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FURTHER CONVENTIONS FOR NMR CHEMICAL SHIFTS
(IUPAC Recommendations 2006)

Prepared for publication by

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6 39 **Abstract:** IUPAC has published a number of recommendations regarding the reporting of
7 40 nuclear magnetic resonance (NMR) data, especially chemical shifts. The most recent
8 41 publication [*Pure Appl. Chem.* **73**, 1795-1818 (2001)] recommended that tetramethylsilane
9 42 (TMS) serve as a universal reference for reporting the shifts of all nuclides, but it deferred
10 43 recommendations for several aspects of this subject. This document first examines the extent
11 44 to which the shielding in TMS itself is subject to change by variation in temperature,
12 45 concentration, and solvent. On the basis of recently published results, it has been established
13 46 that the shielding of TMS (along with that of DSS, often used as a reference for aqueous
14 47 solutions) varies only slightly with temperature but is subject to solvent perturbations of a
15 48 few tenths of a ppm. Recommendations are given for reporting chemical shifts under most
16 49 routine experimental conditions and for quantifying effects of temperature and solvent
17 50 variation, including the use of magnetic susceptibility corrections and of magic-angle
18 51 spinning (MAS).
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22 53 This document provides the first IUPAC recommendations for referencing and
23 54 reporting chemical shifts in solids, based on high-resolution MAS studies. Procedures are
24 55 given for relating ^{13}C NMR chemical shifts in solids to the scales used for high-resolution
25 56 studies in the liquid phase. The notation and terminology used for describing chemical shift
26 57 and shielding tensors in solids is reviewed in some detail, and recommendations are given for
27 58 best practice.
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61 **1. INTRODUCTION***

62
63 IUPAC has published a number of recommendations for handling data relating to nuclear
64 magnetic resonance (NMR) [1-4]. The most recent recommendations in 2001 [4] focused
65 particularly on conventions for reporting chemical shifts. These recommendations included a
66 minor redefinition of the chemical shift δ for a nuclide X:

$$67 \delta_{X, \text{ sample}} = (v_{X, \text{ sample}} - v_{X, \text{ reference}}) / v_{X, \text{ reference}} \quad (1)$$

68
69
70 Eq. 1 differs from previous definitions in deleting a factor of 10^6 , for reasons explained in
71 reference [4]. Because the numerator is normally expressed in Hz whereas the denominator
72 is given in MHz, this formulation leads to values readily expressed in ppm. The suffix “ppm”
73 is interchangeable with “ $\times 10^{-6}$ ” in equations, just as % is interchangeable with $\times 0.01$.

74
75 Also recommended [4] was a unified scale for reporting chemical shifts of any
76 nuclide X relative to a primary internal reference, *viz.* the proton resonance of
77 tetramethylsilane (TMS)[†] in a dilute solution in CDCl_3 (volume fraction $\varphi < 1\%$). To relate
78 data on the unified scale to chemical shifts expressed relative to a secondary reference of the
79 same nuclide X, a quantity \mathcal{E} was defined as the ratio of the secondary (isotope-specific)
80 frequency, v_X^{obs} , to that for ^1H of TMS, $v_{\text{TMS}}^{\text{obs}}$, in the *same* magnetic field. As pointed out in
81 reference [4], \mathcal{E} can conveniently be expressed as a percentage:

$$82 \mathcal{E} / \% = 100 (v_X^{\text{obs}} / v_{\text{TMS}}^{\text{obs}}) \quad (2)$$

83
84
85 The document [4] discussed the use of three techniques for referencing chemical
86 shifts – (a) internal reference; (b) external reference; and (c) substitution method, with the
87 field locked on an internal deuterium resonance for both sample and reference measurements.
88 Methods (a) and (c) were recommended, where feasible, because they avoid the magnetic
89 susceptibility artifact introduced by method (b). An alternative substitution method, with no
90 field-frequency lock (or an external lock) was not discussed there but will be covered in this
91 document primarily because it is commonly used for solids.

92
93 The 2001 recommendations document set aside temporarily a number of more
94 specialized (but nevertheless important) areas for later discussion. As a result, an IUPAC
95 task group has now addressed several matters, as follows:

- 96
- 97 • Temperature dependence of the ^1H chemical shift of TMS
 - 98 • Shape factor for making magnetic susceptibility corrections when an external
99 reference must be used and samples cannot be considered as infinite cylinders
 - Solvent dependence of the ^1H chemical shift of TMS

* Abbreviations used: TMS, tetramethylsilane; DSS, 3-(trimethylsilyl)propane-1-sulfonate, sodium salt – commonly called 2,2-dimethyl-2-silapentane-5-sulfonate, sodium salt; TSP, 3-(trimethylsilyl)-propionate, sodium salt; DMSO, dimethylsulfoxide; THF, tetrahydrofuran; NMR, nuclear magnetic resonance; MAS, magic angle spinning; ZAS, zero-angle spinning; SA, shielding anisotropy; CSA, chemical shift anisotropy

† To be more precise, the dominant proton resonance line from $^{12}\text{C}_4^1\text{H}_{12}^{28}\text{Si}$. Resonances at slightly different chemical shifts can be observed from other isotopomers (usually as ^{13}C and ^{29}Si “satellites”).

- 100 • Alternative scenarios for referencing (with relevant \bar{E} values) for certain nuclides,
101 including ^{15}N
- 102 • Aspects of magic angle spinning for both liquids and solids
- 103 • Procedures for chemical shift referencing in solid samples
- 104 • Terminology for reporting chemical shift/shielding tensors

105
106 Each of these subjects is considered in this document, along with related comments and
107 relevant recommendations for future practice. Section 2 discusses general concepts, whereas
108 Sections 3-8 relate mostly to solutions. Sections 9 and 10 refer mostly to solids.

111 2. GENERAL ASPECTS OF CHEMICAL SHIFTS

112
113 The definition of chemical shift (symbol δ), as expressed in Eq. (1), is based on observation,
114 not theory; that is, δ describes a *measured* value for the nuclide. The value of δ obtained by
115 applying Eq. 1 to a particular nuclide in a given chemical compound can vary substantially,
116 depending on the conditions used for measuring the sample and reference frequencies. The
117 basic requirement for a valid measurement is that the resonance frequencies for sample and
118 reference be obtained under precisely the same value of the magnetic induction, B_0 . In some
119 experimental measurements, as described below, B_0 (sample) $\neq B_0$ (reference) as a result of
120 bulk (isotropic) magnetic susceptibility (BMS) effects, which give rise to demagnetizing
121 fields [5]. In these circumstances, it is essential to apply a suitable correction, as described in
122 Section 5, and it is appropriate to designate a “corrected” or “true” chemical shift to
123 distinguish it from the “apparent” or observed value obtained by rote application of Eq. (1)
124 when an external referencing procedure is employed.

125
126 At the theoretical level, the shielding σ that is the basis for the chemical shift is known
127 to depend on complex intramolecular factors and, except for gases at very low pressure, on
128 many intermolecular factors as well. It is, therefore, important to record any experimental
129 conditions (*e.g.* solvent, temperature, concentration, pressure) that are thought to be
130 significant for the particular investigation and to recognize that the value of δ may vary as
131 these parameters are changed. However, it is generally *not* desirable to speak of “correcting”
132 a chemical shift that has been properly measured under a particular set of conditions or of
133 converting that value to a “true” chemical shift (except as mentioned above for BMS effects).
134 Provided the measurements are made as described in the preceding paragraph, no measured
135 chemical shift is more “correct” than another.

136
137 Nevertheless, it is often highly desirable to compare chemical shifts (even for the
138 same resonance) obtained under different experimental conditions. To make such
139 comparisons or to interpret variations in observed shifts in terms of possible molecular
140 mechanisms, it is important to know whether and how the resonance frequency of a
141 reference, especially that of the universal reference TMS, varies with change in parameters
142 such as temperature and solvent. Those subjects will be addressed in Sections 4-6.

144 3. REFERENCING

145
146 For *internal referencing* in isotropic liquids, the sample and reference compound are
147 molecularly dispersed in a homogeneous liquid contained in a single sample tube (usually
148 cylindrical), within which B_0 is constant [except for unavoidable gradients, which apply

149 equally to sample and reference]. Thus, the measured values of ν_{sample} and $\nu_{\text{reference}}$ can be
150 used directly in Eq. 1 to provide a chemical shift, albeit one that may be highly dependent on
151 intermolecular effects.

152
153 For *external referencing*, the sample and reference substances are physically
154 contained in separate containers within the same magnet gap, often in coaxial cylindrical
155 tubes. If the applied magnetic field H_0 is sufficiently homogeneous (as is normally true),
156 both sample and reference experience the same external field. However, the nuclear
157 induction field (B_0) within each substance depends on its bulk volume magnetic
158 susceptibility, κ_{sample} and $\kappa_{\text{reference}}$, which are normally not identical, and the effect of average
159 shape factors $\bar{\alpha}_{\text{sample}}$ and $\bar{\alpha}_{\text{reference}}$, which are normally very similar. Hence, the measured
160 frequencies must be adjusted to take into account the different values of B_0 – a subject that
161 will be discussed in detail in Section 5.

162
163 Two quite different scenarios arise for chemical shifts measured by the *substitution*
164 *method*. The substitution method implies that the reference is substituted for the sample in
165 the probe, so the measurements of ν_{sample} and $\nu_{\text{reference}}$ are made consecutively, not
166 concurrently. If the magnetic field is thought to have adequate stability for the measurement
167 being conducted, as in most experiments with solid samples and occasionally with some
168 high-resolution studies of liquid samples, the experimenter might rely on this stability,
169 *without a field/frequency lock*, to ensure that H_0 remains the same for the two measurements.
170 This then results in the same situation as in external referencing: in general, $B_0(\text{sample}) \neq$
171 $B_0(\text{reference})$, and a correction is needed for the effect of BMS. (If the sample and reference
172 are both very dilute solutions in the same solvent, then the susceptibility correction may, of
173 course, be negligible.) One important restriction in using the substitution method without a
174 lock is that the magnetic field must not be re-shimmed between the two measurements, since
175 a small but unknown z_0 component often accompanies higher-order field gradient shims.

176
177 The second substitution method uses a field/frequency lock based on a substance
178 (usually involving the ^2H signal of a deuterated solvent) contained *within* each of the two
179 tubes being measured (containing sample of interest and reference respectively). This
180 *internally locked* substitution method presents an entirely different situation. Here, the lock
181 ensures that the instrument alters H_0 in order to maintain B_0 within the tube at a constant
182 value. If the lock substance is identical for the sample and reference measurements and is not
183 influenced appreciably by different intermolecular interactions in the two instances, then
184 $\delta_{\text{sample}}^{\text{D}} = \delta_{\text{reference}}^{\text{D}}$, B_0 is constant, and the measured frequencies may be used in Eq. 1.
185 However, if different lock substances are used, then a correction must be applied to account
186 for the different chemical shifts of these two materials. This matter was discussed in some
187 detail in the 2001 recommendations document [4]. With most recently-installed
188 spectrometers, the manufacturers have built such corrections into the software, but it is
189 important for the experimenter to ascertain whether that has been done and what values of the
190 chemical shifts for the lock compounds have been entered into the spectrometer's look-up
191 tables.

193 4. TEMPERATURE DEPENDENCE OF THE ^1H CHEMICAL SHIFT OF TMS

194
195 Most NMR studies are carried out at a single temperature, often the ambient temperature of
196 the probe. In some instances, however, it is important to examine the variation of one or
197 more chemical shifts within a sample as the probe temperature is varied. Such chemical
198 shifts are measured with respect to TMS, and the implicit assumption is often made that the

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3 199 ^1H chemical shift of TMS does not vary with temperature. However, that assumption has no
4 200 theoretical basis, since excitation of vibrational and rotational modes with increased
5 201 temperature may alter the intramolecular shielding of TMS, and changes in solvent effects
6 202 may also influence the intermolecular shielding of TMS.
7 203

8 204 The only method that, at present, seems feasible for determining the temperature
9 205 dependence of the chemical shift of TMS is to measure the ^1H TMS resonance as a function
10 206 of temperature relative to a substance that is believed to have a resonance frequency
11 207 independent of temperature. This concept was introduced by Jameson and Jameson in 1973,
12 208 [6] when they measured the ^1H resonance of neat TMS relative to the resonance of ^{129}Xe in
13 209 xenon gas. An isolated Xe atom has no vibrational or rotational modes that can be excited,
14 210 and collisional effects on the resonance frequency, which can be substantial in ^{129}Xe , could in
15 211 principle be negated by extrapolation to zero pressure. Those studies [6, 7], extended by
16 212 Morin *et al.* in 1982 [8] to account for the magnetic susceptibility of TMS, reported a rather
17 213 significant temperature coefficient for the TMS chemical shift. However, these
18 214 investigations suffered from the shortcomings in sensitivity and reliability inherent in the use
19 215 of the 90 and 100 MHz NMR instruments of that period.
20 216

21 217 In reviewing the literature, we determined that the existing data were inadequate to
22 218 serve as the basis for an IUPAC recommendation. Accordingly, members of our task group
23 219 undertook new experimental observations, based on the Jameson concept but using ^3He gas at
24 220 low pressure, together with modern 400 MHz NMR instrumentation [9]. ^3He has better NMR
25 221 sensitivity than ^{129}Xe and is far less susceptible to interatomic interactions. In fact, its
26 222 resonance frequency was found not to have any significant pressure dependence from about
27 223 0.1 to 2.1 atmospheres. Thus, we believe that ^3He is an excellent temperature-independent
28 224 standard.
29 225

30 226 In this investigation [9] the ^1H chemical shift of TMS in dilute solution in CDCl_3 (the
31 227 primary reference recommended in reference [4]) was found to vary only slightly with
32 228 temperature (with an average temperature coefficient of approximately -5×10^{-4} ppm/ $^\circ\text{C}$) over
33 229 a temperature range of more than 200°C (-75°C to $+130^\circ\text{C}$). This is approximately a factor
34 230 of six smaller than the temperature coefficient reported for neat TMS in 1982 [8].
35 231

36 232 Subsequently Hoffman [10] repeated some measurements and extended the work to
37 233 cover TMS in a number of commonly used organic solvents (CDCl_3 , CD_3OD , CD_3CN ,
38 234 $\text{DMSO}-d_6$, acetone- d_6 , and THF- d_8). He also investigated aqueous solutions, using TMS and
39 235 two more soluble derivatives, DSS and TSP. Although the published results show non-linear
40 236 behavior, particularly at low temperatures, overall the results can be approximated over wide
41 237 temperature ranges by average temperature coefficients for TMS in the range of 0 ppm/ $^\circ\text{C}$ to
42 238 -6×10^{-4} ppm/ $^\circ\text{C}$.
43 239

44 240 These studies necessitated the use of external referencing, since the ^3He gas and the
45 241 solutions of TMS were in separate compartments of coaxial sample tubes. The authors
46 242 corrected for the temperature variation of volume magnetic susceptibility, an effect that was
47 243 comparable in magnitude with the observed changes in chemical shift and of opposite sign.
48 244 Because of uncertainties in the magnitudes of magnetic susceptibilities and in temperature
49 245 calibration, we believe that the resulting chemical shift data must be used with caution.
50 246 However, the totality of these results makes it clear that the chemical shift of TMS (as well as
51 247 that of DSS, the reference recommended for aqueous solutions [3]) has a very small
52 248 temperature dependence, usually amounting to only 0.01 ppm over a temperature range of
53 249 about 20°C , which is often smaller than other experimental uncertainties. Thus the vast

250 majority of NMR data referenced to TMS and DSS require no adjustment to account for
 251 differing temperatures of acquisition.

252
 253 These findings permit us to make two recommendations, as follows:

254
 255 *Recommendation 1: The acquisition temperature should be stated (including an estimate of*
 256 *“ambient” probe temperature) when chemical shift data are reported, but for temperatures*
 257 *in the region of 25°C it is neither necessary nor desirable to adjust the observed chemical*
 258 *shift data to any “standard” temperature.*

259
 260 *Recommendation 2: In instances where it is desired to make comparisons of chemical shifts*
 261 *measured with respect to the ¹H resonance of TMS over a large temperature range between*
 262 *–20°C to 80°C, IUPAC recommends that a value of -5×10^{-4} ppm/°C for the temperature*
 263 *coefficient of the chemical shift of TMS be used, or that data from references [9] and [10] be*
 264 *consulted for values at specific temperatures or for temperatures outside this range.*

265 266 267 **5. MAGNETIC SUSCEPTIBILITY CORRECTION. SHAPE FACTOR**

268
 269 The observed shift, δ_{obs} , of a signal arising from a homogeneous liquid sample consists of two
 270 components: chemical shift δ (including the effects of intermolecular interactions), and BMS
 271 shift δ_{κ} , [11].[‡] The latter is typically 3 ppm but usually varies by less than 1 ppm between
 272 solvents. The BMS shift is identical in ppm (independent of the nuclide observed) for all
 273 signals in a homogeneous sample. In this case no susceptibility measurement or correction is
 274 required if the chemical shift is reported relative to an internal reference [4]. However, the
 275 BMS shift needs to be taken into account when comparing samples that are physically
 276 separated, such as in external referencing, as described in Section 3. The BMS shift depends
 277 on the shape factor and magnetic susceptibility, as quantified in Eq. 3 (in SI units):[§]

$$278 \quad \delta = \delta_{\text{obs}} + \delta_{\kappa} = \delta_{\text{obs}} + \left(\frac{1}{3} - \bar{\alpha}\right)(\kappa - \kappa_{\text{ref}}) \quad (3)$$

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

287
 288 Table 1 lists the theoretical shape factors for some simple sample shapes. Whilst
 289 nearly all solution-state NMR experiments are conducted with cylindrical samples (generally
 290 of effectively infinite length) oriented parallel to the applied magnetic field, there is particular
 291 significance in the shape factor for cylindrical samples with the cylinder axis at the magic
 292 angle, 54.736°, to B_0 since this is $1/3$, which means that the correction factor for BMS is zero.

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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.

[‡] Eq. 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.

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

$$295 \quad \delta_\kappa = \frac{\kappa}{3} \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad (4)$$

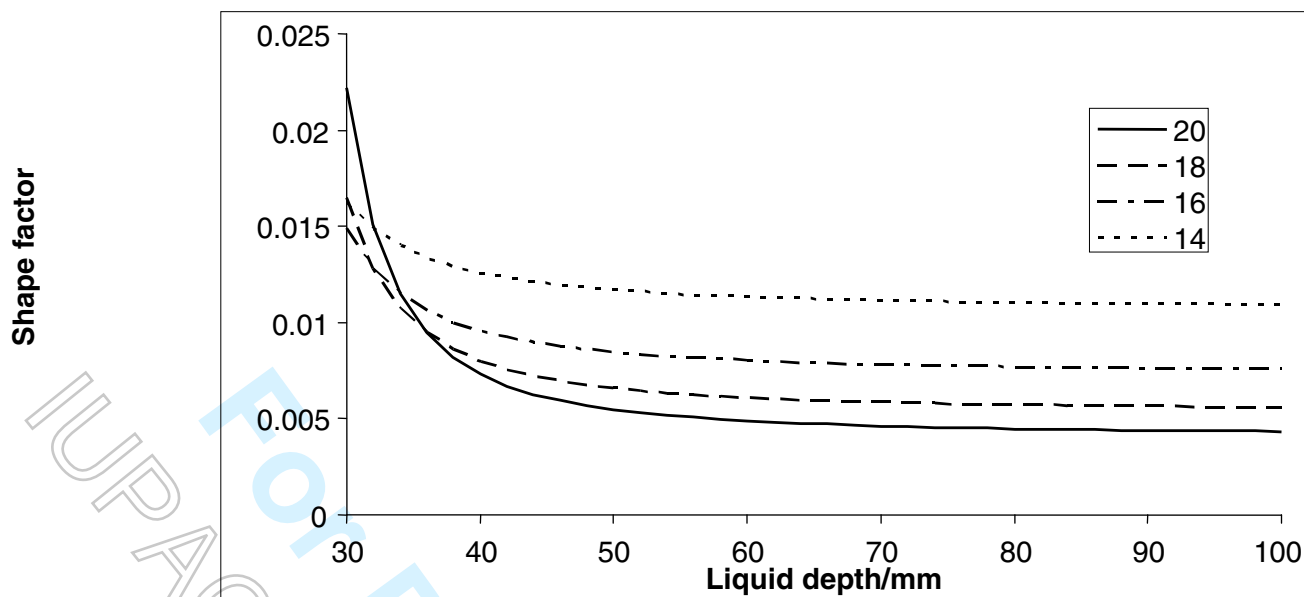
296 This situation holds also for points along the central axis of any cylindrically symmetrical
 297 object aligned with the magic angle. Moreover, for infinite cylinders inclined at the magic
 298 angle to \mathbf{B}_0 , even points away from the central axis have a time-averaged shape factor of $1/3$,
 299 during sample rotation, and hence the shift effect of isotropic magnetic susceptibility
 300 averages to zero. Indeed, this is true for a cylindrical sample tube of finite length and for any
 301 shape cylindrically symmetrical about the magic angle. However, spinning at the magic angle
 302 is necessary to eliminate off-axis and end effects. The required spin rates are discussed in
 303 [14]. Then, chemical shift measurements made at the magic angle by replacement require no
 304 (isotropic) BMS corrections, a feature which is of particular significance for solids (see
 305 section 9) but is also valid for solutions. Magic-angle spinning measurements are therefore
 306 superior to external referencing. The idea of external referencing for both ^1H and ^{13}C using
 307 1% TMS in deuteriochloroform in conjunction with the recommended Ξ values is thus a
 308 straightforward proposition for MAS NMR studies.

309
 310 For all but the simplest shapes, the calculation and measurement of shape factors are
 311 complex issues that are beyond the scope of these recommendations. However, Hoffman [15]
 312 recently applied the basic theory to determine the shape factor for typical NMR sample tubes,
 313 using the geometry and receiver coil configuration of a superconducting magnet. For a 5 mm
 314 NMR sample tube with liquid 20 mm above and 20 mm below the center of the receiver coil,
 315 the effective average shape factor, expressed in SI units, is approximately 0.007, as indicated
 316 in Fig. 1, which is adapted from reference [15]. The factor $(1/3 - \bar{\alpha})$ thus differs by only 2%
 317 from the theoretical value of $1/3$. For many purposes this difference is negligible, but it may
 318 be significant when the BMS must be determined in order to compare chemical shifts in
 319 solvents of considerably different magnetic susceptibility. Moreover, the shape factor may be
 320 considerably larger for sample volumes or instrument parameters (including size and location
 321 of receiver coil) that differ from the parameters used to derive Fig. 1.

322
 323
 324 **Table 1. Shape factors for selected samples**
 325

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	$1/3$
Infinite horizontal cylinder	$1/2$
Infinite cylinder at angle θ to the field	$(1 - \cos^2 \theta)/2$

326
 327 **Figure 1.** Shape factors for a 5 mm NMR tube whose bottom is at various depths (14, 16, 18
 328 and 20 mm) below the receiver-coil center. This figure is adapted from reference [15]
 329 and depends on a number of parameters assumed there for instrument geometry and
 330 receiver coil sensitivity.
 331



332
333
334
335 The volume susceptibility of most solvents, in SI units, lies in the range -4.91 ppm for
336 nitromethane to -14.53 ppm for diiodomethane, where ppm indicates " $\times 10^{-6}$ " [12]. For
337 common NMR solvents at room temperature it ranges from -5.66 ppm for acetone- d_6 to
338 -9.15 ppm for chloroform- d [15, 16]. Estimates for magnetic susceptibility at other
339 temperatures can usually be made by assuming a constant molar susceptibility and applying
340 corrections for solvent density.

341
342 Most tabulated values of bulk isotropic magnetic susceptibility have been measured
343 using a magnetic susceptibility balance [17]. In addition, various NMR methods have been
344 proposed for measuring magnetic susceptibility, some depending on the use of the geometry
345 of an iron-core magnet in which the sample tube axis is at 90° to the magnetic field axis [18,
346 19]. Others employ a spherical sample holder inside a cylindrical sample tube [19, 20] or
347 rely on gross distortion of line-shape when the bottom of the sample tube is close to the
348 receiver coil [16].

349
350 A more promising modern NMR method for measuring susceptibility makes use of
351 measurements from coaxial cylindrical sample tubes spun (a) about an axis oriented
352 parallel to the magnetic field axis and spun (b) at the magic angle. The true chemical shift (δ
353 in Eq. 3) can be measured directly by MAS because the BMS shift is zero. Small errors in
354 the magic angle lead to large changes in resonance frequency, but the magic angle can be set
355 precisely, as discussed in Section 9, to yield an accuracy in δ of 0.0004 ppm. Since $\delta_{\text{obs, vertical}}$
356 depends only on *differences* in susceptibilities, the measurement is normally repeated with a
357 sample of accurately known susceptibility, such as water. The differences $\Delta\delta$, along with the
358 known susceptibility κ_0 , are then used in Eq. 5 to determine κ :

$$359 \quad \kappa = \frac{\Delta\delta_{\text{obs, vertical}} - \Delta\delta_{\text{magic}}}{\frac{1}{3} - \bar{\alpha}} + \kappa_0 \quad (5)$$

360
361 In Section 6, we shall apply this technique to investigate the effect of solvent variation on the
362 TMS chemical shift. Two recommendations follow from the discussion in this section:

363

364 *Recommendation 3: In situations where it is necessary to use an external reference or to*
 365 *compare chemical shifts of samples in separate tubes oriented parallel to \mathbf{B}_0 , the BMS shift,*
 366 *symbol δ_κ , should be quantified and subtracted from the observed shift, symbol δ_{obs} , to yield*
 367 *the chemical shift, symbol δ . The BMS shift may be calculated from Eq. 3, with α*
 368 *approximated as indicated in the text.*

370 *Recommendation 4: In line with general IUPAC recommendations, SI units and conventions*
 371 *should be used for shape factor, symbol α , and volume magnetic susceptibility, symbol κ .*
 372 *Because cgs units have been widely used in tabulations of susceptibility data, the convention*
 373 *should always be explicitly stated. The diamagnetic susceptibilities of common NMR*
 374 *solvents are small and are conveniently quoted in ppm.*

376 6. SOLVENT EFFECTS ON THE ^1H CHEMICAL SHIFT OF TMS

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

383 In some instances, where solvent effects on the chemical shift of a sample are
 384 significant in the interpretation of data, it may be important to take into account the change in
 385 shielding of TMS with solvent variation. Clearly such changes can be measured only with
 386 samples that are physically separated from each other, thus requiring either correction for
 387 magnetic susceptibility or measurements at precisely the magic angle. Table 2 provides
 388 results for TMS in ten solvents, where corrections for magnetic susceptibility have been made
 389 using Eq. 3. The last column provides data obtained by MAS for five of the solvents, where
 390 no correction is required. The agreement is excellent.

392 Although the results in Table 2 should not be regarded as having the quantitative
 393 reliability of critically evaluated data from several independent studies, they illustrate quite
 394 well the magnitude of change in shielding of the protons in TMS with change of solvent. As
 395 a non-polar molecule, with approximately tetrahedral geometry, TMS is expected to interact
 396 with solvent molecules only rather weakly. Nevertheless, the results in Table 2 show that the
 397 ^1H resonance of TMS in a variety of non-aromatic solvents varies over a range of more than
 398 0.2 ppm at room temperature (25°C). For aromatic solvents, the variation is appreciably
 399 larger, as expected because of well-known ring current effects.

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

405 Solvent	$\delta_{\text{obs}}/\text{ppm}^a$	κ/ppm^b	δ/ppm^c	$\delta_{\text{MAS}}/\text{ppm}^d$
406 Chloroform- <i>d</i>	0.00	-9.153	0.00	0.000
407 Acetone- <i>d</i> ₆	0.97	-5.700	-0.16	-0.160
408 Acetonitrile- <i>d</i> ₃	0.83	-6.597	-0.01	-0.011
409 DMSO- <i>d</i> ₆	0.54	-7.730	0.07	0.062
410 D ₂ O	0.01	-8.840	-0.09	<i>e</i>

411	Methanol- d_4	0.72	-6.606	-0.11	-0.106 ^f
412	THF- d_8	0.31	-7.914	-0.10	-0.109
413	Benzene- d_6	-0.01	-7.82	-0.45	<i>e</i>
414	Nitrobenzene- d_5	-0.03	-7.28	-0.64	<i>e</i>
415	Toluene- d_8	0.05	-7.72	-0.42	<i>e</i>

416

417 ^a Apparent ¹H chemical shift of TMS in various solvents in coaxial tubes spun parallel to **B**₀,
 418 relative to TMS in CDCl₃ as an external reference; based on experimental data from
 419 references [10, 16].

420 ^b Volume magnetic susceptibility, from various published sources but presented here in SI
 421 units [12, 13, 15, 16].

422 ^c δ from Eq. 3, using a shape factor of 0.007.

423 ^d ¹H chemical shift of TMS in various solvents relative to TMS in CDCl₃ in coaxial tubes
 424 spun at the magic angle; see reference [21].

425 ^e Not determined.

426 ^f Measured using non-deuterated methanol as the solvent.

427

428 7. A STANDARD STATE FOR THE ¹H TMS REFERENCE?

429 The 2001 recommendations document [4] pointed out the desirability in principle of having a
 430 physico-chemical *standard state* for TMS, in which relevant parameters such as
 431 concentration, temperature and pressure are specified. A study reported in that document
 432 showed that the chemical shift of TMS in CDCl₃ was constant below a volume fraction $\varphi \approx$
 433 1%; hence, a precise “standard” concentration was considered unnecessary for most
 434 purposes. We now know (Section 4) that the temperature variation is also small, usually
 435 amounting to only 0.01 ppm over a temperature range of about 20 °C, and thus requiring no
 436 adjustment for the vast majority of NMR data referenced to TMS. The effect of pressure has
 437 not been studied in detail, but the TMS chemical shift data in reference [10] did not display
 438 any large variation at the highest temperatures, where vapor pressures were sometimes in the
 439 tens of atmospheres. For practical applications, virtually all measurements are made at
 440 ambient pressure of approximately 1 atm, or with air removed to leave the sample under its
 441 own vapour pressure. This leads to a recommendation:

442

443 *Recommendation 5: For samples subject to ambient atmospheric pressure, the applied*
 444 *pressure may be assumed to be 1 atm, but any substantial variation from 1 atm should be*
 445 *stated. In conformity with earlier IUPAC recommendations, [1, 2] information should be*
 446 *supplied on treatment of samples to remove oxygen.*

447

448 With the accumulation of reasonably reliable data for change of the resonance
 449 frequency of TMS with temperature, concentration, solvent and pressure, as described in this
 450 document and the 2001 recommendations [4], it is becoming feasible to consider a standard
 451 state for referencing chemical shifts. With ever-improving measurement techniques, there
 452 may be specific applications where an agreed standard state will be desirable. However, for
 453 the vast majority of NMR studies, there seems to be insufficient value to warrant the
 454 complexity of converting chemical shift data to such a “standard state.” IUPAC believes that
 455 the recommendations given in this document and in references [3] and [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 CDCl₃ at 25°C under a standard atmosphere. Full details of any conversion process should be given (e.g., source and application of magnetic susceptibility data, 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 ³He in the neutral helium atom, for which shielding computations should be accurate. In fact, the 2001 recommendations [4] mentioned the desirability of using ³He 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 ³He to TMS in CDCl₃ [9,10]. Meanwhile, *ab initio* calculations are reported to give an accurate value of 59.93677 ppm for the absolute shielding of ³He (reference [22], page 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 \mathcal{E} VALUES

The IUPAC recommendations 2001 [4] included tables of \mathcal{E} values, one for each magnetic nuclide. Data from the tables have been widely disseminated in magnetic resonance journals and in other ways. Except for the rare earths, where only approximate values of \mathcal{E} were available, IUPAC recommended that the values of \mathcal{E} 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 has sometimes been questioned, since it might appear that newer results or correction of any errors in the tables 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. To allow changes to be made from time to time in these values would result in inconsistent and confusing comparisons.

Although the values published in the 2001 document were carefully reviewed, they were extracted from various sources, as described in that article [4]. It was clear when the tables were formulated that errors could have occurred and that all results were not of equivalent accuracy. However, *for the intended purpose*, we believe that the values in Tables 1 and 2 in the 2001 document [4] are of adequate accuracy. For example, it has come to our attention that in processing data for the 2001 paper an error was made in reporting \mathcal{E} for ³He. If a value for \mathcal{E} were derived from data in recent publications, such as reference [9], a value differing by about 6 ppm would be obtained, but this change in \mathcal{E} would be of no practical significance. We reaffirm the recommendation *not* to update the values in Table 1 of the 2001 document [4]. However, as noted in that document, for specific studies investigators should report their experimental results in a way that meets their needs for consistency, without suggesting a re-evaluation for \mathcal{E} .

505 The recommendation regarding δ values does not apply to other results cited in the
506 2001 document. For example, we have learned (M. Jaszunski, private communication) that a
507 typographical error in the IUPAC "Green Book" [23] for the value of the magnetic moment
508 of ^{207}Pb resulted in incorrect values for several derived quantities in the 2001 document.**
509 The correct value is given in the latest edition of the Green Book [available in provisional
510 form on the IUPAC web site, www.iupac.org].

511 For conciseness, Tables 1-3 in the 2001 document [4] list a value of δ for only one
512 substance for each magnetic nuclide. However, it was recognized there that a number of
513 alternative compounds have been widely used as references. Several of these, including DSS
514 as a reference for aqueous solutions, were noted in the 2001 document [4]. The most
515 appropriate δ value for ^{15}N has been the subject of some discussion. Nitromethane was given
516 in the tables on the basis of its historically wide use for ^{14}N , but liquid ammonia is often cited
517 as a reference for ^{15}N , particularly in literature related to biochemical applications, and was
518 recommended by IUPAC/IUPAB for use in such applications [3].

519

520 *Recommendation 7: In addition to the recommended values in Tables 1-3 of reference [4],*
521 *the values of δ listed in Table 4 of reference [4] may be said to be recommended by IUPAC,*
522 *but it should be clearly stated which compound is being cited.*

523

524 9. REFERENCING IN SOLIDS

525

526 Chemical shift referencing in high-resolution MAS NMR experiments on solids is
527 complicated by several factors not encountered in solution-state NMR. At present no strategy
528 is in general use for providing an internal lock of any sort in MAS NMR of solids, and
529 referencing is usually done using the substitution method without a lock. In the absence of a
530 field/frequency lock, the precision of any shift measurement relies upon the inherent stability
531 of the static magnetic field. This is usually not an important consideration for solids, as
532 linewidths are significantly larger than for solutions and many modern superconducting
533 magnets have drift rates measured in Hz per week or month at ^1H frequencies. However, the
534 highest field solenoids often have significant drift rates, being built closer to the limit of
535 current technology. In this instance, field stabilization has been achieved by a calibrated
536 linear ramp of correction current to the room temperature (RT) compensation coil [26] or
537 alternatively by use of a separate external lock probe [27].

538

539 The use of an external reference in solid-state MAS experiments typically involves
540 removal of the NMR probe from the magnet to change samples. When field stability is not
541 the limiting factor, the repositioning of the probe accurately into the magnet can be a
542 significant experimental source of referencing error. Each different experimental situation
543 needs to be characterized with respect to the repeatability of resonance measurements, with
544 values of ± 0.03 ppm to ± 0.01 ppm being readily achieved [26]. An important consideration
545 here is the setting of the room temperature shims. Without an internal lock, the current
546 settings should not be changed between samples, otherwise z_0 imperfections will affect the

** The value of the maximum observable component of the magnetic moment of ^{207}Pb is given in the Green Book as +0.582 583(9) instead of the correct value of +0.592 583(9) [24], a difference on the second digit. The correct values for ^{207}Pb in Table 1 of reference 4 are: magnetic moment, $\mu/\mu_{\text{N}} = 1.026\ 38$; magnetogyric ratio, $\gamma/10^7\ \text{rad s}^{-1}\ \text{T}^{-1} = 5.676\ 25$; relative receptivities $D^{\text{P}} = 2.11 \times 10^3$; $D^{\text{C}} = 12.4$. Jaszunski and co-workers [25] recently presented an analysis of the precise values of magnetic moments for a number of bare nuclei.

547 subsequent shift measurements. Fortunately, in the typical MAS situation no adjustment of
548 the RT shims is required for different samples.

549 As discussed in Section 5, shift referencing for solution-state experiments using
550 substitution by an external standard is complicated by the demagnetizing fields [5] associated
551 with the normal sample geometry and with differing isotropic magnetic susceptibilities.
552 However, these artifacts can be corrected as indicated in Section 5. For solids, the situation is
553 more complicated since anisotropies in magnetic susceptibilities also affect the situation (see
554 below). However, for the central axis of cylindrical samples, such as in typical solid-state
555 rotors under magic-angle spinning (MAS) conditions, the (isotropic) BMS effect is zero, so
556 that replacement samples of standard substances may be used for referencing to give correct
557 chemical shifts. For off-center positions in cylindrical samples of infinite length, the average
558 of the demagnetizing field over a rotor period is zero [28, 29].

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

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

573 A substantial caveat to the above discussion arises when the sample in question is a
574 solid which possesses an anisotropic magnetic susceptibility [30, 31]. Demagnetizing fields
575 from anisotropic bulk magnetic susceptibility do not average to zero under MAS. Moreover,
576 such fields are dependent upon the size, shape and relative orientations of the particles
577 comprising the sample. In most situations these effects can be argued to be more likely to
578 produce a broadening of the observed resonances than to any resonance shifts.

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

590 Since many MAS arrangements are not convenient for liquid samples, additional
591 secondary narrow line references have been developed for solid-state measurements. For
592 example, the recent study by Morcombe and Zilm [26] provided accurate data (± 2 Hz, or
593 0.01 ppm) on ^{13}C chemical shifts for several potential reference compounds in both solid and
594 solution states, under MAS and with the conventional geometry for high-resolution NMR –

spinning parallel to 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 [26] to be related to the IUPAC recommended scale, the DSS scale, and to neat external TMS according to

$$\delta_{\text{MAS}}^{1\% \text{ TMS in CDCl}_3} = \delta_{\text{MAS}}^{\text{neat TMS}} - 0.71 = \delta_{\text{MAS}}^{5\% \text{ DSS in D}_2\text{O}} - 2.72 = \delta_{\text{MAS}}^{\text{solid adamantane}} + 37.77 \quad (6)$$

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_2O relative to neat TMS.

IUPAC recommends that the chemical shifts of all nuclides be referred to the ^1H resonance of TMS in CDCl_3 , $\varphi = 1\%$. Such a presentation is particularly useful with widespread use of heteronuclear correlation methods. Referencing of ^{13}C chemical shifts to ^1H shifts in MAS experiments can be done using \mathcal{E} values, reported here as $100 \times$ the ratio of the ^{13}C to ^1H resonance frequencies for the methyl groups in the indicated samples:

$$\mathcal{E}^{1\% \text{ TMS}} \text{ for } ^{13}\text{C} \text{ of TMS (1\% in CDCl}_3) = 25.145020\% \quad (7)$$

$$\mathcal{E}_{\text{MAS}}^{\text{neat TMS}} \text{ for } ^{13}\text{C} \text{ in neat TMS} = 25.145003_8\% \quad (8)$$

$$\mathcal{E}_{\text{MAS}}^{\text{DSS}} \text{ for } ^{13}\text{C} \text{ of 5\% DSS in D}_2\text{O} = 25.144954_8\% \quad (9)$$

Eq. (7) gives the IUPAC-recommended value [4]. Eqs. 8 and 9 give values reported by Morcombe and Zilm as the average of eight MAS measurements [26]. The value in Eq. 9 differs very slightly from that reported by Markley *et al.* [3], 25.144952_8 , which appears to be just outside the claimed experimental uncertainties. Equation (10) lists the \mathcal{E} values (relative to neat TMS) for the two adamantane ^{13}C signals under MAS conditions [26].

$$\mathcal{E}^{\text{adamantane}} \text{ relative to neat TMS} = 25.145972(7) \& 25.145745(7) \quad (10)$$

In all of the above, operation at room temperature 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 [32], so changes in probe temperature can easily produce large shifts in the average field as well as affect the MAS lineshape. 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 8: With MAS, sample replacement methods suffice to determine chemical shift measurements on solids. For ^{13}C , equation 6 provides relations that can be used to convert data measured under MAS for solids relative to neat TMS or to the high-frequency signal for adamantane to the standard 1% TMS in CDCl_3 or to DSS in water.

633
634 *Recommendation 9: For reporting chemical shifts in solids, IUPAC endorses the unified*
635 *chemical shift scale established for solutions. Equations 7-10 provide relations that may be*
636 *useful in converting results to the virtually equivalent recommended scales based on the*
637 *proton resonance of TMS in CDCl₃ and the proton resonance of DSS in aqueous solution.*

638
639 Clearly relationships for other nuclides remain to be determined.

641 10. TERMINOLOGY FOR SHIELDING AND CHEMICAL SHIFT TENSORS

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

649
650 The shielding tensor can be decomposed to a symmetric part and an antisymmetric
651 part. The latter, which in some cases will be zero because of local symmetry around the
652 nucleus in question, may contribute to relaxation but does not give rise to an observable
653 chemical shift, even in solids [33]. We consider here only the symmetric part, where $\sigma_{ij} =$
654 σ_{ji} . Then only 6 different elements are necessary. Transformation to a suitable set of axes,
655 X, Y and Z (the principal axis system, PAS) will diagonalise the matrix to give 3 principal
656 components ($\sigma_{XX}, \sigma_{YY}, \sigma_{ZZ}$). The remaining three variables determine the orientation of the
657 PAS in, say, a molecule-fixed or crystal-fixed set of axes. These six variables can be
658 predicted by suitable quantum mechanical computations (though most programs usually
659 calculate all nine components by default).

660
661 All six variables can be obtained experimentally, but many results come from
662 experiments on powdered samples (either from analysis of bandshapes of static samples or of
663 spinning sideband manifolds, which generally yield only the principal components).
664 Alternatives to the principal components are often reported. The *isotropic average*

$$665 \sigma_{\text{iso}} = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) \quad (11)$$

666
667 is invariably one of these, but there is divergence in the literature regarding the remaining two
668 (see below). In order to avoid any problems arising from this situation:

669
670 *Recommendation 10: The three principal components themselves should always be listed*
671 *explicitly (but see also recommendation 15).*

672
673 Unfortunately, there are a number of different conventions in use regarding matters of
674 notation in this area, which are sometimes confused in the literature and are often
675 inadequately defined. There are two conventions for labelling the axes, which became
676 established following the important textbooks of Haeberlen [34] and Mehring [35], both
677 appearing in 1976. In 1993, the “Maryland Group” [36] recommended additional
678 terminology. Also, it is widely recognized that shielding [and other] tensors can be expressed
679 more fundamentally in a spherical, rather than a Cartesian representation. Finally, it has been
680 suggested that [37] 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.

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

$$|\sigma_{ZZ} - \sigma_{\text{iso}}| \geq |\sigma_{XX} - \sigma_{\text{iso}}| \geq |\sigma_{YY} - \sigma_{\text{iso}}| \quad (12)$$

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, (13) and (14), have grown up for shielding anisotropy:

$$\Delta\sigma = \sigma_{ZZ} - \frac{1}{2}(\sigma_{XX} + \sigma_{YY}) \quad (13)$$

$$\zeta = \sigma_{ZZ} - \sigma_{\text{iso}} \quad (14)^{\dagger\dagger}$$

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

$$\Delta\sigma = \frac{3}{2}\zeta \quad (15)$$

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 (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 $\frac{1}{2}(\sigma_{XX} + \sigma_{ZZ})$, 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:

^{††} Haerberlen [34] 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.

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

718

719 Thus η is zero if the tensor is axial ($\sigma_{XX} = \sigma_{YY}$), which can occur for both positive and
 720 negative cases of anisotropy, and its maximum value is unity, when $\sigma_{YY} = \frac{1}{2}(\sigma_{XX} + \sigma_{ZZ})$
 721 $= \sigma_{\text{iso}}$. Note that η cannot be negative. The Haerberlen convention relates directly to the
 722 definition of the tensor axis system in the molecular or crystallographic frame.

723

724 “**Mehring notation.**” This alternative notation uses numerical subscripts instead of
 725 letters and simply designates the components in order of increasing shielding as:

726

$$\sigma_{11} \leq \sigma_{22} \leq \sigma_{33} \quad (17)$$

727

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

$$\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (18)$$

729

730 (analogous to (11)) but the relationships for anisotropy and asymmetry (analogous to (13),
 731 (14) and (16)) are more difficult to express than under the Haerberlen convention, since they
 732 depend on the position of σ_{22} between σ_{11} and σ_{33} .^{§§} Moreover, when relating components to
 733 molecular or crystallographic systems, a change of order may be necessary. These are reasons
 734 for preferring the Haerberlen convention. However, the benefit of the Mehring convention is
 735 that components for a range of related compounds are more readily compared, since there is
 736 no discontinuity when the middle component passes through the average of the outer
 737 components. Of course, computer programs for generating principal components from
 738 spectral analysis may easily calculate values of anisotropy and asymmetry under the Mehring
 739 labelling of components.

740

741 “**Maryland notation.**” The relevant literature on shielding tensors prior to 1993 is
 742 entirely couched in terms of principal components and anisotropy/asymmetry. However, in
 743 that year an *ad hoc* group of NMR spectroscopists held discussions at a Summer School in
 744 College Park, Maryland, USA and proposed [36] that the anisotropy/asymmetry convention
 745 be replaced by *span* (Ω) and *skew* (κ^{***}), with the following definitions:

746

$$\Omega = \sigma_{33} - \sigma_{11} \quad (19)$$

747

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

748

749 The components in this notation are always labelled in the Mehring order $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$.
 750 The span is an easily envisaged unsigned quantity that describes the full range of the
 751 observed spectrum, and comparisons between related systems are straightforward. A
 752 variation in sign is imposed on the skew, which is positive if $\sigma_{22} > \sigma_{\text{iso}}$ and negative if $\sigma_{22} <$
 753 σ_{iso} . Thus, the skew carries the physical insight of a prolate ($\kappa = +1$) or oblate ($\kappa = -1$)
 754 σ_{iso} .

755

§§ A few authors have incorrectly used definitions equivalent to Eq. (16) in combination with labelling 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.

756 ellipsoid representing axially symmetric shielding tensors. The situation with σ_{22} mid-way
 757 between σ_{11} and σ_{33} corresponds to $\kappa = 0$ (*i.e.* to $\eta = 1$ in the anisotropy/asymmetry
 758 convention). Whilst these parameters give a readily envisaged picture for shielding powder
 759 patterns or spinning sideband manifold intensities, they are not readily related to theory, as
 760 discussed below.

761
 762 **Recommendations on notation.** Both the Mehring and Haerberlen notations have
 763 continued to be used widely in the literature, causing occasional confusion, especially among
 764 new practitioners. However, each has its advantages, as has been pointed out, and it is not
 765 feasible at present for IUPAC to recommend that one notation should be used in all
 766 circumstances. Nevertheless, there are conventions that should be followed:

767
 768 *Recommendation 11: Haerberlen notation, with capital X, Y, Z subscript letters for the*
 769 *principal components of shielding tensors, should be used whenever relationships to*
 770 *molecular- or crystal-fixed axes are discussed.*

771
 772 *Recommendation 12: Given the wide use of both $\Delta\sigma$ and ζ we recommend either symbol as*
 773 *acceptable for reporting shielding anisotropy. η is the recommended symbol for shielding*
 774 *anisotropy (biaxiality). Definitions of these symbols should always be given.*

775
 776 *Recommendation 13: The use of anisotropy/asymmetry, rather than span/skew, is generally*
 777 *recommended. Span/skew may be used to describe or compare powder patterns or spreads*
 778 *of spinning sidebands, but they are not suitable parameters to define shielding tensors.*

779
 780 **Spherical tensor representation.** As Haerberlen (ref. [34], page 10) and Grant [37]
 781 have pointed out, at a fundamental level tensors are better represented in spherical fashion,
 782 such that a general second-order property σ may be written as:

$$783 \quad \sigma = \sigma^{(0)} + \sigma^{(1)} + \sigma^{(2)} \quad (21)$$

784
 785 where the number in brackets refers to tensor rank, with $\sigma^{(0)}$ as the isotropic value, $\sigma^{(1)}$ as the
 786 generally-ignored anti-symmetric part (with 3 components), and $\sigma^{(2)}$ as a symmetric part
 787 (with 6 different components, but subject to a zero trace). Spherical tensors are intrinsically
 788 involved in considering the effects of tensor quantities on density matrix evolution and hence
 789 on spectra, so the use of this representation is inevitable for such work. However, they are not
 790 normally quoted for experimental results. It is worth noting that:

$$791 \quad \sigma_0^{(2)} = \sqrt{\frac{3}{2}}\zeta \quad (22)$$

$$792 \quad \sigma_{\pm 2}^{(2)} = \frac{1}{2}(\sigma_{XX} - \sigma_{YY}) = \frac{1}{2}\eta\zeta \quad (23)$$

793
 794
 795
 796 The proportionalities in these equations indicate that shielding anisotropy and asymmetry can
 797 readily be related to spherical tensor components, thus facilitating theoretical interpretation,
 798 whereas the relation between spherical tensor components and span/skew is more obscure
 799 (*i.e.* there are no simple proportionalities of the type given in Eqs. (22) and (23)).

800
 801 **Icosahedral representation.** The comparison of shielding tensors, using a single
 802 scalar that represents their differences, requires using different statistical weights for different
 803 shielding components in some commonly-used representations. To eliminate this problem
 804 Grant and co-workers have introduced the icosahedral representation [37]. In this

805 representation the six components are equally distributed on the unit sphere, *i.e.* the spatial
 806 distance among all the components is the same, and therefore they can be treated with equal
 807 statistical weight when comparing shielding tensors. While the icosahedral representation is
 808 valuable for comparing tensors, it should be considered merely as a working representation.

809
 810 **Shielding & Chemical Shifts.** Confusion between shielding and chemical shift has
 811 been a problem in NMR for many years. Recently, the exclusive use of symbols σ for the
 812 former and δ for the latter has greatly assisted in eliminating the confusion.

813
 814 Isotropic chemical shifts are defined [23] in such a way that their direction is in the
 815 opposite sense from that of shielding. This arises from the definition given in equation (1),
 816 where:

$$817 \nu_{X, \text{sample}} = \frac{\gamma}{2\pi} B_0 (1 - \sigma_{X, \text{sample, iso}}) \quad (24)$$

818
 819 and $\nu_{X, \text{reference}}$ is similarly defined for the resonance of a reference compound.

820
 821 Most research papers regard the chemical shift and the shielding of a given nucleus
 822 as separate but related tensors, although this concept is not universally accepted.^{†††} If distinct
 823 tensors are accepted, then anisotropies (and skews) for chemical shifts are logically opposite
 824 in sign for those of shielding tensors (*e.g.* $\Delta\delta \equiv -\Delta\sigma$). The symbol ζ for anisotropy is,
 825 however, ambiguous unless a subscript (*i.e.* σ or δ) is used to distinguish shielding and shift.
 826 Asymmetry is unaffected, being the same for shielding and chemical shift. Span is
 827 unaffected, provided it is considered as a modulus, *i.e.* $\Omega = |\sigma_{33} - \sigma_{11}|$. Subscripts can be used
 828 with skew symbols to indicate whether they are for shift (κ_δ) or shielding (κ_σ).

829
 830
 831 *Recommendation 14: We fully endorse the use of the symbols σ and δ for shielding and*
 832 *chemical shift respectively and urge their exclusive use in NMR notation for these properties.*

833
 834 Whilst chemical shifts are defined and quoted as relative to a reference, theoreticians
 835 always compute, at least initially, absolute shielding values. Therefore there is merit in
 836 retaining the symbols σ_{iso} , σ_{XX} etc. to refer only to absolute shielding.

837
 838 *Recommendation 15: When it is necessary to report shielding tensor components on a*
 839 *relative basis (to either σ_{ref} or σ_{iso}) such data should always be explicitly indicated as $\sigma_{\text{iso}} -$*
 840 *σ_{ref} , $\sigma_{XX} - \sigma_{\text{iso}}$ etc.*

841
 842 The term "shielding" has in recent years been modified in many papers to "chemical
 843 shielding". There are reasons for discouraging this terminology, given that it was not in use
 844 in the earliest years of NMR. In the first place it gives the wrong impression, since shielding
 845 is properly described as electronic or magnetic, rather than "chemical" (whereas "chemical
 846 shift" correctly expresses the eponymous phenomenon, which is experimentally rather than
 847 theoretically based). Secondly, anisotropy in "chemical" shielding becomes abbreviated as
 848 CSA, which is then confused with chemical shift anisotropy, exacerbating the sign problem.

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 ††† Arguments for treating chemical shift and shielding as separate tensors [38] and counter-arguments [39] have been given in the literature.

850 *Recommendation 16: The term shielding anisotropy should be used, with attendant*
851 *abbreviation SA, giving a distinction from CSA (which then refers unambiguously to*
852 *chemical shift anisotropy).*

854
855 In principle, conventions recommended for shielding tensors should be consistent
856 with those in general use for other tensor properties relevant to NMR. However, this is a
857 problem, since such conventions vary significantly and it is outside the brief of this task
858 group to make proposals for matters other than shielding and chemical shift notation.
859 Nonetheless, to provide a link between the various common conventions, we mention in the
860 Appendix some of the usages for the relevant tensors.

861 11. CONCLUDING REMARKS

863 These recommendations are intended to underline the importance of reporting chemical shifts
864 in a consistent way in the literature. The recommendations are distributed through the
865 document, since it is important that they be read in the context of the relevant sections. As
866 pointed out in several instances, these recommendations extend and clarify recommendations
867 made in reference [4] and, where relevant, in reference [3], which deals primarily with
868 biopolymers. All the recommendations in the three documents are based on a practical
869 approach for reporting observations in both solids and liquids that should encourage
870 compliance with minimal effort. The distinction between chemical shift and shielding, in
871 both liquids and solids, is emphasized to encourage authors to make clear the relations
872 between experimentally determined values and the underlying theoretical constructs.

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875
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APPENDIX: NMR Tensors other than Shielding

885

886 A number of tensor quantities, in addition to shielding, affect NMR properties. Principal
887 among these are dipolar coupling, indirect "scalar" coupling and quadrupolar coupling. For
888 completeness, we mention below usages for these tensors:

889

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

893

$$894 \quad D = (\mu_o / 4\pi)(\hbar / 2\pi)\gamma_i\gamma_j/r_{ij}^3 \quad \text{in frequency units}^{\text{¥}} \quad (25)$$

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

$$897 \quad D_{XX} = D_{YY} = D (\equiv D_{\perp} \text{ say}) \quad (26)$$

$$898 \quad D_{ZZ} = -2D (\equiv D_{\parallel} \text{ say}) \quad (27)$$

899 Thus, use of anisotropy notation gives:

$$900 \quad \Delta D = -3D \quad (28)$$

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

903

- 904 (b) Indirect ("scalar") coupling has no special characteristics. Any asymmetry (η_J) is
905 almost always ignored (though this is rarely theoretically justifiable), and an
906 anisotropy convention is generally adopted:

$$907 \quad \Delta J = J_{\parallel} - J_{\perp} \quad (29)$$

908

- 909 (c) Quadrupolar coupling is not, in general, axially symmetric but its isotropic average is
910 zero. Most references [40, 41] choose the components such that $|\chi_{ZZ}| \geq |\chi_{YY}| \geq |\chi_{XX}|^{\text{§}}$.
911 Unfortunately, because the isotropic average is zero, this places the components in the
912 algebraic order χ_{ZZ} , χ_{XX} , χ_{YY} (or the reverse), which is neither sensible nor consistent
913 with shielding notation. Quadrupolar interactions are generally expressed in terms of
914 a "quadrupole coupling constant", χ^{\ddagger} , defined as the largest component:

$$915 \quad \chi_{\parallel} = \chi_{ZZ} \equiv \chi = e^2 q_{ZZ} Q / \hbar \quad (30)$$

916 This quantity may be either positive or negative, since both q_{ZZ} and Q can be
917 separately positive or negative. Given the zero isotropic average, an anisotropy ($= \chi_{\parallel}$
918 $- \chi_{\perp}$ in an axial case) may be simply defined by:

$$919 \quad \Delta\chi = \frac{3}{2}\chi, \quad (31)$$

920

¥ Some authors [42] 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
labelled 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].

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2
3 920 though this parameter is seldom listed. However, the second parameter (*i.e.* the
4 921 asymmetry η_Q , which ranges from 0 to 1) takes the same form as for shielding
5
6 922 (though with X and Y reversed):
7

8 923
$$\eta_Q = (\chi_{XX} - \chi_{YY}) / \chi_{ZZ} \quad (32)$$

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