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Chemical Shift Standards in High-Resolution Solid-State NMR (1) ^{13}C, ^{29}Si, and ^{1}H Nuclei

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Synopsis. The resonance frequencies of ^{13}C, ^{29}Si, and ^{1}H nuclei in pure tetramethylsilane have been measured accurately by spinning the liquid sample at the magic angle, which are free from the effects of the bulk magnetic susceptibility and the solvent. Using the above resonance positions, the chemical shifts of several second shift-standard materials have been determined with much improved accuracy and precision.

The chemical shift can be expressed as the deviation of the resonance frequency from that of a standard sample. An external reference is usually used in solid-state NMR, where we should be careful of the effect of the bulk magnetic susceptibility.[1,2] In high-resolution solid-state NMR of ^{13}C, ^{29}Si, and ^{1}H, few papers have been presented, in which the chemical shifts have been determined accurately by directly referring to the signal of tetramethylsilane (TMS), except for the Earl and VanderHart's work.[3] In our previous paper,[4] we have reported chemical shift values of several second shift-standard materials in ^{13}C, ^{29}Si, ^{31}P, ^{23}Na, ^{27}Al, and ^{11}B NMR, although the accuracies were not so good as in solution NMR.

In the present work, we can trace the spectra of pure tetramethylsilane with high resolution in the instrumental set-up for solid-state NMR by the magic-angle spinning (MAS) of the liquid sample, to the extent that the error in the first standard is negligible. The resonance position obtained by the above method is free from the solvent effect and the effect of the bulk magnetic susceptibility. Thus, we can determine the "absolute chemical shifts" of the materials to be investigated with markedly improved accuracy.

Experimental

Materials were available commercially. They were used as supplied.

The instrument used for the NMR measurements was a Bruker MSL400 pulsed spectrometer, whose magnetic field strength was 9.4 T. The resonance frequencies were 100.614, 79.496, and 400.136 MHz for ^{13}C, ^{29}Si, and ^{1}H, respectively. The commercial MAS probehead supplied by Bruker was used, in which a double-bearing type rotor made of zirconia was spun at spinning rates between 3 and 4 kHz for solid samples. Sealed inserts which fit the inside of the rotor[5] were used to spin the liquid samples at spinning rates of 0.5 to 1 kHz. A spherical container made of Pyrex was also used to check the effect of the bulk magnetic susceptibility. One did not need to remove the probehead from the magnet bore when the sample was exchanged, which excluded the error in the chemical shift caused by the replacement of the probehead. Temperature was 294 K. Before the NMR measurements, the magnetic field was carefully shimmed to achieve a linewidth less than 0.010 ppm for liquid samples when the magic-angle spinning was applied.

The chemical shifts were determined by use of an external reference. The drift of the magnetic field was less than 0.006 ppm per day, and thus, the drift of the magnetic field was negligible compared to the other experimental errors during a day. Most part of the experimental errors came from the residual linewidth and the line shape both of which caused by the field inhomogeneity and the sample nature.

Results and Discussion

Accurate Determination of Chemical Shifts. TMS can be used as the first standard in ^{13}C, ^{29}Si, and ^{1}H measurements, where pure liquid should be used to avoid the solvent effect. TMS is highly volatile, and a resonance line with a relatively broad linewidth is obtained for a sealed sample in the static state. On the other hand, we can get a very sharp line by spinning the sealed sample at the magic angle. The residual linewidths are 0.008 ppm in the decoupled spectra of ^{13}C and ^{29}Si, and 0.012 ppm in the ^{1}H spectra. Small peaks are observed on both sides of the intense peak in the ^{13}C spectra, which are originated from the coupling with ^{29}Si, where the coupling constant $^{1}J(^{13}\mathrm{C}-^{29}\mathrm{Si})$ is 51.4 Hz. The coupling constants with ^{1}H can be determined accurately from the ^{1}H-coupled spectrum, which are $^{1}J(^{13}\mathrm{C}-^{1}\mathrm{H})=118.06\pm0.03$ Hz, $^{3}J(^{13}\mathrm{C}-^{1}\mathrm{H})=2.16\pm0.03$ Hz, and $^{2}J(^{29}\mathrm{Si}-^{1}\mathrm{H})=6.59\pm0.01$ Hz. This high resolution enables the accurate determination of the chemical shifts.

Tables 1 and 2 summarize the results on the second standard materials frequently used in high-resolution

Table 1. ^{13}C Chemical Shifts[a)]

Compounds	δ[b)] ppm	FWHM[c)] ppm
[Pure liquids]		
Tetramethylsilane	0	0.008
Benzene	128.475 (0.005)	0.006
Chloroform	77.966 (0.005)	0.020
[Solids]		
Adamantane	38.520 (0.005)	0.050
	29.472 (0.004)	0.049
Glycine	176.46 (0.02)	0.40
	43.67 (0.01)	0.90
Hexamethylbenzene	132.07 (0.04)	0.83
	17.17 (0.02)	0.80
Tetrakis(trimethylsilyl)silane	3.517 (0.005)	0.077
Silicone rubber	d) 1.422 (0.004)	0.030
	e) 1.412 (0.004)	0.030

a) All the samples are spinning at the magic angle. b) Numbers in the parentheses are experimental errors. c) Full width at half maximum. d) $\nu_r \leqslant 1.0$ kHz. e) $\nu_r \geqslant 2.5$ kHz.

Table 2. ^{29}Si Chemical Shifts[a)]

Compounds	δ ppm	FWHM ppm
[Pure liquids]		
Tetramethylsilane	0	0.008
Hexamethyldisiloxane	6.679 (0.004)	0.011
[Solids]		
Sodium 3-(trimethlsilyl)-propionate-d_4[b)]	1.669 (0.022)	0.17
	1.445 (0.012)	0.16
	av. 1.50 (0.03)	
Sodium 3-(trimethylsilyl)-propionate[b)]	1.682 (0.022)	0.24
	1.459 (0.012)	0.17
	1.158 (0.022)	0.28
	av. 1.50 (0.03)	
Sodium 3-(trimethylsilyl)-propane-1-sulfonate[b)]	1.534 (0.012)	0.22
	av. 1.46 (0.03)	
Hexamethylcyclotrisiloxane	−9.66 (0.05)	1.0
Tetrakis(trimethylsilyl)silane	−9.843 (0.006)	0.040
	−135.402 (0.007)	0.059
Silicone rubber	[c)] −22.319 (0.005)	0.030
	[d)] −22.333 (0.008)	0.031

a) All the samples are spinning at the magic angle. b) Shift values of main peaks are listed. Average values indicated by av. are determined by artificial broadening. c) $\nu_r \leqslant 1.0$ kHz. d) $\nu_r \geqslant 2.0$ kHz.

Table 3. ^{1}H Chemical Shifts[a)]

Compounds	δ ppm	FWHM ppm
[Pure liquids]		
Tetramethylsilane	0	0.012
Benzene	6.771 (0.005)	0.011
Chloroform	7.392 (0.005)	0.006
Cyclohexane	1.482 (0.005)	0.014
Water	4.877 (0.005)	0.024
[Solids]		
Adamantane	1.85 (0.15)	2.5[b)]
d-Camphor	1.1 (0.1)	2.7[b)]
Tetrakis(trimethylsilyl)silane	0.247 (0.011)	0.80[b)]
Silicone rubber	[c)] 0.123 (0.003)	0.048
	[d)] 0.119 (0.003)	0.047

a) All the samples are spinning at the magic angle. b) The linewidth depends on the spinning rate. The listed values were obtained at ν_r=4.04, 3.59, and 4.01 kHz for adamantane, *d*-camphor, and tetrakis(trimethylsilyl)silane, respectively. c) $\nu_r \leqslant 1.0$ kHz. d) $\nu_r \geqslant 2.5$ kHz.

solid-state ^{13}C and ^{29}Si NMR. Among the solid materials, adamantane, tetrakis(trimethylsilyl)silane ($Si(Si(CH_3)_3)_4$; TKS),[6)] and silicone rubber have markedly narrow resonance lines, where the dipolar coupling with ^{1}H nuclei is weak due to fast molecular motions. Cross polarization (CP) is not efficient in TKS and silicone rubber. On the other hand, glycine and hexamethylbenzene need cross polarization to get ^{13}C signals with a good signal to noise ratio. To set up the ^{29}Si CP/MAS experiment, sodium 3-(trimethylsilyl)propionate-d_4 ($(CH_3)_3SiCD_2CD_2COONa$; TSPA-d_4), sodium 3-(trimethylsilyl)propionate ($(CH_3)_3SiCH_2CH_2COONa$; TSPA), and sodium 3-(trimethylsilyl)propane-1-sulfonate (sodium 4,4-dimethyl-4-silapentane-1-sulfonate; $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$; DSS) are suitable. However, they have a fine structure in the spectra, as shown in Fig. 1, which is considered to be caused by the crystallographic inequivalence in the solid state. The most intense peaks have chemical shift values of 1.445, 1.459, and 1.534 ppm in TSPA-d_4, TSPA, and DSS, respectively.

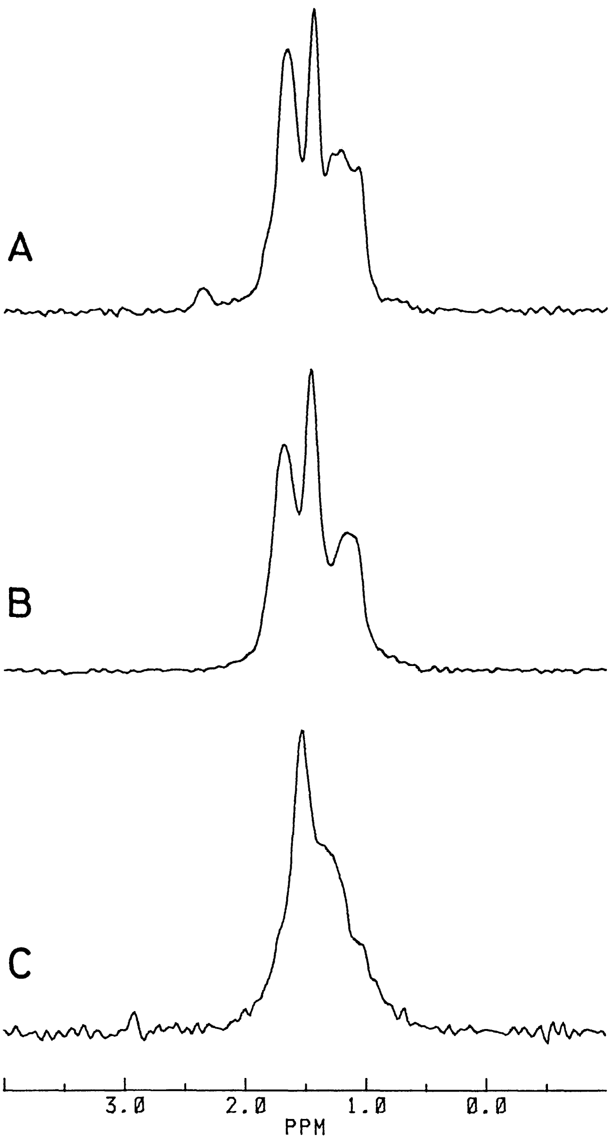

Fig. 1. ^{29}Si CP/MAS NMR spectra of (A) TSPA-d_4, (B) TSPA, and (C) DSS, measured at ν_0=79.496 MHz.

The homonuclear dipole-dipole interaction between ^{1}H spins cannot be usually suppressed by the magic-angle spinning of the normal rate. In this work, the chemical shift values of weakly-coupled ^{1}H are determined only by MAS, which results are summarized in Table 3.

The spectra of silicone rubber have a fine structure in the range of the spinning rate between 1.4 and 2.0 kHz, while only one component is observed outside the range. Thus, the shift values outside the above range are listed in the tables.

Table 4. Summary of the Experiments on the Effect of the Bulk Magnetic Susceptibility[a)]

Nucleus	Shape	Mode	δ / ppm	FWHM / ppm
^{13}C	Cylinder	MAS	128.475 (0.005)	0.006
	Cylinder	Static	128.51 (0.05)	0.22
	Sphere	Static	128.45 (0.05)	0.19
^{1}H	Cylinder	MAS	6.771 (0.005)	0.011
	Cylinder	Static	6.78 (0.03)	0.22
	Sphere	Static	6.76 (0.02)	0.050

a) The sample is pure benzene.

Effect of Bulk Magnetic Susceptibility on the Shift. Earl and VanderHart[3)] have suggested that the bulk magnetic susceptibility effect is negligible for an infinitely long cylinder spinning about its cylindrical axis which is inclined at the magic angle from the direction of the field. Even if the length of the cylinder is finite, the susceptibility effect is expected to be negligible in the MAS experiment, being derived from VanderHart et al.[7)]

We have checked the above suggestions in practical samples. Three types of experiments have been carried out: First, the resonance frequency of a cylindrical sample is measured under MAS, using the sealed insert with a cylindrical hole. Second, the resonance frequency of a cylindrical sample is measured without the spinning. Third, the spectra of a spherical sample is measured in the static state. In the first and the second experiments, the cylindrical axis is inclined at the magic angle from the direction of the field.

We have measured ^{13}C and ^{1}H signals of pure benzene, the results of which are summarized in Table 4. The resonance positions of the spherical samples are free from the susceptibility effect. As shown in table, the effect is negligible for the cylindrical sample under MAS as well as in the static state. The inclination of the cylindrical axis might be important to cancel the effect. Thus, the MAS experiment can determine "the absolute chemical shift" free from the susceptibility effect and the solvent effect.

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