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NMR NOMENCLATURE. NUCLEAR SPIN PROPERTIES AND CONVENTIONS FOR CHEMICAL SHIFTS

(IUPAC Recommendations 2001)

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NMR nomenclature. Nuclear spin properties and conventions for chemical shifts

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Abstract: A unified scale is recommended for reporting the NMR chemical shifts of *all* nuclei relative to the ^{1}H resonance of tetramethylsilane (TMS). The unified scale is designed to provide a precise ratio, Ξ, of the resonance frequency of a given nuclide to that of the primary reference, the ^{1}H resonance of TMS in dilute solution (volume fraction, $\varphi < 1\%$) in chloroform. Referencing procedures are discussed, including matters of practical application of the unified scale. Special attention is paid to recommended reference samples, and values of Ξ for secondary references on the unified scale are listed, many of which are the results of new measurements.

Some earlier recommendations relating to the reporting of chemical shifts are endorsed. The chemical shift, δ, is redefined to avoid previous ambiguities but to leave practical usage unchanged. Relations between the unified scale and recently published recommendations for referencing in aqueous solutions (for specific use in biochemical work) are discussed, as well as the special effects of working in the solid state with magic-angle spinning. In all, nine new recommendations relating to chemical shifts are made.

Standardized nuclear spin data are also presented in tabular form for the stable (and some unstable) isotopes of all elements with nonzero quantum numbers. The information given includes quantum numbers, isotopic abundances, magnetic moments, magnetogyric ratios and receptivities, together with quadrupole moments and line-width factors where appropriate.

1. INTRODUCTION

A distinguishing feature of nuclear magnetic resonance (NMR) is that signals are isotope-specific. In other words, each signal can be firmly linked to a particular element and nuclide. Two features follow: Firstly, there is a close connection with chemistry and, in particular, with the periodic table, since almost all elements can be studied; secondly, the spin properties of each isotope need to be clearly tabulated and firmly understood. It is a principal purpose of this document to provide such information.

Any scientific discipline relies for its effectiveness upon communication of ideas and results, which can only occur if there is an agreed basis for the meaning of the terminology used. The process of communication is greatly eased if there are universally recognized conventions for measurement and reporting of quantities with their units and symbols. The aim of this document is to set down such a set of meanings and conventions in relation to chemical shifts (and shielding) and to list resonance frequencies for reference signals for each magnetically active nucleus.

Within IUPAC, Commission I.5 has been responsible for molecular structure and spectroscopy. Until now, this Commission has produced only three reports [1–3] specifically relating to NMR. The two earlier reports refer to chemical shifts. The more recent of these two publications is 25 years old, and the NMR world has changed beyond recognition since then. Recently, however, conventions for chemical shifts of five nuclei of wide biochemical interest have been included in "Recommendations for the presentation of NMR structures of proteins and nuclei acids" [4] by Commission I.7, Biophysical Chemistry. The current document addresses the same issue for general chemical usage and

extends the conventions to the entire range of active nuclei, providing a more comprehensive guide to the factors important in chemical shift referencing. A unified list of properties of NMR-observable nuclei is also included herein.

2. NUCLEAR SPIN PROPERTIES

The phenomenon of NMR is based upon the magnetic properties of various isotopes of elements in the periodic table. It is, therefore, important to have an accessible unified list of these properties. These are contained in Tables 1–3 of this article, which include the following for each stable isotope and each long-lived radioactive isotope with nonzero spin:

(i) The nuclear spin quantum number, I, of the ground state of the nucleus.[*] This defines the magnitude of the spin angular momentum vector (and hence magnetic dipole moment—see below). The z-component quantum number is then denoted by m_I.

(ii) The standard isotopic natural abundance, x, expressed as a mole fraction in %.

(iii) The magnetic dipole moment, μ, of the nuclide, in terms of the nuclear magneton, μ_N. It should be noted that we have chosen to use the full vector magnitude of μ, given by:

$$|\mu| / \mu_N = |\gamma| \hbar [I(I + 1)]^{1/2} / \mu_N \tag{1}$$

where γ is the magnetogyric ratio and $\hbar$ is the Planck constant divided by 2π. Many lists prefer to give only the maximum value of the z-component of μ, namely, $\mu_z = \gamma \hbar I$, frequently without explicitly stating this fact. The sign of μ given in Tables 1–3 refers to its direction compared to the related spin angular momentum vector.

(iv) The magnetogyric ratio, γ (sometimes called the gyromagnetic ratio). The SI base units of this quantity are (angular frequency) / (magnetic induction) normally given as rad s^{-1} T^{-1}.

(v) The receptivity, of a nucleus in natural abundance, which influences the NMR signal strength. A common definition [5] involves the proportionality of receptivity to $\gamma^3 x I (I + 1)$. In practice, it is useful to list such receptivities relative to those of the commonly used nuclei ^{1}H (proton) and ^{13}C, giving receptivity ratios D^p and D^C, respectively. Both these quantities are given in Tables 1 and 2.

(vi) The quadrupole moment, Q, for nuclei with spin quantum number $I > \frac{1}{2}$ (Tables 2 and 3 only). These data fall naturally in the region of 10^{-30} m^2, i.e., fm^2. However, quadrupole moments are often expressed in units of 10^{-28} m^2, called a barn, where 1 barn = 100 fm^2.

(vii) The line-width factor, ℓ, for quadrupolar nuclei. This is defined [5] by:

$$\ell = Q^2 (2I + 3)/[I^2(2I - 1)] \tag{2}$$

When taken in conjunction with the relative receptivity (e.g., as D^C/ℓ), this quantity gives a guide to the ease with which spectra can be obtained for different quadrupolar nuclei in solution for similar site symmetries and molecular mobilities. However, in practice, both symmetry and mobility may vary widely, thus introducing variations that may amount to several powers of ten.

Table 1 gives the data for the spin-$\frac{1}{2}$ nuclei in the periodic table, whereas Table 2 refers to quadrupolar nuclei. These two tables omit the lanthanide and actinide nuclei, which are separately listed in Table 3. Many of the data in Tables 1–3 have been taken from the IUPAC "Green Book" [6], but additional information is included (particularly on resonance frequencies and quadrupole moments). A version of Tables 1–3 has been published [7]. However, the tables given here contain revised resonance frequencies for consistency with the recommended primary reference, as described in Section 3.5. In

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[*]NMR is entirely concerned with the nuclear spin in the lowest-energy nuclear state, though Mössbauer spectroscopy involves values of I in higher-energy nuclear states.

Table 1 The spin properties of spin-$\frac{1}{2}$ nuclei[a].

Isotope[b]	Natural abundance,[c] $x/\%$	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7$ rad s^{-1} T^{-1}	Frequency ratio,[e] $\Xi/\%$	Reference compound	Sample conditions[f]	Literature for Ξ	Relative receptivity[g] D^p	D^C
^{1}H	99.9885	4.837 353 570	26.752 2128	100.000 000[h]	Me$_4$Si	CDCl$_3$; $\varphi = 1\%$	–	1.000	5.87×10^3
^{3}H[i]	–	5.159 714 367	28.534 9779	106.663 974	Me$_4$Si-t_1	j	10	–	–
^{3}He	1.37×10^{-4}	-3.685 154 336	-20.380 1587	76.179 437	He	gas	11	6.06×10^{-7}	3.56×10^{-3}
^{13}C	1.07	1.216 613	6.728 284	25.145 020	Me$_4$Si	CDCl$_3$; $\varphi = 1\%$	12,13	1.70×10^{-4}	1.00
^{15}N	0.368	-0.490 497 46	-2.712 618 04	10.136 767	MeNO$_2$	neat/CDCl$_3$[k]	9	3.84×10^{-6}	2.25×10^{-2}
^{19}F	100	4.553 333	25.181 48	94.094 011	CCl$_3$F	j	14	0.834	4.90×10^3
^{29}Si	4.6832	-0.961 79	-5.3190	19.867 187	Me$_4$Si	CDCl$_3$; $\varphi = 1\%$	15	3.68×10^{-4}	2.16
^{31}P	100	1.959 99	10.8394	40.480 742	H$_3$PO$_4$	j	16	6.65×10^{-2}	3.91×10^2
^{57}Fe	2.119	0.156 9636	0.868 0624	3.237 778	Fe(CO)$_5$	C$_6$D$_6$[l]	9	7.24×10^{-7}	4.25×10^{-3}
^{77}Se	7.63	0.926 775 77	5.125 3857	19.071 513	Me$_2$Se	neat/C$_6$D$_6$[k]	9	5.37×10^{-4}	3.15
^{89}Y	100	-0.238 010 49	-1.316 2791	4.900 198	Y(NO$_3$)$_3$	H$_2$O/D$_2$O[m]	9	1.19×10^{-4}	0.700
^{103}Rh	100	-0.1531	-0.8468	3.186 447[n,o]	Rh(acac)$_3$[p]	CDCl$_3$; sat.	18	3.17×10^{-5}	0.186
(^{107}Ag)	51.839	-0.196 898 93	-1.088 9181	4.047 819	AgNO$_3$	D$_2$O, sat.	9	3.50×10^{-5}	0.205
^{109}Ag	48.161	-0.226 362 79	-1.251 8634	4.653 533	AgNO$_3$	D$_2$O, sat.	9	4.94×10^{-5}	0.290
(^{111}Cd)	12.80	-1.030 3729	-5.698 3131	21.215 480	Me$_2$Cd	neat[j]	19	1.24×10^{-3}	7.27
^{113}Cd[q]	12.22	-1.077 8568	-5.960 9155	22.193 175	Me$_2$Cd	neat[j]	19	1.35×10^{-3}	7.94
(^{115}Sn)	0.34	-1.5915	-8.8013	32.718 749	Me$_4$Sn	neat/C$_6$D$_6$[k]	9	1.21×10^{-4}	0.711
(^{117}Sn)	7.68	-1.733 85	-9.588 79	35.632 259	Me$_4$Sn	neat/C$_6$D$_6$[k]	9	3.54×10^{-3}	20.8
^{119}Sn	8.59	-1.813 94	-10.0317	37.290 632	Me$_4$Sn	neat/C$_6$D$_6$[k]	9	4.53×10^{-3}	26.6
(^{123}Te)	0.89	-1.276 431	-7.059 098	26.169 742	Me$_2$Te	neat/C$_6$D$_6$[k]	9	1.64×10^{-4}	0.961
^{125}Te	7.07	-1.538 9360	-8.510 8404	31.549 769	Me$_2$Te	neat/C$_6$D$_6$[k]	9	2.28×10^{-3}	13.4
^{129}Xe	26.44	-1.347 494	-7.452 103	27.810 186	XeOF$_4$	neat[j]	20,21	5.72×10^{-3}	33.6
^{183}W	14.31	0.204 009 19	1.128 2403	4.166 387	Na$_2$WO$_4$	D$_2$O, 1 M	11	1.07×10^{-5}	6.31×10^{-2}
^{187}Os	1.96	0.111 9804	0.619 2895	2.282 331	OsO$_4$	CCl$_4$, 0.98 M	22	2.43×10^{-7}	1.43×10^{-3}
^{195}Pt	33.832	1.0557	5.8385	21.496 784[n]	Na$_2$PtCl$_6$	D$_2$O, 1.2 M	9	3.51×10^{-3}	20.7
^{199}Hg	16.87	0.876 219 37	4.845 7916	17.910 822	Me$_2$Hg[r]	neat	11	1.00×10^{-3}	5.89
(^{203}Tl)	29.524	2.809 833 05	15.539 3338	57.123 200[s]	Tl(NO$_3$)$_3$	j	24	5.79×10^{-2}	3.40×10^2

Table 1 (*Continued*).

Isotope[b]	Natural abundance,[c] $x/\%$	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7$ rad s^{-1} T^{-1}	Frequency ratio,[e] $\Xi/\%$	Reference compound	Sample conditions[f]	Literature for Ξ	Relative receptivity[g] D^p	D^C
^{205}Tl	70.476	2.837 470 94	15.692 1808	57.683 838	Tl(NO$_3$)$_3$	[j]	25	0.142	8.36×10^2
^{207}Pb	22.1	1.009 06	5.580 46	20.920 599	Me$_4$Pb	neat/C$_6$D$_6$[k]	9	2.01×10^{-3}	11.8

[a]A complete list for stable nuclei, but excluding the lanthanides, the actinides and most radioactive isotopes.

[b]Nuclei in parentheses are considered to be not the most favorable of the element concerned for NMR.

[c]Data are "representative isotopic compositions", taken from Rosman *et al.* [8], pp. 98–104. For the error limits, see Rosman *et al.* [8].

[d]Data derived from the compilation in Mills *et al.* [6], pp. 98–104, which lists values of $\mu_{max}/\mu_N = \gamma\hbar I/\mu_N$. For the error limits, see Mills *et al.* [6].

[e]Ratios of the resonance frequency of the reference to that of the protons of TMS at infinite dilution (in practice at $\varphi = 1\%$) in CDCl$_3$.

[f]M = molarity in mol dm^{-3} (solution); m = molality in mol kg^{-1} (solution). Some results from ref. 9 were initially referenced [7] to a TMS concentration of 4.75 m in CDCl$_3$, but the values are corrected to refer to a dilute ($\varphi = 1\%$) solution of TMS in CDCl$_3$.

[g]D^p is the receptivity [5] relative to that of ^{1}H, whereas D^C is relative to ^{13}C.

[h]Value by definition (see the text).

[i]Radioactive (half-life 12 y).

[j]See literature cited.

[k]Small amount of lock substance ($\varphi < 10\%$) in neat liquid.

[l]$\varphi = 20\%$ of C$_6$D$_6$ in Fe(CO)$_5$.

[m]H$_2$O/D$_2$O solution, concentration not reported.

[n]Alternatively, the precise values 3.160 000 MHz and 21.400 000 have been suggested [17] as the references for ^{103}Rh and ^{195}Pt, respectively.

[o]Subject to considerable variation with temperature.

[p]acac ≡ acetylacetonato

[q]Long-lived radioactive isotope.

[r]The high toxicity of this compound means its direct use should be strongly discouraged [23].

[s]Deduced from refs. 24 and 25.

Table 2 The spin properties of quadrupolar nuclei[a].

Isotope[b]	Spin[c]	Natural abundance,[c] $x/\%$	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7$ rad s^{-1} T^{-1}	Quadrupole moment[e] Q/fm^2	Frequency ratio,[e] $\Xi/\%$	Reference sample	Sample conditions[g]	Literature for Ξ	Line-width factor,[h] ℓ/fm^4	Relative receptivity[j] D^p	D^C
^{2}H	1	0.0115	1.212 600 77	4.106 627 91	0.2860	15.350 609	(CD$_3$)$_4$Si	neat	15	0.41	1.11×10^{-6}	6.52×10^{-3}
^{6}Li	1	7.59	1.162 5637	3.937 1709	−0.0808	14.716 086	LiCl	D$_2$O, 9.7 m	9	0.033	6.45×10^{-4}	3.79
^{7}Li	3/2	92.41	4.204 075 05	10.397 7013	−4.01	38.863 797	LiCl	D$_2$O, 9.7 m	9	21	0.271	1.59×10^3
^{9}Be	3/2	100	−1.520 136	−3.759 666	5.288	14.051 813	BeSO$_4$	D$_2$O, 0.43 m	9	37	1.39×10^{-2}	81.5
^{10}B	3	19.9	2.079 2055	2.874 6786	8.459	10.743 658	BF$_3$·Et$_2$O	CDCl$_3$[k]	29	14	3.95×10^{-3}	23.2
^{11}B	3/2	80.1	3.471 0308	8.584 7044	4.059	32.083 974	BF$_3$·Et$_2$O	CDCl$_3$[k]	29	22	0.132	7.77×10^2
^{14}N	1	99.632	0.571 004 28	1.933 7792	2.044	7.226 317	CH$_3$NO$_2$	neat/CDCl$_3$[ℓ]	9	21	1.00×10^{-3}	5.90
^{17}O	5/2	0.038	−2.240 77	−3.628 08	−2.558	13.556 457	D$_2$O	neat	9	2.1	1.11×10^{-5}	6.50×10^{-2}
^{21}Ne	3/2	0.27	−0.854 376	−2.113 08	10.155	7.894 296[m]	Ne	gas, 1.1 MPa	9	140	6.65×10^{-6}	3.91×10^{-2}
^{23}Na	3/2	100	2.862 9811	7.080 8493	10.4	26.451 900	NaCl	D$_2$O, 0.1 M	9	140	9.27×10^{-2}	5.45×10^2
^{25}Mg	5/2	10.00	−1.012 20	−1.638 87	19.94	6.121 635	MgCl$_2$	D$_2$O, 11 M	9	130	2.68×10^{-4}	1.58
^{27}Al	5/2	100	4.308 6865	6.976 2715	14.66	26.056 859	Al(NO$_3$)$_3$	D$_2$O, 1.1 m	9	69	0.207	1.22×10^3
^{33}S	3/2	0.76	0.831 1696	2.055 685	−6.78	7.676 000	(NH$_4$)$_2$SO$_4$	D$_2$O, sat.	9	61	1.72×10^{-5}	0.101
^{35}Cl	3/2	75.78	1.061 035	2.624 198	−8.165	9.797 909	NaCl	D$_2$O, 0.1 M	9	89	3.58×10^{-3}	21.0
^{37}Cl	3/2	24.22	0.883 1998	2.184 368	−6.435	8.155 725	NaCl	D$_2$O, 0.1 M	9	55	6.59×10^{-4}	3.87
^{39}K	3/2	93.2581	0.505 433 76	1.250 0608	5.85	4.666 373	KCl	D$_2$O, 0.1 M	9	46	4.76×10^{-4}	2.79
(^{40}K)	4	0.0117	−1.451 3203	−1.554 2854	−7.3	5.802 018	KCl	D$_2$O, 0.1 M	31	5.2	6.12×10^{-7}	3.59×10^{-3}
(^{41}K)	3/2	6.7302	0.277 396 09	0.686 068 08	7.11	2.561 305[n]	KCl	D$_2$O, 0.1 M	31	67	5.68×10^{-6}	3.33×10^{-2}
^{43}Ca	7/2	0.135	−1.494 067	−1.803 069	−4.08	6.730 029[o]	CaCl$_2$	D$_2$O, 0.1 M	32	2.3	8.68×10^{-6}	5.10×10^{-2}
^{45}Sc	7/2	100	5.393 3489	6.508 7973	−22.0	24.291 747	Sc(NO$_3$)$_3$	D$_2$O, 0.06 M	9	66	0.302	1.78×10^3
^{47}Ti	5/2	7.44	−0.932 94	−1.5105	30.2	5.637 534	TiCl$_4$	neat[p]	9	290	1.56×10^{-4}	0.918
^{49}Ti	7/2	5.41	−1.252 01	−1.510 95	24.7	5.639 037	TiCl$_4$	neat[p]	9	83	2.05×10^{-4}	1.20
(^{50}V)[q]	6	0.250	3.613 7570	2.670 6490	21.0	9.970 309	VOCl$_3$	neat/C$_6$D$_6$[ℓ]	9	17	1.39×10^{-4}	0.818
^{51}V	7/2	99.750	5.838 0835	7.045 5117	−5.2	26.302 948	VOCl$_3$	neat/C$_6$D$_6$[ℓ]	9	3.7	0.383	2.25×10^3
^{53}Cr	3/2	9.501	−0.612 63	−1.5152	−15.0	5.652 496	K$_2$CrO$_4$	D$_2$O, sat.	9	300	8.63×10^{-5}	0.507
^{55}Mn	5/2	100	4.104 2437	6.645 2546	33.0	24.789 218	KMnO$_4$	D$_2$O, 0.82 m	9	350	0.179	1.05×10^3
^{59}Co	7/2	100	5.247	6.332	42.0	23.727 074	K$_3$[Co(CN)$_6$]	D$_2$O, 0.56 m	9	240	0.278	1.64×10^3
^{61}Ni	3/2	1.1399	−0.968 27	−2.3948	16.2	8.936 051	Ni(CO)$_4$	neat/C$_6$D$_6$[ℓ]	33	350	4.09×10^{-5}	0.240
^{63}Cu	3/2	69.17	2.875 4908	7.111 7890	−22.0	26.515 473	[Cu(CH$_3$CN)$_4$][ClO$_4$]	CH$_3$CN, sat.[r]	9	650	6.50×10^{-2}	3.82×10^2
^{65}Cu	3/2	30.83	3.074 65	7.604 35	−20.4	28.403 693	[Cu(CH$_3$CN)$_4$][ClO$_4$]	CH$_3$CN, sat.[r]	9	550	3.54×10^{-2}	2.08×10^2
^{67}Zn	5/2	4.10	1.035 556	1.676 688	15.0	6.256 803	Zn(NO$_3$)$_2$	D$_2$O, sat.	9	72	1.18×10^{-4}	0.692
(^{69}Ga)	3/2	60.108	2.603 405	6.438 855	17.1	24.001 354	Ga(NO$_3$)$_3$	D$_2$O, 1.1 m	34	390	4.19×10^{-2}	2.46×10^2

Table 2 (*Continued*).

Isotope[b]	Spin[c]	Natural abundance,[c] $x/\%$	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7\ \text{rad s}^{-1}\ \text{T}^{-1}$	Quadrupole moment[e] Q/fm^2	Frequency ratio,[e] $\Xi/\%$	Reference sample	Sample conditions[g]	Literature for Ξ	Line-width factor,[h] ℓ/fm^4	Relative receptivity[i] D^P	D^C
^{71}Ga	3/2	39.892	3.307 871	8.181 171	10.7	30.496 704	Ga(NO$_3$)$_3$	D$_2$O, 1.1 m	34	150	5.71×10^{-2}	3.35×10^2
^{73}Ge	9/2	7.73	$-0.972\ 2881$	$-0.936\ 0303$	-19.6	3.488 315	(CH$_3$)$_4$Ge	neat[s]	35	28	1.09×10^{-4}	0.642
^{75}As	3/2	100	1.858 354	4.596 163	31.4	17.122 614	NaAsF$_6$	CD$_3$CN, 0.5 M	9	1300	2.54×10^{-2}	1.49×10^2
(^{79}Br)	3/2	50.69	2.719 351	6.725 616	31.3	25.053 980	NaBr	D$_2$O, 0.01 M	9	1300	4.03×10^{-2}	2.37×10^2
^{81}Br	3/2	49.31	2.931 283	7.249 776	26.2	27.006 518	NaBr	D$_2$O, 0.01 M	9	920	4.91×10^{-2}	2.88×10^2
^{83}Kr	9/2	11.49	$-1.073\ 11$	$-1.033\ 10$	25.9	3.847 600[t]	Kr	gas	36	50	2.18×10^{-4}	1.28
(^{85}Rb)	5/2	72.17	1.601 3071	2.592 7050	27.6	9.654 943	RbCl	D$_2$O, 0.01 M	9	240	7.67×10^{-3}	45.0
^{87}Rb[q]	3/2	27.83	3.552 582	8.786 400	13.35	32.720 454	RbCl	D$_2$O, 0.01 M	9	240	4.93×10^{-2}	2.90×10^2
^{87}Sr	9/2	7.00	$-1.209\ 0236$	$-1.163\ 9376$	33.5	4.333 822	SrCl$_2$	D$_2$O, 0.5 M	37	83	1.90×10^{-4}	1.12
^{91}Zr	5/2	11.22	$-1.542\ 46$	$-2.497\ 43$	-17.6	9.296 298	Zr(C$_5$H$_5$)$_2$Cl$_2$	CH$_2$Cl$_2$, sat.[r]	9	99	1.07×10^{-3}	6.26
^{93}Nb	9/2	100	6.8217	6.5674	-32.0	24.476 170	K[NbCl$_6$]	CH$_3$CN, sat.[u]	9	76	0.488	2.87×10^3
^{95}Mo	5/2	15.92	-1.082	-1.751	-2.2	6.516 926	Na$_2$MoO$_4$	D$_2$O, 2 M[v]	9	1.5	5.21×10^{-4}	3.06
(^{97}Mo)	5/2	9.55	-1.105	-1.788	25.5	6.653 695	Na$_2$MoO$_4$	D$_2$O, 2 M[v]	9	210	3.33×10^{-4}	1.95
^{99}Tc[q]	9/2	–	6.281	6.046	-12.9	22.508 326	NH$_4$TcO$_4$	D$_2$O[w]	9	12	–	–
^{99}Ru	5/2	12.76	-0.7588	-1.229	7.9	4.605 151	K$_4$[Ru(CN)$_6$]	D$_2$O, 0.3 M	9	20	1.44×10^{-4}	0.848
^{101}Ru	5/2	17.06	-0.8505	-1.377	45.7	5.161 369	K$_4$[Ru(CN)$_6$]	D$_2$O, 0.3 M	9	670	2.71×10^{-4}	1.59
^{105}Pd	5/2	22.33	-0.760	-1.23	66.0	4.576 100	K$_2$PdCl$_6$	D$_2$O, sat.	22	1400	2.53×10^{-4}	1.49
(^{113}In)	9/2	4.29	6.1124	5.8845	79.9	21.865 755	In(NO$_3$)$_3$	D$_2$O, 0.1 M[x]	34	470	1.51×10^{-2}	88.5
^{115}In[q]	9/2	95.71	6.1256	5.8972	81.0	21.912 629	In(NO$_3$)$_3$	D$_2$O, 0.1M[x]	34	490	0.338	1.98×10^3
^{121}Sb	5/2	57.21	3.9796	6.4435	-36.0	23.930 577	KSbCl$_6$	CH$_3$CN, sat.[u]	9	410	9.33×10^{-2}	5.48×10^2
(^{123}Sb)	7/2	42.79	2.8912	3.4892	-49.0	12.959 217	KSbCl$_6$	CH$_3$CN, sat.[u]	9	330	1.99×10^{-2}	1.17×10^2
^{127}I	5/2	100	3.328 710	5.389 573	-71.0	20.007 486	KI	D$_2$O, 0.01 M	9	1600	9.54×10^{-2}	5.60×10^2
^{131}Xe[j]	3/2	21.18	0.893 1899	2.209 076	-11.4	8.243 921[y]	XeOF$_4$	neat	9	170	5.96×10^{-4}	3.50
^{133}Cs	7/2	100	2.927 7407	3.533 2539	-0.343	13.116 142	CsNO$_3$	D$_2$O, 0.1 M	9	0.016	4.84×10^{-2}	2.84×10^2
(^{135}Ba)	3/2	6.592	1.081 78	2.675 50	16.0	9.934 457	BaCl$_2$	D$_2$O, 0.5 M	9,38	340	3.30×10^{-4}	1.93
^{137}Ba	3/2	11.232	1.210 13	2.992 95	24.5	11.112 928	BaCl$_2$	D$_2$O, 0.5 M	9,38	800	7.87×10^{-4}	4.62
^{138}La[q]	5	0.090	4.068 095	3.557 239	45.0	13.194 300	LaCl$_3$	D$_2$O/H$_2$O[z]	39	120	8.46×10^{-5}	0.497
^{139}La	7/2	99.910	3.155 6770	3.808 3318	20.0	14.125 641	LaCl$_3$	D$_2$O, 0.01 M	11	54	6.05×10^{-2}	3.56×10^2
^{177}Hf	7/2	18.60	0.8997	1.086	336.5	(4.007)[A]	–	–		1.5×10^4	2.61×10^{-4}	1.54
^{179}Hf	9/2	13.62	-0.7085	-0.6821	379.3	(2.517)[A]	–	–		1.1×10^4	7.45×10^{-5}	0.438
^{181}Ta	7/2	99.988	2.6879	3.2438	317.0	11.989 600[B]	KTaCl$_6$	CH$_3$CN, sat.	40	1.4×10^4	3.74×10^{-2}	2.20×10^2

(continues on next page)

Table 2 (*Continued*).

Isotope[b]	Spin[c]	Natural abundance,[c] $x/\%$	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7$ rad s^{-1} T^{-1}	Quadrupole moment[e] Q/fm^2	Frequency ratio,[e] $\Xi/\%$	Reference sample	Sample conditions[g]	Literature for Ξ	Line-width factor,[h] ℓ/fm^4	Relative receptivity[i] D^p	D^C
(^{185}Re)	5/2	37.40	3.7710	6.1057	218.0	22.524 600[B]	KReO$_4$	D$_2$O, 0.1 M	40	1.5×10^4	5.19×10^{-2}	3.05×10^2
^{187}Re[q]	5/2	62.60	3.8096	6.1682	207.0	22.751 600[B]	KReO$_4$	D$_2$O, 0.1 M	40	1.4×10^4	8.95×10^{-2}	5.26×10^2
^{189}Os[j]	3/2	16.15	0.851 970	2.107 13	85.6	7.765 400[B]	OsO$_4$	CCl$_4$, 0.98 M	22	9800	3.95×10^{-4}	2.32
(^{191}Ir)	3/2	37.3	0.1946	0.4812	81.6	(1.718)[A]	–	–		8900	1.09×10^{-5}	6.38×10^{-2}
^{193}Ir	3/2	62.7	0.2113	0.5227	75.1	(1.871)[A]	–	–		7500	2.34×10^{-5}	0.137
^{197}Au	3/2	100	0.191 271	0.473 060	54.7	(1.729)[A]	–	–		4000	2.77×10^{-5}	0.162
^{201}Hg[j]	3/2	13.18	-0.723 2483	-1.788 769	38.6	6.611 583[C]	(CH$_3$)$_2$Hg[D]	neat	41	2000	1.97×10^{-4}	1.16
^{209}Bi	9/2	100	4.5444	4.3750	-51.6	16.069 288	Bi(NO$_3$)$_3$	HNO$_3$/D$_2$O/H$_2$O[E]	9	200	0.144	8.48×10^2

[a]Excluding the lanthanides, actinides, and most radioactive isotopes.

[b]Nuclei in parentheses are considered to be not the most favorable of the element concerned for NMR.

[c]Data are "representative isotopic compositions", taken from Rosman *et al.* [8], pp. 98–104. For the error limits on the natural abundances, see Rosman *et al.* [8].

[d]Data derived from the compilation in Mills *et al.*[6] pp. 98–104, which lists values of $\mu_{max} / \mu_N = \gamma \hbar I / \mu_N$. For the error limits, see Mills *et al.* [6].

[e]Data from Mills *et al.* [6], pp. 98–104 (taken mostly from Pyykko [26] and Raghavan [27]) and updated from Pyykko [28]. It should be noted that reported values of Q may be in error by as much as 20–30%. For the error limits, see Pyykko [28].

[f]Ratio of the resonance frequency of the reference to that of the protons of TMS at infinite dilution (in practice at $\varphi = 1\%$) in CDCl$_3$.

[g]M = molality in mol dm^{-3} (solution); m = molality in mol kg^{-1} (solvent). Some results from ref. 9 were initially referenced [7] to a TMS concentration of 4.75 m in CDCl$_3$, but the values are corrected to refer to a dilute ($\varphi = 1\%$) solution of TMS in CDCl$_3$.

[h]$\ell = (2I+3)Q^2/I^2(2I-1)$ [5]. The values are quoted, arbitrarily, to 2 significant figures.

[i]D^p is the receptivity [5] relative to that of ^{1}H whereas D^C is relative to ^{13}C. The values are given to three significant figures only.

[j]A useful isotope of $I = \frac{1}{2}$ exists.

[k]15% by volume of BF$_3$.Et$_2$O in CDCl$_3$.

[l]Small amount of lock substance ($\varphi \leq 10\%$) in neat liquid, except for ^{61}Ni (where $\varphi = $ ca. 20% of C$_6$D$_6$ is involved).

[m]Ξ In reasonable agreement with a value deduced from a ratio given in ref. 30.

[n]Ξ deduced from data in ref. 31.

[o]Ξ deduced from a ratio given in ref. 32.

[p]Plus C$_6$D$_{12}$ ($\varphi = 10\%$) for field/frequency lock purposes.

[q]Radioactive, with a long half-life.

[r]Containing a little C$_6$D$_6$ ($\varphi \leq 10\%$).

[s]With conversion factors applied by Granger.

[t]The data in ref. 36 are only accurate to 4 decimal places. The proposal herein is that Ξ (^{83}Kr) is defined to the 6 decimal places given.

[u]In CH$_3$CN/CD$_3$CN for ^{93}Nb, ^{121}Sb, and ^{123}Sb.

[v]Plus a small quantity of NaOH.

[w]Semisaturated in H$_2$O/D$_2$O.

[x]Plus 0.5 M DNO$_3$.

[y]Calculated from the value for ^{129}Xe via the ^{129}Xe:^{131}Xe frequency ratio.

[z]For the solution conditions, see the reference.

[A]Value calculated from literature data on nuclear magnetic moments.

[B]The proposal herein is to define to 6 decimal places, but line-widths are generally such that this is unnecessarily accurate.

[C]Deduced from the ^{201}Hg:^{199}Hg ratio given in ref. 41.

[D]The high toxicity of this compound means its direct use should be strongly discouraged [23].

[E]Saturated in conc. HNO_3, then diluted with an equal volume of D_2O.

Table 3 The spin properties of lanthanide and actinide nuclei[a].

Isotope	Spin	Natural abundance x/%	Magnetic moment μ/μ_N	Magnetogyric ratio $\gamma/10^7$ rad s^{-1} T^{-1}	Quadrupole moment[b] Q/fm^2	NMR frequency[c] Ξ/%
^{141}Pr	5/2	100	5.0587	8.1907	–5.89	(30.62)
^{143}Nd	7/2	12.2	–1.208	–1.457	–63.0	(5.45)
^{145}Nd	7/2	8.3	–0.744	–0.898	–33.0	(3.36)
^{147}Sm[d]	7/2	14.99	–0.9239	–1.115	–25.9	(4.17)
^{149}Sm	7/2	13.82	–0.7616	–0.9192	7.4	(3.44)
^{151}Eu	5/2	47.81	4.1078	6.6510	90.3	(24.86)
^{153}Eu	5/2	52.19	1.8139	2.9369	241.2	(10.98)
^{155}Gd	3/2	14.80	–0.33208	–0.82132	127.0	(3.07)
^{157}Gd	3/2	15.65	–0.43540	–1.0769	135.0	(4.03)
^{159}Tb	3/2	100	2.600	6.431	143.2	(24.04)
^{161}Dy	5/2	18.91	–0.5683	–0.9201	250.7	(3.44)
^{163}Dy	5/2	24.90	0.7958	1.289	264.8	(4.82)
^{165}Ho	7/2	100	4.732	5.710	358.0	(21.34)
^{167}Er	7/2	22.93	–0.63935	–0.77157	356.5	(2.88)
^{169}Tm	1/2	100	–0.4011	–2.218	–	(8.29)
^{171}Yb	1/2	14.28	0.85506	4.7288	–	17.499306[e]
^{173}Yb	5/2	16.13	–0.80446	–1.3025	280.0	(4.821)
^{175}Lu	7/2	97.41	2.5316	3.0552	349.0	(11.404)
^{176}Lu[d]	7	2.59	3.3880	2.1684	497.0	(8.131)
^{235}U[d]	7/2	0.7200	–0.43	–0.52	493.6	1.841400[f]

[a]These nuclides are sufficiently little used that values for line-width factors and relative receptivities are not listed here. However, for ^{169}Tm, $D^p = 5.70 \times 10^{-4}$ and $D^C = 3.35$, while for ^{171}Yb, $D^p = 7.89 \times 10^{-4}$ and $D^C = 4.63$.
[b]For the limits of accuracy, see ref. 28.
[c]Values in brackets are approximate (calculated from the magnetogyric ratios).
[d]Long-lived radioactive isotope.
[e]Reference: Yb(η-C$_5$Me$_5$)$_2$(THF)$_2$, 0.171 M in THF solution (THF $\equiv$ tetrahydrofuran) [42].
[f]Reference: UF$_6$ (with $\varphi = 10$% of C$_6$D$_6$) [43].

addition, some new measurements of resonance frequencies are reported in Tables 1–3, and information about solution conditions and relevant references has been added.

3. CHEMICAL SHIFTS

3.1 Background

Since the discovery of the chemical shift in 1950, NMR spectroscopy has become of vital importance to chemistry and related disciplines. The term chemical shift refers to a difference in resonance frequency (conventionally expressed as a fraction—see below) between nuclei in different chemical sites (or for samples under different physical conditions). Such effects are caused by variations in shielding by the electronic environment of the nuclei in question, and the concept of chemical shift is described by eq. 3:

$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma) \tag{3}$$

In this equation, the resonance frequency ν (normally in the radio frequency region) is related to the applied magnetic flux density B_0 by the magnetogyric ratio of the nucleus and the shielding constant σ.

In the International System of Units (SI), ν is expressed in hertz, Hz, (and is normally in the range of tens or hundreds of MHz), B_0 is in tesla, T, and σ is a dimensionless fraction (generally reported in parts per million, ppm). Equation 3 is usually applied to the situation in isotropic media (liquids, solutions, and gases), for which σ can be represented as a scalar quantity. However, the value of σ depends on molecular orientation in the applied magnetic field and can be represented by a scalar quantity only because of the averaging caused by rapid isotropic molecular tumbling. Therefore, σ is a second-rank tensor and must be used in that form for many situations in the solid state and in liquid crystals (and their solutions).

Whereas frequencies can be measured very precisely, the same cannot be said of B_0. Thus, although in principle chemists would like to know the absolute value of σ, it has long been recognized that only relative values can normally be obtained with precision. Therefore, from the early days of NMR the concept of a standard reference signal has been developed. This requires a number of choices, among which are:

(i)   whether to base chemical shifts on resonance frequencies or on shielding,
(ii)   which compound to use as a reference,
(iii)   what further conditions to specify for the reference situation, and
(iv)   whether to use separate references for different nuclei or to attempt to link them.

These matters will be dealt with in detail below.

In the early days of NMR, resonance was normally achieved by varying the applied field B_0. It therefore seemed natural for positive chemical shifts to refer to situations where the sample resonated at a higher field than that of the reference. Equation 3 shows that this corresponds to greater shielding for the sample than for the reference—a convention that was popular with theoreticians, who are principally concerned with σ. The first clear consensus on an experimental reference compound for proton NMR (by far the most popular nucleus at the time owing to its high sensitivity) was tetramethylsilane (TMS), introduced in 1958 by Tiers [44]. However, both for proton NMR and for other nuclei, various chemical shift scales were used, with some increasing in the direction of increasing magnetic field and others increasing in the direction of decreasing field (which corresponds to increasing frequency).

The convention recommended by IUPAC in the 1972 document [1], which mostly concerned proton NMR, was that given in eq. 4:

$$\delta_{X,sample} = \left(\frac{\nu_{X,sample} - \nu_{X,reference}}{\nu_{X,reference}} \right) \times 10^6 \tag{4}$$

in which the chemical shift of a resonance for nucleus X is defined. For protons referenced to TMS this convention gives positive values with increasing frequency, and most proton chemical shifts then turn out to be positive. A second IUPAC report [2] in 1976 extended the recommendations to include nuclei other than protons, always with a high-frequency-positive convention.

Of course, since σ is, in principle, a tensor quantity, so is δ. However, the present document deals only with the isotropic average value of δ, which is the usual value of relevance for solution-state NMR. The tensor properties of σ and δ may be the subject of a later document.

3.2 Recommendations endorsed

At this point, it is appropriate to list those recommendations of the previous two IUPAC reports on NMR which relate to chemical shifts [1,2] (including presentation of spectra) and which we endorse, with one exception noted under item 6. These relate to notational matters and are particularly directed at publications in chemical journals. In several places, we use different wording from the original reports and in some cases extended meanings:

1. The nucleus giving rise to the spectrum concerned should always be explicitly stated in full or in abbreviation (e.g., ^{10}B NMR or boron-10 NMR). The isotopic mass number should be given except in cases without ambiguity. In the case of hydrogen NMR, the *de facto* usage is proton NMR, deuterium NMR, or tritium NMR, in spite of the inconsistency of the wording. Abbreviations such as PMR for proton NMR are strongly discouraged. The term "multinuclear NMR" is clumsy (a repeated word "nuclear") and so is also to be discouraged. Where reference to a variety of nuclei is required, multinuclear magnetic resonance should be written in full.

2. The graphical presentation of spectra should show frequency increasing to the left and positive intensity increasing upwards.

3. The dimensionless scale for chemical shifts should be tied to a reference, which should be clearly stated. The procedures used must be carefully defined.

4. The dimensionless scale factor for chemical shifts should generally be expressed in parts per million, for which ppm is the appropriate abbreviation. The radio frequency of the reference, appropriate to the nucleus in question and to the spectrometer in use, should always be quoted, with sufficient accuracy in relation to the numerical values of shifts listed. Unfortunately, older software supplied by manufacturers to convert from frequency units to ppm in FT NMR sometimes uses the carrier frequency in the denominator instead of the true frequency of the reference, which can lead to significant errors.

5. The chemical shift scale should be defined with respect to resonance frequencies, with the appropriate sign convention (i.e., a positive sign should imply the sample resonates to high frequency from that of the reference). In order to avoid ambiguities of sign, the term "chemical shift" should *not* be used to describe variations in shielding.

6. The symbol δ (lower case Greek delta) should be used for chemical shift scales with the sign convention given above. Such a symbol should *never* be used to refer to shielding. These recommendations cohere with the definition of the δ-scale adopted in refs. 1 and 2. The definition of δ in eq. 4 leads to a value with no units, and the 1972 document recommended that "ppm" be not stated explicitly (e.g., $\delta = 5.00$, *not* $\delta = 5.00$ ppm). However, this convention is widely ignored. Therefore, we do *not* endorse the omission of "ppm" in reporting values of δ (see Section 3.3).

7. The nucleus in question should be indicated as a subscript or in brackets, e.g., δ_C or $\delta(^{13}C)$, unless there is no ambiguity.

8. As far as possible, full information should be given in publications regarding any factor that might influence chemical shifts, such as:

    (i)   The physical state of the sample (solid, liquid, solution, or gas), with additional relevant facts where necessary.
    (ii)   For solutions, the name of the solvent and the concentration of solute.
    (iii)   The nature of the reference procedure, e.g., internal, external (coaxial tubes or substitution), absolute frequency. (This aspect is discussed in detail in later sections of this article.)
    (iv)   The name of the secondary referencing compound local to the nucleus in question and its concentration. Note, however, that no reference compound needs to be added to the sample if the unified scale described in Section 3.5 is used, although a chemical shift value with respect to a recommended secondary reference compound, obtained via the unified scale, may still be quoted. In exceptional cases, where an isotope-specific secondary reference compound must be used in the experimental measurement, a clear description of the referencing procedure should be given.
    (v)   The temperature and (if different from ambient) the pressure of the sample.
    (vi)   Whether oxygen and other gases have been removed from the sample.
    (vii)   Any chemicals present in the sample, in addition to the solvent and the compound under investigation, and details of their concentrations.

3.3 Definition and reporting of δ scales

As mentioned above, the IUPAC Recommendation [1] dating from 1972 defined the proton chemical shift scale in such a way that δ has no quoted units but is presumed to be in ppm. However, this recommendation not to use "ppm" has *not* received acceptance in practice. It is a simple matter to rewrite eq. 4 in a general way that can lead validly to the units of ppm. We now *define* the chemical shift (for any nucleus X, using its local reference substance) by eq. 5:

$$\delta_{X,sample} = (\nu_{X,sample} - \nu_{X,reference})/\nu_{X,reference} \tag{5}$$

that is, *without* the factor of 10^6. This leads, in general, to a very small number, $M \times 10^{-n}$. Normal practice has been and will doubtless continue to be to use $n = 6$ and thus to express δ in ppm. With eq. 5 as the *definition* of δ, eq. 6 provides a simple procedure for *calculating* the value of δ in ppm from measured frequencies:

$$\delta_{X,sample}/ppm = \frac{(\nu_{X,sample} - \nu_{X,reference})/Hz}{\nu_{X,reference}/MHz} \tag{6}$$

where the *factor* of 10^6 difference in the units of numerator and denominator is appropriately represented by the units ppm.

This redefinition allows values to be quoted also in parts per billion, ppb $= 10^{-9}$, (as is appropriate for some isotope effects) by expressing the numerator in eq. 6 in millihertz (mHz). Alternatively, the units of eq. 6 could be altered to give % (relevant for some heavy-metal chemical shifts), but ppm will undoubtedly remain as the most common usage. *IUPAC therefore recommends that the chemical shift δ be defined by eq. 5 and that δ normally be expressed in ppm.*

3.4 Referencing procedures

Accurate and consistent referencing is easy to visualize but hard to implement. For mobile isotropic media (liquids, solutions, and gases) there are several possible methods:

(a) *Internal referencing*, where the reference compound is added directly to the system under study. This method is used almost universally for ^{1}H and ^{13}C NMR. However, it is clearly limited by the solubility, miscibility, or mutual reactions of the sample components and may be difficult to implement for many samples in which a variety of nuclei are studied.

(b) *External referencing*, involving sample and reference contained separately in coaxial cylindrical tubes. A single spectrum is recorded, which includes signals from both the sample and the reference compound.

(c) *Substitution method*: The use of separate cylindrical tubes for the sample and reference compound, with (in principle) spectra recorded individually for each. It is similar to external referencing in that sample and reference materials are not mixed, but there are significant differences in the two procedures, as described later, which arise because of the common use of precise field/frequency locking (usually via the ^{2}H signal of a deuterated solvent). If locking is not used, the magnet should not be reshimmed between running the sample and reference solutions, since this changes the applied magnetic field.

(d) Referencing via direct measurement of the absolute frequency of the field/frequency lock signal, usually provided by the ^{2}H resonance of an internally contained deuterated compound (frequently the solvent). This method is discussed more fully in Section 3.6.

(e) Application of magic-angle spinning, usually with the substitution method, but also conceivably with coaxial tubes—see Section 3.8.

These methods all have various advantages and disadvantages. For (a) the shielding of the reference nucleus depends, to a greater or lesser extent, on the solvent, on the solute under study, and on the con-

centration of both solute and reference owing to the effects of intermolecular interactions. These effects may be minimized by a judicious choice of solvent and reference compound, but they cannot be eliminated. External reference procedures (b) generally require corrections arising from differences in bulk magnetic susceptibility between sample and reference. These corrections depend on the geometry employed for the sample containers. For the usual coaxial cylindrical arrangement, the correction is [45]

$$(\delta_{\text{true}} - \delta_{\text{obs}}) = k(\kappa_{\text{sample}} - \kappa_{\text{reference}}) \tag{7}$$

where k refers to the relevant volume magnetic susceptibility (in rationalized units) and ideally $k = +1/6$ for a tube perpendicular to B_0, $k = -1/3$ for a tube parallel to B_0 (as is usual for a superconducting magnet), and $k = 0$ for a tube inclined at the magic angle. These theoretical factors are calculated for infinite cylinders. In practice, they depend on the length of the liquid column and other geometrical factors that are not always under control. No correction is needed for spherical samples, but the production of a truly spherical sample cell is generally not feasible. [Equation 7 is consistent with SI notation. A corresponding expression in cgs form would substitute $k_{\text{cgs}} = 4\pi k_{\text{SI}}$ along with a $\Delta\chi_V$ term numerically equal to $\Delta\kappa/4\pi$. Many lists of magnetic susceptibility data give χ_V rather than κ.]

The substitution method uses the fact that, with the advent of stable, internally solvent-locked spectrometers, it has become feasible to obtain accurate data by measuring the spectra of sample and reference in two separate experiments. If the sample and the reference compound are each dissolved in the same solvent at low concentration (which, where feasible, we recommend), the substitution method is equivalent to use of an internal reference, except that the reference substance does not contaminate the sample or interact with it, chemically or physically. If the reference compound is a nearly neat liquid with only a small amount of the deuterated "solvent" to serve as a lock, the measured chemical shifts may be slightly different from those obtained with an internal reference because of differing molecular interactions. It might appear that a magnetic susceptibility correction would be needed if the susceptibilities of sample and reference differ, but this is not the case. With the field/frequency lock established via the deuterated solvent, the applied magnetic field simply shifts slightly to maintain the magnetic induction inside the sample tube constant so as to keep the ^{2}H nuclei on resonance. There is, thus, a distinct difference between the commonly used *internally locked* system, in which the magnetic induction B_0 is maintained constant and an *unlocked* (or *externally locked*) system in which the applied field H_0 is constant.

If the lock signal of the sample differs from that of the reference, a lock correction may need to be applied according to:

$$\delta_{\text{true}} = \delta_{\text{measured}} + \left(\delta_{\text{sample}}^{\text{lock}} - \delta_{\text{reference}}^{\text{lock}}\right) \tag{8}$$

Except for very strongly hydrogen-bonded systems [46–48], no primary isotope effects between proton and deuterium have been firmly established, and none are expected on theoretical grounds. Hence, the difference between deuterium lock frequencies in eq. 8 may be obtained from a table of proton chemical shifts. However, when polyhydrogenated groups are involved, corrections may be needed for secondary isotope effects [46] arising from ^{1}H $\rightarrow$ ^{2}H replacement. When high precision is required the measurement of the shift difference between the locks may be obtained via direct observation of the deuterium spectrum of the two solvents, placed in coaxial tubes.

However, for most modern spectrometers, the manufacturers have incorporated compensating procedures for lock changes, largely for the users' convenience of retaining the spectral window in the same position on the screen or chart. Unfortunately, these procedures vary between manufacturers and between spectrometers of different ages from the same manufacturer, so no completely general comments on this question can be made here. NMR spectroscopists must refer to the relevant operating manual for details. In most cases with modern instruments, the effect is to keep the magnetic field inside the samples constant when different lock compounds are used. In such situations, the correction term in brackets in eq. 8 is not necessary. Of course, the accuracy of the result clearly depends on what the

manufacturers use for the term in brackets, generally present in a "look-up" table in the spectrometer software. *We recommend that manufacturers give clear, explicit, and accurate guidance on their procedures in this matter and quote their "look-up" tables prominently.*

Another situation where isotope shifts have some effect is when signals of the reference compound are affected, for instance for ^{19}F measurements. In this case, the signal is split into four lines with intensities approximately 27:27:9:1 because the natural-abundance isotopic ratio ^{35}Cl:^{37}Cl is ca. 3:1. Since CFCl$_3$ is firmly accepted as the local reference for ^{19}F, it is not reasonable to suggest a new alternative. It is recommended that the reference signal is that of CF(^{35}Cl)$_2$(^{37}Cl).

Earlier IUPAC documentation [1,2] did not suggest any specific composition for the reference sample, or choice of solvents. Ideally, for most referencing methods, a nonpolar solvent consisting of nearly spherical molecules should be used, and measurements should be extrapolated to zero reference concentration. Clearly, such procedures are not generally feasible, so that caution always needs to be exercised when comparing shift data from different sources.

3.5 Unified scale

As NMR studies of various nuclei were initiated, each was, of necessity, treated independently, with some substance containing the nuclide being studied selected as a reference compound. The result is a vast collection of data in the literature for multinuclear magnetic resonance based on a large array of reference compounds. The proliferation of reference substances is, however, unnecessary and in some ways unhelpful. In a given magnetic field, all resonance frequencies form a single spectral range, and it is only because different nuclides resonate at markedly different frequencies that use of separate references has arisen. With modern instruments, in which all frequencies are derived from a single source, it is therefore possible to relate the observed frequencies of all nuclides in a particular sample to that of a single primary reference—preferably the proton resonance of TMS.[*]

There are, however, two reasons for wishing to retain the concept of a separate reference for each nucleus: (*i*) It is convenient to speak of, say, an aromatic ^{13}C resonance at *x* ppm from the ^{13}C line of TMS, rather than always quoting a frequency to many significant figures, and (*ii*) many data tabulations are available with values only expressed relative to separate heteronuclear references. Thus, for a unified scale to be of practical use, there must be agreed frequency relations between a set of commonly used secondary (heteronuclear) references and the primary reference. Measurements of such relations have been reported sporadically since the time of early double-resonance experiments [49], and it has been proposed to relate the separate reference frequencies to a primary standard originally defined for a magnetic field such that the ^{1}H TMS signal is at exactly 100 MHz. These frequencies have been given [49] the symbol $\varXi$ (capital Greek xi), and some tabulations have been presented [5,14,50–52]. However, it is clearer and more appropriate for users of modern high-field NMR spectrometers simply *to define $\varXi$ as the ratio of the secondary (isotope-specific) frequency to that of ^{1}H in TMS in the same magnetic field. Therefore, it is convenient to express $\varXi$ as a percentage* by the use of eq. 9:

$$\varXi \,/\,\% = 100\left(\nu_X^{obs} / \nu_{TMS}^{obs} \right) \tag{9}$$

where ν_{TMS}^{obs} is the measured ^{1}H frequency of TMS. The use of percentage ensures that values of $\varXi$ with this recommendation are numerically identical to those based on the earlier [49] definition.

Recently, the question of a unified reference has been addressed for multinuclear studies in biomolecular NMR: Wishart *et al.* [53] surveyed the relevant literature, pointed out inconsistencies in

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[*]TMS has a low boiling point (28 °C), which can be advantageous in facilitating removal from nonvolatile samples after use, but can in other circumstances be a severe disadvantage. To overcome this problem, a substance such as [(CH$_3$)$_3$Si]$_4$C (m.p. 267 °C), can be used as a reference [54] and the results converted to the TMS standard.

existing practices, and proposed the use of a single internal reference—for their purposes, one that is highly soluble in water (sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS*, preferably deuterated at the CH_2 positions). Operationally, as discussed in the following sections, it is often easier to obtain the necessary heteronuclear frequency data directly via the lock signal than to make additional measurements with various reference materials for different nuclei.

IUPAC recommends that a unified chemical shift scale for all nuclides be based on the proton resonance of TMS as the primary reference. This recommendation is in line with the "Recommendations for presentation of NMR structures of proteins and nucleic acids", recently promulgated [4] by IUPAC in conjunction with the International Union of Biochemistry and Molecular Biology and the International Union of Pure and Applied Biophysics, which include recommended Ξ values for several nuclei of importance in such studies for aqueous solutions, but which uses the proton resonance of DSS as the primary standard because of its solubility in water (see Section 3.9).

In conformity with other areas in physical chemistry, it would be desirable to define a precise standard state—for example, pure liquid TMS or TMS at infinite dilution in $CDCl_3$ at 293 K and 1 bar. [Indeed, in principle a better standard might be ^{3}He or ^{129}Xe in the gaseous state at a very low pressure (see ref. 55 and references therein), but this is not practicable.] However, in this document we concentrate on aspects that are of immediate practical utility. Temperature and pressure effects on chemical shifts for solutions and solid samples are sufficiently small for the lighter elements to be generally ignored for most chemical usage of NMR (largely carried out at ambient probe temperature and pressure), so we make no detailed recommendations regarding these parameters. References 55 and 56 contain some data on the temperature dependence of ^{1}H and ^{13}C resonances for TMS. Variations of solvent and/or change in sample concentration are known to have important effects on many chemical shifts, but they are relatively small for a symmetrical, nonpolarizable molecule like TMS.

To assess the magnitude of the concentration effect, measurements have been obtained [12] of the proton chemical shift for TMS in solutions of volume fractions, $\varphi = 0.01\%$, 1%, and 80% in $CDCl_3$ (see the Appendix). The ^{1}H NMR frequency of TMS ($\varphi = 1\%$) in chloroform is essentially at the infinite dilution level, the value for a $\varphi = 0.01\%$ solution differing by of the order of $10^{-7}\%$ in Ξ, which is normally reported to only $10^{-6}\%$. However, for a $\varphi = 80\%$ solution Ξ is $9 \times 10^{-6}\%$ larger than for a $\varphi = 1\%$ solution. *Therefore, for the primary reference in multinuclear magnetic resonance, we recommend a dilute solution (approximately $\varphi = 1\%$ or less) of TMS in $CDCl_3$. This recommendation does not preclude the use of TMS in other solvents as alternative references for ^{1}H NMR, and it is consistent with the use of DSS in aqueous solutions (see Section 3.7).*

These recommendations should not be taken in any way to preclude the design and implementation of experiments to measure specific properties, such as very high precision relative frequency measurements and special sample arrangements designed to minimize certain molecular interactions. Data will continue to be reported in the most effective way for the purpose at hand, but we believe that adoption of the unified chemical shift scale will facilitate comparison of the vast majority of NMR frequency measurements. The choice of the base reference as the proton signal of TMS is in accord with the virtually universal use of this signal as a reference for proton NMR.**

If the recommendation for use of a unified scale is widely adopted, future measurements should be reported as Ξ values. However, to assure consistency with data already in the literature, it is important to have a set of Ξ values of sufficient accuracy to permit conversion between the primary TMS reference and at least one secondary homonuclear reference for each nuclide (other than ^{1}H). Tables 1–3 list values of Ξ for a number of commonly used secondary references, which are hereby recommended

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*The name sodium 3-(trimethylsilyl)propane-1-sulfonate is strictly the correct one for this compound.

**With hindsight, it might have been better to choose the ^{29}Si signal of TMS since that is arguably even less susceptible to outside influence than the ^{1}H resonance (silicon being at the symmetry center of the molecule). However, because of the large amount of literature based on the proton signal, we recommend that the primary reference remain the ^{1}H signal of TMS.

for further use. These values come from a number of sources, as indicated in the tables. However, it should be noted that a number of these compounds are hazardous [for example, Me_2Se, Me_2Te, $Ni(CO)_4$, and, especially, Me_2Hg]. The unified scale has the advantage that its use avoids direct handling of any secondary references (see Section 3.6). For most of the nuclides listed in Table 3, there are few data available, and the values of $\varXi$ are simply approximations based on magnetogyric ratios.

However, for Tables 1 and 2, values of $\varXi$ are stated for almost all nuclides to $10^{-6}\%$. For 69 of the most commonly studied nuclides, careful measurements of $\varXi$ have been made specifically for the purpose of this tabulation. The frequencies of ^{13}C and ^{29}Si were determined for samples of TMS in dilute solution in $CDCl_3$ [12,13,15]. The remaining 67 measurements were made [9] by the substitution method (as described in the Appendix). Since all observation frequencies and the ^2H lock frequency are derived from a single source, the measured frequencies ($\varXi$) are reproducible to better than $10^{-7}\%$ and are reported to $10^{-6}\%$. Experimental details are given in the Appendix. Values of $\varXi$ for the remaining 30 nuclides in Tables 1 and 2 are taken from published values, which have been converted to be consistent with the choice of the ^1H signal for TMS in very dilute solution as the primary reference. The literature cited should be consulted for details of the experimental procedure and for estimates of experimental precision and accuracy.

For ^1H and ^{13}C NMR, internal referencing has been used almost exclusively, primarily to avoid bulk magnetic susceptibility effects, which can be of the same magnitude as some chemical shift differences that are interpretable with regard to chemical structure. The recommended reference for these nuclides is, therefore, TMS in a dilute solution in $CDCl_3$, and for consistency this reference is recommended also for ^{29}Si. For most other nuclides, magnetic susceptibility effects are small relative to chemical shift differences, and many of the published data have been reported relative to an external or replacement reference, often a neat liquid where feasible. To provide maximum utility, most of the entries in Tables 1 and 2 refer to such neat liquids or concentrated solutions, usually with a minimum amount of deuterated substance added to provide a stable lock. Of course, a very large number of such reference materials and lock substances could be used, but as described in Section 3.6, it is relatively simple to convert from one to another if necessary.

Values of $\varXi$ can generally be determined to $10^{-6}\%$, which represents resonance measurement differences of only 0.01 ppm for nuclides with large values of γ to 0.5 ppm for nuclides with very low γ values (an imprecision that is usually negligible compared with their generally large chemical shift ranges). Under the unified scale, chemical shifts can thus be reported to a precision that is often dependent on line-width or other sample-related factors, rather than instrumental factors. Since literature data for a number of nuclides are usually referred to a secondary reference and hence are often of considerably lower precision, small discrepancies in values of $\varXi$ are of little practical consequence in most instances.

3.6 Practical application of the unified scale

Modern NMR spectrometers invariably include field/frequency locking and frequency synthesizers, so that all frequencies are reliably interrelated by locking to a master clock frequency. There are two ways in which this fact can be used to determine chemical shifts, either directly on the $\varXi$ scale or with respect to a recognized reference for the nucleus in question. These two ways are equivalent to the use of the conventional internal reference and substitution methods, respectively. In the former case, if a nucleus X is to be studied, and the sample can be prepared with a small amount of TMS, then two direct frequency measurements made while maintaining the same ^2H locking conditions will provide the chemical shift of X on the unified scale according to eq. 9. If this procedure is applied to a series of samples, the effect is to replace "medium effects" on the shielding of X (given by measurements using a reference compound containing the nuclide X) by medium effects on the shielding of ^1H in TMS. In general, this should result in a reduction of medium effects due to the referencing procedure, which is desirable. Clearly, the substitution method can be used similarly and is particularly valuable when it is not

convenient to add TMS to the sample. Equation 9 is still pertinent. However, as noted in Section 3.4, medium effects may vary to some extent if different concentrations of sample and reference are used.

In the future, reporting of chemical shift data as Ξ values may become more common and acceptable. Conversion of Ξ values to conventional chemical shifts relative to a reference of an X-containing compound requires only subtraction of the Ξ value of a suitable homonuclear reference, as given in Tables 1 and 2, followed by division by the Ξ value of the homonuclear reference. Thus:

$$\delta_X \text{ / ppm} = 10^6 \, (\Xi_{X,\text{sample}} - \Xi_{X,\text{reference}}) \, / \, \Xi_{X,\text{reference}} \tag{10}$$

The widespread use of a ^{2}H lock for NMR measurements on isotropic samples suggests a modification of the substitution approach, since the relevant reference frequency should not vary with time. Thus, the chemical shifts of the X nuclei can, in principle, be determined on the unified (TMS-based) scale merely by measuring the resonance frequency of the sample and using a predetermined reference frequency for the nuclide in question. Thus, only one (sample) tube is required and no reference substance needs to be added. The predetermined reference frequency is obtained by measuring the proton resonance of TMS under similar conditions to the sample (i.e., with the same lock compound) in a single experiment for the spectrometer being used. Then, the frequency of the usual secondary reference for the X nucleus can be calculated using the predetermined value of ν_{TMS}:

$$\nu_{\text{reference}} = \nu_{\text{TMS}} \times \Xi_{\text{reference}} \, / \, 100\% \tag{11}$$

where $\Xi_{\text{reference}}$ takes the appropriate value given in Tables 1–3. Thence, the chemical shift (or the value of Ξ_X) for the sample can be readily derived. If the lock substance in the sample solution is not the same as that of the reference solution, a lock correction must be applied (eq. 8).

As an example, suppose that a ^{77}Se resonance has been measured on a compound dissolved in acetone-d$_6$, resulting in a value:

$$\nu_{\text{sample}} = 76\,344\,378 \text{ Hz}$$

On this spectrometer, the ^{1}H resonance of a $\varphi = 1\%$ solution of TMS in CDCl$_3$ has been found at 400 103 342 Hz when the spectrometer was installed. The reference frequency of selenium is then, from Table 1:

$$400\,103\,342 \text{ Hz} \times 19.071\,513 \div 100 = 76\,305\,761 \text{ Hz}$$

The proton chemical shifts of the resonances of the lock compounds are:

$$\delta_H(\text{CHCl}_3) = 7.27 \text{ ppm and } \delta_H(\text{acetone}) = 2.17 \text{ ppm}$$

Then:

$$\delta_{\text{Se, sample}} = (76\,344\,378 - 76\,305\,761)/76.305\,761 + (2.17 - 7.27) = 501.0 \text{ ppm}$$

Since this is still basically a substitution method, an error will arise if the ^{2}H frequency of the solvent has been influenced by the particular sample used. For many samples that consist of dilute solutions the error is small, and for many nuclei with large chemical shift ranges the error introduced in this way is probably smaller than would occur if a homonuclear (X) reference were used in the conventional manner.

Reporting of Ξ_X and δ_X measurements in future heteronuclear magnetic resonance studies will ultimately lead to a large set of consistent data, provided that values of $\Xi_{X,\text{ref}}$ are established and used consistently in all future work. Therefore, particularly for comparison with chemical shifts reported relative to a homonuclear (X) reference via conventional internal referencing procedures, it is essential that the values of Ξ in Tables 1 and 2 represent the accepted values for the substances listed (which are the "best" available at the present time). *We therefore recommend that the defined local chemical shift scale zero values are established as those listed in Tables 1 and 2, and that such definitions are not subject to future change arising from remeasurement even where this results in increasing accuracy for the ref-*

erence compound in question. However, the values of Ξ for "rare earth" nuclei in Table 3 should be regarded as provisional, pending more accurate measurement.

The Unified Scale offers many advantages over other methods of referencing. However, serious errors can occur in reading and displaying frequencies in some spectrometers unless care is taken. The software in NMR spectrometers is continually evolving, and even some spectrometers of relatively recent vintage are configured to display frequencies that are rounded off or that appear with many digits that do not correctly represent the frequency of a peak indicated by the cursor. The correct information is available in the appropriate parameter tables, but the authors of this document have found that in instruments that are several years old it may be necessary to seek the correct file and not rely on what appears to be an "obvious" display. Although the situation has improved with the latest version of commercial instruments, *we strongly recommend that each user verify that his/her own instrument correctly determines one or more values of Ξ as given in Tables 1–3.*

3.7 Alternative reference compounds

Many of the elements have more than one proposed reference compound for the chemical shift scale mentioned in the literature. The majority are secondary reference standards chosen for convenience. Although our recommendation stands for the compounds listed in Tables 1 and 2, there are some situations where an alternative reference has to be used. One of these cases occurs when ^1H, ^{13}C, ^{15}N, ^{29}Si, and other nuclei have to be referenced in highly polar solvents such as water, where TMS is only very sparingly soluble. For those situations, DSS or its partially deuterated form, $Me_3SiCD_2CD_2CD_2SO_3Na$, is the recommended primary reference [53,57]. {Sodium 3-(trimethylsilyl)propanoate (TSP) is another salt that has been suggested [58].} When DSS is used as a reference, it has been recommended [4] that ^1H chemical shifts be denoted by the symbol δ_{DSS} to distinguish them from those referenced to TMS. However, the resonances of DSS and TMS, *both dissolved in the same solvent*, are very close: On the scale with TMS as zero, DSS has a chemical shift of $\delta = 0.0173$ ppm in dilute aqueous solution, while in dilute solution in di[($^2H_3$)methyl] sulfoxide (DMSO-d_6), the chemical shift of DSS is $\delta = -0.0246$ ppm [4]. For most purposes, these differences are negligible (falling well below the anticipated range of solvent effects), and *data from the TMS and DSS scales may be validly compared without correction for the different ^1H reference.*

Table 4 repeats the recommended values of Ξ from ref. 4, along with data for additional references proposed in the literature for nitrogen, and compares them with our recommendations in Tables

Table 4 Alternative secondary references.

Isotope	Alternative secondary references			Literature	Recommended secondary references[a]		
	Reference compound	Sample conditions	NMR frequency Ξ / %		Reference compound	Sample conditions	NMR frequency Ξ / %
^1H	DSS	Internal	100.000 000	4	TMS	Internal[b]	100.000 000
^2H	DSS	Internal	15.350 608	4	TMS	Internal[b]	15.350 609
^{13}C	DSS	Internal	25.144 953	4	TMS	Internal[b]	25.145 020
^{31}P	$(CH_3O)_3PO$	Internal	40.480 864	4	H_3PO_4 (85%)	External	40.480 742
^{15}N	NH_3 (liquid)	External	10.132 912	4	CH_3NO_2	External	10.136 767
^{15}N	$[(CH_3)_4N]I$	Internal[c]	10.133 356	59,60			
^{14}N	$[(CH_3)_4N]I$	Internal[c]	7.223 885	59	CH_3NO_2	External	7.226 717

[a]See Tables 1 and 2.
[b]Volume fraction $\varphi = 1\%$ in $CDCl_3$.
[c]0.075 M in DMSO-d_6.

1 and 2. For ^{13}C studies in aqueous solution, ref. 4 recommends using the ^{13}C methyl resonance of DSS, rather than that of TMS, as the secondary reference. Carbon-13 chemical shifts based on DSS and TMS differ by about 2 ppm, which can cause confusion if not clarified. *We recommend that when ^{13}C chemical shifts are referenced to DSS, that point should be made clear by using a notation such as $\delta_{DSS}(^{13}C)$.*

Reference 4 recommends use of trimethyl phosphate (internal) as a secondary reference for ^{31}P studies in aqueous solution, whereas Table 1 recommends 85% phosphoric acid (external), which has been used more widely, particularly for chemical systems where use of an internal reference is not feasible. The two secondary references differ by about 3 ppm, so *it is important to specify which is being used.*

Several reference compounds have been used historically for nitrogen NMR, partly resulting from the very different properties and natural abundances of the two nuclides (^{14}N and ^{15}N). Nitromethane as either an internal or external reference has been the most widely used for ^{14}N and to some extent for ^{15}N, while liquid ammonia has been a popular external reference for ^{15}N. Ammonium and tetramethylammonium salts have been used as internal references for both ^{14}N and ^{15}N. Reference 4 recommends liquid NH$_3$ as a secondary reference for ^{15}N in aqueous solutions, since most biochemical applications of ^{15}N NMR have used this reference. In Tables 1 and 2 *we recommend nitromethane as a reference*, in line with common usage in many other applications. The values of Ξ for different nitrogen reference compounds are presented in Table 4, along with those for tetramethylammonium iodide, which has been suggested as an internal reference for both ^{14}N and ^{15}N since the tetrahedral geometry results in sharp lines for both isotopomers.

For most of the nuclei listed in Tables 1 and 2, Ξ values are listed for only one homonuclear reference, since conversions to other reference compounds can be readily made from literature values.

3.8 Magic-angle spinning

It has been shown [61–63] that, in theory, bulk isotropic magnetic susceptibility effects are eliminated by spinning an infinitely long cylindrical sample with its axis at the magic angle (54.7°) to the static magnetic field of an NMR spectrometer. Therefore, in principle, magic-angle spinning (MAS) can be used in the external referencing method to obtain chemical shifts free from bulk susceptibility problems. Whereas this technique was proposed in the context of solid-state NMR (see below), its utility applies equally well to the solution state [64,65]. In practice, an infinitely long cylinder is not necessary to reduce bulk susceptibility effects on chemical shifts to an acceptable level. Strictly speaking, to correct for *isotropic* bulk magnetic susceptibility effects, it is also not necessary to spin at the magic angle, but merely to orient the cylinder containing the sample at the magic angle (see eq. 7). However, spinning may narrow the lines significantly and so is normally essential for accurate chemical shift measurement.

3.9 Solids

Sample-handling procedures differ substantially for solids from those appropriate for solutions, and there are clear advantages to using suitable solids as secondary references. This is almost always done using sample replacement. However, the spectrometers are generally used without field/frequency locking, so that the resulting chemical shifts are inevitably less accurate than those for solutions. This is not a significant problem, because line-widths are usually substantially greater than those for solutions and they impose an upper limit to accuracy. High-resolution NMR of solids almost invariably relies on magic-angle spinning, and, as discussed in Section 3.8, this eliminates the effects of differences in bulk isotropic magnetic susceptibilities. Early papers [61,62] addressed this matter, and a recent review by VanderHart [45], which refers to both liquids and solutions, further discusses the influence of MAS for referencing spectra. Unfortunately, the situation is simple only for systems with isotropic magnetic susceptibility. VanderHart [45] discusses the case of anisotropic susceptibility, but there has been to date

little experimental work in this area. However, in general it may be taken that, within the accuracy of measurement, referencing by sample replacement under MAS conditions in an unlocked but stable spectrometer is to a good approximation equivalent to the substitution method as described in Section 3.5.

Several papers [66–68] take advantage of the MAS technique to suggest secondary solid standards for practical use in solid-state NMR. For example, the ^{13}C signals of solid adamantane, glycine, hexamethylbenzene, and $[(CH_3)_3Si]_4Si$ have been referenced to those for liquids and solutions using MAS, and data were reported to accuracies in the region of 0.004–0.04 ppm.

Chemical shift referencing for solid-state NMR is not yet at the stage where much further discussion is warranted here, so the only recommendation that we make is for referencing procedures to be always clearly and carefully stated in publications.

4. SUMMARY OF RECOMMENDATIONS

In addition to the endorsements of earlier Recommendations stated in Section 3.2 above, IUPAC recommends the following:

(a)　Equation 5 should be used to define chemical shift scales, with symbol δ and with ppm (or ppb or %, as appropriate) explicitly stated after the numerical values. Equation 6 provides a simple way to calculate chemical shift values in ppm.

(b)　The ^1H signal of tetramethylsilane in dilute solution (ca. volume fraction $\varphi = 1\%$ in $CDCl_3$) should be used as the primary *internal* or substitution reference for the resonance frequencies (and hence chemical shifts) for *all* nuclei. However, for aqueous solutions, the recommendations of ref. 4 are supported.

(c)　The secondary references listed in Tables 1 and 2 may be used for the nuclei of the various elements, with their Ξ taking the fixed values given (not subject to revision).

(d)　Internal referencing may be used for solutions, but its limitations should be recognized.

(e)　For solution-state measurements, referencing via an internal ^2H lock signal may be used, either to give the value of Ξ directly or to calculate the chemical shift with respect to the relevant secondary reference (via eq. 8, where relevant).

(f)　Referencing by the substitution method with field/frequency lock spectrometers may also be used for solutions.

(g)　External referencing for either liquids or solids may be carried out with magic-angle spinning.

(h)　External referencing by means other than (f) and (g) is to be discouraged unless corrections are applied for bulk magnetic susceptibility effects.

(i)　In all circumstances, and especially where strict adherence to these Recommendations is not feasible, details of experimental procedures should be given clearly so that results may be validly intercompared.

ACKNOWLEDGMENTS

APPENDIX

As noted in the body of this document, a number of new experimental measurements have been made to verify values of Ξ for various nuclides. Experimental details are given here.

Concentration dependence of δ_H (TMS) [12]. Measurements were made with a Varian VXR-500S spectrometer, sample at ambient probe temperature (about 23 °C), locked onto the signal for $CDCl_3$. Measured ^{1}H frequencies were as follows:

$\varphi = 0.01\%$:   499.872 5048 MHz
$\varphi = 1\%$:   499.872 5054 MHz
$\varphi = 80\%$:   499.872 5495 MHz

Ξ for ^{13}C and [29]Si. Three measurements were made of Ξ (^{13}C) for TMS in $CDCl_3$ at $\varphi = 1\%$, all at ambient probe temperature using the following spectrometers: Varian VXR-500S [13], $\Xi = 25.145$ 0188%; Varian Unity-300 [12], $\Xi = 25.145\ 0202\%$; and Varian Inova-500 [13], $\Xi = 25.145\ 0196\%$. The reported value [15] (Table 1) of Ξ ([29]Si) for TMS in $CDCl_3$ at $\varphi = 1\%$ was obtained at ambient probe temperature using a Bruker Avance-400 spectrometer.

Other values of Ξ. Most of the remaining 67 new measurements presented in Tables 1 and 2 were made by the substitution method (as described above) with a Bruker Model MSL spectrometer, operating at a nominal frequency of 300 MHz for ^{1}H, and with corrections applied for the lock signals (see equation 8) [9]. However, Ξ was measured for the following nuclei using a Bruker Avance-400 spectrometer: [2]H, [17]O, [45]Sc, [47]Ti, [49]Ti, [55]Mn, [75]As, [81]Br, [87]Rb, [127]I, [131]Xe, [133]Cs, [135]Ba, and [137]Ba. The [21]Ne value was measured [9] using a Chemagnetics Infinity 600. All 67 measurements were made at ambient probe temperature, approximately 298–300 K. The replacement reference samples used were either a concentrated solution (m = 4.75 mol kg^{-1}, $\varphi = 80\%$) of TMS in $CDCl_3$, or a $\varphi = 1\%$ solution of TMS in $CDCl_3$. In the former case, the values have been converted to refer to TMS ($\varphi = 1\%$) in $CDCl_3$ (see above).

REFERENCES

1. "Recommendations for the presentation of NMR data for publication in chemical journals", *Pure Appl. Chem.* **29**, 627 (1972).
2. "Presentation of NMR data for publication in chemical journals – B. Conventions relating to spectra from nuclei other than protons", *Pure Appl. Chem.* **45**, 217 (1976).
3. R. K. Harris, J. Kowalewski, S. C. de Menezes. "Parameters and symbols for use in nuclear magnetic resonance", *Pure Appl. Chem.* **69**, 2489 (1997).
4. J. L. Markley, A. Bax, Y. Arata, C. W. Hilbers, R. Kaptein, B. D. Sykes, P. E. Wright, K. Wüthrich. "Recommendations for the presentation of NMR structures of proteins and nucleic acids", *Pure Appl. Chem.* **70**, 117 (1998).
5. *NMR and the Periodic Table*, R. K. Harris and B. E. Mann (Eds.), Academic Press (1978).
6. I. Mills, T. Cvitaš, K. Homann, N. Kallay, K. Kuchitsu. *Quantities, Units and Symbols in Physical Chemistry*, 2nd ed., published for IUPAC by Blackwell Scientific Publications (1993).
7. R. K. Harris. *Encyclopedia of Nuclear Magnetic Resonance*, D. M. Grant and R. K. Harris (Eds.-in-Chief), **5**, 3301, Wiley, Chichester (1996).
8. K. J. R. Rosman and P. D. P. Taylor. *Pure Appl. Chem.* **70**, 217 (1998).

9. P. Granger, J. Raya, M. Bourdonneau, L. Helm, T. Meersmann. Measurements previously unpublished in the primary literature. See the Appendix for details.

10. J. P. Bloxsidge, J. A. Elvidge, J. R. Jones, R. B. Mane, M. Saljoughian. *Org. Magn. Reson.* **12**, 574 (1979).

11. R. Hoffman. Private communication.

12. H. J. C. Yeh. Previously unpublished work.

13. A. M. Kenwright. Previously unpublished work.

14. S. Brownstein and J. Bornais. *J. Magn. Reson.* **38**, 131 (1980).

15. B. Ancian. Previously unpublished work.

16. H. T. Edzes. *Magn. Reson. Chem.* **30**, 850 (1992).

17. P. L. Goggin, R. J. Goodfellow, F. J. S. Reed, *J. Chem. Soc., Dalton Trans.* 576 (1974); S. J. Anderson, J. R. Barnes, P. L. Goggin, R. J. Goodfellow. *J. Chem. Res. (M)*, 3601 (1978).

18. R. Benn and A. Rufinska. *Angew. Chem., Int. Ed. Engl.* **25**, 861 (1986).

19. J. D. Kennedy and W. McFarlane. *J. Chem. Soc., Perkin Trans.* **2** 1187 (1977).

20. M. Gerken and G. J. Schrobilgen. *Coord. Chem. Rev.* **197**, 335 (2000).

21. G. A. Schumacker and G. J. Schrobilgen. *Inorg. Chem.* **23**, 2923 (1984).

22. C. Brevard. Previously unpublished work.

23. M. B. Blayney, J. S. Winn, D. W. Nierenberg. *Chem. Eng. News* May 12, 7 (1997); T. Y. Toribara, T. W. Clarkson, D. W. Nierenberg. *Chem. Eng. News* June 16, 6 (1997); D. Love. *Chem. Eng. News* July 14, 7 (1997); R. K. Harris. *Chem. Eng. News* July 14, 7 (1997).

24. J. F. Hinton, G. L. Turner, G. Young, K. R. Metz. *Pure Appl. Chem.* **54**, 2359 (1982).

25. J. F. Hinton and R. W. Briggs. *J. Magn. Reson.* **25**, 555 (1977).

26. P. Pyykko. *Z. Naturforsch., A* **47**, 189 (1992).

27. P. Raghavan. *At. Data Nucl. Data Tables* **42**, 189 (1989).

28. P. Pyykko. *Mol. Phys.* **99**, 1617 (2001).

29. J. D. Kennedy. In *Multinuclear NMR*, J. Mason (Ed.), Ch. 8, p. 221, Plenum Press (1987).

30. J. T. LaTourrette, W. E. Quinn, R. F. Ramsey. *Phys. Rev.* **107**, 1202 (1957).

31. W. Sahm and A. Schwenk. *Z. Naturforsch.*, *A* **29**, 1754 (1974).

32. O. Lutz, A. Schwenk, A. Uhl. *Z. Naturforsch., A* **30**, 1122 (1975).

33. N. Hao, M. J. McGlinchey, B. G. Sayer, G. J. Schrobilgen. *J. Magn. Reson.* **46**, 158 (1982).

34. J. Kodweiss, O. Lutz, W. Messner, K. R. Mohn, A. Nolle, B. Stütz, D. Zepf. *J. Magn. Reson.* **43**, 495 (1981).

35. J. Kaufmann, W. Sahm, A. Schwenk. *Z. Naturforsch., A* **26**, 1384 (1971).

36. D. Brinkman. *Helv. Phys. Acta* **41**, 367 (1968).

37. W. Sahm and A. Schwenk. *Z. Naturforsch. A* **29**, 1763 (1974).

38. O. Lutz and H. Oehler. *Z. Physik A* **288**, 11 (1978).

39. O. Lutz and H. Oehler. *J. Magn. Reson.* **37**, 261 (1980).

40. C. Brevard and P. Granger. *Handbook of High Resolution Multinuclear NMR*, Wiley, New York (1981).

41. G. Wu and R. E. Wasylishen. *Magn. Reson. Chem.* **31**, 537 (1993).

42. A. G. Avent, M. A. Edelman, M. F. Lappert, G. A. Lawless. *J. Am. Chem. Soc.* **111**, 3423, (1989).

43. H. LeBail, C. Chachaty, P. Rigny, R. Bougon. *C. R. Acad. Sci.* **297**, 451 (1983).

44. G. V. D. Tiers. *J. Phys. Chem.* **62**, 1151 (1958).

45. D. L. VanderHart. *Encyclopedia of Nuclear Magnetic Resonance*, D. M. Grant and R. K. Harris (Eds.-in-Chief), **5**, 2938, Wiley, Chichester (1996).

46. P. E. Hansen. *Prog. Nucl. Magn. Reson. Spectrosc.* **20**, 207 (1988).

47. D. F. Evans. *J. Chem. Soc., Chem. Comm.* 1226 (1982).

48. L. J. Altman, D. Laungani, G. Gunnarson, H. Wennerström, S. Forsen. *J. Amer. Chem. Soc.* **100**, 8264 (1978).

49. W. McFarlane. *Proc. R. Soc. London, Ser.* A **306**, 185 (1968) and references therein.

50. W. McFarlane. *Annu. Rep. NMR Spectrosc.* **1**, 135 (1968).
51. R. K. Harris and B. J. Kimber. *J. Magn. Reson.* **17**, 174 (1975).
52. D. Canet, C. Goulon-Ginet, J. P. Marchal. *J. Magn. Reson.* **22**, 537 (1976).
53. D. S. Wishart, C. G. Bigam, J. Yao, F. Abildgaard, H. J. Dyson, E. Oldfield, J. L. Markley, B. D. Sykes. *J. Biomol. NMR* **6**, 135 (1995).
54. N. N. Zemlyanskii and O. K. Sokolikova. *Russ. J. Anal. Chem.* **36**, 1421 (1981).
55. C. J. Jameson, A. K. Jameson, S. M. Cohen. *J. Magn. Reson.* **19**, 385 (1975).
56. F. G. Morin, M. S. Solum, J. D. Withers, D. M. Grant. *J. Magn. Reson.* **48**, 138 (1982).
57. G. V. D. Tiers and A. Kowalewsky. Paper presented to the Division of Physical Chemistry, 137th ACS National Meeting, Cleveland, Ohio, 1960; Abstracts, p. 1712; G. V. D. Tiers and R. I. Coon. *J. Org. Chem.* **26**, 2097 (1961).
58. G. V. Tiers and A. Kowalewsky. Division of Physical Chemistry, 137th ACS National Meeting, Cleveland, Ohio, 1960; L. Pohl and M. Ecke. *Angew Chem., Int. Ed. Engl.* **8**, 381 (1969); D. H. Live and S. I. Chan. *Org. Magn. Reson.* **5**, 275 (1973).
59. E. D. Becker. *J. Magn. Reson.* **4**, 142(1971).
60. E. D. Becker, R. B. Bradley, T. Axenrod. *J. Magn. Reson.* **4**, 136 (1971).
61. D. Doskočilová and B. Schneider. *Macromolecules* **5**, 125 (1972).
62. D. Doskočilová, D. D. Tao, B. Schneider. *Czech. J. Phys. B* **25**, 202 (1975).
63. W. L. Earl and D. L. VanderHart. *J. Magn. Reson.* **48**, 35 (1982).
64. A. N. Garroway. *J. Magn. Reson.* **49**, 168 (1982).
65. S. Hayashi, M. Yanagisawa, K. Hayamizu. *Anal. Sci.* **7**, 955 (1991).
66. S. Hayashi and K. Hayamizu. *Bull. Chem. Soc. Jpn* **62**, 2429 (1989).
67. S. Hayashi and K. Hayamizu. *Bull. Chem. Soc. Jpn.* **64**, 685 (1991).
68. S. Hayashi and K. Hayamizu. *Bull. Chem. Soc. Jpn.* **64**, 688 (1991).