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Variations on the chemical shift of TMS

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Abstract

The chemical shift of TMS is commonly assumed to be zero. However, it varies by over 1 ppm for ^{1}H and 4 ppm for ^{13}C and shows a correlation with the physical properties of the solvent. Using the commonly accepted convention that TMS always resonates at zero leads to significant errors when comparing chemical shifts in different solvents. A new method for measuring absolute chemical shift with a conventional NMR spectrometer is demonstrated. The observed chemical shift is corrected by measuring and correcting for susceptibility and shape factor. Practical suggestions are made for modifying the current chemical shift standard while maintaining compatibility with earlier literature.

Keywords: Chemical shift; Magnetic susceptibility; Standards; Solvents; Temperature

1. Introduction

A reliable method for comparing chemical shifts under varying conditions is required for studying the effects of solvent, temperature and concentration. To this end, IUPAC recently published a unified prime standard (^{1}H of dilute TMS in $CDCl_3$) for measuring chemical shifts [1]. However, the standard is unclear regarding other solvents and the effect of temperature on the chemical shift of TMS. If, as is usually the case, one assumes that the chemical shift of TMS is zero in every solvent, then this can lead to errors of over 1 ppm for ^{1}H NMR and by extension using the Ξ system [1] for other nuclei. (There is one report of the chemical shift of TMS in benzene-d_6 being −0.5 ppm and a paper on the chemical shifts of TMS in a variety of protiated solvents that have gone largely unnoticed [2,3].) This effect cannot be ignored when you consider that the nominal chemical shift range of ^{1}H is only 10 ppm.

In order to compare samples in different solvents one needs to know the susceptibility difference and shape factor of the sample (Eq. (1)) because the susceptibility affects the observed absorption frequency. These parameters are difficult to measure with a standard NMR spectrometer and have therefore been widely ignored in the literature. Nonetheless, the difficulty in measuring these parameters, even if errors remain in the second decimal place, cannot be used as an excuse for sweeping under the carpet such glaring inaccuracies of over 1 ppm. For this purpose, I have developed a method to measure the susceptibilities and shape factor that, with care, can be used to determine the absolute chemical shift relative to the IUPAC [1] prime standard (^{1}H of dilute TMS in $CDCl_3$).

An example of such an inaccuracy is the aromatic solvent isotope shift (ASIS) [2,4–10] of chloroform. If we assume TMS to have a zero chemical shift (measured in the normal manner with deuterium lock) in both chloroform-d and benzene-d_6 then the ASIS effect is 1.06 ppm but when its correct value is measured (by exchanging samples without lock and correcting for susceptibility effects) it is 42% larger: 1.51 ppm.

The ability to compare chemical shifts between solvents has the potential to open up the study of weak intermolecular effects on the chemical shifts of ^{1}H. This is important for solvation studies and supra-molecular chemistry. Until now this has been restricted to nuclei with larger chemical shift ranges such as ^{13}C and the noble gases. The reason is clear when we see that the difference in chemical shift of chloroform in the highly polarizable solvent methylene iodide as compared with

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chloroform-d is 0.25 ppm assuming TMS to have a zero chemical shift in both solvents. Using the corrected method suggested here, it is over twice as large at 0.54 ppm.

Besides the solvent effect, the chemical shift of TMS in chloroform-d is dependent on temperature. Based on previous measurements of the temperature dependence of neat TMS's chemical shift [11,12] the temperature dependence of the IUPAC prime standard can be determined. This may find application in improving the accuracy of thermodynamic studies. However, further work will be required to check the accuracy of the literature before this can be put into general use.

2. Shape factor for magnetic susceptibility correction

Magnetic susceptibility changes the observed chemical shift (δ_o) of a nucleus from its true chemical shift (δ) [13]. Therefore, exchanging a chemical shift reference sample with a sample of different susceptibility yields an observed chemical shift that differs from the true chemical shift. This effect is proportional to its volume magnetic susceptibility (K in ppm) multiplied by the sample's shape factor (a, Eq. (1)) [13]

$$\delta = \delta_o - aK. \tag{1}$$

The shape factor can be calculated theoretically from the geometry of the sample. However it is easily affected by small changes in the geometry that occur between NMR tubes and probe coils, so empirical methods are better for practical purposes. IUPAC suggests ignoring the bulk susceptibility factor by choosing a geometry that has a shape factor of zero such as a shape cylindrically symmetrical about the magic angle [1]. This is impractical for a normal high-resolution NMR probe where the sample is cylindrically aligned with the magnetic field although it would be possible using a CP-MAS or HR-MAS probe. In principle, this could be achieved using a spherical sample, however, slight deformations in spherical cavities and the emergent stem effect yield greater errors than measuring a cylindrical sample and correcting for its susceptibility effects [14].

The shape factor for an infinitely long cylinder aligned with the magnetic field is $4\pi/3$ (4.189) [13]. In a conventional NMR spectrometer, a 5 mm outer diameter (4.2 mm inner diameter) sample with a depth of 40–50 mm and the bottom of the tube between 18 and 20 mm below the coil center is typically used. This configuration is a cylinder that is far from infinite in length. In fact, the cylinder length is only a few times longer than the coil length. Therefore both the length of the sample and the coil geometry affect the shape factor.

To measure the shape factor one must start with a sample that is a little closer to an infinite cylinder. By removing the thermocouple from the probe it is possible to place the bottom of the sample 25 mm below the coil center rather than the usual 20 mm. Using a narrower tube increases the length to diameter ratio. I used a 1.2 mm internal diameter tube containing methylene chloride (that yields a proton singlet whose chemical shift is not over-dependent on temperature) with a liquid depth of over 100 mm held concentrically in a regular NMR tube starting with the bottom of the outer tube 25 mm below the coil center. The shift of the signal was measured. The tube was ejected, raised by 1 mm, reinserted, reshimmed and a new chemical shift measured. This was repeated until a depth of 15 mm was reached. The tube was then returned to a 25 mm depth and the shift remeasured in order to correct for magnet drift.

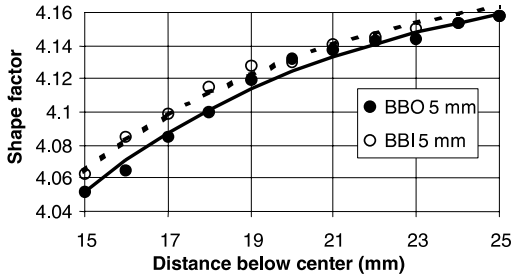

Fig. 1. Shape factor for a long cylinder (4.2 mm diameter) terminating a finite distance below the coil center.

A plot of observed shift against sample depth was fitted to an exponential function. An extrapolation of the observed shift to infinite depth (δ_∞) was assumed to correspond to a shape factor of 4.189. This led to a shape factor for the narrow tube at 25 mm deep of 4.180 for a Bruker 5 mm BBO probe (coil length 20.0 mm) and 4.185 for a BBI probe (coil length 18.5 mm). The experiment was repeated starting with a narrow tube at 25 mm depth then replacing it with a regular NMR tube (4.2 mm inner diameter) and raising the NMR tube 1 mm at a time and remeasuring until a depth of 15 mm was reached. Finally the narrow tube was reinserted at 25 mm depth in order to correct for any magnet drift. The observed chemical shift was then used to determine the shape factor (Eq. (2)). The shape factor was correlated to an exponential function for depths (d) between 15 and 25 mm below. For BBO it was $4.189 - 1.01 \exp[-0.634(d - 1.8)]$ for BBI it was $4.189 - 0.98 \exp[-0.658(d - 1.8)]$ (Fig. 1)

$$a = 4.189 + (\delta_o - \delta_\infty)/K. \tag{2}$$

3. Magnetic susceptibility measurement

In the past, magnetic susceptibility has been measured using a magnetic susceptibility balance [15] or by NMR using a horizontally aligned electromagnet [16,17]. The magnetic susceptibility balance may be

more accurate than the NMR method proposed here but requires extra instrumentation and careful measurement.

To measure susceptibility with a vertically aligned magnet, one can take advantage of the dependence of the observed shift on shape factor to its extreme. A sample containing a solution with a depth of at least 45 mm and the bottom 20 mm below the coil center that exhibits a strong singlet is first set up and shimmed in the normal manner. The tube is then raised so that the bottom is 2 mm below the coil center and the spectrum acquired (Fig. 2). The linewidth (w) for the same solvent was found to vary by around 10% between round-bottomed tubes (Wilmad 507-PP) but for a single tube at a specific field strength, it was repeatable with a standard deviation of 0.1%. Flat-bottomed tubes yielded a lineshape that was less consistent. The width was also dependent on the amount of oxygen in the air (due to the high paramagnetism of oxygen) around the tube so separate calibrations were needed when using air and nitrogen flow. For variable temperature work, nitrogen flow was used because the volume paramagnetism of oxygen in the air varies with temperature. The lineshape was also found to change slightly between probes. Oxygen dissolved in the solvent has a significant effect. Chloroform-d has a susceptibility of −0.719 at 0.93 bar and −0.725 under vacuum. The samples in this work were air saturated at 0.93 bar unless otherwise stated because most NMR work is carried out air saturated. Therefore, to achieve the most consistent results for susceptibility, one must use the same tube in the same probe with the same atmosphere. The signal near the bottom of the tube is most shifted but is not as intense as signal arising from the higher part of the tube and therefore only affects measurements near the baseline. It is the difference between the resonance frequencies at bottom and further up the tube that is affected by the susceptibility. The linewidth at some arbitrary level near the baseline depends linearly on susceptibility based on the comparison of several solvents (Table 1 and Fig. 3).

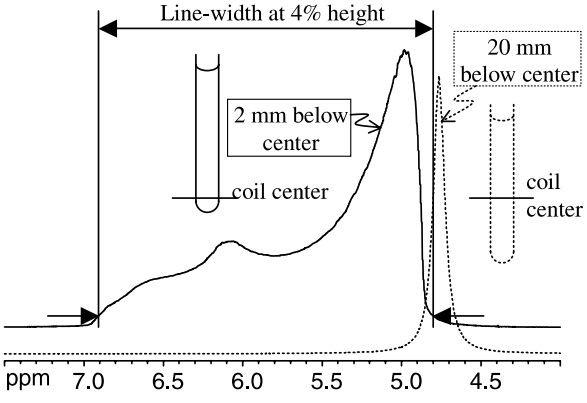

Fig. 2. Typical lineshape produced by this method.

Table 1
Correlation of susceptibility with linewidth

Solvent	Susceptibility[a]	Linewidth (ppm)
Acetone (0.2% water)	−0.458	1.441
Methanol	−0.525	1.664
Toluene	−0.622	1.898
Water	−0.715	2.178
Methyl iodide	−0.911	2.785
Bromoform	−0.937	2.909

[a] In ppm, derived from [18,19] as explained in the text.

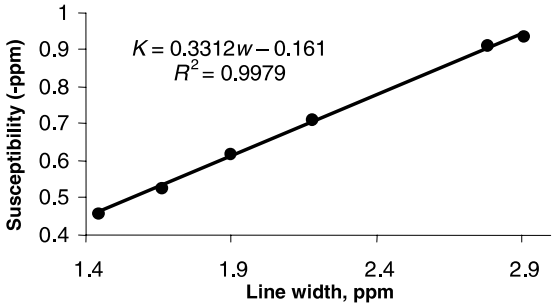

Fig. 3. Correlation of susceptibility with linewidth for a specific NMR tube and probe.

In order to yield the maximum consistency, the lineshape was also checked with a depth of 1 and 3 mm. This was found by trial and error to have a minimal affect at 4% of the peak height when the spectrum was processed using 5 Hz line broadening in and automatic baseline flattening.

For protiated solvents, saturation becomes an issue and slightly affects the susceptibility measurements. To avoid the effect, protiated solvents were off-tuned enough to increase the 90° pulse width to 60 μs (about three turns on a manually tuned Bruker 5 mm probe).

This linewidth can be calibrated against samples of known susceptibilities such as water (−0.715) and acetone (containing 0.2% water) (−0.458). By comparing several solvents, the value of the susceptibility can be determined to a standard deviation of 0.009 (0.04 ppm in chemical shift) provided that the same tube and probe are used (Fig. 3). The remaining errors may be due to impurity of the solvent, inconsistencies in the conditions of the literature measurements or intrinsic inaccuracies in the NMR method.

Deuterated solvents have slightly different susceptibilities than their equivalent protiated solvent. For example, the volume susceptibility (ppm) is −0.720 for H_2O (20 °C) versus −0.704 for D_2O [18,19] or it is (as measured in this work at 25 °C) −0.622 for THF versus −0.646 for THF-d_8.

The susceptibility is temperature dependent, changing by up to 0.002 ppm/K. Account for this must be taken when measuring chemical shifts at different temperatures.

In this work, the measurements were carried out at $25 \pm 0.5\,^{\circ}C$. Where the magnetic susceptibility was available from the literature, an average of the literature values from two sources [18,19] at 20 °C was used and multiplied by a factor of 0.992 to correct for the 5 °C temperature difference. In the case of water and D_2O, literature values were available for different temperatures so a better approximation could be made by interpolation.

4. Rigorous determination of chemical shifts using the prime standard

To rigorously measure chemical shifts the substitution method, corrected for magnetic susceptibility is proposed. First, the susceptibilities of the *prime standard* for chemical shift (^1H of dilute TMS in $CDCl_3$ [1]) and the sample are measured as described above. To compare another chemical shift, the prime standard was measured without lock and replaced with the sample and measured. The prime standard was then returned and remeasured. The final measurement is to correct for drift and is usually repeatable to about 1 Hz. The factor limiting the accuracy is the susceptibility measurement that leads to a standard deviation of error of 0.04 ppm. For example, for DMSO-d_5 (the residual proton signal) in DMSO-d_6 using the substitution method yielded an observed chemical shift, δ_o, of 3.07 relative to dilute TMS in $CDCl_3$. Eq. (3) gives the true chemical shift

$$\begin{aligned}\delta &= \delta_o - a(K_{\text{DMSO-d}_6} - K_{\text{CDCl}_3}) \\ &= 3.07 - 4.124(-0.606 + 0.728) = 2.56\,\text{ppm}. \end{aligned} \quad (3)$$

Likewise, the TMS peak in DMSO-d_6 has an observed chemical shift of 0.56 ppm and a true chemical shift of 0.06 ppm. However, decades of scientific work have referenced TMS to zero in any solvent [1]. Changing the reference to reflect the true chemical shift relative to the prime standard of IUPAC would cause confusion. I suggest, and this is only a suggestion that would have to be approved by IUPAC and subsequently the NMR scientific community, that we continue to use the proton resonance of TMS in each solvent as the 0 ppm but remain aware of the true chemical shift of TMS, using it as a correction factor when comparing chemical shifts between solvents. For solvents, such as trifluoracetic acid-d (not studied here), in which TMS is unstable, I suggest referencing to the prime standard. Table 2 shows the chemical shifts of some common NMR solvents relative to the TMS in the same solvent and the correction factors for the chemical shift of TMS relative to the prime standard.

The variation of chemical shifts with temperature is used to study equilibrium effects between different chemical and physical states. However, the chemical shifts of almost all samples, including the primary standard, vary with temperature. The only reported exceptions are noble gases, as their pressure tends to zero because they are not subject to intramolecular effects. Measurements of neat TMS relative to ^{129}Xe have provided an absolute chemical shift scale from −60 to 20 °C [11,12].

Here, the primary standard has been compared with neat TMS and combined with the reported measurements [11,12] to yield its temperature dependence. The IUPAC standard [1] only hints at this temperature effect. IUPAC suggests 293 K (19.85 °C) as a standard temperature. In this work I have primarily obtained results at 25 °C and so have chosen this temperature to be the prime standard. The chemical shift of neat TMS is $-0.06 - 4.2 \times 10^{-3}T - 4 \times 10^{-6}T^2$ (T is temperature in °C) and that of dilute TMS in $CDCl_3$ is $0.079 - 2.8 \times 10^{-3}T - 1.24 \times 10^{-5}T^2$ (Table 3 and Fig. 4).

While these findings show that the chemical shift of TMS varies significantly with temperature, there are limitations to the data available from the literature. The data are available over a relatively small range of

Table 2
Chemical shifts of some common NMR solvents

Solvent	δ_H (TMS)[a]	δ_H (solvent)[b]	δ_C (solvent)[c]
Acetone-d_6	−0.16	2.04	28.92, 205.19
Acetonitrile-d_3	−0.07	1.94	0.30, 117.31
Benzene-d_6	−0.45	7.16	127.68
Bromoform-d	0.15	6.84	11.85
Chloroform-d	0.00	7.26	76.98
Deuterium oxide	−0.08	4.80	
DMF-d_7	−0.12	2.75, 2.89, 8.01	29.69, 34.50, 162.09
DMSO-d_6	0.06	2.50	39.98
Methanol-d_4	−0.11	3.30, 4.85	47.84
Methylene chloride-d_2	0.03	5.31	53.37
1-Methylnaphthalene-d_{10}	−0.73	2.21, 6.96, 7.11, 7.21, 7.24, 7.47, 7.58, 7.61	18.08, 123.67, 124.87, 124.96, 125.05, 126.00, 126.12, 127.98, 132.80, 133.68, 133.79
Nitrobenzene-d_5	−0.64	7.51, 7.68, 8.12	122.88, 128.90, 134.26, 147.94
Pyridine-d_5	−0.58	7.21, 7.58, 8.74	123.31, 135.30, 149.70
1,1,2,2-Tetrachloroethane-d_2	−0.03	5.99	73.99
THF-d_8	−0.02	1.72, 3.58	24.28, 66.36
Toluene-d_8	−0.42	2.08, 6.97, 7.01, 7.10	20.01, 124.71, 127.55, 128.45, 137.07

[a] At 25 °C relative to dilute TMS in $CDCl_3$. Use as a correction factor when comparing solvents by adding it to the chemical shift relative to TMS in that solvent.

[b] Relative to $\delta_H(\text{TMS}) = 0$ in the same solvent.

[c] Relative to ^1H frequency of TMS in the same solvent × 0.25145020, where 0.25145020 is $\Xi(^{13}C)/100$.

Table 3
Effect of temperature on chemical shift and susceptibility

Substance	Susceptibility (ppm)			Chemical shift (ppm)		
	$a+$	$bT+$	cT^2	$a+$	$bT+$	cT^2
TMS	−0.536	1.17×10^{-3}	-2.7×10^{-6}	−0.06	-4.2×10^{-3}	-4×10^{-6}
TMS in $CDCl_3$	−0.776	9.5×10^{-4}		0.079	-2.85×10^{-3}	-1.24×10^{-5}
TMS in THF-d_8	−0.684	1.51×10^{-3}		0.16	-6.1×10^{-3}	-2.4×10^{-5}

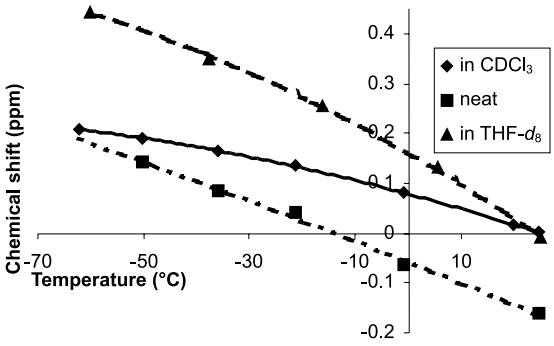

Fig. 4. Variation of the chemical shift of TMS with temperature.

temperatures and is based on only one report [11]. The use of ^{3}He would be preferable to ^{129}Xe as its chemical shift is 2 orders of magnitude less sensitive to physical effects [20]; it yields a stronger NMR signal and can be used at lower temperatures. Therefore further research is required to check the results before they can be relied upon. However, this effect should not be ignored as it has the potential to significantly affect thermodynamic measurements.

For nuclei other than ^{1}H, the chemical shift is measured relative to the prime standard multiplied by a factor ($\Xi/100$) for each nucleus as tabulated in the IUPAC standard [1]. For ^{13}C $\Xi/100$ is 0.25145020 and for ^{29}Si it is 0.19867187. Relative chemical shifts for different nuclei can be measured by this method with a precision of 0.002 ppm [1] although differences in the shape factor between nuclei arising from the use of different coils in the probe may reduce the accuracy. However, their absolute shifts are only accurate to 0.04 ppm due to limitations in the accuracy of susceptibility. Table 2 shows the proton and ^{13}C chemical shifts of some common NMR solvents. The chemical shifts (except for chloroform-d) are only given to two decimal places due to their limited absolute accuracy.

5. Determination of chemical shifts using secondary standards

The rigorous method is somewhat cumbersome and is impractical for most routine NMR. Therefore a practical method, especially suited to dilute diamagnetic samples, based on secondary standards is proposed. The spectrum is acquired as usual, with lock and no exchange of samples. The chemical shift is then compared with that of the solvent (or some other dissolved and well characterized signal such as TMS or TSP) as tabulated (Table 2). For example, returning to chloroform in benzene-d_6, referencing benzene-d_5 to 7.16 ppm (i.e., TMS in benzene-$d_6 = 0$) we get the chemical shift for chloroform in benzene-d_6 as 6.10 ppm. This, I suggest, should be the chemical shift normally quoted. However, if you wish to compare the chemical shift with that in another solvent such as chloroform in chloroform-d then you have to apply the correction factor and subtract 0.45 ppm yielding a chemical shift relative to the prime standard of 5.65 ppm.

6. What affects the chemical shift of TMS?

Intermolecular effects arising from the polarizability and magnetic anisotropy affect the chemical shift of TMS just as they affect other compounds.

In ^{1}H NMR, magnetic anisotropy is most marked with aromatic solvents yielding TMS chemical shifts in a range completely separate from that of other solvents (Fig. 5 and Table 4). This effect is called the aromatic solvent induced shift (ASIS). In the case of TMS, the shift is caused by weak σ–π bonding between the methyl of the TMS and benzene ring. On average, the methyl tends to be more above than to the edge of the benzene

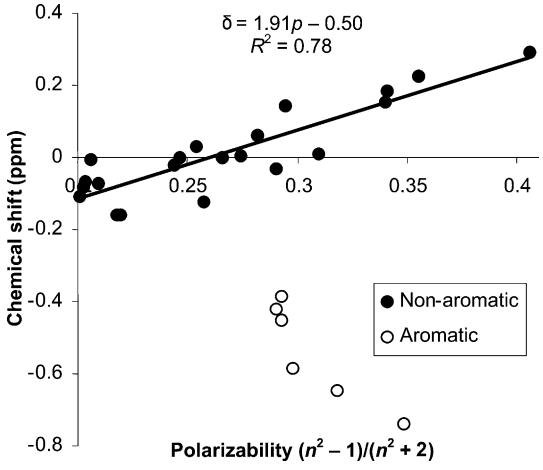

Fig. 5. ^{1}H chemical shift of TMS versus polarizability.

Table 4
Chemical shifts of TMS and ^{129}Xe and physical parameters for solvents

Solvent	δ_H (TMS)	δ_C (TMS)	δ_{Xe}[a]	n[b]	Polarizability	Susceptibility[c]
Acetone-d_6	−0.16	−1.07	175	1.355	0.218	−0.441
Acetonitrile-d_3	−0.07	−1.15		1.340	0.210	−0.501
Benzene-d_6	−0.45	−0.81		1.498	0.293	−0.622
Bromoform	0.18	1.51	285	1.5976	0.341	−0.937[c]
Bromoform-d	0.15	1.60		1.595	0.340	−0.925
Carbon disulfide	0.23	0.60	225	1.6279	0.355	−0.699[c]
Carbon tetrachloride	0.14		222	1.5011	0.295	−0.691[c]
Chloroform	0.01	0.01	217	1.4603	0.274	−0.736[c]
Chloroform-d	0.000	−0.029		1.444	0.266	−0.753
Deuterium oxide	−0.08	−0.88		1.327	0.202	−0.699[c]
DMF-d_7	−0.12	−0.74		1.428	0.257	−0.569
DMSO-d_6	0.06	−0.36		1.475	0.282	−0.606
Methanol	−0.07	−1.50	148	1.329	0.203	−0.525[c]
Methanol-d_4	−0.11	−1.59		1.325	0.201	−0.510[c]
Methylene chloride	0.00	−0.45	192	1.4243	0.246	−0.725
Methylene chloride-d_2	0.03	−0.44		1.421	0.254	−0.733
Methylene iodide	0.29	2.80	335	1.7464	0.406	−1.142
Methyl iodide	0.01	0.76	209	1.5314	0.310	−0.911[c]
1-Methyl naphthalene-d_{10}	−0.74	−0.81		1.6140	0.349	−0.749
Nitrobenzene-d_5	−0.64	−1.23		1.5490	0.318	−0.579
Pyridine-d_5	−0.58	−0.82		1.5070	0.298	−0.590
1,1,2,2-Tetrachloroethane-d_2	−0.03	0.17		1.4390	0.291	−0.824
THF-d_8	−0.02	−1.05		1.403	0.244	−0.636
TMS	−0.16	−0.78	158	1.3580	0.220	−0.526
Toluene	−0.38	−0.78		1.4969	0.293	−0.615[c]
Toluene-d_8	−0.42	−0.84		1.493	0.291	−0.614
Vacuum	−0.27		0	1.0000	0.000	0.000
Water	−0.01	−0.75	196	1.333	0.206	−0.719[c]

[a] Ref. [21].
[b] Refs. [18,26].
[c] In ppm, individual values marked are derived from [18,19] as explained in the text.

ring causing an up-field shift in both proton and carbon. The effect on the proton chemical shift of TMS is between the 0.4 and 1.0 ppm.

Weak intermolecular forces are evident by the correlation of chemical shift with polarizability (Figs. 5 and 6). Previous reports have made a correlation between the chemical shift of dissolved ^{129}Xe and a function, $100[(n^2-1)/(2n^2+1)]^2$, of the refractive index (n) of the solvent [21]. A better correlation is achieved if the chemical shift is correlated to the polarizability parameter (p, used for solubility studies [22]) that is in itself a function of the refractive index $(n^2-1)/(n^2+2)$. The ^{13}C chemical shift of dissolved methane also shows such a correlation [23] as do the chemical shifts of dissolved ^{83}Kr [24], ^{21}Ne [25], and ^{3}He [20]. It is therefore not surprising that, in the absence of an ASIS effect, TMS also shows such a correlation, albeit weaker.

The correlation of chemical shifts between the noble gases and between them and methane is much better than between the noble gases and polarizability [20]. The poorer correlation with TMS and ^{129}Xe (Fig. 7) suggests

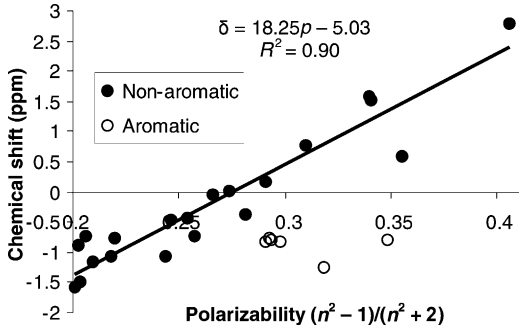

Fig. 6. ^{13}C chemical shift of TMS versus polarizability.

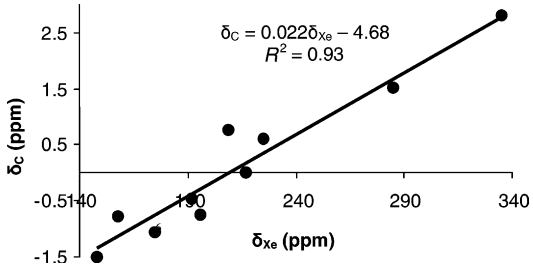

Fig. 7. Correlation of ^{13}C TMS and ^{129}Xe chemical shifts (Xe shifts for protiated solvents are compared with TMS shifts for some deuterated solvents).

that there are additional weak chemical effects in addition to the polarizability.

There is one point that does not fit this trend at all. This is for low-pressure ^{129}Xe [21] and TMS vapor in a vacuum (Table 4). Both deviate significantly from line. In the case of TMS it is easy to suspect some intramolecular effect. Also, initial measurements of ^{29}Si chemical shifts (methylene iodide 0.36, chloroform-d −0.05 and TMS −0.40) suggest that polarizability is not the major factor affecting silicon chemical shifts.

7. Experimental

DMSO-d_6 was a commercial sample nominally 99.9% atom D was found to contain 0.06% water and 0.01% D_2O. Acetone-d_6 99.9% atom D was found to contain 0.1% water of which 1/3 was deuterated. THF, THF-d_8 (99.5% atom D), and C_6D_6 were dried over alkali metal. Chloroform, chloroform-d, and TMS were dried over P_2O_5. Acetonitrile-d_3 was 99.2% D. Chloroform and bromoform were purified to remove ethanol stabilizer by washing six times with water and distilling from P_2O_5. Methanol was dried by reacting with a little piece of potassium and distilled. Toluene was redistilled. All other solvents were commercial products used without further purification.

Spectra were measured on Bruker DRX-400 and Bruker AMX-300 spectrometers at a temperature of $25 \pm 0.5\,^{\circ}C$ and saturated with air at a pressure of 0.93 bar unless stated otherwise. Temperatures were calibrated according to a methanol NMR thermometer [27]. Where sensitivity was insufficient to directly observe the ^{13}C or ^{29}Si signal of TMS, HSQC [28] was used to observe the signal indirectly.

8. Conclusions

The IUPAC chemical shift standard [1] requires slight modification to give consistent results for different solvents and at different temperatures. A method for making such measurements is achievable on a standard NMR spectrometer. This method will yield more consistency in the reporting of chemical shifts if implemented. It is suggested that the chemical shift be referenced to ^1H of TMS = 0 in the same solvent unless comparison is required with other solvents.

The chemical shift of TMS mostly depends on solvent anisotropy and polarizability.

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