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FURTHER CONVENTIONS FOR NMR SHIELDING AND CHEMICAL SHIFTS

(IUPAC Recommendations 2008)

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Further conventions for NMR shielding and chemical shifts

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Abstract: IUPAC has published a number of recommendations regarding the reporting of nuclear magnetic resonance (NMR) data, especially chemical shifts. The most recent publication [*Pure Appl. Chem.* **73**, 1795 (2001)] recommended that tetramethylsilane (TMS) serve as a universal reference for reporting the shifts of all nuclides, but it deferred recommendations for several aspects of this subject. This document first examines the extent to which the ^{1}H shielding in TMS itself is subject to change by variation in temperature, concentration, and solvent. On the basis of recently published results, it has been established that the shielding of TMS in solution [along with that of sodium-3-(trimethylsilyl)propanesulfonate, DSS, often used as a reference for aqueous solutions] varies only slightly with temperature but is subject to solvent perturbations of a few tenths of a part per million (ppm). Recommendations are given for reporting chemical shifts under most routine experimental conditions and for quantifying effects of temperature and solvent variation, including the use of magnetic susceptibility corrections and of magic-angle spinning (MAS).

This document provides the first IUPAC recommendations for referencing and reporting chemical shifts in solids, based on high-resolution MAS studies. Procedures are given for relating ^{13}C NMR chemical shifts in solids to the scales used for high-resolution studies in the liquid phase. The notation and terminology used for describing chemical shift and shielding tensors in solids are reviewed in some detail, and recommendations are given for best practice.

Keywords: nuclear magnetic resonance; recommendations; chemical shifts; conventions; IUPAC Physical and Biophysical Chemistry Division; shielding tensors.

CONTENTS

1. INTRODUCTION*

IUPAC has published a number of recommendations for handling data relating to nuclear magnetic resonance (NMR) [1–4]. The most recent recommendations in 2001 [4] focused particularly on conventions for reporting chemical shifts. These recommendations included a minor redefinition of the chemical shift δ for a nuclide X:

$$\delta_{\text{sample}}(X) = [\nu_{\text{sample}}(X) - \nu_{\text{reference}}(X)]/\nu_{\text{reference}}(X) \tag{1}$$

Equation 1 differs from previous definitions in deleting a factor of 10^6, for reasons explained in ref. [4]. Because the numerator is normally expressed in Hz whereas the denominator is given in MHz, this formulation leads to values readily expressed in ppm. The suffix "ppm" is interchangeable with "$\times 10^{-6}$" in equations, just as "%" is interchangeable with "$\times 0.01$". The signs that can be attached to Larmor frequencies are ignored herein.

Also recommended [4] was a unified scale for reporting chemical shifts of any nuclide X (other than ^{1}H) in any sample relative to a primary internal reference, viz. the proton resonance of tetramethylsilane (TMS)** in a dilute solution in $CDCl_3$ (volume fraction $\varphi < 1\,\%$). To relate data on the unified scale to chemical shifts expressed relative to a secondary reference of the same nuclide X, a quantity $\varXi$ (Greek capital Xi) was defined as the ratio of the secondary (isotope-specific) frequency, $\nu^{\text{obs}}(X)$, to that for ^{1}H of TMS in $CDCl_3$, $\nu^{\text{obs}}_{\text{TMS}}$, in the *same* magnetic field:

$$\varXi = \nu^{\text{obs}}_{\text{sample}}(X)/\nu^{\text{obs}}_{\text{TMS}} \tag{2}$$

As pointed out in ref. [4], $\varXi$ can conveniently be expressed as a percentage. The tables of $\varXi$, reported therein, for the secondary references of all nonradioactive (together with a few radioactive) but NMR-active nuclides, are condensed to a convenient form for reference in Appendix 1.

The document [4] discussed the use of three techniques for referencing chemical shifts: (a) internal reference; (b) external reference; and (c) substitution method, with the field locked on an internal deuterium resonance for both sample and reference measurements. Methods a and c were recommended, where feasible, because they avoid the magnetic susceptibility artifact introduced by method b. An alternative substitution method, with no field-frequency lock (or an external lock) was not discussed there but will be covered in this document primarily because it is commonly used for solids.

The 2001 recommendations document set aside temporarily a number of more specialized (but nevertheless important) areas for later discussion. As a result, an IUPAC task group has now addressed several matters, as follows:

- temperature dependence of the ^{1}H chemical shift of TMS
- shape factor for making magnetic susceptibility corrections when an external reference must be used and samples cannot be considered as infinite cylinders
- solvent dependence of the ^{1}H chemical shift of TMS
- alternative scenarios for referencing (with relevant $\varXi$ values) for certain nuclides, including ^{15}N
- aspects of MAS for both liquids and solids
- procedures for chemical shift referencing in solid samples
- terminology for reporting chemical shift/shielding tensors

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*Abbreviations used: TMS, tetramethylsilane; DSS, sodium-3-(trimethylsilyl)propanesulfonate — commonly called sodium-2,2-dimethyl-2-silapentane-5-sulfonate, sodium salt; TSP, sodium-3-(trimethylsilyl)propionate; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; NMR, nuclear magnetic resonance; MAS, magic-angle spinning; ZAS, zero-angle spinning; PAS, principal axis system; SA, shielding anisotropy; CSA, chemical shift anisotropy; cgs, centimeter gram second system of units.
**To be more precise, the dominant proton resonance line from $^{12}C_4{}^1H_{12}{}^{28}Si$. Resonances at slightly different chemical shifts can be observed from other isotopomers (usually as ^{13}C and ^{29}Si "satellites").

Each of these subjects is considered in this document, along with related comments and relevant recommendations for future practice. Section 2 discusses general concepts, whereas Sections 3–8 relate mostly to solutions. Sections 9 and 10 refer mostly to solids.

2. GENERAL ASPECTS OF CHEMICAL SHIFTS

The definition of chemical shift (symbol δ), as expressed in eq. 1, is based on observation, not theory; that is, δ describes a *measured* value for the nuclide. The value of δ obtained by applying eq. 1 to a particular nuclide in a given chemical compound can vary substantially, depending on the conditions used for measuring the sample and reference frequencies. The basic requirement for a valid measurement is that the resonance frequencies for sample and reference be obtained under precisely the same value of the magnetic induction, B_0. In some experimental measurements, as described below, B_0 (sample) $\neq B_0$ (reference) as a result of bulk (isotropic) magnetic susceptibility (BMS) effects, which give rise to demagnetizing fields [5]. In these circumstances, it is essential to apply a suitable correction, as described in Section 5, and it is appropriate to designate a "corrected" or "true" chemical shift to distinguish it from the "apparent" or observed value obtained by rote application of eq. 1 when an external referencing procedure is employed.

At the theoretical level, the shielding σ that is the basis for the chemical shift is known to depend on complex intramolecular factors and, except for gases at very low pressure, on many intermolecular factors as well. It is, therefore, important to record any experimental conditions (e.g., solvent, temperature, concentration, pressure) that are thought to be significant for the particular investigation and to recognize that the value of δ may vary as these parameters are changed. However, it is generally *not* desirable to speak of "correcting" a chemical shift that has been properly measured under a particular set of conditions or of converting that value to a "true" chemical shift (except as mentioned above for BMS effects). Provided the measurements are made as described in the preceding paragraph, no measured chemical shift is more "correct" than another.

Nevertheless, it is often highly desirable to compare chemical shifts (even for the same resonance) obtained under different experimental conditions. To make such comparisons or to interpret variations in observed shifts in terms of possible molecular mechanisms, it is important to know whether and how the resonance frequency of a reference, especially that of the universal reference TMS, varies with change in parameters such as temperature and solvent. Those subjects will be addressed in Sections 4–6.

3. REFERENCING

For *internal referencing* in isotropic liquids, the sample and reference compound are molecularly dispersed in a homogeneous liquid contained in a single sample tube (usually cylindrical), within which B_0 is constant (except for unavoidable gradients, which apply equally to sample and reference). Thus, the measured values of ν_{sample} and $\nu_{reference}$ can be used directly in eq. 1 to provide a chemical shift, albeit one that may be highly dependent on intermolecular effects[*].

For *external referencing*, the sample and reference substances are physically confined in separate containers within the same magnet gap, often in coaxial cylindrical tubes. If the applied magnetic field H_0 is sufficiently homogeneous (as is normally true), both sample and reference experience the same external field. However, the magnetic induction field (B_0) within each substance depends on its bulk volume magnetic susceptibility, κ_{sample} and $\kappa_{reference}$, which are normally not identical, and the effect of average shape factors $\bar{\alpha}_{sample}$ and $\bar{\alpha}_{reference}$, which are normally very similar. Hence, the measured

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*Care must be taken when dealing with situations involving hydrogen bonding or with ionic interactions in aqueous solutions (including those involving DSS or TSP as references) and when measuring stability constants by means of NMR.

frequencies must be adjusted to take into account the different magnitudes of B_0 — a subject that will be discussed in detail in Section 5.

Two quite different scenarios arise for chemical shifts measured by the *substitution method*. The substitution method implies that the reference is substituted for the sample in the probe, so the measurements of v_{sample} and $v_{reference}$ are made consecutively, not concurrently. If the magnetic field is thought to have adequate stability for the measurement being conducted, as in most experiments with solid samples and occasionally with some high-resolution studies of liquid samples, the experimenter might rely on this stability, *without a field/frequency lock*, to ensure that H_0 remains the same for the two measurements. This then results in the same situation as in external referencing: in general, B_0(sample) ≠ B_0(reference), and a correction is needed for the effect of BMS. (If the sample and reference are both very dilute solutions in the same solvent, then the susceptibility correction may, of course, be negligible.) One important restriction in using the substitution method without a lock is that the magnetic field must not be re-shimmed between the two measurements, since a small but unknown z_0 component often accompanies higher-order field gradient shims.

The second substitution method uses a field/frequency lock based on a substance (usually involving the ^{2}H signal of a deuterated solvent) contained *within* each of the two tubes being measured (containing sample of interest and reference, respectively). This *internally locked* substitution method presents an entirely different situation. Here, the lock ensures that the instrument alters H_0 in order to maintain B_0 within the tube at a constant magnitude. If the lock substance is identical for the sample and reference measurements and is not influenced appreciably by different intermolecular interactions in the two instances, then $\delta_{sample}(D) = \delta_{reference}(D)$, B_0 is constant, and the measured frequencies may be used in eq. 1. However, if different lock substances are used, then a correction must be applied to account for the different chemical shifts of these two materials. This matter was discussed in some detail in the 2001 recommendations document [4]. With most recently installed spectrometers, the manufacturers have built such corrections into the software, but it is important for the experimenter to ascertain whether that has been done and what values of the chemical shifts for the lock compounds have been entered into the spectrometer's look-up tables.

4. TEMPERATURE DEPENDENCE OF THE ^{1}H CHEMICAL SHIFT OF TETRAMETHYLSILANE

Most NMR studies are carried out at a single temperature, often the ambient temperature of the probe. In some instances, however, it is important to examine the variation of one or more chemical shifts within a sample as the probe temperature is varied. Such chemical shifts are measured with respect to TMS, and the implicit assumption is often made that the ^{1}H chemical shift of TMS does not vary with temperature. However, that assumption has no theoretical basis, since excitation of vibrational and rotational modes with increased temperature may alter the intramolecular shielding of TMS, and changes in solvent effects may also influence the intermolecular shielding of TMS.

The only method that, at present, seems feasible for determining the temperature dependence of the chemical shift of TMS is to measure the ^{1}H TMS resonance as a function of temperature relative to a substance that is believed to have a resonance frequency independent of temperature. This concept was introduced by Jameson and Jameson in 1973 [6], when they measured the ^{1}H resonance of neat TMS relative to the resonance of ^{129}Xe in xenon gas. An isolated Xe atom has no vibrational or rotational modes that can be excited, and collisional effects on the resonance frequency, which can be substantial in ^{129}Xe, could in principle be negated by extrapolation to zero pressure. Those studies [6,7], extended by Morin et al. in 1982 [8] to account for the magnetic susceptibility of TMS, reported a rather significant temperature coefficient for the TMS chemical shift. However, these investigations suffered from the shortcomings in sensitivity and reliability inherent in the use of the 90- and 100-MHz NMR instruments of that period.

In reviewing the literature, we determined that the existing data were inadequate to serve as the basis for an IUPAC recommendation. Accordingly, members of our task group undertook new experimental observations, based on the Jameson and Jameson concept but using ^{3}He gas at low pressure, together with modern 400-MHz NMR instrumentation [9]. ^{3}He has higher NMR sensitivity than ^{129}Xe and is far less susceptible to interatomic interactions. In fact, its resonance frequency was found not to have any significant pressure dependence from about 0.1 to 2.1 atmospheres (0.01 to 0.21 MPa). Thus, we believe that ^{3}He is an excellent temperature-independent standard.

In this investigation [9] the ^{1}H chemical shift of TMS in dilute solution in CDCl$_3$ (the primary reference recommended in ref. [4]) was found to vary only slightly with temperature (with an average temperature coefficient of approximately -5×10^{-4} ppm/K) over a temperature range of more than 200 K (-75 to $+130$ °C). This is approximately a factor of six smaller than the temperature coefficient reported for neat TMS in 1982 [8].

Subsequently, Hoffman [10] repeated some measurements and extended the work to cover TMS in a number of commonly used organic solvents (CDCl$_3$, CD$_3$OD, CD$_3$CN, [^{2}H$_6$] DMSO, [^{2}H$_6$] acetone, and [^{2}H$_8$] THF). He also investigated aqueous solutions, using TMS and two more soluble derivatives, sodium-3-(trimethylsilyl)propanesulfonate (DSS) and TSP. Although the published results show nonlinear behavior, particularly at low temperatures, overall the results can be approximated over wide temperature ranges by average temperature coefficients for TMS in the range of 0 to -6×10^{-4} ppm/K.

These studies necessitated the use of external referencing, since the ^{3}He gas and the solutions of TMS were in separate compartments of coaxial sample tubes. The authors corrected for the temperature variation of volume magnetic susceptibility, an effect that was comparable in magnitude with the observed changes in chemical shift and of opposite sign. Because of uncertainties in the magnitudes of magnetic susceptibilities and in temperature calibration, we believe that the resulting chemical shift data must be used with caution. However, the totality of these results makes it clear that the chemical shift of TMS (as well as that of DSS, the reference recommended for aqueous solutions [3]) has a very small temperature dependence, usually amounting to only 0.01 ppm over a temperature range of about 20 K, which is often smaller than other experimental uncertainties. Thus, the vast majority of NMR data referenced to TMS and DSS require no adjustment to account for differing temperatures of acquisition.

These findings permit us to make two recommendations, as follows:

> **Recommendation 1**: The acquisition temperature should be stated (including an estimate of "ambient" probe temperature) when chemical shift data are reported, but for temperatures in the region of 25 °C it is neither necessary nor desirable to adjust the observed chemical shift data to any "standard" temperature.

> **Recommendation 2**: In instances where it is desired to make comparisons of chemical shifts measured with respect to the ^{1}H resonance of TMS over a large temperature range between -20 to 80 °C (253 to 353 K), IUPAC recommends that a value of -5×10^{-4} ppm/K for the temperature coefficient of the chemical shift of TMS be used, or that data from refs. [9,10] be consulted for values at specific temperatures and for temperatures outside this range.

5. MAGNETIC SUSCEPTIBILITY CORRECTION: SHAPE FACTOR

The observed shift, δ^{obs}, of a signal arising from a homogeneous liquid sample consists of two components: chemical shift δ (including the effects of intermolecular interactions), and BMS shift δ_κ [11].*

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*In solids, liquid crystals, and other non-isotropic systems, a chemical shift anisotropy component also exists, as will be discussed in Section 9.

The latter is typically 3 ppm but usually varies by less than 1 ppm between solvents. The BMS shift is identical for all signals in a homogeneous sample (independent of the nuclide observed if expressed as a ratio, rather than as a frequency).

In this case, no susceptibility measurement or correction is required if the chemical shift is reported relative to an internal reference [4]. However, the BMS shift needs to be taken into account when comparing samples that are physically separated, such as in external referencing, as described in Section 3. The BMS shift depends on the shape factor and magnetic susceptibility, as quantified in eq. 3 (in SI electromagnetic units):*

$$\delta = \delta^{\mathrm{obs}} + \delta_\kappa = \delta^{\mathrm{obs}} + \left(\frac{1}{3} - \bar{\alpha}\right)\left(\kappa - \kappa_{\mathrm{ref}}\right) \tag{3}$$

where $\bar{\alpha}$ is the effective average shape factor, κ is the dimensionless volume magnetic susceptibility of the sample, and κ_{ref} is the susceptibility of the reference liquid or solution. Knowledge of theoretical shape factors and experimental magnetic susceptibilities is clearly necessary to carry out external referencing procedures. SI units and conventions for susceptibility and shape factor are used throughout this document in line with IUPAC recommendations. However, most published tables of magnetic susceptibilities (e.g., [12,13]) are in cgs units. To convert from cgs units to SI, magnetic susceptibilities must be multiplied by 4π and shape factors must be divided by 4π.

Table 1 lists the theoretical shape factors for some simple sample shapes. Whilst nearly all solution-state NMR experiments are conducted with cylindrical samples (generally of effectively infinite length) oriented parallel to the applied magnetic field, there is particular significance in the shape factor for cylindrical samples with the cylinder axis at the magic angle, 54.736°, to B_0 since this is $1/3$, which means that δ_κ, the correction for BMS, is zero.

Table 1 Theoretical shape factors for selected samples.

Shape in a vertical magnetic field	Shape factor
Infinite vertical cylinder	0
Sphere, infinite cylinder at the magic angle, or any shape cylindrically symmetrical about the magic angle	$\frac{1}{3}$
Infinite horizontal cylinder	$\frac{1}{2}$
Infinite cylinder at angle θ to the field	$\frac{1}{2}(1 - \cos^2\theta)$

This fact becomes clearer when δ_κ for an infinite cylinder is put into a form familiar to solid-state NMR spectroscopists:

$$\delta_\kappa = \frac{\kappa}{3}\left(\frac{3\cos^2\theta - 1}{2}\right) \tag{4}$$

where θ is the angle between the cylinder axis and the applied magnetic field B_0. This situation holds also for points along the central axis of any cylindrically symmetrical object aligned with the magic angle. Moreover, for infinite cylinders inclined at the magic angle with respect to B_0, even points away from the central axis have a time-averaged shape factor of $1/3$, during sample rotation, and hence the shift effect of isotropic magnetic susceptibility averages to zero. Indeed, this is true for a cylindrical sample

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*Equation 3 assumes that the magnetic susceptibility is independent of magnetic field. This is true of most diamagnetic and paramagnetic systems but not for ferromagnetic and superconductive materials. In any case, the BMS shift is usually much larger than the chemical shift for ferromagnetic and superconductive materials, so chemical shifts cannot be measured reliably.

tube of finite length and for any shape cylindrically symmetrical about the magic angle. However, spinning at the magic angle is necessary to eliminate off-axis and end effects. The required spin rates are discussed in [14]. Then, chemical shift measurements made at the magic angle by replacement require no (isotropic) BMS corrections, a feature which is of particular significance for solids (see Section 9) but is also valid for solutions. MAS measurements, therefore, provide a superior method of external referencing. The idea of external referencing for both ^{1}H and ^{13}C using TMS, volume fraction 1 %, in deuterochloroform in conjunction with the recommended Ξ values is thus a straightforward proposition for MAS NMR studies.

For all but the simplest shapes, the calculation and measurement of shape factors are complex issues that are beyond the scope of these recommendations. However, Hoffman [15] recently applied the basic theory to determine the shape factor for typical NMR sample tubes, using the geometry and receiver coil configuration of a superconducting magnet. For a 5-mm NMR sample tube with liquid 20 mm above and 20 mm below the center of the receiver coil, the effective average shape factor, expressed in SI units, is approximately 0.007, as indicated in Fig. 1, which is adapted from ref. [15]. The factor $(\frac{1}{3} - \bar{\alpha})$ thus differs by only 2 % from the theoretical value of ⅓. For many purposes, this difference is negligible, but it may be significant when the BMS must be determined in order to compare chemical shifts in solvents of considerably different magnetic susceptibility. Moreover, the shape factor may be considerably larger for sample volumes or instrument parameters (including size and location of receiver coil) that differ from the parameters used to derive Fig. 1.
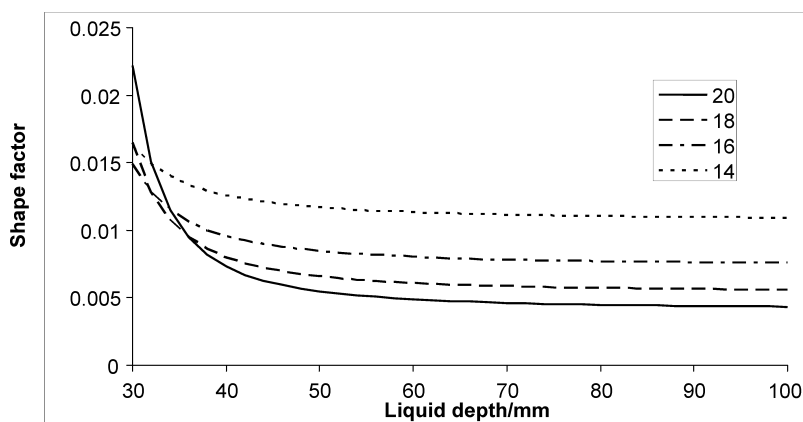
Fig. 1 Shape factors for a 5-mm NMR tube whose bottom is at various depths (14, 16, 18, and 20 mm) below the receiver-coil center. This figure is adapted from ref. [15] and depends on a number of parameters assumed there to account for instrument geometry and receiver coil sensitivity.

The volume susceptibility of most solvents, in SI units, lies in the range –4.91 ppm for nitromethane to –14.53 ppm for di-iodomethane, where ppm indicates "× 10^{-6}" [12]. For common NMR solvents at room temperature (RT), it ranges from –5.66 ppm for [^{2}H$_6$] acetone to –9.15 ppm for [^{2}H] chloroform [15,16]. Estimates for magnetic susceptibility at other temperatures can usually be made by assuming a constant molar susceptibility and applying corrections for solvent density.

Most tabulated values of bulk isotropic magnetic susceptibility have been measured using a magnetic susceptibility balance [17]. In addition, various NMR methods have been proposed for measuring magnetic susceptibility, some depending on the use of the geometry of an iron-core magnet in which the sample tube axis is at 90° to the magnetic field axis [18,19]. Others employ a spherical sample holder inside a cylindrical sample tube [19,20] or rely on gross distortion of line-shape when the bottom of the sample tube is close to the receiver coil [16].

A more promising modern NMR method for measuring susceptibility makes use of measurements from coaxial cylindrical sample tubes spun (a) about at an axis oriented parallel to the magnetic field axis and (b) at the magic angle. The true chemical shift (δ in eq. 3) can be measured directly by MAS because the BMS shift is zero. Small errors in the magic angle lead to large changes in resonance frequency, but the magic angle can be set accurately, as discussed in Section 9, to yield a precision in δ of 0.0004 ppm. Since $\delta^{\text{obs, vertical}}$ depends only on *differences* in susceptibilities, the measurement is normally repeated with a sample of accurately known susceptibility, such as water. The differences $\Delta\delta$, along with the known susceptibility κ_0, are then used in eq. 5 to determine κ:

$$\kappa = \frac{\Delta\delta^{\text{obs,vertical}} - \Delta\delta^{\text{magic}}}{\frac{1}{3} - \bar{\alpha}} + \kappa_0 \tag{5}$$

In Section 6, we shall apply this technique to investigate the effect of solvent variation on the TMS chemical shift. Two recommendations follow from the discussion in this section:

> ***Recommendation 3***: In situations where it is necessary to use an external reference or to compare chemical shifts of samples in separate tubes oriented parallel to $\boldsymbol{B}_0$, the BMS shift, symbol δ_κ, should be quantified and subtracted from the observed shift, symbol δ^{obs}, to yield the chemical shift, symbol δ. The BMS shift may be calculated from eq. 3, with $\bar{\alpha}$ approximated as indicated in the text.

> ***Recommendation 4***: In line with general IUPAC recommendations, SI units and conventions should be used for average shape factor, symbol $\bar{\alpha}$, and volume magnetic susceptibility, symbol κ. Because cgs units have been widely used in tabulations of susceptibility data, the convention should always be explicitly stated. The diamagnetic susceptibilities of common NMR solvents are small (of the order of 10^{-6}) and are conveniently quoted in ppm.

6. SOLVENT EFFECTS ON THE ^{1}H CHEMICAL SHIFT OF TETRAMETHYLSILANE

The proton chemical shift of TMS in any solvent is *by definition* (eq. 1) exactly *zero* when TMS is used as an internal reference or as a reference in the substitution method with an internally locked field. However, the *magnetic shielding* of the protons in TMS, measured relative to some "absolute" reference, such as a bare proton or low-pressure monatomic gas, depends not only on intramolecular electron currents but also on perturbations from the solvent environment.

In some instances, where solvent effects on the chemical shift of a sample are significant in the interpretation of data, it may be important to take into account the change in shielding of TMS with solvent variation. Clearly, such changes can be measured only with samples that are physically separated from each other, thus requiring either correction for magnetic susceptibility or measurements at precisely the magic angle. Table 2 provides results for TMS in 10 solvents (as well as for neat TMS and for DSS in D_2O), where corrections for magnetic susceptibility have been made using eq. 3. The last column provides data obtained by MAS for nine of the samples, where no correction is required. The agreement is excellent.

Although the results in Table 2 should not be regarded as having the quantitative reliability of critically evaluated data from several independent studies and are subject to correction in the future, they illustrate quite well the magnitude of change in shielding of the protons in TMS with change of solvent. As a nonpolar molecule, with approximately tetrahedral geometry, TMS is expected to interact with solvent molecules only rather weakly. Nevertheless, the results in Table 2 show that the ^{1}H resonance of TMS in a variety of non-aromatic solvents varies over a range of more than 0.2 ppm at RT (25 °C). For aromatic solvents, the variation is appreciably larger, as expected because of well-known ring current effects.

Table 2 Change of the ^{1}H chemical shift in TMS with variation of solvent.

Solvent	δ^{obs}/ppm[a]	κ/ppm[b]	δ/ppm[c]	δ^{MAS}/ppm[d]
[2H] Chloroform	0.00	–9.153	0.00	0.000
[2H6] Acetone	0.97	–5.700	–0.16	–0.160
[2H3] Acetonitrile	0.83	–6.597	–0.01	–0.011
[2H6] DMSO	0.54	–7.730	0.07	0.062
[2H4] Methanol	0.72	–6.606	–0.11	–0.106[e]
[2H8] THF	0.31	–7.914	–0.10	–0.109
[2H6] Benzene	–0.01	–7.82	–0.45	[f]
Nitro [2H5] benzene	–0.03	–7.28	–0.64	[f]
[2H8] Toluene	0.05	–7.72	–0.42	[f]
TMS (neat liquid)	0.58[g]	–6.90	–0.15	–0.124[h]
D_2O (saturated solution)	0.01	–8.840	–0.09	–0.071[h]
DSS in D_2O (10 mmol/dm^3)[i]	0.03	–8.840	–0.07	–0.056[h]

[a]Apparent ^{1}H chemical shift of TMS in various solvents in coaxial tubes spun parallel to $\boldsymbol{B}_0$, relative to TMS in CDCl$_3$ as an external reference; based on experimental data from refs. [10,16] except where noted.
[b]Volume magnetic susceptibility, where "ppm" is equivalent to "×10^{-6}", from various published sources but presented here in SI units [12,13,15,16].
[c]δ from eq. 3, using a shape factor of 0.007.
[d] [1]H chemical shift of TMS in various solvents relative to TMS in CDCl$_3$ in coaxial tubes spun at the magic angle; from ref. [21] except where noted.
[e]Measured using nondeuterated methanol as the solvent.
[f]Not determined.
[g]Unpublished result supplied by R. Hoffman.
[h]Unpublished data supplied by F. Ziarelli and A. Thevand, University of Aix-Marseille.
[i]Included for comparison of Ξ and Ξ^{DSS}; see Section 8.

7. A STANDARD STATE FOR THE ^{1}H TMS REFERENCE?

The 2001 recommendations document [4] pointed out the desirability in principle of having a physico-chemical *standard state* for TMS, in which relevant parameters such as concentration, temperature, and pressure are specified. A study reported in that document showed that the chemical shift of TMS in CDCl$_3$ was constant below a volume fraction $\varphi \approx 1$ %; hence, a precise "standard" concentration was considered unnecessary for most purposes. We now know (Section 4) that the temperature variation is also small, usually amounting to only 0.01 ppm over a temperature range of about 20 °C, and thus requiring no adjustment for the vast majority of NMR data referenced to TMS. The effect of pressure has not been studied in detail, but the TMS chemical shift data in ref. [10] did not display any large variation at the highest temperatures, where vapor pressures were sometimes in the tens of atmospheres. For practical applications, virtually all measurements are made at ambient pressure of approximately 1 bar (ca. 1 atm), or with air removed to leave the sample under its own vapor pressure.

Removal of oxygen from a sample is not expected to affect chemical shifts determined by the internal reference or locked substitution method or with MAS. However, external referencing or the unlocked substitution method introduces a susceptibility artifact that is dependent on the concentration of dissolved paramagnetic oxygen — for example, a change in δ_κ (see eq. 3) of about 0.07 ppm is expected for water saturated with air (volume fraction 21 % oxygen). This leads to a recommendation:

Recommendation 5: For samples subject to ambient atmospheric pressure, the pressure need not be more precisely specified, but any substantial variation from 1 bar (ca. 1 atm) should be stated. In conformity with earlier IUPAC recommendations [1,2], information

should be supplied if a sample has been treated to remove oxygen. Particular care should be taken to give adequate details if external referencing is used.

With the accumulation of reasonably reliable data for change of the resonance frequency of TMS with temperature, concentration, solvent, and pressure, as described in this document and the 2001 recommendations [4], it is becoming feasible to consider a standard state for referencing chemical shifts. With ever-improving measurement techniques, there may be specific applications where an agreed standard state will be desirable. However, for the vast majority of NMR studies, there seems to be insufficient value to warrant the complexity of converting chemical shift data to such a "standard state." IUPAC believes that the recommendations given in this document and in refs. [3,4] are sufficient in most applications to promote consistency with minimal effort by investigators. However, there are instances where comparisons between results carried out under different conditions are to be made, and the following recommendation is for those cases.

> *Recommendation 6*: When it is essential to compare data obtained at different temperatures or pressures or with different solvents, chemical shifts should be referenced to the proton signal of TMS as its concentration tends to zero in $CDCl_3$ at 25 °C under a standard atmosphere (0.1 MPa = 1 bar). *Full* details of any conversion process should be given (e.g., source and application of magnetic susceptibility data, effect of dissolved oxygen, source of temperature conversions), along with an estimate of additional uncertainties introduced in the conversion.

Perhaps the ultimate standard state would be the bare proton, which is used as the basis of absolute shielding calculations. Connection to the experimental regime might best be obtained via a nuclide such as ^{3}He in the neutral helium atom, for which shielding computations should be accurate. In fact, the 2001 recommendations [4] mentioned the desirability of using ^{3}He in the gaseous state at very low pressure as a universal reference, rather than TMS, but discarded it as not practicable. Since that time, measurements have been reported relating the NMR frequency of ^{3}He to TMS in $CDCl_3$ [9,10]. Also, ab initio calculations are reported to give an accurate value of 59.93677 ppm for the absolute shielding of ^{3}He (ref. [22], p. 154). These results suggest that refinements in accuracy of the experimental data and perhaps further improvements in theory might provide a seamless connection between the bare proton and shielding in TMS.

8. COMMENTS ON Ξ VALUES

In 2001, IUPAC recommended that new data for *all* nuclides other than ^{1}H be reported as Xi (Ξ) values, as defined in eq. 2, relative to the ^{1}H resonance of TMS in $CDCl_3$ with the *same* magnetic induction $\boldsymbol{B}_0$ [4]. For NMR of proteins and nucleic acids in aqueous solutions, IUPAC and the International Union of Biochemistry and Molecular Biology (IUBMB) [3] recommended reporting Ξ relative to the ^{1}H resonance of DSS as an internal reference, with the use of DSS clearly designated as Ξ^{DSS}. Neat liquid TMS has also been used as a reference for solid-state NMR, particularly because of its larger ^{13}C signal. As indicated in Section 9, its use as the basis for Ξ can be designated by $\Xi^{neat\ TMS}$. We affirm the recommendation [4] to use TMS in $CDCl_3$ as the basis of the Ξ system but recognize that TMS has been and may continue to be used under other circumstances. It is important that any deviant uses be clearly identified to avoid confusion. This leads to a recommendation:

> *Recommendation 7*: Ξ always represents the ratio of the resonance frequency of a nuclide other than ^{1}H to the ^{1}H frequency of TMS (or DSS for aqueous solutions) but of no other compound. Ξ with no qualification (as in ref. [4]) represents the ratio where the denomina-

tor is the ^{1}H resonance frequency of TMS in CDCl$_3$ at a volume fraction of 1 % or less. Any other conditions, including the use of a dilute aqueous solution of DSS, should be clearly delineated by a superscript or other unambiguous notation.

The two frequencies forming the Ξ ratio must be measured in the same magnetic field $\boldsymbol{B}_0$. Thus, all comments in Section 2 regarding the factors involved in referencing methods — internal, external, unlocked substitution, and locked substitution — apply when a value of Ξ is determined. When Ξ is measured in CDCl$_3$ with TMS as an internal reference or with the locked substitution method (or in aqueous solution with DSS as internal reference), the two frequencies are clearly determined in the same $\boldsymbol{B}_0$. When the frequency of nuclide X is measured with the magnetic field locked on another solvent, the value of $\boldsymbol{B}_0$ is altered. Many spectrometers now have software that corrects the reported frequency to a constant field. For those that do not, ref. [4] describes in some detail just how the correction should be made. With the unlocked substitution method and normal high-resolution geometry (sample tube axis parallel to $\boldsymbol{H}_0$), a correction is required also for magnetic susceptibility unless the resonance frequency of X is measured in CDCl$_3$ at low concentration. With MAS, no correction is needed.

The values of δ for TMS and DSS shown in Table 2 may be used when needed to relate values of Ξ referred to DSS or neat liquid TMS. It should be noted that the ^{1}H chemical shifts of DSS and TMS in the same solvent (D$_2$O or DMSO) were shown to differ by about 0.02 ppm [3], but DSS in water is displaced from TMS in CDCl$_3$ by 0.07 ppm (see Table 2). Further useful relations for ^{13}C chemical shifts and values of Ξ are given in Section 9.

The IUPAC recommendations 2001 [4] included tables of Ξ values, one for each magnetic nuclide, which are intended to facilitate comparison with data obtained using secondary (homonuclear) references. Data from the tables have been widely disseminated in magnetic resonance journals and in other ways. Appendix 1 provides a single table of Ξ values reproduced directly from Tables 1, 2, and 4 of ref. [4], *with one change* — the value of Ξ for ^{3}He. Except for the rare earths, where only approximate values of Ξ were available, IUPAC recommended that the values of Ξ in the 2001 document [4] "are not subject to future change arising from remeasurement even where this results in increasing accuracy for the reference compound in question." This recommendation echoed a similar recommendation by IUPAC/IUBMB [3]. The immutability of these Ξ values has sometimes been questioned, since it might appear that newer, more accurate, results should be incorporated, as is the case with most scientific data. However, the principal purpose for the tables is to provide a *consistent* set of numbers that can be used to provide a link between data for various nuclides referred to the universal TMS reference and results already in the literature where each nuclide is referenced separately. In general, the values of Ξ that are given here are of sufficient accuracy relative to previously published data to permit valid comparisons. To allow changes to be made from time to time in these values would result in inconsistent and confusing comparisons.

The Ξ value for ^{3}He in Appendix 1 represents the sole exception to this policy. After publication of the 2001 recommendations [4], it was discovered that an error in data processing had resulted in a value that was incorrect by 6 ppm — a very large discrepancy for a nuclide with a sharp resonance and an expected range of chemical shifts that is relatively small. In view of the potential future importance of ^{3}He as a fundamental standard, as discussed in Section 7, we concluded after careful consideration and consultation that this error should be corrected. Fortunately, it appears that no results have been published using the erroneous value of Ξ (with the exception of ref. [10]), largely because ^{3}He has been little studied.

For conciseness, Tables 1–3 in the 2001 document [4] list a value of Ξ for only one substance for each magnetic nuclide. However, it was recognized that a number of alternative compounds have been widely used as references. Several of these, including DSS as a reference for aqueous solutions, were noted in the 2001 document [4]. The most appropriate Ξ value for ^{15}N has been the subject of some discussion. Nitromethane was given in the tables on the basis of its historically wide use for ^{14}N, but liq-

uid ammonia is often cited as a reference for ^{15}N, particularly in literature related to biochemical applications, and was recommended by IUPAC/IUPAB for use in such applications [3]. For convenient reference, Appendix 1 includes Ξ values for several alternatives from ref. [3].

> ***Recommendation 8***: The values of Ξ in Appendix 1 may be regarded as IUPAC recommended, but it should be clearly stated which compound is being cited.

Although not related to Ξ values, this is an appropriate place to point out that we have learned (M. Jaszunski, private communication) that a typographical error in the IUPAC "Green Book", 2nd edition [23], for the value of the magnetic moment of [207]Pb resulted in incorrect values for several derived quantities in Table 1 of the 2001 document [4]*. The correct value of the magnetic moment is given in the third edition of the "Green Book" [26].

9. REFERENCING IN SOLIDS

Chemical shift referencing in high-resolution MAS NMR experiments on solids is complicated by several factors not encountered in solution-state NMR. At present, no strategy is in general use for providing an internal lock of any sort in MAS NMR of solids, and referencing is usually done using the substitution method without a lock. In the absence of a field/frequency lock, the precision of any shift measurement relies upon the inherent stability of the static magnetic field. This is usually not an important consideration for solids, as linewidths are significantly larger than for solutions and many modern superconducting magnets have drift rates measured in Hz per week or per month at ^{1}H frequencies. However, the highest field solenoids often have significant drift rates, being built closer to the limit of current technology. In this instance, field stabilization has been achieved by a calibrated linear ramp of correction current to the RT compensation coil [27] or alternatively by use of a separate external lock probe [28].

Referencing by the unlocked substitution method in solid-state MAS experiments typically involves removal of the NMR probe from the magnet to change samples. When field stability is not the limiting factor, the repositioning of the probe accurately into the magnet can be a significant experimental source of referencing error. Each different experimental situation needs to be characterized with respect to the repeatability of resonance measurements, with values of ±0.03 to ±0.01 ppm being readily achieved [27]. An important consideration here is the setting of the RT shims. Without an internal lock, the current settings should not be changed between samples, otherwise z_0 imperfections will affect the subsequent shift measurements. Fortunately, in the typical MAS situation no adjustment of the RT shims is required for different samples.

As discussed in Section 5, shift referencing for solution-state experiments using substitution by an external standard is complicated by the demagnetizing fields [5] associated with the normal sample geometry and with differing isotropic magnetic susceptibilities. These artifacts can be corrected as indicated in Section 5. For solids, the situation is somewhat simpler as far as the effect of *isotropic* magnetic susceptibility is concerned. For the central axis of cylindrical samples inclined at the magic angle, such as in typical solid-state rotors, the (isotropic) BMS effect is actually zero, so that replacement samples of standard substances may be used for referencing to give correct chemical shifts. For off-center positions in cylindrical samples of infinite length, the average of the demagnetizing field over a rotor period is also zero [29,30].

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*The value of the maximum observable component of the magnetic moment of [207]Pb was given in the "Green Book" as +0.582 583(9) instead of the correct value of +0.592 583(9) [24], i.e., a difference in the second decimal place. The correct values for [207]Pb, to replace those in Table 1 of ref. [4], are: magnetic moment, $\mu/\mu_N = 1.026\ 38$; magnetogyric ratio, $\gamma/10^7$ rad s^{-1} T^{-1} = 5.676 25; relative receptivities $D^p = 2.11 \times 10^3$; $D^C = 12.4$. Jaszuński, Jackowski, and coworkers [25] recently presented an analysis of the precise values of magnetic moments for a number of bare nuclei.

For a finite length of cylindrical sample (such as in a typical MAS rotor) or for other geometries, the shape factors for the demagnetizing fields are more complex, as mentioned in Section 5; yet they can still be shown to vanish under the averaging of MAS [14]. Since demagnetizing fields are small for typical diamagnetic susceptibilities, the net field at any particular point can be thought of as the sum of the individual fields from other portions of the sample. In the simplest model, one can then mentally divide the sample into a collection of spheres, each producing its own dipolar demagnetizing field. The net field seen by a nucleus in one sphere due to all others will be the sum of these dipolar fields. Since the field from each dipole averages to zero under MAS, the net field from the entire sample is also zero regardless of the complexity of the sample shape.

As long as the probe is repositioned accurately, an external reference sample is in theory then just as good as having one contained in the same rotor. MAS NMR measurements for liquid samples in this regard are superior to measurements with internal reference compounds as the latter can incur sizeable and often unpredictable solvent shifts (see Section 6).

However, there are complications for solids which arise from *anisotropy* in magnetic susceptibility [31,32]. Demagnetizing fields from anisotropic BMS do not average to zero under MAS. Moreover, such fields are dependent upon the size, shape, and relative orientations of the particles comprising the sample. Fortunately for questions of chemical shift referencing, in most situations experimental experience shows that these effects are more likely to produce a relatively symmetrical broadening of the observed resonances rather than to cause any resonance shifts. For microcrystalline samples, the extent of any possible shift will depend on particle sizes, crystal habit, and sample shape and at present is a largely unexplored issue.

The accuracy of the MAS will typically also not be of concern, as it will have already been set to deal with the much larger anisotropy of chemical shifts. In ^{13}C MAS experiments, it is common practice to set the magic angle accurately enough to remove the last few Hz of broadening from the line shape of a standard sample such as glycine or hexamethylbenzene. For the sake of discussion, assume a 150 ppm chemical shift anisotropy (axial symmetry), and an operating frequency for ^{13}C of 125 MHz. A residual broadening $\Delta\delta$ of 0.04 ppm or 5 Hz implies an angle mis-set $\Delta\theta$ of only 0.0108°. The demagnetizing field term corresponding to the shift anisotropy is simply $\kappa/3$, which (with a typical $|\kappa|$ of <4 ppm) results in an insignificant broadening of ~0.0011 ppm, and a shift in peak position of less than half this amount. To produce an error of 0.01 ppm, the angle would need to be mis-set by at least 0.10°, a huge value by the standards of most solid-state NMR laboratories.

Since many MAS arrangements are not convenient for liquid samples, additional secondary narrow line references have been developed for solid-state measurements. For example, the recent study by Morcombe and Zilm [27] provided accurate data (±2 Hz, or 0.01 ppm) on ^{13}C chemical shifts for several potential reference compounds in both solid and solution states, under MAS and with the conventional geometry for high-resolution NMR — spinning parallel to $\boldsymbol{B}_0$, i.e., zero-angle spinning (ZAS). Adamantane is a suitable compound because its ^{13}C resonances are particularly narrow, and, being a plastic crystal, it has an isotropic magnetic susceptibility. The ^{13}C shift scale based on the high-frequency (methylene) carbon signal for this standard has been found [27] to be related to the IUPAC-recommended scale, the DSS scale, and to neat external TMS according to

$$\delta_{\text{MAS}}^{1\,\%\,\text{TMS in CDCl}_3} = \delta_{\text{MAS}}^{\text{neat TMS}} - 0.71 \text{ ppm} = \delta_{\text{MAS}}^{0.5\,\%\,\text{DSS in D}_2\text{O}} - 2.72 \text{ ppm} = \delta_{\text{MAS}}^{\text{solid adamantane}} + \quad (6)$$
$$37.77 \text{ ppm}$$

These relations refer to ^{13}C in the indicated substances and states, with all samples subject to MAS. Thus, –0.71 ppm is the solvent effect on the ^{13}C resonance of TMS in CDCl$_3$ relative to neat TMS, and 2.01 ppm is the chemical shift for ^{13}C of DSS in D$_2$O relative to neat TMS.

IUPAC recommends that the chemical shifts of all nuclides be referred to the ^{1}H resonance of TMS in CDCl$_3$, $\varphi \le 1$ %, as the primary internal reference. However, as discussed in Sections 7 and 8, a low volume fraction of TMS in other solvents or of DSS in water may be a useful internal reference.

With MAS, susceptibility artifacts are suppressed, so that external referencing to neat TMS and referencing by the unlocked substitution method are also feasible. Presentation of results as Ξ values is particularly useful with widespread use of heteronuclear correlation methods. Referencing of ^{13}C chemical shifts to ^{1}H shifts in MAS experiments can be done using Ξ values, reported here as $100 \times$ the ratio of the ^{13}C to ^{1}H resonance frequencies for the methyl groups in the indicated samples:

$$\Xi(^{13}C \text{ for vol. fract. } 0.1 \text{ % TMS in CDCl}_3) = 25.145\ 020 \text{ %} \tag{7}$$

$$\Xi(^{13}C \text{ for neat liquid TMS}) = 25.145\ 004 \text{ %} \tag{8}$$

$$\Xi(^{13}C \text{ for 10 mmol/dm}^3 \text{ DSS in D}_2\text{O}) = 25.144\ 953 \text{ %} \tag{9}$$

The notation for Ξ conforms to Recommendation 7. Equation 7 gives the IUPAC-recommended value relative to the ^{1}H resonance frequency of TMS in CDCl$_3$ [4]. Equation 8 gives the value relative to the ^{1}H frequency of neat TMS, reported by Morcombe and Zilm as the average of eight MAS measurements [27]. Equation 9 is the value recommended by IUPAC/IUBMB relative to the ^{1}H frequency of DSS [3]. The value in eq. 9 differs very slightly from that reported by Morcombe and Zilm [26], 25.144 954$_8$ %, which was based on a DSS sample of much higher concentration. Each of the values given in eqs. 7–9 represents the frequency ratio in a single homogeneous sample, so it is irrelevant whether the measurement is made under MAS or ZAS conditions.

Equation 10 lists the Ξ values (relative to TMS in CDCl$_3$) for the two adamantane ^{13}C signals under MAS conditions [27]:

$$\Xi[^{13}C \text{ for adamantane (s)}] = 25.145\ 970 \text{ % and } 25.145\ 743 \text{ %} \tag{10}$$

for the methylene and methine resonances, respectively. These values are computed from data in [26], using measurements made with MAS to eliminate susceptibility artifacts.

In all of the above, operation at RT has been assumed. Accurate measurements at extreme excursions of temperature are complicated by the effect of probe components on the magnetic field experienced by the sample. These demagnetizing fields are the dominant sources of field inhomogeneity [33], so changes in probe temperature can easily produce large shifts in the average field as well as affect the MAS line shape. Accurate referencing in this case requires knowledge of the temperature dependence of the chemical shift of the reference compound (see Section 4) as well as how the net field shifts as the probe temperature changes.

> ***Recommendation 9***: With MAS, sample replacement methods suffice to determine chemical shift measurements on solids. For ^{13}C, eq. 6 provides relationships that can be used to interconvert data measured under MAS for solids relative to several references — neat TMS; the high-frequency signal for adamantane; the IUPAC standard TMS in CDCl$_3$, volume fraction 1 %; and DSS in water.

> ***Recommendation 10***: For reporting chemical shifts in solids, IUPAC endorses the unified chemical shift scale established for solutions. Equations 7–10 provide relationships that may be useful in converting ^{13}C results to the virtually equivalent recommended scales based on the proton resonance of TMS in CDCl$_3$ and the proton resonance of DSS in aqueous solution.

Clearly, relationships for other nuclides remain to be determined.

10. TERMINOLOGY FOR SHIELDING AND CHEMICAL SHIFT TENSORS

Thus far, this document has dealt only with situations in which the chemical shift and corresponding shielding are effectively isotropic — as a result of rapid molecular tumbling in liquids or the use of MAS in solids. In general, however, shielding and chemical shift must be regarded as anisotropic quantities described by second-rank tensors $\boldsymbol{\sigma}$ and $\boldsymbol{\delta}$. In the most general case, nine elements are required to represent such a tensor (a 3×3 matrix). In 3-dimensional Cartesian space, these may be specified (e.g., for the shielding tensor, $\boldsymbol{\sigma}$) by σ_{ij} where $i,j = x$, y, or z.

The shielding tensor can be decomposed to a symmetric part and an antisymmetric part. The latter, which in some cases will be zero because of local symmetry around the nucleus in question, may contribute to relaxation but does not give rise to an observable chemical shift, even in solids [34]. We consider here only the symmetric part, where $\sigma_{ij} = \sigma_{ji}$. Then, only 6 different elements are necessary. Transformation to a suitable set of axes X, Y, and Z (the principal axis system, PAS) will diagonalize the matrix to give three principal components (σ_{XX}, σ_{YY}, σ_{ZZ}). The remaining three variables determine the orientation of the PAS in, say, a molecule- or crystal-fixed set of axes. These six variables can be predicted by suitable quantum mechanical computations (though most programs usually calculate all nine components by default).

All six variables can be obtained experimentally, but many results come from experiments on powdered samples (either from analysis of bandshapes of static samples or of spinning sideband manifolds, which generally yield only the principal components). Alternatives to the principal components are often reported. The *isotropic average*

$$\sigma_{\text{iso}} = \tfrac{1}{3}\,(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) \tag{11}$$

is invariably one of these, but there is divergence in the literature regarding the remaining two (see below). In order to avoid any problems arising from this situation, Recommendation 11 is essential.

> ***Recommendation 11***: The three principal components of the shielding or chemical shift tensors should always be listed explicitly (see also Recommendation 15).

Unfortunately, there are a number of different conventions in use regarding matters of notation in this area, which are sometimes confused in the literature and are often inadequately defined. There are two conventions for labeling the axes, which became established following the important textbooks of Haeberlen [35] and Mehring [36], both appearing in 1976. In 1993, the "Maryland Group" [37] recommended additional terminology. Also, it is widely recognized that shielding (and other) tensors can be expressed more fundamentally in a spherical, rather than a Cartesian representation. Finally, it has been suggested that [38] for computational purposes an icosahedral representation may be convenient. We summarize each of these five approaches, pointing out their interrelations, then provide a series of recommendations for future usage.

"Haeberlen notation"

This notation relates each of the three principal components to σ_{iso} as follows:

$$\left|\sigma_{ZZ} - \sigma_{\text{iso}}\right| \ \geq\ \left|\sigma_{XX} - \sigma_{\text{iso}}\right| \ \geq\ \left|\sigma_{YY} - \sigma_{\text{iso}}\right| \tag{12}$$

Thus, σ_{ZZ} is the principal component farthest from the isotropic value, and σ_{YY} is closest to σ_{iso}, but this means that the ordering of the components can be either $\sigma_{ZZ} \geq \sigma_{YY} \geq \sigma_{XX}$, or $\sigma_{ZZ} \leq \sigma_{YY} \leq \sigma_{XX}$, depending on the chemical system in question.

As mentioned above, for many purposes (especially in connection with theory), it is useful to express shielding tensor data using three other parameters as well as the principal components. One of

these is invariably the isotropic average, defined in eq. 11. The second parameter is generally referred to as *shielding anisotropy*. Unfortunately, two definitions (eqs. 13 and 14), have grown up for shielding anisotropy

$$\Delta\sigma = \sigma_{ZZ} - \tfrac{1}{2}\left(\sigma_{XX} + \sigma_{YY}\right) \tag{13}$$

$$\zeta = \sigma_{ZZ} - \sigma_{\text{iso}} \tag{14}*$$

It is easily shown that the two definitions of anisotropy are closely related by

$$\Delta\sigma = \tfrac{3}{2}\zeta \tag{15}$$

Clearly, one is redundant, but both are in common use, sometimes leading to misunderstandings when data from different sources are compared.

Shielding anisotropy may be either positive ($\sigma_{ZZ} > \sigma_{\text{iso}}$) or negative ($\sigma_{ZZ} < \sigma_{\text{iso}}$) — or, of course, zero (e.g., for cubic nuclear environments). In terms of the position of σ_{YY}, the changeover from positive anisotropy to negative occurs when this variable passes through $\tfrac{1}{2}(\sigma_{XX} + \sigma_{ZZ})$, at which point the relationship in eq. 12 causes an interchange of subscripts *XX* and *ZZ*. This oddity makes for difficulties in comparing tensor components or anisotropies for a series of related molecules and has sometimes led to misunderstandings.

The third parameter is usually called *shielding asymmetry*** and is given the symbol η, defined as

$$\eta = \left(\sigma_{YY} - \sigma_{XX}\right)/\zeta \equiv 3\left(\sigma_{YY} - \sigma_{XX}\right)/2\Delta\sigma \tag{16}$$

Thus, η is zero if the tensor is axial ($\sigma_{XX} = \sigma_{YY}$), which can occur for both positive and negative cases of anisotropy, and its maximum value is unity, when $\sigma_{YY} = \tfrac{1}{2}(\sigma_{XX} + \sigma_{ZZ}) = \sigma_{\text{iso}}$. Note that η cannot be negative. The Haeberlen convention for the tensor eigenvalues relates directly to the corresponding tensor eigenvectors, i.e., to the principal axes.

"Mehring notation"

This alternative notation uses numerical subscripts instead of letters and simply designates the components in order of increasing shielding as

$$\sigma_{11} \leq \sigma_{22} \leq \sigma_{33} \tag{17}$$

In this notation, the definition of isotropic shielding, σ_{iso}, is, clearly,

$$\sigma_{\text{iso}} = \tfrac{1}{3}\left(\sigma_{11} + \sigma_{22} + \sigma_{33}\right) \tag{18}$$

(analogous to eq. 11) but the relationships for anisotropy and asymmetry (analogous to eqs. 13, 14, and 16) are more difficult to express than under the Haeberlen convention, since they depend on the posi-

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*Haeberlen [35] used the symbol δ rather than ζ for the latter quantity, but this is to be strongly discouraged since δ is in universal use for chemical shifts relative to the signal for a reference compound.

**This name is not ideal since it also represents a type of anisotropy. A better word might be biaxiality. Also, the use of a ratio for this parameter is not ideal, since a better match with spherical tensor notation would be achieved (see eq. 25) by, for example, $\eta\zeta$. However, we believe that introduction of a new parameter at this stage cannot be justified.

tion of σ_{22} between σ_{11} and σ_{33}.* Moreover, when relating components to molecular or crystallographic systems, a change of order may be necessary. These are reasons for preferring the Haeberlen convention. However, the benefit of the Mehring convention is that components for a range of related compounds are more readily compared, since there is no discontinuity when the middle component passes through the average of the outer components. Of course, computer programs for generating principal components from spectral analysis may easily calculate values of anisotropy and asymmetry under the Mehring labeling of components.

"Maryland notation"

The relevant literature on shielding tensors prior to 1993 is entirely couched in terms of principal components and anisotropy/asymmetry. However, in that year an ad hoc group of NMR spectroscopists held discussions at a summer school in College Park, Maryland, USA and proposed [37] that the anisotropy/asymmetry convention be replaced by *span* (Ω) and *skew* (κ)**, with the following definitions:

$$\Omega = \sigma_{33} - \sigma_{11} \tag{19}$$

$$\kappa = 3(\sigma_{iso} - \sigma_{22})/\Omega \tag{20}$$

The components in this notation are always labeled in the Mehring order $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$. The span is an easily envisaged unsigned quantity that describes the full range of the observed spectrum, and comparisons between related systems are straightforward. A variation in sign is imposed on the skew, which is positive if $\sigma_{22} > \sigma_{iso}$ and negative if $\sigma_{22} < \sigma_{iso}$. Thus, the skew carries the physical insight of a prolate ($\kappa = +1$) or oblate ($\kappa = -1$) ellipsoid representing axially symmetric shielding tensors. The situation with σ_{22} midway between σ_{11} and σ_{33} corresponds to $\kappa = 0$ (i.e., to $\eta = 1$ in the anisotropy/asymmetry convention). Whilst these parameters give a readily envisaged picture for shielding powder patterns or spinning sideband manifold intensities, they are not readily related to theory, as discussed below, and are not therefore suitable for describing the interaction tensor itself.

Recommendations on notation

Both the Mehring and Haeberlen notations have continued to be used widely in the literature, causing occasional confusion, especially among new practitioners. However, each has its advantages, as has been pointed out, and it is not feasible at present for IUPAC to recommend that one notation should be used in all circumstances. Nevertheless, there are conventions that should be followed:

> **Recommendation 12**: Haeberlen notation, with capital X, Y, Z subscript letters for the principal components of shielding tensors, should be used whenever relationships to molecular- or crystal-fixed axes are discussed.

> **Recommendation 13**: Given the wide use of both $\Delta\sigma$ and ζ, we recommend either symbol as acceptable for reporting shielding anisotropy. η is the recommended symbol for shielding anisotropy (biaxiality). Definitions of these symbols should always be given.

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*A few authors have incorrectly used definitions equivalent to eq. 16 in combination with labeling components always in the Mehring order $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$. Whilst this consistently produced positive values for $\Delta\sigma$, it allowed values of η between 0 and 3, and the extreme values both correspond to axial symmetry. In the view of the Task Group, there is no merit in this notation and its use should be discouraged/discontinued.

**Note that the symbol κ is used herein for both magnetic susceptibility and skew.

Recommendation 14: The use of anisotropy/asymmetry, rather than span/skew, is generally recommended. Span/skew may be used to describe or compare powder patterns or spinning sideband amplitudes, but they are not suitable parameters to define shielding tensors.

Spherical tensor representation

As Haeberlen (ref. [35], page 10) and Grant [38] have pointed out, at a fundamental level tensors are better represented in spherical fashion, such that a general second-order property $\boldsymbol{\sigma}$ may be written as

$$\boldsymbol{\sigma} = \sigma^{(0)} + \sigma^{(1)} + \sigma^{(2)} \tag{21}$$

where the number in brackets refers to tensor rank, with $\sigma^{(0)}$ as the isotropic value, $\sigma^{(1)}$ as the generally ignored, anti-symmetric part (with three components), and $\sigma^{(2)}$ as a symmetric part (with six different components, but subject to a zero trace). Spherical tensors are intrinsically involved in considering the effects of tensor quantities on density matrix evolution and hence on spectra, so the use of this representation is inevitable for such work. However, they are not normally quoted for experimental results. It is worth noting that

$$\sigma_0^{(2)} = \sqrt{\tfrac{3}{2}}\zeta \tag{22}$$

$$\sigma_{\pm 2}^{(2)} = \tfrac{1}{2}(\sigma_{XX} - \sigma_{YY}) = \tfrac{1}{2}\eta\zeta \tag{23}$$

The proportionalities in these equations indicate that shielding anisotropy and asymmetry can readily be related to spherical tensor components, thus facilitating theoretical interpretation, whereas the relation between spherical tensor components and span/skew is more obscure (i.e., there are no simple proportionalities of the type given in eqs. 22 and 23).

Icosahedral representation

The comparison of shielding tensors, using a single scalar that represents their differences, requires using different statistical weights for different shielding components in the commonly used representations since these contain different types of metrics (e.g., scalars, ratios, and angles). To eliminate this problem, Grant and coworkers have introduced the icosahedral representation [38]. In this representation, the six components are equally distributed on the unit sphere, i.e., the spatial distance among all the components is the same, and therefore they can be treated with equal statistical weight when comparing shielding tensors. This is particularly important when the statistical propagation of errors is considered. While the icosahedral representation is especially valuable for comparing tensors, and hence as a working representation, it is less easy to envisage than the normally used parameters and its use has not been widely taken up to date.

Shielding and chemical shifts

Confusion between shielding and chemical shift has been a problem in NMR for many years. Recently, the exclusive use of symbols σ for the former and δ for the latter has greatly assisted in eliminating the confusion.

Isotropic chemical shifts are defined [23] in such a way that their direction is in the opposite sense from that of shielding. This arises from the definition given in eq. 1, where

$$\nu_{\text{sample}}(X) = \frac{\gamma}{2\pi} B_0 \left[1 - \sigma_{\text{sample, iso}}(X) \right] \tag{24}$$

and $\nu_{\text{reference}}(X)$ is similarly defined for the resonance of a reference compound.

Most research papers regard the chemical shift and the shielding of a given nucleus as separate but related tensors, although this concept is not universally accepted.* If distinct tensors are accepted, then anisotropies (and skews) for chemical shifts are logically opposite in sign for those of shielding tensors (e.g., $\Delta\delta \equiv -\Delta\sigma$). The symbol ζ for anisotropy is, however, ambiguous unless a subscript (i.e., σ or δ) is used to distinguish shielding and shift. Asymmetry is unaffected, being the same for shielding and chemical shift. Span is unaffected, provided it is considered as a modulus, i.e., $\Omega = |\sigma_{33} - \sigma_{11}|$. Subscripts can be used with skew symbols to indicate whether they are for shift (κ_δ) or shielding (κ_σ).

> ***Recommendation 15***: We fully endorse the use of the symbols σ and δ for shielding and chemical shift respectively and urge their exclusive use in NMR notation for these properties.

Whilst chemical shifts are defined and quoted as relative to a reference, theoreticians always compute, at least initially, absolute shielding values. Therefore, there is merit in retaining the symbols σ_{iso}, σ_{XX}, etc. to refer only to absolute shielding.

> ***Recommendation 16***: When it is necessary to report shielding tensor components on a relative basis (to either σ_{ref} or σ_{iso}) such data should always be explicitly indicated as $\sigma_{iso} - \sigma_{ref}$, $\sigma_{XX} - \sigma_{iso}$, etc.

The term "shielding" has in recent years been modified in many papers to "chemical shielding". There are reasons for discouraging this terminology, given that it was not in use in the earliest years of NMR. In the first place, it gives the wrong impression, since shielding is properly described as electronic or magnetic, rather than "chemical" (whereas "chemical shift" correctly expresses the eponymous phenomenon, which is experimentally rather than theoretically based). Secondly, anisotropy in "chemical" shielding becomes abbreviated as CSA, which is then confused with chemical shift anisotropy, exacerbating the sign problem.

> ***Recommendation 17***: The term "shielding anisotropy" should be used, with attendant abbreviation SA, giving a distinction from CSA (which then refers unambiguously to chemical shift anisotropy).

In principle, conventions recommended for shielding tensors should be consistent with those in general use for other tensor properties relevant to NMR. However, this is a problem, since such conventions vary significantly and it is outside the brief of this task group to make proposals for matters other than shielding and chemical shift notation. Nonetheless, to provide a link between the various common conventions, we mention in Appendix 2 some of the usages for the relevant tensors.

11. CONCLUDING REMARKS

These recommendations are intended to underline the importance of reporting chemical shifts in a consistent way in the literature. *Seventeen specific recommendations are distributed through the document, since it is important that they be read in the context of the relevant sections.* As pointed out in several instances, these recommendations extend and clarify recommendations made in ref. [4] and, where relevant, in ref. [3], which deals primarily with biopolymers. All the recommendations in the three documents are based on a practical approach for reporting observations in both solids and liquids that should

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*Arguments for treating chemical shift and shielding as separate tensors [39] and counter-arguments [40] have been given in the literature.

encourage compliance with minimal effort. The distinction between chemical shift and shielding, in both liquids and solids, is emphasized to encourage authors to make clear the relations between experimentally determined values and the underlying theoretical constructs.

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APPENDIX 1: RECOMMENDED VALUES OF Ξ FOR VARIOUS NUCLIDES[a]

Isotope	Frequency ratio, Ξ/%	Reference compound	Reference compound conditions[a]
[1]H	100.000 000	Me_4Si	$CDCl_3$, $\varphi = 1$ %
	100.000 000[b]	DSS methyl signal	D_2O
[2]H	15.350 609	$(CD_3)_4Si$	neat
[3]H	106.663 974	Me_4Si-t_1	
[3]He	76.178 976[c]	He	gas
[6]Li	14.716 086	LiCl	D_2O, 9.7 mol/kg
[7]Li	38.863 797	LiCl	D_2O, 9.7 mol/kg
[9]Be	14.051 813	$BeSO_4$	D_2O, 0.43 mol/kg
[10]B	10.743 658	$BF_3.Et_2O$	$CDCl_3$, $\varphi = 15$ %
[11]B	32.083 974	$BF_3.Et_2O$	$CDCl_3$, $\varphi = 15$ %
[13]C[d]	25.145 020	Me_4Si	$CDCl_3$, $\varphi = 1$ %
	25.144 953[b]	DSS methyl signal	D_2O
[14]N	7.226 317	$MeNO_2$	neat/$CDCl_3$[e]
[15]N	10.136 767	$MeNO_2$	neat/$CDCl_3$[e]
	10.132 912[b]	NH_3 (liquid)	external
[17]O	13.556 457	D_2O	neat
[19]F	94.094 011	CCl_3F	
[21]Ne	7.894 296	Ne	gas, 1.1 MPa

(*continues on next page*)

Isotope	Frequency ratio, $\Xi/\%$	Reference compound	Reference compound conditions[a]
^{23}Na	26.451 900	NaCl	D_2O, 0.1 mol/dm^3
^{25}Mg	6.121 635	MgCl$_2$	D_2O, 11 mol/dm^3
^{27}Al	26.056 859	Al(NO$_3$)$_3$	D_2O, 1.1 mol/kg
^{29}Si	19.867 187	Me$_4$Si	CDCl$_3$, $\varphi = 1$ %
^{31}P	40.480 742	H$_3$PO$_4$	external
	40.480 864[b]	(MeO)$_3$PO	internal
^{33}S	7.676 000	(NH$_4$)$_2$SO$_4$	D_2O, satd.
^{35}Cl	9.797 909	NaCl	D_2O, 0.1 mol/dm^3
^{37}Cl	8.155 725	NaCl	D_2O, 0.1 mol/dm^3
^{39}K	4.666 373	KCl	D_2O, 0.1 mol/dm^3
^{40}K	5.802 018	KCl	D_2O, 0.1 mol/dm^3
^{41}K	2.561 305	KCl	D_2O, 0.1 mol/dm^3
^{43}Ca	6.730 029	CaCl$_2$	D_2O, 0.1 mol/dm^3
^{45}Sc	24.291 747	Sc(NO$_3$)$_3$	D_2O, 0.06 mol/dm^3
^{47}Ti	5.637 534	TiCl$_4$	neat/C$_6$D$_{12}$[e]
^{49}Ti	5.639 037	TiCl$_4$	neat/C$_6$D$_{12}$[e]
^{50}V	9.970 309	VOCl$_3$	neat/C$_6$D$_6$[e]
^{51}V	26.302 948	VOCl$_3$	neat/C$_6$D$_6$[e]
^{53}Cr	5.652 496	K$_2$CrO$_4$	D_2O, satd.
^{55}Mn	24.789 218	KMnO$_4$	D_2O, 0.82 mol/kg
^{57}Fe	3.237 778	Fe(CO)$_5$	C$_6$D$_6$, $\varphi = 80$ %
^{59}Co	23.727 074	K$_3$[Co(CN)$_6$]	D_2O, 0.56 mol/kg
^{61}Ni	8.936 051	Ni(CO)$_4$	neat/C$_6$D$_6$, $\varphi = 80$ %
^{63}Cu	26.515 473	[Cu(MeCN)$_4$][ClO$_4$]	CH$_3$CN, satd./C$_6$D$_6$[e]
^{65}Cu	28.403 693	[Cu(MeCN)$_4$][ClO$_4$]	CH$_3$CN, satd./C$_6$D$_6$[e]
^{67}Zn	6.256 803	Zn(NO$_3$)$_2$	D_2O, satd.
^{69}Ga	24.001 354	Ga(NO$_3$)$_3$	D_2O, 1.1 mol/kg
^{71}Ga	30.496 704	Ga(NO$_3$)$_3$	D_2O, 1.1 mol/kg
^{73}Ge	3.488 315	Me$_4$Ge	neat
^{75}As	17.122 614	NaAsF$_6$	CD$_3$CN, 0.5 mol/dm^3
^{77}Se	19.071 513	Me$_2$Se	neat/C$_6$D$_6$[e]
^{79}Br	25.053 980	NaBr	D_2O, 0.01 mol/dm^3
^{81}Br	27.006 518	NaBr	D_2O, 0.01 mol/dm^3
^{83}Kr	3.847 600	Kr	Gas
^{85}Rb	9.654 943	RbCl	D_2O, 0.01 mol/dm^3
^{87}Rb	32.720 454	RbCl	D_2O, 0.01 mol/dm^3
^{87}Sr	4.333 822	SrCl$_2$	D_2O, 0.5 mol/dm^3
^{89}Y	4.900 198	Y(NO$_3$)$_3$	H_2O/D_2O
^{91}Zr	9.296 298	Zr(C$_5$H$_5$)$_2$Cl$_2$	CH$_2$Cl$_2$, satd./C$_6$D$_6$[e]
^{93}Nb	24.476 170	K[NbCl$_6$]	CH$_3$CN, satd./CD$_3$CN[e]
^{95}Mo	6.516 926	Na$_2$MoO$_4$	D_2O, 2 mol/dm^3
^{97}Mo	6.653 695	Na$_2$MoO$_4$	D_2O, 2 mol/dm^3
^{99}Tc	22.508 326	NH$_4$TcO$_4$	H_2O/D_2O
^{99}Ru	4.605 151	K$_4$[Ru(CN)$_6$]	D_2O, 0.3 mol/dm^3
^{101}Ru	5.161 369	K$_4$[Ru(CN)$_6$]	D_2O, 0.3 mol/dm^3

Isotope	Frequency ratio, Ξ /%	Reference compound	Reference compound conditions[a]
^{103}Rh	3.186 447	Rh(acac)$_3$	CDCl$_3$, satd.
^{105}Pd	4.576 100	K$_2$PdCl$_6$	D$_2$O, satd.
^{107}Ag	4.047 819	AgNO$_3$	D$_2$O, satd.
^{109}Ag	4.653 533	AgNO$_3$	D$_2$O, satd.
^{111}Cd	21.215 480	Me$_2$Cd	neat
^{113}Cd	22.193 175	Me$_2$Cd	neat
^{113}In	21.865 755	In(NO$_3$)$_3$	D$_2$O, 0.1 mol/dm^{3f}
^{115}In	21.912 629	In(NO$_3$)$_3$	D$_2$O, 0.1 mol/dm^{3f}
^{115}Sn	32.718 749	Me$_4$Sn	neat/C$_6$D$_6$[e]
^{117}Sn	35.632 259	Me$_4$Sn	neat/C$_6$D$_6$[e]
^{119}Sn	37.290 632	Me$_4$Sn	neat/C$_6$D$_6$[e]
^{121}Sb	23.930 577	KSbCl$_6$	CH$_3$CN, satd./CD$_3$CN[e]
^{123}Sb	12.959 217	KSbCl$_6$	CH$_3$CN, satd./CD$_3$CN[e]
^{123}Te	26.169 742	Me$_2$Te	neat/C$_6$D$_6$[e]
^{125}Te	31.549 769	Me$_2$Te	neat/C$_6$D$_6$[e]
^{127}I	20.007 486	KI	D$_2$O, 0.01 mol/dm^3
^{129}Xe	27.810 186	XeOF$_4$	neat
^{131}Xe	8.243 921	XeOF$_4$	neat
^{133}Cs	13.116 142	CsNO$_3$	D$_2$O, 0.1 mol/dm^3
^{135}Ba	9.934 457	BaCl$_2$	D$_2$O, 0.5 mol/dm^3
^{137}Ba	11.112 928	BaCl$_2$	D$_2$O, 0.5 mol/dm^3
^{138}La	13.194 300	LaCl$_3$	D$_2$O/H$_2$O
^{139}La	14.125 641	LaCl$_3$	D$_2$O, 0.01 mol/dm^3
^{177}Hf	(4.007)	–	
^{179}Hf	(2.517)	–	
^{181}Ta	11.989 600	KTaCl$_6$	CH$_3$CN, satd.
^{183}W	4.166 387	Na$_2$WO$_4$	D$_2$O, 1 mol/dm^3
^{185}Re	22.524 600	KReO$_4$	D$_2$O, 0.1 mol/dm^3
^{187}Re	22.751 600	KReO$_4$	D$_2$O, 0.1 mol/dm^3
^{187}Os	2.282 331	OsO$_4$	CCl$_4$, 0.98 mol/dm^3
^{189}Os	7.765 400	OsO$_4$	CCl$_4$, 0.98 mol/dm^3
^{191}Ir	(1.718)	–	
^{193}Ir	(1.871)	–	
^{195}Pt	21.496 784	Na$_2$PtCl$_6$	D$_2$O, 1.2 mol/dm^3
^{197}Au	(1.729)	–	
^{199}Hg	17.910 822	Me$_2$Hg[g]	neat
^{201}Hg	6.611 583	Me$_2$Hg[g]	neat
^{203}Tl	57.123 200	Tl(NO$_3$)$_3$	
^{205}Tl	57.683 838	Tl(NO$_3$)$_3$	
^{207}Pb	20.920 599	Me$_4$Pb	neat/C$_6$D$_6$[e]
^{209}Bi	16.069 288	Bi(NO$_3$)$_3$	HNO$_3$/D$_2$O/H$_2$O

[a]Further details are to be found in ref. [4].
[b]This value, taken from ref. [3], represents Ξ^{DSS}, rather than Ξ itself as defined in Section 8. The difference of approximately 0.07 ppm, as indicated in Table 2, should be taken into account when comparisons are made between values of Ξ and Ξ^{DSS}.

(*continues on next page*)

[c]This value is changed from that given in ref. [4], as described in the text. The revised value, taken from data given in reference [9], takes into account the very significant magnetic susceptibility correction for helium gas vs. the primary reference sample of TMS in $CDCl_3$.

[d]Values for Ξ for ^{13}C solid-state NMR are given in Section 9, eqs. 7–10

[e]Small amount of deuterated compound added to neat liquid or nondeuterated solvent to provide a lock signal.

[f]Plus 0.5 mol/dm³ DNO_3.

[g]This compound is highly toxic (as may be some of the other references listed) and should not be used directly.

APPENDIX 2: NMR TENSORS OTHER THAN SHIELDING

A number of tensor quantities, in addition to shielding, affect NMR. Principal among these are dipolar coupling, indirect *J*-coupling and quadrupolar coupling. For completeness, we mention below usages for these tensors:

(a) Simple dipolar coupling is axial (so that $\eta_D = 0$) and its isotropic average is zero. Therefore, apart from orientation information, such coupling between a pair of nuclei *i* and *j* is fully defined by the dipolar coupling constant, *D*:

$$D = \left(\mu_o/4\pi\right)\left(\hbar/2\pi\right)\gamma_i\gamma_j/r_{ij}^3 \text{ in frequency units*} \tag{25}$$

The *Z* axis is automatically given by the internuclear vector r_{ij}. The usual formulae then result in

$$D_{XX} = D_{YY} = D \ (\equiv D_\perp) \tag{26}$$

$$D_{ZZ} = -2D \ (\equiv D_{//}) \tag{27}$$

Thus, use of anisotropy notation gives

$$\Delta D = -3D \tag{28}$$

The dipolar tensor may become non-axial when there is molecular-level mobility, causing averaging.

(b) Indirect coupling generally has a non-zero isotropic average and is not axially symmetric. However, any asymmetry (η_J) is almost always ignored (though this is rarely theoretically justifiable), and an anisotropy convention is generally adopted

$$\Delta J = J_{//} - J_\perp \tag{29}$$

where the subscripts indicate components parallel and perpendicular to the assumed symmetry axis.

(c) Quadrupolar coupling is not, in general, axially symmetric but its isotropic average is zero. Most references [42,43] choose the components such that $|\chi_{ZZ}| \geq |\chi_{YY}| \geq |\chi_{XX}|$**. Unfortunately, because the isotropic average is zero, this places the components in the algebraic order χ_{ZZ}, χ_{XX}, χ_{YY} (or the reverse), which is neither sensible nor consistent with shielding notation. Quadrupolar interactions are generally expressed in terms of a "quadrupole coupling constant", $\chi^\dagger$, defined as the largest component

$$\chi_{ZZ} \equiv \chi = e^2 q_{ZZ}Q/h \tag{30}$$

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*Some authors [41] attribute a negative sign to this parameter.

**Frequently, it is the components of the electric field gradient, V_{jj} or eq_{jj}, which are listed, rather than those of the coupling constant. Note that it is normal for the components to be labeled *XX*, *YY*, and *ZZ* rather than 11, 22, and 33.

[†]An alternative symbol, C_Q, is frequently used for this quantity, though χ is recommended by IUPAC [23].

This quantity may be either positive or negative, since both q_{ZZ} and Q can be separately positive or negative. Given the zero isotropic average, an anisotropy ($= \chi_{//} - \chi_{\perp}$ in an axial case) may be simply defined by

$$\Delta\chi = \tfrac{3}{2}\,\chi \tag{31}$$

though this parameter is seldom listed. However, the second parameter (i.e., the asymmetry η_Q, which ranges from 0 to 1) takes the same form as for shielding (though with X and Y reversed)

$$\eta_Q = (\chi_{XX} - \chi_{YY})/\chi_{ZZ} \tag{32}$$