Ab initio calculation of ^{29}Si NMR chemical shifts for the clusters of $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$ and $\text{Si}(\text{OH})_6^{-2}$

Masami KANZAKI*

Department of Mechanical Sciences Tokyo, Institute of Technology, Meguro-ku, Tokyo 152, Japan

Abstract

In order to identify five-coordinated $\text{Si}(\text{Si}^{\text{V}})$ species in crystalline and amorphous silicates by NMR spectroscopy, ^{29}Si NMR chemical shifts for the clusters of $\text{Si}(\text{CH}_3)_4$ (TMS), $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$ and $\text{Si}(\text{OH})_6^{-2}$ were calculated using ab initio molecular orbital theory. The calculated shifts relative to TMS cluster were -71.7 and -179.0 ppm for $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_6^{-2}$, respectively, and are in good agreement with observed shifts. The calculated shift for $\text{Si}(\text{OH})_5^-$ was -127.4 ppm, falls just between the shifts of $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_6^{-2}$. The chemical shift for Si^{V} species in polymerized silicates is expected to appear at about -150 ppm, if the effect of polymerization is considered. Present calculation thus supports the assignment of -150 ppm peak as Si^{V} species, which has been found in the alkali-silicate glasses quenched from high pressures.

Introduction

Si is commonly coordinated by four oxygen ions in both crystalline and amorphous silicates at ambient pressure. Application of pressure, however, stabilizes six-coordinated $\text{Si}(\text{Si}^{\text{VI}})$ species, and a number of high-pressure crystalline silicates with Si^{VI} in the structure have been reported (e.g., Finger and Hazen, 1991). Electron density distributions around Si nuclei in Si^{IV} and Si^{VI} species are different due to change in first-neighbour oxygen arrangements. Therefore they give different magnetic shielding to central ^{29}Si nuclei, which are readily distinguished as separated peaks (different chemical shifts) by ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy (Kirkpatrick, 1988; Stebbins, 1995). However identification of species has been empirical and largely relying on comparison with crystalline silicates of known structures. Recently a peak with chemical shift of about -150 ppm has been observed in the alkali-silicate glasses quenched from high pressures (Stebbins and McMillan 1989; Xue *et al.*, 1991). This shift falls just between those of Si^{IV} and Si^{VI} species, so these authors have assigned the peak as a Si^{V} species. However no Si^{V} species has been observed in crystal-

* Present address: Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-01, Japan

line silicates, except in a high-pressure CaSi_2O_5 phase (Y. Kudoh and M. Kanzaki, in preparation). Thus the assignment of Si^{V} species is rather tentative so far. Although Si^{V} species is merely reported, it has been assumed to appear as an intermediate complex during dissolution and polymerization processes of silicate minerals (e.g., Lasaga and Gibbs, 1990). The Si^{V} species is also proposed to be an intermediate state for viscous flow and diffusion processes in silicate melts (e.g., Stebbins, 1995; and other chapters in this review volume). Therefore in order to understand these processes at microscopic level, it is important to identify and characterize Si^{V} species.

Without crystalline references for Si^{V} species, we have to rely on theoretical approach. Ab initio molecular orbital calculation has been successfully applied to obtain the local geometry, energy, electronic structure and vibrational properties of silicates (e.g., Gibbs, 1982). The calculation can now predict accurate magnetic shielding tensor for small molecules or clusters (e.g., Keith and Bader, 1993). In this study, we calculated magnetic shielding tensors of the clusters $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$ and $\text{Si}(\text{OH})_6^{2-}$, which mimic Si^{IV} , Si^{V} and Si^{VI} species in silicates, respectively. These calculations also have direct application for identification of these species in aqueous solution. Although similar calculations have been already reported (e.g., Tossell, 1990; 1991), they could not be directly compared with observed NMR spectra. This is because observed NMR shift is measured relative to a reference material (tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$ for ^{29}Si NMR), while the calculated shift was relative to bare nucleus. In this study, however, we have calculated shielding tensor for TMS cluster as well. By taking a difference of calculated shifts between TMS and the cluster of interest, now the difference can be directly compared with the observed shift. In this study, the chemical shifts for $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$ and $\text{Si}(\text{OH})_6^{2-}$ are calculated using this procedure and are reported below.

Calculation method

In this study, Gaussian 94 program (Frisch *et al.*, 1995) was employed for ab initio molecular orbital calculation. Restricted Hartree-Fock calculation with 6-31G(d) basis set (Hehre *et al.*, 1986) was used for optimization of cluster geometries. All clusters ($\text{Si}(\text{CH}_3)_4$, $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$ and $\text{Si}(\text{OH})_6^{2-}$) were successfully optimized without symmetrical constraint. Vibrational frequency calculations of these clusters were performed at same basis set. No imaginary frequency was found, thus the optimized clusters were indeed in stable geometries.

For calculation of ^{29}Si NMR shielding tensor, we used continuous set of gauge transformation (CSGT) method implemented in Gaussian 94, which yields accurate magnetic response properties (Keith and Bader, 1993). We employed robust 6-311+G(2df,p) basis set for CSGT calculation, while using the structures obtained at

FIG. 1. Optimized geometries of the clusters Si(OH)_4 (a), Si(OH)_3^- (b), and Si(OH)_6^{2-} (c) at 6-31G(d) basis set (stereo drawing). Large circle: oxygen; medium circle: silicon; small solid circle: hydrogen.

6-31G(d) basis set. In order to check the accuracy of predicted shift with this procedure, we calculated the shifts for SiH_4 and SiF_4 clusters. The obtained shifts relative to that of TMS cluster for SiH_4 and SiF_4 were -88.1 and -112.2 ppm, respectively and were within 5 ppm of observed shifts. When smaller basis sets were employed, for example 6-31G(d) for CSGT calculation, the predicted shifts were unreliable. Thus we have used above basis sets for following shielding tensor calculation.

Results and discussion

Optimized geometries

Geometries of fully optimized clusters at 6-31G(d) basis set are shown in Figure 1, and selected geometrical parameters and energies are listed in Table 1. The optimized

TABLE 1. Geometries and energies of $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$, and $\text{Si}(\text{OH})_6^{-2}$ at HF/6-31G(d).

cluster	R(Si-O) (Å)	<O-Si-O (°)	E (Hartree) [#]
$\text{Si}(\text{OH})_4$	1.629	106.38, 115.84	-590.892 (-591.075)*
$\text{Si}(\text{OH})_5^-$	1.742, 1.790	176.3, 87.8-92.0	-666.343 (-666.564)*
	1.696-1.702	115.5-122.3	
$\text{Si}(\text{OH})_6^{-2}$	1.810	90.0	-741.581 (-741.853)*

[#]: 1 Hartree=4.3597x10⁻¹⁸ Joules

*:Energy at HF/6-311+G(2df,p)

structure of $\text{Si}(\text{OH})_4$ cluster is shown in Fig. 1a. It possesses *S₄* symmetry. The geometry, total energy and vibrational frequencies were identical with the results of Hess *et al.* (1987), who have performed similar calculation at identical basis set. For $\text{Si}(\text{OH})_5^-$ cluster, it converged to a distorted trigonal bipyramid configuration as shown in Fig. 1b. The Si-O distances vary from 1.696 to 1.790 Å with longer distances for apical oxygens. This local geometry was consistent with the calculation by Lasaga and Gibbs (1990) with 3-21G(d) basis set and by Kubicki *et al.* (1993) with MP2/6-31G(d) calculation (latter includes electron-correlation correction). These studies as well as present study indicate that the $\text{Si}(\text{OH})_5^-$ cluster is stable. Kubicki *et al.* (1993) have calculated the reaction pathway for the formation of $\text{Si}(\text{OH})_5^-$ from $\text{Si}(\text{OH})_4$ plus OH^- . Based on their calculation, the abundance of $\text{Si}(\text{OH})_5^-$ in aqueous solution will be well below the detection limit of current spectroscopy. This could explain why $\text{Si}(\text{OH})_5^-$ cluster has not been observed so far.

The geometry of the $\text{Si}(\text{OH})_6^{-2}$ cluster has reported by Gibbs (1982) with minimal basis set (STO-3G). For our knowledge, no calculation for the $\text{Si}(\text{OH})_6^{-2}$ cluster with 6-31G(d) basis set or larger has been reported, although Lasaga and Gibbs (1987) briefly mentioned the calculation of H_8SiO_6 cluster. The optimized structure is shown in Figure 1c. The structure is very close to regular octahedron if hydrogens are ignored. The Si-O distances were 1.810 Å. Thaumassite ($\text{Ca}_3\text{Si}(\text{OH})_6\text{CO}_3\text{SO}_4\cdot 12\text{H}_2\text{O}$) has $\text{Si}(\text{OH})_6^{-2}$ species in its structure, and its Si-O distance is about 1.78 Å (Effenberger *et al.*, 1983), slightly shorter than calculated one. The O-Si-O angles are 90.0°, more regular than those observed in thaumasite (86.5–93.4°).

²⁹Si NMR chemical shifts of the clusters

Calculated ²⁹Si NMR shielding tensors (diagonal elements only) are shown in Table 2. We noted that the shielding increases with increasing coordination number as

TABLE 2. Calculated ^{29}Si NMR shielding tensors (ppm) for the clusters of $\text{Si}(\text{CH}_3)_4$, $\text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_5^-$, and $\text{Si}(\text{OH})_6^{-2}$

	σ_{XX}	σ_{YY}	σ_{ZZ}	σ^i	σ^a	δ
$\text{Si}(\text{CH}_3)_4$ (TMS)	385.5	385.6	385.7	385.6	0.1	0
$\text{Si}(\text{OH})_4$	451.9	452.0	468.1	457.3	16.2	-71.7
$\text{Si}(\text{OH})_5^-$	423.9	546.3	568.7	513.0	83.5	-127.4
$\text{Si}(\text{OH})_6^{-2}$	560.0	560.0	573.8	564.6	13.8	-179.0

σ_{XX} , σ_{YY} , σ_{ZZ} : diagonal elements of shielding tensor

σ^i : isotropic component ($= (\sigma_{\text{XX}} + \sigma_{\text{YY}} + \sigma_{\text{ZZ}}) / 3$)

σ^a : anisotropic component ($= \sigma_{\text{ZZ}} - (\sigma_{\text{XX}} + \sigma_{\text{YY}}) / 2$)

δ_A : isotropic chemical shift ($= \sigma_{\text{TMS}}^i - \sigma_A^i$)

observed for Si^{IV} and Si^{VI} species in crystalline solids (Kirkpatrick, 1988; Grimmer *et al.*, 1980). The tensors of the clusters have not been measured and thus can not be directly compared. However difference of isotropic component of tensors (σ^i) between cluster of interest and a reference (TMS in this case), which corresponds to isotropic chemical shift (δ), can be compared with observed ^{29}Si MAS NMR shift. For $\text{Si}(\text{OH})_4$ cluster, chemical shift was calculated as -71.7 ppm (δ in Table 2). The shift can be compared with observed shifts of $\text{Si}(\text{OH})_4$ species in sodium silicate solutions (Engelhardt *et al.*, 1975). Observed chemical shift for the species was -70 to -72 ppm depending on Na/Si ratio, excellent agreement with calculated one. For $\text{Si}(\text{OH})_6^{-2}$, calculated shift was -179.0 ppm. The observed shifts of $\text{Si}(\text{OH})_6^{-2}$ in both natural and synthetic thaumasites were -178 to -182 ppm (Grimmer *et al.*, 1980), and again the agreement is excellent. Calculated anisotropic component of $\text{Si}(\text{OH})_6^{-2}$ was 13.8 ppm (Table 2), and is in reasonable agreement with observed 9.8 ppm (Grimmer *et al.*, 1980).

The calculated shift for $\text{Si}(\text{OH})_5^-$ was -127.4 ppm, just between the shifts of $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_6^{-2}$. The anisotropic component of tensor for $\text{Si}(\text{OH})_5^-$ is quite large (83.5 ppm) compared to those of $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_6^{-2}$, reflecting lower symmetry of the cluster (Fig. 1b). As mentioned before, no $\text{Si}(\text{OH})_5^-$ species has been observed to date, therefore we can not compare with observed shift. However good agreements between observed and calculated shifts for other clusters ensure that the shift for $\text{Si}(\text{OH})_5^-$ is predicted within 5 ppm of accuracy.

Tossell (1991) has calculated the shielding tensors for $\text{Si}(\text{OH})_4$, as well as deprotonated clusters. Reported σ^i for $\text{Si}(\text{OH})_4$ with S_4 symmetry after correction (467.8 ppm) was consistent with our calculation (457.3 ppm). However he reported that

the value for a T_d symmetry cluster is more than 100 ppm shielded from that of S_4 symmetry (see Table 2 of his paper). This difference is too large to be real, therefore the calculation is not quite reliable. Tossell (1990) has also calculated the shielding tensors for SiO_5^{-6} cluster. Reported σ^i was 594 ppm, whereas that of our calculation for $\text{Si}(\text{OH})_5^-$ was 513.0 ppm. The difference is quite large, however, the correction used for Tossell (1991) was not employed in this earlier study. The correction reduced the shielding tensors about 50 ppm for Si^{IV} clusters (Table 2 of Tossell, 1991). Therefore the difference would be reduced by this correction. We also noted that the geometry of SiO_5^{-6} cluster, which was taken from optimized $\text{Si}(\text{OH})_5^-$ cluster geometry at 3-21G(2d) basis set with D_{3h} symmetry, has significantly shorter Si-O distances (1.718 Å for apical, 1.639 Å for equatorial) compared with present (Table 1) and other calculations (Lasaga and Gibbs, 1990; Kubicki *et al.*, 1993). The difference of geometries as well as deprotonation might be also responsible for the difference of isotropic tensor components. Unlike Tossell's calculations, present calculations are well supported from observed chemical shifts, thus our results would be more reliable.

As mentioned before, the assignment of -150 ppm peak in the alkali-silicate glasses as Si^{V} species has been proposed (Stebbins and McMillan, 1989; Xue *et al.*, 1991). This peak is about 20 ppm more shielded than that of $\text{Si}(\text{OH})_5^-$ cluster. The difference is due to the difference of degree of polymerization between these species. Si^{V} species is mostly observed in the alkali-silicate glasses ($\text{Na}_2\text{Si}_2\text{O}_5$ and $\text{A}_2\text{Si}_4\text{O}_9$; $\text{A} = \text{Na}, \text{K}$) which are well polymerized, whereas the cluster is a monomer. In order to incorporate the effect of polymerization on the chemical shift, we must use larger clusters which include bridging oxygens around central Si atom. However it would be quite expensive calculations at moment. Therefore the effect of polymerization is considered here empirically. The effect of polymerization on chemical shift for Si^{IV} species is well established (Kirkpatrick, 1988). The chemical shifts for Si^{IV} species with three and four bridging oxygens (Q^3 and Q^4) are 20 to 30 ppm more shielded from that of monomer (Q^0). The effect is not well established for Si^{VI} species, though the chemical shifts for most Si^{VI} species observed in both crystalline and amorphous alkali-silicates are about -200 ppm (Xue *et al.*, 1991), whereas those of $\text{Si}(\text{OH})_6^{-2}$ in thaumasite is about -180 ppm. Thus polymerized Si^{VI} species are about 20 ppm more shielded from that of monomer, similar behavior observed for Si^{IV} species. This shielding changes are best illustrated in the NMR spectra of $\text{Na}_2\text{Si}_4\text{O}_9$ glasses quenched from high pressures (Fig. 2 of Xue *et al.*, 1991). The broad peaks of Si^{IV} and Si^{VI} species appear at around -95 and -198 ppm, and are about 20 ppm more shielded than those of corresponding $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_6^{-2}$ clusters, respectively. It is reasonable to assume similar change in chemical shift for Si^{V} species as well. Thus Si^{V} species is expected to have a chemical shift about 20 ppm more shielded from $\text{Si}(\text{OH})_5^-$ cluster (i.e., -150 ppm). This is consistent with observed -147 ppm peak in alkali-silicate glasses (Xue *et al.*, 1991). The -150 ppm peak has also been

observed from high-pressure run products of CaSiO_3 system (Kanzaki and Stebbins, 1991). We identified this -150 ppm containing phase as a CaSi_2O_5 phase, and its structure indeed contains Si^{V} species (Kudoh and Kanzaki, in preparation). Thus present calculation supports the assignment of -150 ppm peak to Si^{IV} species as previously suggested (Stebbins and McMillan, 1989; Xue *et al.*, 1991). These results demonstrated that the NMR chemical shift of Si-containing clusters can be predicted with reasonable accuracy using ab initio molecular orbital calculation.

Acknowledgements—Comments from reviewers are appreciated. The author acknowledges support from the Grant-in-Aid for Priority-Area-Research (“Magma”), Ministry of Education, Science and Culture of Japan.

References

- EFFENBERGER, H., KIRFEL, A., WILL, G. and ZOBETZ, E. (1983) A further refinement of the crystal structure of thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6\text{CO}_3\text{SO}_4 \cdot 12\text{H}_2\text{O}$. *Neues Jahrb. Min. Monatsh.*, **1983**, H. 2, 60–68.
- ENGELHARDT, G., ZEIGAN, D., JANCKE, H., HOEBBEL, D. and WIEKER, W. (1975) ^{29}Si -NMR-spektroskopie an silicatlösungen II. Zur abhängigkeit der struktur der silicatanionen in wässrigen natrium silicatlösungen vom Na:Si-verhältnis. *Z. Anorg. Allg. Chem.*, **418**, 17–28.
- FINGER, L. W. and HAZEN, R. M. (1991) Crystal chemistry of six-coordinated silicon: a key to understanding the Earth's deep interior. *Acta Cryst.*, **B47**, 561–580.
- FRISCH, M. J., TRUCKS, G. W., SCHLEGEL, H. B., GILL, P. M. W., JOHNSON, B. G., ROBB, M. A., CHEESEMAN, J. R., KEITH, T., PETERSSON, G. A., MONTGOMERY, J. A., RAGHAVACHARI, K., AL-LAHAM, M. A., ZAKRZEWSKI, V. G., ORTIZ, J. V., FORESMAN, J. B., PENG, C. Y., AYALA, P. Y., CHEN, W., WONG, M. W., ANDERS, J. L., REPLOGLE, E. S., GOMPERTS, R., MARTIN, R. L., FOX, D. J., BINKLEY, J. S., DEFREES, D. J., BAKER, J., STEWART, J. P., HEAD-GORDON, M., GONZALEZ, C., and POPLE, J. A. (1994) Gaussian 94, Revision B. 2., Gaussian Inc., Pittsburgh, Pennsylvania.
- GIBBS, G. V. (1982) Molecules as models for bonding in silicates. *Am. Mineral.*, **67**, 421–450.
- GRIMMER, A. R., WIEKER, W., von LAMPE, F., FECHNER, E., PETER, R. and MOLGEDEY, G. (1980) Hochauflösende ^{29}Si -NMR an festen Silicaten: anisotropie der chemischen Verschiebung in Thaumasit. *Zeit. Chem.*, **20**, 453.
- HEHRE, W. J., RADOM, L., SCHLEYER, P. v. R. and POPLE, J. A. (1986) *Ab Initio Molecular Orbital Theory*, John Wiley and Sons, New York, 548pp.
- HESS, A. C., McMILLAN, P. F. and O'KEEFFE, M. (1987) Ab initio field of the S_4 conformation of H_4SiO_4 . *J. Phys. Chem.*, **91**, 1395–1396.
- KANZAKI, M., STEBBINS, J. F. and XUE, X. (1991) Characterization of quenched high pressure phases in the system CaSiO_3 by XRD and ^{29}Si NMR. *Geophys. Res. Lett.*, **18**, 463–466.
- KEITH, T. A., and BADER, R. F. W. (1993) Calculation of magnetic response properties using a continuous set of gauge transformations. *Chem. Phys. Lett.*, **210**, 223–231.
- KIRKPATRICK, R. J. (1988) MAS NMR spectroscopy of minerals and glasses. In “Spectroscopy Methods in Mineralogy and Geology”, ed. Hawthorne, F. C., *Rev. Mineral.*, **18**, 341–403.
- KUBICKI, J. D., XIAO, Y. and LASAGA, A. C. (1993) Theoretical reaction pathways for the formation of $[\text{Si}(\text{OH})_5]^-$ and the deprotonation of orthosilicic acid in basic solution. *Geochim. Cosmochim. Acta*, **57**, 3847–3853.

- LASAGA, A. C. and GIBBS, G. V. (1987) Applications of quantum mechanical potential surfaces to mineral physics calculations. *Phys. Chem. Min.*, **14**, 107–117.
- LASAGA, A. C. and GIBBS, G. V. (1990) Ab-Initio quantum mechanical calculations of water-rock interactions: adsorption and hydrolysis reactions. *Am. J. Sci.*, **290**, 263–295.
- STEBBINS, J. F. (1995) Dynamics and structure of silicate and oxide melts: Nuclear magnetic resonance studies. In “Structure, Dynamics and Properties of Silicate Melts”, ed. Stebbins, J. F., McMillan, P. F. and Dingwell, D. B., *Rev. Mineral.*, **32**, 191–246.
- STEBBINS, J. F. and McMILLAN, P. F. (1989) Five- and six-coordinated Si in $K_2Si_4O_9$ liquid at 1.9 GPa and 1200°C. *Am. Mineral.*, **74**, 965–968.
- TOSSELL, J. A. (1990) Calculation of NMR shieldings and other properties for three and five coordinate Si, three coordinate O and some siloxane and boroxol ring compounds. *J. Non-Crystal. Solids*, **120**, 13–19.
- TOSSELL, J. A. (1991) Calculation of the effect of deprotonation on the Si NMR shielding for the series $Si(OH)_4$ to SiO_4^{4-} . *Phys. Chem. Min.*, **17**, 654–660.
- XUE, X., STEBBINS, J. F., KANZAKI, M., McMILLAN, P. F. and POE, B. (1991) Pressure-induced silicon coordination and tetrahedral structural changes in alkali oxide-silica melts up to 12 GPa: NMR, Raman, and infrared spectroscopy. *Am. Mineral.*, **76**, 8–26.

Received October 31, 1995; accepted January 21, 1996