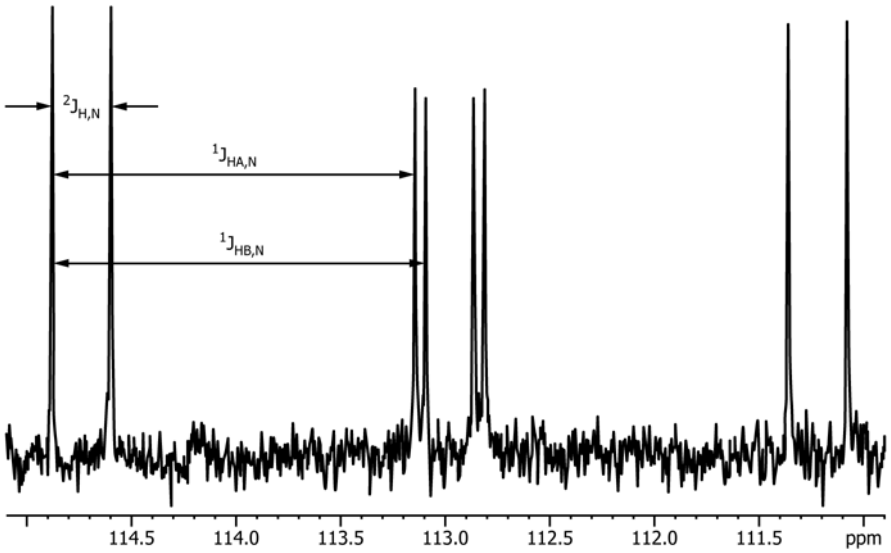

FIG. X1.3 Fully Coupled 50.7-MHz ^{15}N Spectrum of 90 % Formamide in Dimethyl Sulfoxide-d_6 Showing the Outer Four Signals Taller than the Inner Four as a Result of Relaxation Effects and Two Different One-Bond Coupling Constants Caused by Restricted Rotation about the Carbon-Nitrogen Bond

four signals have a significantly longer T_1 than the inner four: 15.3 and 13.9 s, respectively, at 500 MHz.

X1.2.7.4 The time-domain-weighting (window) function should be set (as described in the following) to achieve the effective line width, *w*. Display the spectrum without any line broadening and measure the observed line width at the half height of the peak. If the observed line width is less than Ξ(%)/50 Hz, then the broadening should be increased to approximately (Ξ(%)/50) − *w* Hz (see Note X1.14). If the line is very broad then, it may be necessary to reduce the width resulting from time-domain weighting, as described in X1.2.7.6.

NOTE X1.14—The sensitivity test is affected by field homogeneity. If the broadening factor is set too low, then field homogeneity becomes the overriding factor. The value, Ξ (%), is defined as the frequency of the signal divided by the ^{1}H resonance frequency of dilute TMS dissolved in the sample. If TMS is unstable in the sample, then Ξ(%) can be measured to within 3 ppm by exchange with a sample of dilute TMS in chloroform-*d*.

X1.2.7.5 Set the transmitter frequency such that the sensitivity reference is in the center of the spectral width. Ensure that there is a signal-free region toward lower frequency from the reference, starting near the center half of the spectrum (but far enough away that any included NMR signals contribute less

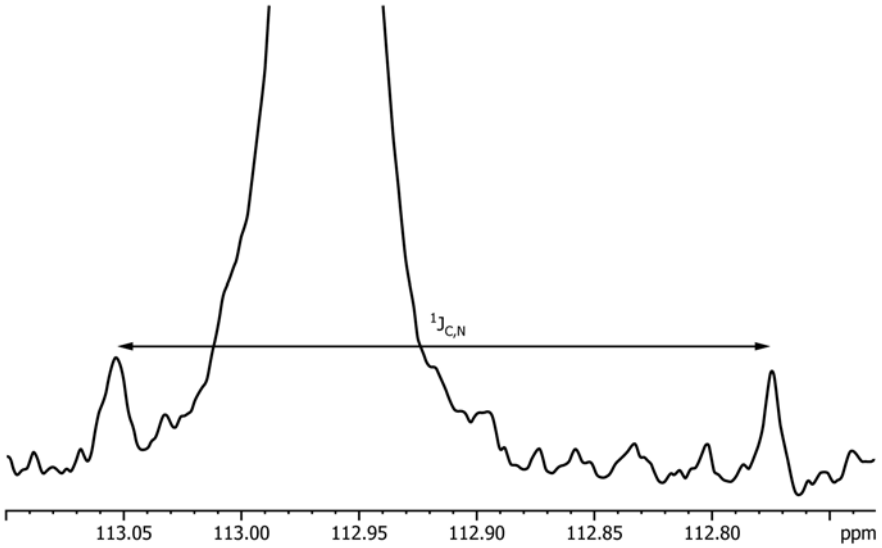

FIG. X1.4 Proton Decoupled 50.7-MHz ^{15}N Spectrum of 90 % Formamide Showing ^{13}C Satellites

than 1 % to the noise) and (for 3 % accuracy) continuing for 1000 times the apodization function broadening. The frequency difference between the reference peak and the beginning of the noise region for a pure Lorentzian signal shall be at least

$$\frac{w \times \sqrt{100 \times S/N \; - 1}}{2} \tag{X1.3}$$

where:

w = width at half height of a reference signal component plus the broadening, and
S/N = signal-to-noise ratio.

(1) For a mixed Lorentzian/Gaussian signal, the frequency difference between the reference peak and the beginning of the noise region will be smaller and can be found by solving the following nonlinear equation for x where k = proportion of Gaussian character:

$$\frac{1}{100 \times S/N}\left(\frac{1-k}{\pi} + k\sqrt{\frac{4\ln(2)}{\pi}}\right) = \frac{1-k}{\pi\left(1 + \frac{4x^2}{w^2}\right)} + k\sqrt{\frac{4\ln(2)}{\pi}}\exp\left(-\frac{4\ln(2)x^2}{w^2}\right) \tag{X1.4}$$

X1.2.7.6 Where these criteria cannot be met, the apodization broadening may be reduced or the noise region restricted, or both. However, the accuracy of the noise measurement will be reduced to 1/√(width of noise region divided by the apodization function broadening) (see Note X1.15). Because of hardware limitations of some spectrometers, it will not be possible to measure or test some nuclei reliably. The value, T_1, should be between 10 and 100 s, but this may not always be possible as stated in X1.2.

NOTE X1.15—For example, the ^{127}I resonance of KI (0.01 mol L^{-1}) in D_2O at 400 MHz has a line width of 1.9 kHz. If the S/N ratio is 1000:1, then the start of the noise measurement $\{w\sqrt{[100 \times (S/N - 1)]}\}/2$ where w = 1.9 kHz + 1.9 kHz broadening = 3.8 kHz) away from the resonance would be 601 kHz to lower frequency and should continue for 1.9 MHz while remaining in the center half of the spectrum. This would require a 10-MHz spectral width. If the spectrometer is only capable of a 4-MHz spectral width, then one could reduce the line broadening to 600 Hz and use a 600-kHz noise region starting 400 kHz to lower frequency of the signal.

X1.2.7.7 The T_1 relaxation time of the nucleus in the sample used should be measured under vacuum and air at a known pressure over the range of magnetic fields for which it is to be used.

X1.2.7.8 The T_1 of the actual sample used shall be measured to determine the relaxation delay (recycle time) required for the sensitivity measurement.

X1.2.7.9 Note that if the signal is a multiplet, different lines may have different T_1s, although they are only likely to differ by a few percent (see Note X1.13). The T_1 of each line in the coupled multiplet should be measured, and the longest one used for calculating the relaxation delay, even if the spectrum is to be decoupled.

X1.3 *Sample Preparation*:

X1.3.1 Each sample shall be identifiable, and a certificate containing information about the sample shall be available as described in 5.2.

X1.3.1.1 Additional information should include: contents of the sample and their concentrations including isotopic abundances, safety data sheets for the sample materials, approximate T_1 of the reference signal, partial pressure of oxygen if this significantly affects the T_1, shelf life in the dark and when exposed to light, spectral parameters of the sample, and degradation product spectral parameters. The purity (both chemical and isotope) of the sample materials should be selected to allow the desired measurement accuracy to be achieved.

X1.3.1.2 For sensitivity measurements, the inner diameter (id) of the sample container shall be stated along with tolerances from the manufacturer as described in 5.3.1.

X1.3.1.3 Sample concentrations are defined as described in 5.4. The isotopic abundance of the nuclei to be measured, and those that couple to it should be known so that the concentration of the relevant isotopomer(s) (see Note X1.16) is/are

known to within 1 %. Because the relative natural abundances of many nuclei may naturally vary by more than 1 %, the isotope ratios should be determined (see Note X1.17). The deuteration ratio of the solvent should meet a minimum standard as defined in 5.4.2.

NOTE X1.16—For example, the relevant isotopomer of $[(CH_3)_3Si]_2O$ for ^{29}Si sensitivity is $^{12}C_6{}^1H_{18}{}^{16}O^{28}Si^{29}Si$ (Fig. X1.2).

NOTE X1.17—For example, a commercial sample of hexamethyldisiloxane was found to have the isotope distribution in Table X1.1.

X1.3.1.4 Whether a w/w method or a v/v method is used for sample preparation, care shall be taken to assure better than 1 % accuracy in the measurements. Any impurities in the final sample (including water) shall be in accordance with 5.4 and 5.5. The combined error in concentration and isotopic abundance(s) of the relevant isotopomer(s) should not exceed 1 %. The final concentration and isotopic abundance and their uncertainties shall be stated.

X1.3.1.5 For routine use (but not for specification purposes), a relaxation agent, such as 0.2 % $Cr(acac)_3$, may be added to the sample to permit more rapid data acquisition provided that it does not significantly reduce the sample shelf life or change the line width of the resonance in question.

X1.3.1.6 The sample should be sealed to prevent evaporation. The sample should be sealed under nitrogen or argon if the relaxation times of the nuclei are greater (see Note X1.18) than 0.2 s or if oxygen may react (see Note X1.19) with the sample. Where the sample has a short relaxation time and is stable to air (see Note X1.20), it may be sealed under air. Where possible, the sample should be prepared so that the pressure in the tube is near atmospheric.

NOTE X1.18—For example, the ^6Li T_1 of ^6LiCl (1 mol L^{-1}) in D_2O at 500 MHz is approximately 150 s. Although there is no suspicion that it will react with atmospheric oxygen, its relaxation time will be reduced and its signal broadened by the presence of oxygen; therefore, such a sample should be sealed under nitrogen or argon.

NOTE X1.19—For example, if $TiCl_4$ is used a standard for ^{49}Ti sensitivity, its T_1 is 0.2 s at 400 MHz, too short for oxygen to affect significantly its T_1. However, it reacts vigorously with airborne humidity and shall be sealed under an inert atmosphere.

NOTE X1.20—For example, NaCl in D_2O (which may be used as a sensitivity standard for ^{35}Cl, ^{37}Cl, and ^{23}Na) is stable in air and the longest T_1 for these nuclei at 400 MHz is that of ^{23}Na, which is 0.1 s.

X1.3.1.7 For long-term storage, the samples should be maintained as described in 5.5.3.

X1.4 *Data Acquisition*:

X1.4.1 *Preliminary Experimental Procedures*—The experimental procedures described in Section 6 should be carried out before any measurements.

TABLE X1.1 Isotope Distribution of Commercial Sample of Hexamethyldisiloxane

Isotope	Measured Abundance	"Natural" Abundance	Variation
^{12}C	99.05 %	98.89 %	
^{13}C	0.95 %	1.11 %	−146 ‰
^{28}Si	93.62 %	92.23 %	
^{29}Si	4.48 %	4.67 %	−55 ‰
^{30}Si	2.90 %	3.10 %	−78 ‰

X1.4.1.1 Where ideal homogeneity is not achievable, homogeneity should be adjusted as well as possible. The contribution of inhomogeneity to the effective line width plus line broadening should be less than 1 %. The contribution of inhomogeneity to the signal height at a distance of five times the sum of the effective line width and line broadening should be less than 1 % of the main signal height. There should be no major splittings or humps arising from inhomogeneity.

X1.4.2 *Data Acquisition Parameters*—For a standard acquisition, the following parameters should be used:

X1.4.2.1 *Spectral Region*—In accordance with X1.2.7.5 and X1.2.7.6, the transmitter frequency should be set on the main signal resonance or should be within $1/16\pi t$ Hz of the resonance, where t = pulse duration in seconds, to maintain 99 % of the signal. If decoupling is used, the decoupling parameters, such as peak power in Hertz, mean power levels in Hertz, and decoupling modulation pattern, shall be specified.

X1.4.2.2 *Equilibration Delay*—At least five times the (longest if a multiplet) T_1 relaxation time reduced by the acquisition time. If NOE effects on signal intensities are to be eliminated by using no decoupling during the equilibration delay, the relaxation delay should be $[\ln(1 - NOE) + 5]\ T_1$ and should not be reduced by the acquisition time; the use of decoupling during any part of the pulse sequence shall be fully specified.

X1.4.2.3 The preacquisition delay for dead time should be set so that the S/N ratio is maximized. If acoustic ringing distortion is present, the test may be carried out with acoustic ringing suppression (**29, 30**, pp. 235-236). If acoustic ringing suppression is used, the associated pulse sequence shall be specified.

X1.4.2.4 *Pulse Flip Angle*—90°.

X1.4.2.5 *Data Acquisition Time*—At least 1.5 ÷ line-broadening as defined in X1.5.1.

X1.4.2.6 *Number of Transients*—At least that required to achieve a S/N ratio of 100:1.

X1.4.2.7 *Receiver Gain*—Optimized to take advantage of the full dynamic range of the receiver.

X1.4.2.8 *Spinning Rate*—The measurement should be specified as spinning or nonspinning. If the sample is spinning, its rate shall be specified.

X1.5 *Data Processing*:

X1.5.1 Multiply the time domain data by an exponentially decaying function of the form $e^{-LB \cdot t \cdot \pi}$ where line-broadening (LB, also known as width, in Hertz) is set to the effective line width of the signal (see X1.2.7.4) or less (see X1.2.7.6) but not less than 0.3 Hz, and t in seconds is the time value for each acquired data point.

X1.5.2 Zero fill to at least twice the size of the data table, and calculate the Fourier transform. Apply phase corrections as needed to produce the pure absorption mode spectrum.

X1.5.3 No data smoothing or other types of data manipulation may be applied except as specified in X1.5.1.

X1.6 *S/N Ratio Calculation*:

X1.6.1 The calculations for S/N ratio are carried out on the real part of the pure phase absorption mode spectrum.

X1.6.2 Signal is defined as the amplitude of the tallest resonance measured from the zero-intensity line determined by the baseline correction. Zero- and first-order baseline corrections should be applied to a region of 50 times the sum of the effective line width and line broadening around the signal. This may not necessarily be the resonance nearest the center of the multiplet (see Note X1.21). Where there is more than one maximum signal of theoretically equal height, the mean of the maximum signal heights should be used.

NOTE X1.21—For example, for the ^{15}N multiplet of 90 % v/v formamide in dimethyl sulfoxide-d_6 (Fig. X1.3), the outer four signals are significantly taller than the center four signals as a result of relaxation effects (see Note X1.13); consequently, the outer four signals should be used for sensitivity measurement.

X1.6.3 Noise is defined as two times the rms noise in the region defined in X1.2.7.5. Zero- and first-order baseline corrections should be applied to the noise region.

X1.6.4 To calculate rms noise, the amplitude of each point measured from the zero-intensity line in the region defined in X1.2.7.5 is squared. The squared values are summed, then divided by one less than the number of data points in the region. The square root of this result yields the rms noise using Eq 2.

X1.6.5 S/N = signal ÷ (2 × rms noise).

X1.6.6 Where the natural abundance of the measured isotope is low or where enrichment of the measured isotope is suspected, it may be important to correct the S/N for the actual abundance of the measured isotope in the sample itself by multiplying the raw S/N by the ratio of the average natural abundance of the isotope **(21)** to its measured abundance.

X1.6.7 Any alteration of data points or use of alternative regions for the rms noise calculation is not compliant with this recommendation.

X1.6.8 *Signal Averaging*—If signal averaging is used, the measured sensitivity value shall be adjusted by dividing by the square root of the number of transients.

X1.7 *Reporting Sensitivity*:

X1.7.1 Sensitivity measurement results are reported as described in Section 7.

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