^{29}Si NMR Chemical Shifts of Silicate Species: Ab Initio Study of Environment and Structure Effects

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Abstract: The structure of the silicate species is determined using the Hartree−Fock method, and the ^{29}Si NMR magnetic shielding constants are subsequently calculated using the coupled perturbed Hartree−Fock method with gauge including atomic orbitals. The silicate monomer is modeled as a neutral fully protonated species, H_4SiO_4 and as a monoanion−potassium cation pair, $H_3SiO_4^-K^+$. Hydration by up to four and two water molecules, respectively, is also considered. For both types of environment the ^{29}Si NMR chemical shift is within -71.0 ± 0.5 ppm. The effect of symmetry and degree of condensation is studied for silicate oligomers forming chains (dimer, trimer), rings (trimer, tetramer, pentamer, hexamer), and cages (prismatic hexamer, cubic octamer, hexagonal dodecamer). Lowering the symmetry lowers the shielding. The shift of a Q^n-unit depends on the adjacent bond angles: $\delta_{\mathrm{TMS}}(\mathrm{Q}^n) = -61.23n\langle\rho(\mathrm{SiOSi})\rangle - 60.45\,(4-n)\langle\rho(\mathrm{SiOH})\rangle + 6.58$, with $\rho(\alpha) = \cos\alpha/(\cos\alpha - 1)$. In addition the tetrahedral tetramer is studied. Previous tentative assignments of the signal at −97.3 ppm to this species can be ruled out. It is likely to be due to one of the double-ring structures with 8, 10, or 12 tetrahedra.

1. Introduction

Synthesis of zeolites, a class of microporous aluminosilicate materials, typically involves nucleation and crystal growth from the solution phase. The chemistry of the zeolite formation[1,2] depends on the proton concentration (pH), cation content, gel composition, crystallization temperature, transport properties, solubility of various species, heating rate, aging, etc. In spite of the large and still growing number of studies the mechanism of zeolite crystallization is not fully understood. Identification of the silicate species present in solution plays a key role and ^{29}Si NMR spectroscopy proved to be a powerful technique for this purpose.[3−12] This is due to the high sensitivity of the measured chemical shift to the local environment of the Si atoms, in particular a clear dependence of the shift on the degree of condensation. Identification of different species occuring and disappearing in the course of the synthesis depends on unequivocal assignments. For example the signal observed at −97.3 ppm by Harris et al.[13] has been tentatively assigned to the tetrahedral tetramer,[10] while McCormick and Bell assign it to the hexagonal dodecamer.[4] Later attempts to settle this issue have not been successful.[11] Quantum chemical ab initio calculations provide an excellent means for understanding of the factors which determine the ^{29}Si NMR chemical shifts. They yield detailed structure information at the atomic level and allow predictions of the NMR chemical shifts for these structures. Hence, they can be used to analyze the relation between the structure and the ^{29}Si NMR chemical shift.

The purpose of this study is to investigate (i) for the silicate monomer the dependence of the ^{29}Si NMR chemical shift on the environment and (ii) for a large number of oligomeric silicate species the relation between the ^{29}Si NMR chemical shift and structural features such as the degree of condensation and the point symmetry. For the silicate monomer we compare the fully protonated form (orthosilicic acid, H_4SiO_4) with the potassium monosilicate ($H_3SiO_4^-K^+$) and the respective complexes with an increasing number of water molecules. The silicate oligomers are all fully protonated. They consist of 2−12 SiO_4 units and include chains, rings, and cages.

To our knowledge previous ab initio studies of the ^{29}Si NMR shielding constants have been limited to disiloxane and to orthosilisic acid in different deprotonated states.[14−17] Calculations have also been performed on hydrated Na disilicate species, but no chemical shift calculations were made.[18]

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(1) Davis, M. E.*Chem. Mater.* **1992**, *4*, 756.

(2) Lok, B. M.; Cannan, T. R.; Messina, C. A. *ZEOLITES* **1983**, *3*, 282.

(3) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites* Wiley: Chicester, 1987.

(4) McCormick, A. V.; Bell, A. T. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 97.

(5) Engelhardt, G.; Jancke, H.; Hoebbel, D.; Wieker, W. *Z. Chem.* **1974**, *14*, 109.

(6) Engelhardt, G.; Zeigan, D.; Jancke, H.; Hoebbel, D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1975**, *418*, 17.

(7) Engelhardt, G.; Altenburg, W.; Hoebbel, D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1977**, *428*, 43.

(8) Harris, R. K.; Knight, C. T. G.; Hull, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 1577.

(9) Harris, R. K.; Knight, C. T. G. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1525.

(10) Kinrade, S. D.; Swaddle, T. W. *J. Am. Chem. Soc.* **1986**, *108*, 7159.

(11) Knight, C. T. G.; Kirkpatrick, R. J.; Oldfield, E. *J. Chem. Soc., Chem. Commun.* **1989**, 919.

(12) Mortlock, R. F.; Bell, A. T.; Radke, C. J. *J. Phys. Chem.* **1991**, *95*, 7847.

(13) Harris, R. K.; O'Connor, M. J.; Curzon, E. H.; Howarth, O. W. *J. Magn. Reson.* **1984**, *57*, 115.

(14) Tossel, J. A.; Lazzeretti, P. *Chem. Phys.* **1987**, *112*, 205.

(15) Tossel, J. A. *Phys. Chem. Miner.* **1991**, *17*, 654.

(16) Wolff, R.; Vogel, C.; Radeglia, R. In *Nuclear Magnetic Shieldings and Molecular Structure,* Tossell, J. A., Ed.; Kluwer Academic Publishers: Netherlands, 1993; p 385.

(17) Wolff, R.; Radeglia, R. *J. Mol. Struct. (THEOCHEM)* **1994**, *313*, 111.

(18) Uchino, T.; Sakka, T.; Ogata, Y.; Iwasaki, M. *J. Phys. Chem.* **1992**, *96*, 7308.

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Table 1. ^{29}Si NMR Shielding Constants (ppm) for $Si(CH_3)_4$−TMS, $Si(OH)_4$−Q^0, and $H_8Si_8O_{20}$−$[Q^3]_8$ (Double Four-Membered Ring, C_{4v} Point Group) and Their Differences for Various Basis Sets

basis	TMS	Q^0	$[Q^3]_8$	Q^0−TMS	Q^0−$[Q^3]_8$		polariz fct	primitives/contr fct	contraction
T(O)DZP	396.5	464.8	494.0	68.3	29.2	Si	0.35	(11,7)/[6,4]	{5,2,4×1/4,3×1}
			493.1		28.3	O	1.2	(10,6)/[6,3]	{5,4×1/4,1,1}
						C	0.8	(8,4)/[4,2]	{5,3×1/3,1}
						H	0.8	(4)/[2]	{3,1}
Basis II	395.9	472.4	−	76.5	−	Si	0.35, 1.4	(11,7)/[7,6]	{5,6×1/2,5×1}
						O	1.0	(9,5)/[5,4]	{5,4×1/2,3×1}
						C	1.0	(9,5)/[6,3]	{5,4×1/2,3×1}
						H	0.65	(5)/[3]	{3,1,1}
TZP	399.8	471.2	499.0	71.4	27.8	Si	0.35	(12,9)/[7,5]	{5,1,2,4×1/5,4×1}
			498.2		27.0	O	1.2	(10,6)/[6,3]	{5,5×1/4,1,1}
						C	0.8	(10,6)/[6,3]	{5,5×1/4,1,1}
						H	0.8	(5)/[3]	{3,1,1}
TZP−2P(Si)	385.4	461.9	491.5	76.6	29.6	Si	0.35, 1.4		
			490.6		28.7	O	1.2		
						C	0.8		
						H	0.8		
TZpP	399.7	469.3	−	69.6	−	Si	0.35	(12,9)/[7,6]	{5,1,2,4×1/4,5×1}
						O	1.2	(10,6)/[6,4]	{5,5×1/3,3×1}
						C	0.8	(10,6)/[6,4]	{5,5×1/3,3×1}
						H	0.8	(5)/[3s]	{3,1,1}
TZp2P	389.2	463.3	492.9	74.1	29.6	Si	0.20, 0.61		
			492.0		28.8	O	0.69, 2.08		
						C	0.44, 1.58		
						H	0.46, 1.39		
ref	368.5[a]			72.0[b]	27.3[c]				

[a] Reference 28. [b] Table 3. [c] Reference 9. Cf. ref 3, Table III.1.

2. Methods and Calculations

Since chemical shifts are structure sensitive properties, to be reliable, any chemical shift calculation requires a good quality reference structure. All structures discussed in this study have been optimized within the Hartree−Fock approximation using polarized basis sets. The details of the basis sets are slightly different for the three series of systems. The structures of the *monomeric silicate species* have been optimized without any symmetry restrictions (C_1 point group). A recently optimized[19] double-ζ plus polarization basis set has been selected for all atoms except oxygen for which a triple-ζ basis set was used to account for the negative charge (see Table 1 for details). Polarization functions are added on Si (0.35), H (0.8), and O (1.2), but not on K^+. This basis set is named T(O)DZP. As a test of the quality and balance of these basis sets we calculated the basis set superposition errors (BSSE)[20,21] for the $K^+\cdot H_2O$ and $H_3SiO_4^-\cdot K^+$ H_2O complexes. In the former, the BSSE is 1.1 kJ/mol only and the binding energy is 73.7 kJ/mol, which is very close to the observed heat of complex formation of 71 kJ/mol.[22] The binding energy of the $H_3SiO_4^-\cdot K^+$ H_2O complex equals 503.3 kJ/mol with an BSSE of 5.0 kJ/mol. In both cases, the BSSE is small (about 1−2%) and can be neglected indicating that the basis sets are balanced.

The majority of the structures of the *silicate oligomers* have been previously optimized and are taken from ref 23. A double-ζ contraction of Huzinagas (11s,7p) and (4s) basis sets was used on Si and H, respectively, while on oxygen a valence triple-ζ contraction of Huzinaga's (9s,5p) set was used.[24] Polarization functions with the exponents 0.4 (Si), 0.8 (H), and 1.2 (O) were added. This basis set is labeled t(O)dzp. The following structures have been optimized for this study: the cyclic trimer, the tetrahedral tetramer, the prismatic hexamer (double 3-ring), and the D_{3d} structure of the hexagonal dodecamer.

A third group of structures include among others the *four- and five-membered rings* and the *hexagonal dodecamer* optimized under the constraints of different point groups. The recently optimized SVP basis set[19] was used with the same polarization function exponents which provides a good compromise between accuracy of the predicted structures and computer time consumed for the optimization.

For calculation of the NMR shielding constants we used the coupled perturbed Hartree−Fock (CPHF) method with the gauge including atomic orbitals (GIAO).[25] Since ^{29}Si NMR chemical shifts are usually given with respect to tetramethylsilane (TMS) as a standard, we include calculations on this molecule. All structure optimizations and chemical shift calculations were performed using the TURBOMOLE program package[26] with the SHEILA module for NMR shieldings on different IBM RS/6000 and Silicon Graphics workstations.

Basis Set Selection for Chemical Shift Calculations. While basis sets of double-ζ plus polarization quality are a proven standard for Hartree−Fock structure optimizations, ^{29}Si NMR shielding constants may have different basis set requirements. To identify an appropriate basis set for chemical shift calculations for silicate species we tested several sets derived from the energy-optimized sets of Schäfer et al.[19] The absolute NMR shielding constants were calculated for tetramethylsilane (TMS), $Si(CH_3)_4$, orthosilisic acid (S_4 point group), $Si(OH)_4$, and the double 4-ring (C_{4v} point group), $H_8Si_8O_{20}$. We will make use of the Q^n symbols common among siloxane and silicate chemists. Q^n stands for a SiO_4 unit with n SiOSi links. Hence, any monosilicate species is Q^0, and the double 4-ring (cage) is $[Q^3]_8$. The structures of the three species were completely optimized with the t(O)dzp basis set. [23,24] Table 1 shows the results. We will judge the quality of the basis sets on the difference of the calculated screening constants between Q^0 and TMS, i.e. the chemical shift of the fully protonated monosilicate with respect to TMS, and between $[Q^3]_8$ and Q^0. The basis sets considered include the T(O)DZP set used also for structure optimizations and the full TZP basis set. Moreover, the effect of further splitting the valence p-shell to quadruple-ζ (TZpP) and of adding a second set of polarization functions to either the Si atom only (TZ2P(Si)P) or to all atoms (TZp2P). We compare also with basis set II used by Kutzelnigg et al.[27] While the absolute shielding constants deviate by 15−31 ppm from the best estimate,[28] the deviations for the chemical shifts are smaller. The Q^0−TMS difference varies over 8.3 ppm, while

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(19) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(20) Boys, S. F.; Bernardi, F. B. *Mol. Phys.* **1970**, *19*, 553.

(21) van Duijneveldt, F. B.; Jeanne, G. C. M.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.

(22) Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6133.

(23) Hill, J.-R.; Sauer, J. *J. Phys. Chem.* **1994**, *98*, 1238.

(24) Huzinaga, S. *Approximate Atomic Wave Functions I, II*; Department of Chemistry Report, University of Alberta: Edmonton, Alberta, Canada, 1971.

(25) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455.

(26) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165. TURBOMOLE and TurboNMR are commercially available from MSI, San Diego, CA.

(27) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR Basic Princ. Prog.* **1990**, *23*, 165.

(28) Jameson, C. A. *Chem. Phys. Lett.* **1988**, *149*, 300.

Table 2. Total and Binding Energies (E_{tot}, hartree, and ΔE_{bind}, kJ/mol), as Well as Predicted ^{29}Si NMR Chemical Shifts and Shielding Anisotropies (δ_{TMS} and $|\Delta\sigma_{Si}|$, ppm) for Different Neutral and Ionic Monosilicates

molecules[a]	E_{tot} (T(O)DZP)	ΔE_{bind}[b]	$-\delta_{TMS}$	$\|\Delta\sigma_{Si}\|$[c]
$(HO)_3SiOC_2H_5$	−669.078 99		74.7	35.3
H_4SiO_4	−591.020 85		72.1	35.1
$H_4SiO_4{\cdot}H_2O$	−667.083 35	28.94	71.4	38.0
$H_4SiO_4{\cdot}(H_2O)_2$, I	−743.147 89	63.26	70.7	43.8
$H_4SiO_4{\cdot}(H_2O)_2$, II	743.145 62	57.31	71.2	43.3
$H_4SiO_4{\cdot}(H2O)_3$, I	−819.213 17	99.51	71.8	25.8
$H_4SiO_4{\cdot}(H2O)_3$, II	−819.211 46	95.04	70.6	42.5
$H_4SiO_4{\cdot}(H_2O)_4$	−895.277 06	132.12	70.8	27.2
$H_3SiO_4^-$	−590.431 19		65.9	154.6
$H_3SiO_4^-{\cdot}H_2O$	−666.511 86	76.85	69.8	125.9
$H_3SiO_4^-{\cdot}K^+$	−1189.624 35	503.34	68.3	130.6
$H_3SiO_4^-{\cdot}K^+{\cdot}H_2O$	−1265.707 09	585.45	71.8	112.4
$H_3SiO_4^-{\cdot}K^+{\cdot}(H_2O)_2$	−1341.765 99	604.94	70.9	105.4

[a] I and II denote different structures of the hydration complex. [b] Binding energies with respect to H_4SiO_4, $H_3SiO_4^-$, K^+, or H_2O, $E_{tot}(H_2O) = -76.051\,47$ hartree, $E_{tot}(K^+) = -599.001\,51$ hartree. [c] $|\Delta\sigma_{Si}| = [^3/_2|\Sigma_{ij}\sigma_{ij}^2 - 3\sigma_{iso}^2|]^{1/2}$.

the $[Q^3]_8-Q^0$ difference varies over 1.6 ppm only. This is not unexpected since in both $[Q^3]_8$ and Q^0 we have SiO_4 units, while in TMS we have SiC_4 units. This suggests to use Q^0 as a secondary internal standard in chemical shift calculations on silicate species.

The TZP basis set seems to be the best balanced among all considered sets. It yields NMR chemical shifts which are closest to the observed reference values. Decontraction of its p-space (TZpP basis set) decreases the Q^0−TMS shift, while an increase of this difference is obtained when two sets of polarization functions are used, either on the Si atom only (TZP-2P(Si)) or on all atoms (TZp2P). Even a further decontraction of the sp-space was compensated by the effect of the second set of polarization functions (results are not given in Table 1). Therefore, the TZP basis set was finally chosen for all NMR shielding constant calculations reported in the following.

3. Results and Discussion

Environment Effects for Monosilicate Species. The structure of the $Si(OH)_4$ neutral monomer as an isolated species and solvated by one to four water molecules was optimized. No symmetry restrictions were imposed, i.e. the C_1 point group applies to all structures. Table 2 shows the energies and NMR shielding constants for all structures. Structures in which the number of hydrogen bonds is maximum are preferred. For clusters with two or three water molecules two structure types can be distinguished. For a given cluster size, the number of water−water hydrogen bonds is larger in type II than in type I, while the number of water−$Si(OH)_4$ hydrogen bonds is larger in type I than in type II (see Figure 1 for the complexes with three water molecules as an example). Typically, the energy difference between the two structure types is 5 kJ/mol.

According to the experimental analysis[29,30] the predominant mononuclear silicate present at pH = 11−12 is $Si(OH)_3O^-$. We performed structure optimizations of this anion as an isolated species and also of its complexes with a potassium counterion or/and water molecules. We consider the $H_3SiO_4^-K^+(H_2O)_2$ complex as a simple model of a monosilicate species in aqueous potassium silicate. Figure 2 shows the structures obtained and Table 2 the stabilization energies. As mentioned before the BBSE is small (about 1−2%) and can be neglected. While the first H_2O molecule is strongly bound to the $H_3SiO_4^-K^+$ ion pair (by 82 kJ/mol) with a bidendate structure (Figure 2), the second one is "externally" attached to the K^+ ion of the $H_3SiO_4^-{\cdot}K^+{\cdot}H_2O$ complex with an energy which is smaller than the average hydration energy per H_2O molecule in the neutral $H_4SiO_4{\cdot}nH_2O$ complexes (about 30−36 kJ/mol).

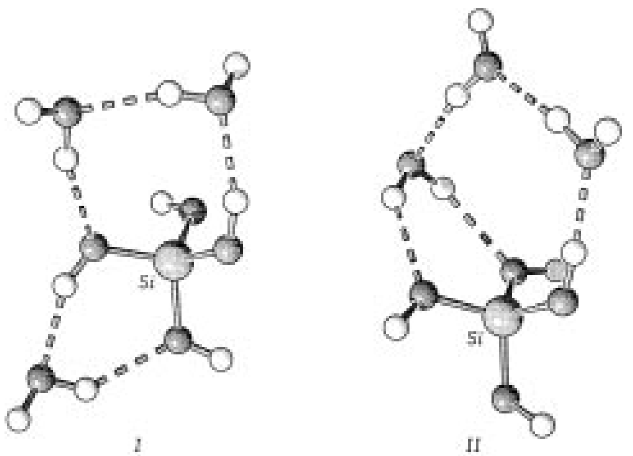

Figure 1. Two structures of the silicate monomer, $Si(OH)_4$, hydrated by three water molecules.

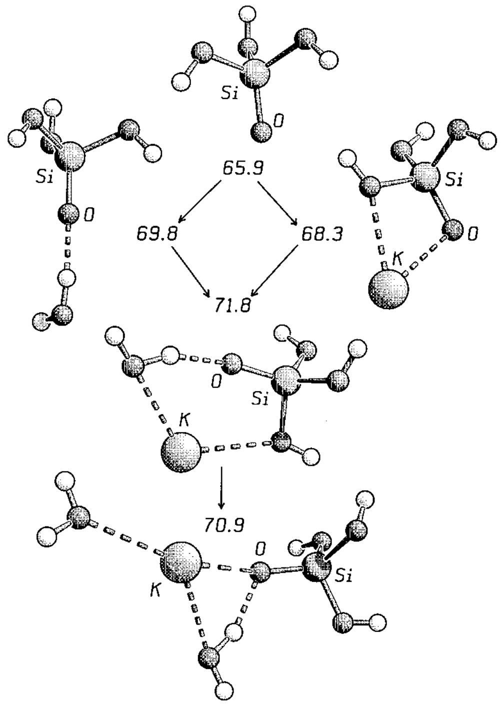

Figure 2. Calculated structures and negative ^{29}Si NMR shifts, $-\delta_{TMS}$, of the monomeric silicate anion $H_3SiO_4^-$ in various environments of water molecules and a potassium cation.

The calculated chemical shifts given in Table 2 show that hydration of the neutral $Si(OH)_4$ species generally lowers the calculated shielding of the Si nucleus in $Si(OH)_4$, but the effect is small and does not exceed 1.5 ppm. There is no trend neither with respect to the number of water molecules nor with respect to the structure type. The shielding of the Si nucleus in the free $H_3SiO_4^-$ anion is lower by 6 ppm than in the neutral $Si(OH)_4$ molecule. However, both the formation of a hydrogen bond in the $H_3SiO_4^-{\cdot}H_2O$ complex and of an ion pair in $H_3SiO_4^-{\cdot}K^+$ bring the shift closer to that of a neutral H_4SiO_4 molecule (cf. Table 2 and Figure 2). In the hydrated state, the shift difference between the fully protonated and the monopotassium monosilicate species fades away: the shift of the $H_3SiO_4^-{\cdot}K^+{\cdot}(H_2O)_2$ complex falls into the 0.5 ppm interval bracketed by the shifts of the two stuctures of the $H_4SiO_4{\cdot}(H_2O)_2$ complex. We note, however, that the shielding anisotropies (absolute values) are much smaller for the neutral complexes

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(29) Iler, R. K. *The Chemistry of Silica*; Wiley-Interscience: New York, 1979, Chapter 6.

(30) Sjoberg, S.; Ohman, L. O.; Ingri, N. *Acta Chem. Scand. Ser.* **1985**, *A39*, 93.

Table 3. ^{29}Si NMR Chemical Shifts, $-\delta_{TMS}$ (ppm), Observed for Monosilicate Species in Different Environments

species		$-\delta_{TMS}$	ref
$(HO)_3SiOC_2H_5$	organic solution	74.2	31
H_4SiO_4	extrapolated, organic solution	72.0	31
$\{H_3SiO_4^-K^+\}_{aq}$	aqueous K silicate solution (K:Si = 1:1; 1:3)	71.5; 72.1	33
$\{H_3SiO_4^-Na^+\}_{aq}$	aqueous Na silicate solution (Na:Si = 1:1; 1:3)	71.4; 71.1	33
$\{H_3SiO_4^-Na^+\}_{aq}$	aqueous Na silicate solution (low Na:Si)	71.3 (70.9−71.7)	5,6

than for the ionic ones. For the ionic species, the anisotropy of the Si shielding tensor decreases as the number of water molecules increases.

We infer from the results of the Table 2 that the ^{29}Si NMR chemical shifts of both the fully protonated and the monopotassium monomeric silicate species in aqueous solution is -71.0 ± 0.5 ppm. These predictions are in excellent agreement with the observed shift data (Table 3). The first point to note is that the shifts observed in different environments fall all in the narrow range between -70.9 and -72.1 ppm. These include results for aqueous potassium and sodium silicate solutions with different alkaline:silica ratio as well as a value for the fully protonated species in organic solution. The latter value of -72.0 ppm was not directly measured, but extrapolated from the series of shifts for the $(HO)_{4-n}Si(OC_2H_5)_n$ ($n = 1-4$) species observed on hydrolysis of $Si(OC_2H_5)_4$.[31] As a further check we calculated the shift for the $(HO)_3SiOC_2H_5$ molecule which was directly observed. Comparison of the observed (Table 3) and the calculated value (Table 2) shows agreement within 0.5 ppm. We conclude that the calculated ^{29}Si NMR chemical shifts of the free H_4SiO_4 and $(HO)_3SiOC_2H_5$ molecules are representative of the shifts measured for these molecules in organic solution.

Silicate Oligomers. Table 4 shows calculated ^{29}Si NMR chemical shifts for fully protonated silicate species the structures of which were determined previously. In addition, the structure of the double 3-ring (prismatic hexamer, $H_6Si_6O_{15}$) was determined within the D_{3h} and C_{3v} point groups (Figure 3). The C_{3v} structure shows Si atoms with different orientations of the OH groups. We used the notation Si_s (staggered) and Si_e (eclipsed). These types of O_3SiOH units occur also in the cubic octamer. We will first look for a relation between the chemical shift and the local structure of the Q^n units. Among others, Engelhardt and Radeglia[32] suggested a relation between the shift and the four SiOSi bond angles of a $Si(OSi)_4$ unit (Q^4). They showed for 21 Q^4 units of solid zeolites and silica polymorphs that a linear relation exists with the average $\langle\rho(\mathrm{SiOSi})\rangle$ of a function ρ of the SiOSi bond angle taken over all four adjacent bonds:

$$\delta_{TMS}(Q^4) = -247.05\langle\rho(\mathrm{SiOSi})\rangle + 2.19$$

The function

$$\rho(\mathrm{SiOSi}) = \cos \mathrm{SiOSi}/(\cos \mathrm{SiOSi} - 1)$$

was found from relating bond polarity to hybridization.

For the Q^n units ($n = 0-3$) of Table 4 we define $\rho(\mathrm{SiOH})$ in addition to $\rho(\mathrm{SiOSi})$ and obtain the following linear relation from the calculated data of Table 4 (23 data points, correlation coefficient $r = 0.9990$, standard deviation $s = 0.35$ ppm):

$$\delta_{TMS}(Q^n) = -61.23n\langle\rho(\mathrm{SiOSi})\rangle - 60.45(4 - n)\langle\rho(\mathrm{SiOH})\rangle + 6.58$$

If we set $n = 4$ we get

$$\delta_{TMS}(Q^4) = -244.91\langle\rho(\mathrm{SiOSi})\rangle + 6.58$$

a result which is very close to Engelhardt and Radeglia's relation, but we did not use any data, neither observed nor calculated ones, for Q^4 units.

The above correlation does not include the result for the tetrahedral tetramer which is also shown in Table 4. Its structure was optimized within the C_1 point group. The SiOSi bond angle in this structure is significantly smaller (118.5°) than in all other structures studied. Even in the other species involving three-membered silicate rings, the cyclic trimer and the prismatic hexamer, this angle is around 135°. The tetrahedral tetramer is also significantly less stable than all other species (vide infra, Table 6). Including the data for the tetrahedral tetramer into the above correlation would double the standard deviation and reduce the similarity with the semiempirical relation of Engelhardt and Radeglia.

Generally, there is a large dependence of the predicted ^{29}Si chemical shifts on the symmetry assumed when determining the structure. Relaxing symmetry constraints usually lowers the shielding and improves the agreement with the experiment. This is seen in Table 4 for the dimer ($C_s - C_1$), the cyclic trimer ($C_{3h} - C_1$), the prismatic hexamer ($D_{3h} - C_{3v}$). Symmetry restrictions which enforce planar rings are also the reason for the relatively large deviations from experiment found for the single four-membered ring (D_{4h}) and double six-membered ring (D_{6h}). A series of structures of single four- and five-membered rings optimized with decreasing symmetry constraints provides further insights. The Hartree−Fock calculations employed the SVP basis set.[19] Figure 4 shows the 4-ring structures obtained and Table 5 the results. For the planar structures of the cyclic tetramer and pentamer comparison with the t(O)dzp results is possible. The change of the basis set leads to small systematic shifts of the Si−O bond length and the shielding constants, but the change of the relative shift with respect to the monomer is 0.5 ppm only or lower. Lowering the symmetry yields more stable structures and ^{29}Si NMR chemical shifts in better agreement with the experiment.

The NMR signals of the single 5- and 6-rings have not been identified in the experimental spectra. Since the shifts calculated for the planar structures are only 2 and 1 ppm lower than the shift of the single 4-ring (Table 4), and since we expect for all three rings a increase by 7−8 ppm when relaxing the symmetry constraints (Table 5), we may expect the chemical shifts of all three species in the -86 and -88 ppm region, which would make it difficult to unequivocally assign a signal observed in this region.

The shift calculations were made on fully protonated silicate species for which no NMR data are reported. However, results are available for the analogous species in aqueous potassium silicate solutions. The small variation of the chemical shift in the various monosilicate species (previous paragraph) explains why such a comparison between calculated and observed data (Table 6) is meaningful. Indeed, for most cases of Table 4 the agreement between calculation (for fully protonated species) and experiment (for the corresponding potassium silicate species) is quite good. In particular the peculiarities of the three-membered ring are well reproduced. The shift of the Q^2 group is less negative in the cyclic trimer than in the cyclic tetramer,

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(31) Unger, B.; Jancke, H.; Hähnert, M.; Stade, H. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 51.

(32) Engelhardt, G.; Radeglia, R. *Chem. Phys. Lett.* **1984**, *108*, 271.

(33) Wijnen, P. W. J. G.; Beelen, T. P. M.; de Haan, J. W.; Rummens, C. P. J.; van Ven, L. J. M.; van Santen, R. A. *J. Non-Cryst. Solids* **1989**, *109*, 85.

Table 4. Total Energies (hartree), Average Si−O Bond Distances, Si−O−Si and Si−O−H Angles (pm and deg), and ^{29}Si Chemical Shifts (ppm, Relative to the Monomer) of the Silicate Species (Structures Obtained with the t(O)dzp Basis Set)

species	formula	point group	E_{tot}(t(O)dzp)	⟨Si−O⟩	⟨SiOSi⟩	⟨SiOH⟩	Q^n site	$-\delta_{Q^0}$[a]
monomer dimer	SiO_4H_4	S_4	−590.985 85	162.8		118.6	Q^0	0.0
	$Si_2O_7H_6$	C_1	−1105.942 44	162.5	138.3	118.5	Q^1	6.0
		C_s	−1105.936 52	162.2	179.5	119.2	Q^1	12.3
linear trimer	$Si_3O_{10}H_8$	C_s	−1620.885 97	162.3	166.2	118.6	Q^1	10.7
				162.3	169.0	120.9	Q^1	14.4
				161.8	167.6	119.8	Q^2	22.9
cyclic trimer	$Si_3O_9H_6$	C_1	−1544.845 75	162.8	135.2	119.6	Q^2	12.7
				162.9	134.8	119.7		12.9
		C_3h[b]	−1544.831 99	162.5	136.7	122.0	Q^2	15.9
cyclic tetramer cyclic	$Si_4O_{12}H_8$	D_4h	−2059.779 14	161.9	163.6	121.6	Q^2	23.7
	$Si_5O_{15}H_{10}$	D_5h	−2574.743 58	161.8	178.6	121.3	Q^2	25.1
pentamer cyclic hexamer	$Si_6O_{18}H_{12}$	D_6h	−3089.692 40	161.8	166.4	121.3	Q^2	24.1
tetrahedral tetramer	$Si_4O_{10}H_4$	C_1	−1907.730 55	163.5	118.5	120.7	Q^3	6.9
				163.5	118.6	121.0		7.3
				163.5	118.5	120.8		7.1
				163.5	118.6	121.2		7.5
prismatic hexamer	$Si_6O_{15}H_6$	D_3h	−2861.555 6 7	162.7	135.7	120.3	Q^3	19.2
		C_3v	−2861.558 42	162.8	134.9	120.4	$Q^3{}_s$	18.6
				162.7	135.1	119.0	$Q^3{}_e$	18.3
cubic octamer	$Si_8O_{20}H_8$	C_4v	−3815.456 52	161.7	151.0	119.4	$Q^3{}_s$	27.8
				161.8	149.8	120.4	$Q^3{}_e$	27.0
		S_2	−3815.458 42	161.8	150.7	119.1	Q^3	27.3
				161.8	150.5	119.9		27.4
				161.7	150.3	119.7		27.1
				161.8	150.0	119.1		26.7
hexagonal dodecamer	$Si_{12}O_{30}H_{12}$	D_6h	−5723.201 80	161.6	154.2	120.1	Q^3	29.1
		D_3d	−5723.426 33	162.1	151.8	119.7	Q^3	28.0

[a] Relative to Q^0, $\delta_{TMS}(Q^0) = -71.4$ ppm. [b] Optimized assuming C_3 resulted in C_{3h}.

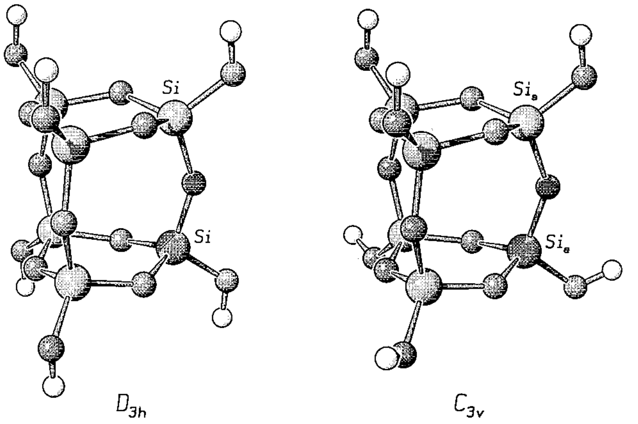

Figure 3. Structures of the double three-membered ring models $Si_6O_{15}H_6$.

and the shift of the Q^3 group is less negative in the primatic hexamer (involving 3-rings) than in the cubic octamer. This is obviously connected with some strain in these rings which is also corroborated by the lower stabilities of the species involving 3-rings. Table 6 also shows the reaction energies for the formation of the rings

$$\mathrm{Si(OH)_4} \rightarrow (1/n)[\mathrm{SiO(OH)_2}]_n + \mathrm{H_2O}$$

and cages

$${}^2/_3\mathrm{Si(OH)_4} \rightarrow {}^2/_3 n[\mathrm{SiO_{1.5}(OH)}]_n + \mathrm{H_2O}$$

from the monomeric species. The largest destabilization and shift deviation from the typical Q^3 range are encountered for the tetrahedral tetramer. Its ^{29}Si NMR signal is expected near the monomer signal, which allows to definitely rule out the suggested assignment of the −25.6 ppm signal to this species. The calculated shifts suggest that the signals both at −27.9 and −25.6 ppm belong to double-ring species with 8 or 12 (or possibly 10) tetrahedra.

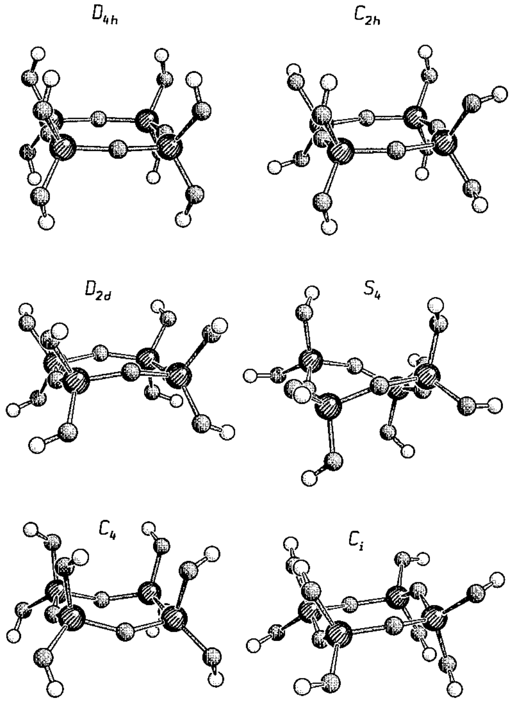

Figure 4. Structures of the single four-membered ring $Si_4O_{12}H_8$ under various symmetry constraints.

4. Conclusion

A method is selected from the available quantum chemical ab initio techniques[19,25,26] that allows accurate predictions of the ^{29}Si NMR chemical shifts for silicate species in solution. It is composed of the HF/T(O)DZP approximation for structure determination and the CPHF/TZP approximation for the subsequent calculation of the shielding constant. It may be referred to as CPHF/TZP//HF/T(O)DZP.

Table 5. Total Energies (hartree), Average Si−O Bond Distances, Si−O−Si and Si−O−H angles (pm and deg), and ^{29}Si NMR Chemical Shifts (ppm, Relative to the Monomer) of Different Silicate Species (Structures Obtained with the SVP Basis Set)

species	point group	E_{tot}(SVP)	⟨Si−O⟩	⟨SiOSi⟩	⟨SiOH⟩	$-\delta^{calc\ a}$
monomer	S_4	−590.591 66	163.3		118.95	0.0[b]
cyclic tetramer	D_4h	−2058.523 74	162.6	163.4	122.0	23.1
	C_2h	−2058.538 70	162.6	161.1	119.0	19.9
			162.6	161.1	120.7	21.5
	D_2d	−2058.539 50	162.7	153.8	119.4	18.2
	S_4	−2058.541 05	162.8	148.8	119.2	15.9
	C_4	−2058.543 38	162.8	147.3	119.7	16.1
	C_i	−2058.547 40	162.9	144.1	119.7	15.0
			163.0	144.1	118.2	13.9
cyclic pentamer	D_5h	−2573.157 18	162.5	178.6	121.6	24.5
	D_5	−2573.182 79	162.4	175.8	119.3	21.9
tetrahedral tetramer	C_1	−1906.550 02	163.9	118.8	121.8	6.4
			163.9	118.9	122.1	6.8
			163.0	118.9	122.1	6.8
			164.0	119.0	121.9	7.0
hexagonal dodecamer	C_6v	−5719.886 79	162.4	155.0	119.6	28.0
			162.5	153.0	120.3	29.5
	C_2h	−5719.888 48	162.5	150.9	120.5	26.7
			162.5	151.2	120.5	26.8
			162.5	150.7	120.5	26.6
	D_3d	−5719.888 64	162.5	151.0	120.6	26.7

[a] Relative to Q^0. [b] $\delta_{TMS}^{calc} = -72.9$ ppm.

Table 6. ^{29}Si NMR Chemical Shifts of Silicate Species Relative to the Monomer (ppm)[a]

species	$-\delta(Q^1)$	$-\delta(Q^2)$	$-\delta(Q^3)$	stability[d]
dimer	8.6			
	6.0−12.3			
linear trimer	8.2	16.7		
	10.7−14.4	22.9		
		10.2		
cyclic trimer		12.7−12.9		−5
cyclic tetramer		16.0		−17
		13.9−16.1		
tetrahedral tetramer			(25.6)[e]	+24
			6.4−7.5	
prismatic hexamer			17.2	+2
			18.3−18.6	
cubic octamer			27.9	−7
			26.7−27.8	
hexagonal dodecamer			25.6[f]	−9
			26.7−28.0	

[a] Comparison of observed (upper row, potassium silicate solution)[b] and predicted values (italics, lower row)[c]. Calculated relative stabilities (kJ/mol) are also given.[d] [b] K:Si = 1, Reference 9. Cf. ref 3, Table III.1. [c] Tables 4 and 5. [d] Energy of formation from the monosilicate species per mole of Si−O−Si bond formed (cf. reactions 1 and 2). Energies obtained with the TZP basis set, except for the cyclic tetramer for which SVP data were used. [e] Reference 10. [f] Reference 4, Table 3.

The chemical shift of the monosilicate species is found to be insensitive to varying environments. Calculations on fully protonated silicate species in the gas phase can be used to predict chemical shifts for anionic silicate species in alkaline solution.

The chemical shifts of the ^{29}Si nuclei in oligomeric species are sensitive to the point group of the species and, in accord to what is known from crystalline silicates, to the average Si−O−Si and Si−O−H angles of the SiO_4 unit considered. A relation is derived which allows to estimate the chemical shift when the bond angles are known. The computational technique presented appears to be a promising tool for determining structures of silicate species in solution when combined with chemical shift measurements.

The assignment of the −97.3 ppm signal to the tetrahedral tetramer can be ruled out. This species which consists of four fused three-membered silicate rings is strained and has SiOSi bond angles as small as 118.5°. It does not fit into the common correlation between average bond angles and chemical shift.

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