Ab Initio ^{27}Al NMR Chemical Shift Calculation for the Clusters of $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$

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$\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$, $\text{Al}(\text{OH})_6^{3-}$ クラスターの非経験的 ^{27}Al NMR 化学シフト計算

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The effect of coordination number on ^{27}Al NMR chemical shift was studied using ab initio molecular orbital calculation. In order to mimic Al of four-, five- and six-coordinations Al, the clusters of $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ were employed for the calculation. The obtained shifts for $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ were +70.3, +31.5 and -3.9 ppm, respectively, and were in reasonable agreement with observed shifts of Al-containing oxides. Present calculation supports the assignment of +30 ppm peak observed in aluminosilicate glasses as five-coordination state. Ab initio molecular orbital calculation can be used to establish the correlation between local structure and NMR chemical shift of Al-containing materials.

[Received August 5, 1996; Accepted September 19, 1996]

Key-words : Molecular orbital calculation, ^{27}Al NMR, Chemical shift, Coordination state

1. Introduction

Aluminum is one of important elements in the ceramics and glasses, as well as minerals. Aluminum can take four-, five- and six-coordination states in crystalline and amorphous oxides. Since the coordination state is important factor for determining physical and chemical properties of materials, the information of Al coordination state is inevitable for Al-containing materials. Unlike other spectroscopies, ^{27}Al NMR spectroscopy is unique in its ability to identify coordination state of Al, and has been extensively applied to Al-containing materials.^{1)–3)} However, the assignment of Al coordination state has been based on an empirical correlation between measured chemical shifts and local structures of known crystalline materials.¹⁾ The empirical correlation would be fine for well known local structure, although it might not be applicable for rarely observed local structure. For example, five-coordination state is rare in crystalline materials, and thus its assignment has been ambiguous, especially for amorphous materials.²⁾ However the rareness of such coordination state in crystals does not necessary mean that it is also rare in the amorphous materials. In order to establish well sounded basis for the chemical shift-local structure correlation, theoretical calculation is needed. Recently ab initio molecular orbital (MO) calculation has been employed to predict magnetic shielding tensor for molecules and clusters.⁴⁾ Taking advantage of this development, chemical shifts of the clusters $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$, which mimic four-, five- and six-coordination Al, respectively, are calculated. As shown below, the calculation can reproduce observed trend in chemical shifts well. ^1H and ^{17}O NMR chemical shifts of the clusters are also reported.

2. Calculation method

The chemical shift calculation is same as our previous study for ^{29}Si NMR.⁵⁾ Gaussian 94 program⁶⁾ was employed for all calculations. In brief, the Hartree-Fock MO calculation with 6-31+G(d) basis set was employed for optimization of cluster geometries. Since all clusters were negatively charged, so a diffuse function was added to the basis set. No symmetrical constraint was forced during the calculation. All clusters were successfully optimized. For the magnetic shielding tensor calculation, the continuous set of

gauge transformation (CSGT) method⁴⁾ with robust 6-311+G(2df, p) basis set was employed. This procedure well reproduced ^{29}Si NMR shifts of Si-containing clusters.⁵⁾

In real NMR experiments, the chemical shift is measured relative to a reference material. Therefore the magnetic shielding tensor of the reference must also be known. Thus AlCl_3 clusters was selected to mimic a commonly used AlCl_3 for ^{27}Al chemical shift reference. For the references of ^1H and ^{17}O NMR shifts, $\text{Si}(\text{CH}_3)_4$ and H_2O were used, respectively. The difference of isotropic tensor components between the reference and the cluster, which corresponds to an isotropic chemical shift, is then calculated.

3. Results and discussion

Geometries of fully optimized Al-containing clusters at Hartree-Fock level calculation with 6-31+G(d) basis set are shown in Fig 1, and structural parameters, the Mulliken charges and total energies are listed in Table 1. The optimized structure of $\text{Al}(\text{OH})_4^-$ possess S_4 symmetry, and has a form similar to that of $\text{Si}(\text{OH})_4$.⁵⁾ The optimized structure of $\text{Al}(\text{OH})_5^{2-}$ was a distorted trigonal bipyramid form, also similar to $\text{Si}(\text{OH})_5^-$.⁵⁾ The optimized structures of the clusters are consistent with observed local structures of corresponding coordination states in Al-containing oxides. The Mulliken charge of Al increases with increasing coordination number. This can be interpreted as an increase of ionicity in Al-O bonding for higher coordination state.

Calculated ^{27}Al NMR shielding tensors are shown in

Fig. 1. Optimized geometries of the clusters $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ at RHF/6-31+G(d). Large circle: aluminum; medium circle: oxygen; small circle: hydrogen.

Table 1. Geometries, Mulliken Charges and Energies of $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ at RHF/6-31+G(d)

cluster	$R_{\text{Al-O}}$ (pm)	$\angle\text{O-Al-O}$ ($^\circ$)	q_{Al}	q_{O}	q_{H}	E (Hartree [#])
$\text{Al}(\text{OH})_4^-$	177.6	105.7, 117.4	0.69	-0.89	0.46	-543.939
$\text{Al}(\text{OH})_5^{2-}$	190.3, 197.6 184.8, 184.9, 186.0	87.1, 87.9, 88.9, 93.8, 93.9 175.0, 114.0, 122.8, 122.9	0.85	-0.97~ -1.14	0.44~ 0.48	-619.224
$\text{Al}(\text{OH})_6^{3-}$	199.6	87.6, 92.4	1.72	-1.25	0.47	-694.339

q_{A} : Mulliken charge for atom A; [#]: 1 Hartree = 4.3597×10^{-18} Joules

Table 2. Calculated ^{27}Al NMR Shielding Tensors (ppm) for the Clusters of AlCl_6^{3-} , $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$

cluster	σ_{XX}	σ_{YY}	σ_{ZZ}	σ^{i}	σ^{a}	δ
AlCl_6^{3-}	592.9	593.2	593.2	593.1	0.2	0.0
$\text{Al}(\text{OH})_4^-$	521.7	523.3	523.4	522.8	0.9	+70.3
$\text{Al}(\text{OH})_5^{2-}$	519.7	578.1	587.0	561.6	38.1	+31.5
$\text{Al}(\text{OH})_6^{3-}$	593.2	593.2	604.7	597.0	11.4	-3.9

 σ_{XX} , σ_{YY} , σ_{ZZ} : diagonal elements of tensors after diagonalization 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 : isotropic chemical shift ($\sigma_{\text{ref}}^{\text{i}} - \sigma_{\text{cluster}}^{\text{i}}$)

Table 2. The isotropic component of shielding tensor increases with increasing coordination number as observed.^{1),3)} For $\text{Al}(\text{OH})_4^-$ cluster, the isotropic chemical shift was calculated as +70.3 ppm. The shift can be compared with observed shifts of +50 to +90 ppm for four-coordination Al in oxides.³⁾ Observed shift for Al with no (Al,Si) neighbor (i.e., Q^0), is about +80 ppm, and is more relevant for comparison. The calculated shift of $\text{Al}(\text{OH})_5^{2-}$ was +31.5 ppm, and is again consistent with observed shifts of +30 to +40 ppm for five-coordination Al in few known crystals.³⁾ For $\text{Al}(\text{OH})_6^{3-}$, the calculated shift was -3.9 ppm. It is again in accord with observed shifts of -10 to +15 ppm for six-coordination Al.³⁾ The chemical shift for five-coordination Al falls just between those of four- and six-coordination states. Similar trend was also observed for ^{29}Si NMR chemical shift.⁵⁾ A peak of about +30 ppm chemical shift found in the aluminosilicate glasses has been empirically assigned to five-coordination Al state.^{1),2)} Present ab initio calculation thus supports this assignment.

Finally, calculated ^1H and ^{17}O NMR chemical shifts of the clusters are shown in Table 3. Since protons in the clusters are introduced to avoid dangling bonds, thus these chemical shifts, especially for proton, might be meaningless values for bulk solids. However, such clusters do exist in aqueous solution or at surface of materials. Therefore these shifts might provide some insight of these environment. ^1H chemical shift increases with increasing coordination number of Al, whereas ^{17}O chemical shift shows opposite trend. The chemical shift of ^{17}O NMR is sensitive to coordination number of Al, thus it might be used to distinguish such local structure.

Although the effect of coordination state of Al on chemical shift was studied here, the effect of more subtle local structural parameters, such as second-neighbor environ-

Table 3. Calculated ^1H and ^{17}O NMR Chemical Shifts (ppm) for the Clusters of AlCl_6^{3-} , $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$

cluster	σ^{i}	σ^{a}	δ
^1H NMR chemical shift			
$\text{Si}(\text{CH}_3)_4$	32.0	9.7	0.0 (ref.)
$\text{Al}(\text{OH})_4^-$	33.4	20.1	-1.4
$\text{Al}(\text{OH})_5^{2-}$	33.5~35.0	16.9~19.1	-1.5~3.0
$\text{Al}(\text{OH})_6^{3-}$	33.9	16.2	-1.9
^{17}O NMR chemical shift			
H_2O	318.8	59.9	0.0 (ref.)
$\text{Al}(\text{OH})_4^-$	321.6	50.7~50.8	-2.8
$\text{Al}(\text{OH})_5^{2-}$	299.3~311.4	51.6~65.9	+19.5~+7.4
$\text{Al}(\text{OH})_6^{3-}$	291.5	42.5	+27.3

 σ^{i} : isotropic component of tensor; σ^{a} : anisotropic component of tensor; δ : isotropic chemical shift

ment, can be studied using larger clusters. Unlike ^{29}Si NMR, the effect of such local structure on chemical shift is not well established for ^{27}Al NMR, partly due to second-order quadrupole broadening. Ab initio MO calculation would be helpful to establish the correlation between chemical shift and local structure for Al-containing materials.

Acknowledgements This study is supported by the Grant-in-Aid for Scientific Research on Priority Areas ("Magma"), the Ministry of Education, Science, Sports and Culture of Japan.

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