Shift References in High-Resolution Solid-State NMR

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Synopsis. The high-resolution solid-state ^{13}C, ^{29}Si, ^{31}P, ^{23}Na, ^{27}Al, and ^{11}B NMR spectra of several compounds have been measured using magic-angle sample spinning. Their isotropic chemical-shift values have been determined accurately to use as shift references in solid-state NMR; this makes comparison between literature shift data possible.

High-resolution solid-state NMR has been widely used for such lighter nuclides as ^{13}C, ^{29}Si, and ^{3}P in the solid state.[1] By using this technique, chemical shifts in solids can be determined accurately, and nonequivalent sites can sometimes be distinguished.

The chemical shift can be expressed as the deviation of the resonance frequency with respect to reference materials. For example, tetramethylsilane (TMS) is universally used as an internal shift reference in liquid-state ^{13}C, ^{1}H, and ^{29}Si NMR. On the other hand, in solid-state NMR, an external reference is used instead of an internal reference. A correction of the bulk magnetic susceptibility is, however, necessary in the case of an external reference, though it is not discussed in the present work.

For the reference materials in solid-state NMR, the following properties are desirable:

(1) The central peak is very sharp under magic-angle sample spinning (MAS).

(2) The material contains a large amount of the observed nuclei, thus making the detection easy.

(3) For the $I \geqq 1$ spins, the crystal symmetry is very high, and so the spins have no electric-field gradient. This means that the center transition ($m=1/2 \leftrightarrow -1/2$) has neither broadening nor a shift caused by the second-order quadrupole effect.

(4) The compounds are available commercially.

(5) The spin-lattice relaxation time of the observed nucleus (or of the proton when the cross-polarization technique is used) is short enough.

(6) The materials are stable in air.

(7) The materials can be used for the set-up of the spectrometer. This means that solid materials are preferable.

Various second-reference materials have been used,[2] but their bases are sometimes ambiguous or have not been described explicitly. While the magnetic field was relatively low, any difference in the second-reference materials was little trouble since the resolution in high-resolution solid-state NMR was not so good as in liquid-state NMR. However, in the high-field NMR instruments recently developed the resolution is sometimes comparable to that in liquid-state NMR, and the chemical shift can be determined very accurately. The use of different second-reference materials might, therefore, now cause some deviation in shift values.

The aim of this paper is to present data on several materials which can be used as second references. This would enable us to compare literature data. We have measured the high-resolution solid-state ^{13}C, ^{29}Si, ^{31}P, ^{23}Na, ^{27}Al, and ^{11}B NMR spectra of several compounds and have determined the isotropic chemical shift accurately.

Experimental

The compounds were available commercially. High-resolution solid-state NMR spectra were measured by the use of a Bruker MSL400 pulsed spectrometer at room temperature. The probe was doubly tuned to the observed nucleus and proton, being capable of proton-dipolar decoupling and cross-polarization if necessary. The magic-angle sample-spinning technique[3] was used to determine the isotropic chemical shift accurately. The spinning rate of the rotor was changed between 2 and 4 kHz; typically, 4 kHz was used. A JEOL FX200 pulsed spectrometer was also used, and the values obtained by the two spectrometers agreed within the limits of experimental error. The static magnetic fields were 9.40 and 4.69 T for MSL400 and FX200 respectively. Since the precision and reproducibility were somewhat better in MSL400, the results obtained by the use of MSL400 will be described here. The higher-frequency shift is expressed as positive.

Results and Discussion

Table 1 summarizes the chemical-shift values of the compounds studied in this work, including the first-reference materials. For practical purposes, materials widely used in liquid-state NMR were selected as the first-reference materials and no correction of the bulk magnetic susceptibility was performed. The experimental errors in Table 1 reflect the reproducibility of the measurements carried out in this work.

^{13}C. The first-reference compound is tetramethylsilane (TMS). It is difficult to deal with neat TMS because of its low boiling point, and the TMS solution might include the solvent effect on the shift. Experimentally, no sharp resonance line of neat TMS was observed in this work. Adamantane, glycine, and hexamethylbenzene have been used as the second-reference compounds. Especially for adamantane, Earl and VanderHart,[4] have measured the chemical shift precisely, getting the value of 29.50 ± 0.10 ppm with respect to TMS. This value is adapted in the present paper, since to our knowledge, this is the most reliable value available at present. VanderHart[5] has also reported field-dependent ^{13}C chemical shifts in solids, among which adamantane shows a field-independent chemical shift. The chemical shifts of glycine and hexamethylbenzene obtained in the present work are given in Table 1.

^{29}Si. The first-reference compound is, again, TMS; TMS is not adequate for routine use for the same reasons as in the case of ^{13}C. The second-reference compounds used are 3-(trimethylsilyl)propionic-d_4 acid sodium salt (TSPA: $(CH_3)_3Si(CD_2)_2COONa$), hexa-

Table 1. Chemical Shifts

Nuclei	Compounds	Chemical shifts (ppm)	
^{13}C	Tetramethylsilane	(0)[a]	
	Adamantane	38.55±0.02	29.50[b]
	Glycine	176.50±0.03	43.70±0.05
	Hexamethylbenzene	132.15±0.03	17.21±0.05
^{29}Si	Tetramethylsilane	(0)[a]	
	3-(trimethylsilyl)propionic-d_4 acid Na salt (TSPA)	1.50[b]	
	Hexamethylcyclotrisiloxane	−9.68±0.05	
	Silicone rubber (Poly(dimethylsiloxane))	−22.42±0.05	
	Hexamethyldisiloxane	6.56±0.05	
^{31}P	85% H_3PO_4	0[b]	
	$(NH_4)_2HPO_4$	1.33±0.02	
	$NH_4H_2PO_4$	1.00±0.03	
^{23}Na	1M NaCl aqueous solution	0[b]	
	NaCl	7.21±0.03	
	NaBr	5.04±0.02	
	NaI	−3.25±0.06	
^{27}Al	1M $AlCl_3$ aqueous solution	0[b]	
	$NaAlO_2$	79.33±0.15	
^{11}B	$(C_2H_5)_2O \cdot BF_3$	0[b]	
	BPO_4	−3.60±0.03	
	$NaBH_4$	−42.06±0.02	

a) This value was not checked in the present work. b) This value is assumed in the present work; therefore, it has no experimental error.

methylcyclotrisiloxane (HMCTS), silicone rubber (poly(dimethylsiloxane)), and hexamethyldisiloxane (HMDS). Among these, TSPA is assumed to have a chemical shift of 1.50 ppm in this work, though there is no clear basis for this assumption. The chemical shifts of $(CH_3)_3Si(CH_2)_3COOH$ (1.54 ppm) and $(CH_3)_3Si(CH_2)_4COOH$ (1.53 ppm)[6] might form a basis. However, the obtained values of HMCTS (−9.68 ppm), silicone rubber (−22.42 ppm), and HMDS (6.56 ppm) are reasonable considering the values in the literature.[6] The error in the value of TSPA is considered to be less than 0.10 ppm, although the shift of TSPA should be related to TMS experimentally.

^{31}P. The first-reference material is 85% H_3PO_4. $(NH_4)_2HPO_4$ (1.33 ppm) and $NH_4H_2PO_4$ (1.00 ppm), which have no crystalline waters, can be used as the second-reference compounds. Some inorganic phosphates contain crystalline waters and/or they are hygroscopic, which influence the chemical shift.

^{23}Na. The first-reference material is a 1M NaCl aqueous solution (1M=1 mol dm^{-3}). NaCl (7.21 ppm), NaBr (5.04 ppm), and NaI (−3.25 ppm) can be the second-reference compounds.

^{27}Al. The first-reference material is a 1 M $AlCl_3$ aqueous solution. $NaAlO_2$ (79.33 ppm) can be the second-reference compound.

^{11}B. The first-reference compound is $(C_2H_5)_2O \cdot BF_3$ (diethyl ether-boron trifluoride (1/1)). This compound is a strong Lewis acid, and it is very reactive. The use of second-reference compounds, such as anhydrous BPO_4 (−3.60 ppm) and $NaBH_4$ (−42.06 ppm), is preferable.

When chemical shifts in solid and liquid states are compared, some problems are left unsolved, as has been pointed above and as will be described below. In the cases of ^{13}C and ^{29}Si, conversions to the TMS reference could not be checked in the present paper, although the ^{13}C reference has previously been checked by Earl and VanderHart.[3] The effect of the bulk magnetic susceptibility should always be taken into consideration when the chemical shifts are discussed in detail.

However, for practical purposes, the determination of a chemical shift by using the external reference described above is sufficient. The shift value can easily be corrected when more reliable reference data are obtained. In order to make this later correction possible, though, it is strongly recommended that the reference materials actually used should be explicitly described in the paper.

References

1) C. A. Fyfe, "Solid State NMR for Chemists," C. F. C. Press, Guelph (1983).

2) In this paper, the first-reference materials are assumed to have a chemical shift of 0 ppm, while the chemical shifts of the second-reference materials are given with respect to that of the first-reference materials.

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