Assessment of the Accuracy of Theoretical Methods for Calculating ^{27}Al Nuclear Magnetic Resonance Shielding Tensors of Aquated Aluminum Species

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Assessment of the accuracy of methods including 29 DFT methods and 2 ab initio wave function theory (WFT) methods for predicting ^{27}Al nuclear magnetic resonance shielding tensors of aquated Al(III) species was carried out. Among all of the tested methods, HF and MP2 methods give the best performance for the calculations of chemical shifts. Among all of the DFT methods with GIAO calculations, O3LYP and MPWKCIS1K are the most accurate models for calculations of chemical shifts, followed in order by BHandHLYP, B98, B97−1, mPW1PW91, PBE1PBE, and MPW1KCIS. Among all of the DFT methods with CSGT calculations, VSXC is the best method for the prediction of chemical shifts, followed in order by TPSSh, B97−2, O3LYP, TPSS, TPSS1KCIS, MPWKCIS1K, BHandHLYP, B97−1, and B98. The popular B3LYP method overestimates largely the chemical shifts with both GIAO and CSGT methods. The calculated results indicate that the predictions of ^{27}Al chemical shifts on the base of the model that includes both explicit solvent effect and bulk solvent effect are most accurate for aquated Al(III) species.

1. Introduction

The aqueous solution chemistry of Al(III) is central to geochemistry, environmental science, and medicine[1] but the nature of the chemical species involved still remains poorly understood and of considerable interest. NMR spectroscopy has proven to be a valuable technique for determining the aluminum species in aqueous solution;[2] however, early ^{27}Al NMR studies indicated that only the species $Al(H_2O)_6^{3+}$, $Al(OH)_4^-$, and Al_{13} with high symmetry can be identified by ^{27}Al NMR technique, and the other hydrolysis products such as $Al(OH)^{2+}$ and $Al(OH)_2^+$ are unable to be characterized by ^{27}Al NMR spectroscopy for broadening of ^{27}Al nuclear resonances induced by low symmetry.[3] To better understand the nature of the chemical species, a number of computational investigations into structures and reactions of various hydrated aluminum species have been undertaken.[4−8] The structures and energies of monomer and polymer of hydrated Al(III) species were investigated by Pophristic et al.[4] and Miao et al.[5] respectively, and the water exchange reactions of aquated Al(III) species were simulated by different theoretical methods.[6,7] The hydrolysis of Al(III) was also investigated using molecular dynamics.[8]

To date only a limited number of ^{27}Al NMR theoretical studies have been attempted.[9−12] To predict the chemical shifts, Tossell calculated the NMR properties of the aquated Al(III) species and Al_{13} polyoxocation with Hartree−Fock method and GIAO formalism,[12] and obtained the comparable results with its experimental data.[9,10] Sykees et al.[11] and Kubicki et al.[12] also combined the Hartree−Fock method and GIAO formalism[13] and calculated the chemical shifts of aqueous aluminum species and aluminum−carboxylate complexes respectively, and their calculated results indicated that the consideration of a second solvation shell around Al(III) can predict ^{27}Al chemical shifts more accurately. A number of methods have been developed for the calculation of molecular NMR properties, and the studies on comparison of calculating models for ^{13}C NMR and ^{9}Be NMR were carried out.[14,15]

The present article seeks to establish conditions for the prediction of accurate ^{27}Al NMR shifts using theoretical calculations and to then use these conditions to predict aluminum chemical shift values for aluminum species with known structures. Because accurate prediction of the NMR properties within the finite basis approximation generally requires gauge-invariant procedures,[13,16] our present study focused on predicting NMR shielding tensors using GIAO[13] and CSGT[16] at both the Hartree−Fock and DFT levels of theory. The effects of solvent on the predicting NMR shifts of aquated Al(III) species was also investigated, in which the effect of a second solvation shell and bulk solvent effect were considered.[7]

2. Computational Methods

2.1. Models. To examine the effects of solvent on the predicting NMR shifts of aquated Al(III) species, three models were proposed, that is, the gas-phase model, supermolecular model, and supermolecule−PCM model.[16] The gas-phase model only involves the gas-phase species ($Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$), which were fully optimized in vacuum. The supermolecular model involves the central gas-phase species and a complete second coordination sphere, and the species ($Al(H_2O)_6^{3+}\cdot 12H_2O$ and $Al(OH)_4^-\cdot 12H_2O$) were denoted as supermolecules. Supermolecule−PCM model is based on the supermolecular model and considered the bulk solvent effect on the supermolecules, and the species ($P-Al(H_2O)_6^{3+}\cdot 12H_2O$ and $P-Al(OH)_4^-\cdot 12H_2O$) in supermolecule−PCM model were denoted as PCM species. The species $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ were chosen as the modeling complexes because the experimental data for their relative chemical shifts was obtained and their hydrated structures were also well established by theoretical methods. According to the reports by Bock et al.[17] and Sillanpaa et al.,[18] a complete second coordination sphere involves 12 water

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TABLE 1: Summary of the DFT Methods Tested

method	type	exchange/correlation functional	*Gaussian 03* keyword	refs
BLYP	pure	Becke88/Lee−Yang−Parr	BLYP	19, 20
BP86	pure	Becke88/Perdew's 1986 GGA	BP86	19, 21
LSDA	pure	Slater's local/Perdew−Wang local	LSDA	22, 23
mPWLYP	pure	Modified Perdew−Wang/ Lee−Yang−Parr	mPWLYP	20, 24
mPWPW91	pure	Modified Perdew−Wang/ Perdew−Wang91	mPWPW91	24
PBE	pure	PBE/PBE	PBEPBE	25
BB95	MDFT	Becke88/Becke95	BB95	26
mPWKCIS	MDFT	Modified Perdew−Wang/KCIS	mPWKCIS	24, 27−30
TPSS	MDFT	TPSS/TPSS	TPSSTPSS	29, 30
TPSSKCIS	MDFT	TPSS/KCIS	TPSSKCIS	27−30
VSXC	MDFT	VSXC/VSXC	VSXC	31
B3LYP	HDFT	Becke88/Lee−Yang−Parr	B3LYP	20, 32, 33
B97−1	HDFT	B97−1/B97−1	B971	34
B97−2	HDFT	B97−2/B97−2	B972	35
B98	HDFT	B98/B98	B98	36
BHandHLYP	HDFT	Becke88/Lee−Yang−Parr	BHandHLYP	37
MPW1K	HDFT	Modified Perdew−Wang Perdew−Wang91	MPWPW91 Iop(3/76=0572004280)	38
mPW1PW91	HDFT	Modified Perdew−Wang Perdew−Wang91	mPW1PW91	24
O3LYP	HDFT	OPTX/Lee−Yang−Parr	O3LYP	39, 40
PBE1PBE	HDFT	PBE/PBE	PBE1PBE	25
X3LYP	HDFT	Becke88 + PW91/Lee−Yang−Parr	X3LYP	41
B1B95	HMDFT	Becke88/Becke95	B1B95	26
BB1K	HMDFT	Becke88/Becke95	BB95 Iop(3/76=0580004200)	42
MPW1B95	HMDFT	Modified Perdew−Wang/Becke95	MPWB95 Iop(3/76=0690003100)	43
MPW1KCIS	HMDFT	Modified Perdew−Wang/KCIS	MPWKCIS Iop(3/76=0850001500)	44
MPWB1K	HMDFT	Modified Perdew−Wang/Becke95	MPWB95 Iop(3/76=0560004400)	43
MPWKCIS1K	HMDFT	Modified Perdew−Wang/KCIS	MPWKCIS Iop(3/76=0590004100)	44
TPSS1KCIS	HMDFT	TPSS exchange/KCIS	TPSSKCIS Iop(3/76=0870001300)	45
TPSSh	HMDFT	TPSS/TPSS	TPSSTPSS Iop(3/76=0900001000)	29, 30

molecules for both $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$, and thereby 12 explicit water molecules were included in the supermolecular model.

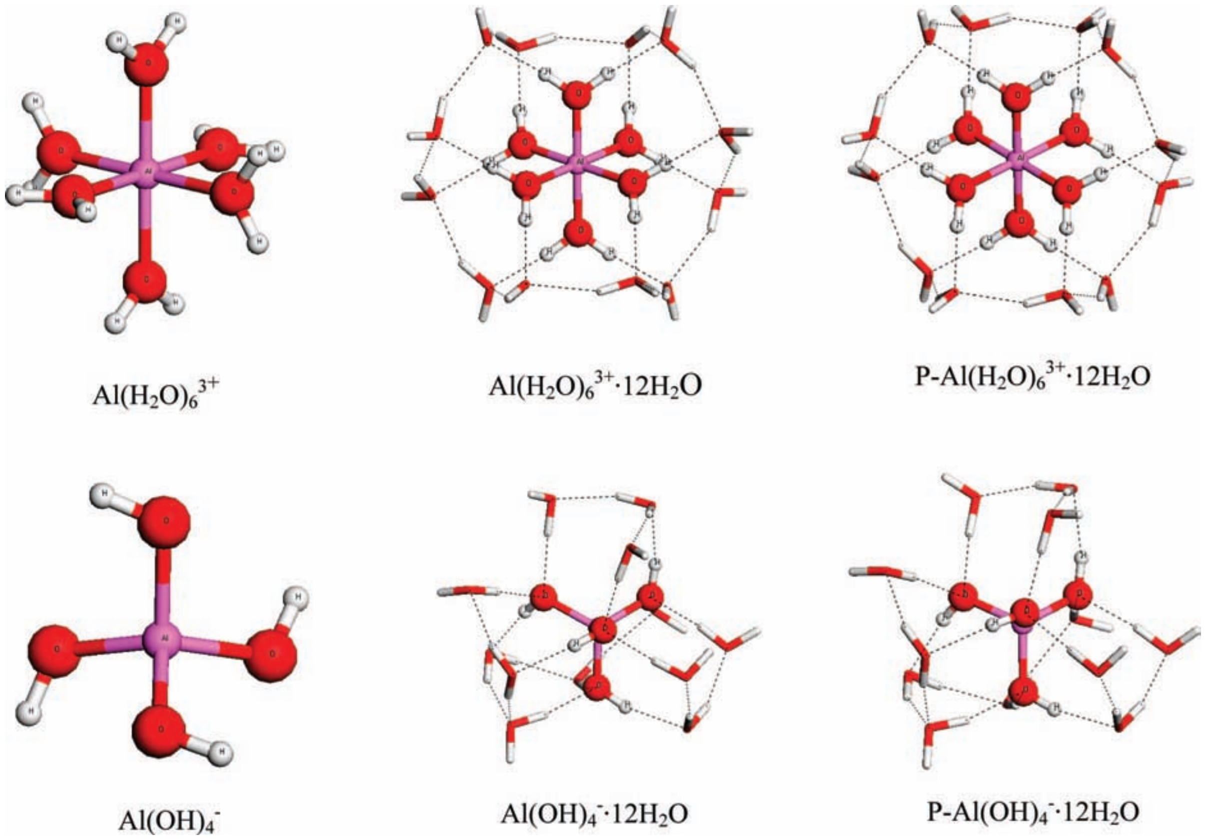
2.2. Theoretical Methods Tested. A number of DFT methods, Hartree−Fock, and MP2 methods were tested. The tested DFT methods include 11 pure DFT or meta DFT methods, 10 hybrid DFT methods, and 8 hybrid meta DFT methods. The tested pure DFT or meta DFT methods include BLYP,[19,20] BP86,[19,21] LSDA,[22,23] mPWLYP,[20,24] mPWPW91,[24] PBE,[25] BB95,[26] mPWKCIS,[24,27−30] TPSS,[29,30] TPSSKCIS,[27−30] and VSXC.[31] The assessed hybrid DFT methods include B3LYP,[20,32,33] B97−1,[34] B97−2,[35] B98,[36] BHandHLYP,[37] MPW1K,[38] mPW1PW91,[24] O3LYP,[39,40] PBE1PBE,[25] and X3LYP,[41] whereas the tested hybrid meta DFT methods include B1B95,[26] BB1K,[42] MPW1B95,[43] MPW1KCIS,[44] MPWB1K,[43] MPWKCIS1K,[44] TPSS1KCIS,[45] and TPSSh.[29,30] All of these tested DFT methods are summarized in Table 1.

2.3. Computational Details. All of the calculations were performed using the program *GAUSSIAN 03*[46] in which GIAO[13] and CSGT[16] methods were implemented. For the gas-phase model and supermolecular model, all of the gas-phase species and supermolecular species were fully optimized in vacuum at B3LYP/6-311+G(d,p) using DFT.[6] For the supermolecule−PCM model, the supermolecular species were reoptimized with PCM model[47] at the same level. In the PCM calculations,[47] a dielectric constant 78.39 for water and UAKS radii were used. To seek the convergence of isotropic absolute shielding constants with respect to basis set, the basis sets 3-21G, 3-21G**, 3-21+G**, 6-31G, 6-31G(d,p), 6-31+G(d,p), 6-311G, 6-311G(d,p), and 6-311+G(d,p) were employed for calculating ^{27}Al NMR absolute shielding constants using Hartree−Fock (DFT/B3LYP) GIAO and CSGT methods. For the supermolecule−PCM species, the chemical shifts of $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ were calculated at the 6-311+G(d,p) level with HF, MP2, and 29 DFT methods, respectively. To examine the effects of solvent on the predicting ^{27}Al NMR chemical shifts, the gas-phase species, supermolecular species, and PCM species for $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ were calculated at 6-311+G(d,p) level using HF GIAO method.

3. Results and Discussion

3.1. Structures of $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$. The structures of $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ for gas-phase, supermolecular, and PCM species are shown in Figure 1. The supermolecular and PCM species for $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ include a complete second solvation shell with 12 explicit water molecules, and they are different from the effect of the bulk solvent water on the structures. From Table 2, one can note that the Al−O bond lengths of supermolecular and PCM species for $Al(H_2O)_6^{3+}$ are closer to the MD data[48] and experimental data[49] than that of the gas-phase species, and the Al−O bond length of PCM species is the closest, which underscores the importance of explicit solvent effect and bulk solvent effect. However, we found the solvent effects have little influence on the structure of $Al(OH)_4^-$. Comparing to the data by molecular dynamics[48] and the corresponding experimental data,[49] one can note that our adopted methods and models are satisfactory for describing the structures of aquated Al(III) species accurately.

3.2. Convergence of Isotropic Absolute Shielding Constant with Respect to Basis Set. The convergence of the GIAO and CSGT methods with respect to basis set is demonstrated in Table 3 for absolute shielding constants calculated at the Hartree−Fock and DFT/B3LYP levels of theory. From the data in Table 3, one can note that the values obtained by GIAO and CSGT methods are close when the basis set is larger than 6-311G, and the shielding constants are converged when the basis set is larger than 6-311G(d,p) for both GIAO and CSGT methods, and thereby the convergence with respect to the basis set is satisfactory for 6-311+G(d,p). CSGT shielding constants are found to converge more smoothly than those by GIAO, and the values by CSGT method are close to the converged value even if the calculations are carried out at small basis set such



$Al(H_2O)_6^{3+}$ $Al(H_2O)_6^{3+}\cdot 12H_2O$ $P\text{-}Al(H_2O)_6^{3+}\cdot 12H_2O$

$Al(OH)_4^-$ $Al(OH)_4^-\cdot 12H_2O$ $P\text{-}Al(OH)_4^-\cdot 12H_2O$

Figure 1. Structures of $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ for gas-phase, supermolecular, and PCM species

TABLE 2: The Al−O Bond Lengths (Å) of $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$

	gas phase	supermolecule	PCM	MD data[a]	exp. data[b]
$Al(H_2O)_6^{3+}$	1.941	1.921	1.915	1.920	1.90
$Al(OH)_4^-$	1.792	1.792	1.793	1.750	

[a] From ref 48. [b] From ref 49.

as 3-21G. In contrast, GIAO shielding constants are found to converge faster than those by CSGT, and the calculated data is satisfactory only at sufficiently large basis sets such as 6-311+G(d,p). Therefore, we expect that our adopted basis set 6-311+G(d,p) is satisfactory to access the accuracy of methods for calculating chemical shifts of aquated Al(III) species.

3.3. Comparison of the Methods for ^{27}Al Chemical Shift. GIAO and CSGT ^{27}Al chemical shifts of $P-Al(OH)_4^-\cdot 12H_2O$ relative to $P-Al(H_2O)_6^{3+}\cdot 12H_2O$ are given in Table 4 at HF, DFT, and MP2 levels of theory using the 6-311+G(d,p) basis. Eleven pure DFT or meta DFT methods, 10 hybrid DFT methods and 8 hybrid meta DFT methods were employed to calculate chemical shifts in the present study. From Table 3, the chemical shift determined by Hartree−Fock with GIAO and CSGT is 79.7 ppm and 82.3 ppm respectively, which are very close to the values by MP2 method (79.7 ppm) and experimental data (80.0 ppm).[50] However, the chemical shifts determined by the functionals of DFT with GIAO and CSGT are different largely, and the largest difference reaches to 30.9 ppm. In the GIAO calculations, the functionals BB95, TPSS, TPSSKCIS, VSXC, B97−2, B1B95, BB1K, MPW1B95, MPWB1K, TPSS1KCIS, and TPSSh do not work, and O3LYP and MPWKCIS1K are two best DFT methods for calculating ^{27}Al NMR, followed in order by BHandHLYP, B98, B97−1, mPW1PW91, PBE1PBE, and MPW1KCIS with unsigned error below 6 ppm. In the GIAO calculations, the most popular functional B3LYP overestimates the value for ^{27}Al NMR by 6.4 ppm, and the largest deviation is up to 32.9 ppm estimated by MPW1K. In the CSGT calculations, VSXC is the best DFT method with the unsigned error 1.7 ppm, followed in order by TPSSh, B97−2, O3LYP, TPSS, TPSS1KCIS, MPWKCIS1K, BHandHLYP, B97−1, and B98 with unsigned error below 8 ppm. In the CSGT calculations, the most popular functional B3LYP overestimates the chemical shift by 9.9 ppm, and the largest deviation is up to 33.9 ppm by MPW1K, indicating that functional MPW1K should be improved for prediction of chemical shifts. Comparing the signed errors between HF and DFT methods, one can note that all of the DFT methods with GIAO and CSGT overestimate the relative chemical shifts, whereas HF method with GIAO underestimates the relative chemical shifts. Comparing the calculated relative chemical shifts using GIAO and CSGT with the same functionals, we found that the GIAO method is more accurate than CSGT to predict the chemical shifts for aquated Al(III) species. Therefore, HF and MP2 methods are the two best methods for calculation of chemical shifts with GIAO and CSGT methods. With GIAO method, O3LYP and MPWKCIS1K are the two best DFT methods, and with CSGT method VSXC is the best DFT method.

In the previous works about prediction of ^{27}Al NMR, the gas-phase species were used to predict the chemical shifts; however, our recent works indicated that the solvent effects are very important for the aquated Al(III) species, and both the explicit solvent effect and the bulk solvent effect have obvious influence on the structure of aquated Al(III) species. To examine the effects of solvent water on the prediction of ^{27}Al chemical shifts, the Hartree−Fock GIAO and CSGT calculations on the gas-phase, supermolecular, and PCM species for $Al(H_2O)_6^{3+}$ and $Al(OH)_4^-$ were carried out. As shown in Table 5, the deviation

TABLE 3: Convergence of Hartree−Fock (DFT) GIAO and CSGT Isotropic Absolute Shielding Constants (σ, in ppm) with Respect to Basis Set

	HF				DFT/B3LYP			
	GIAO		CSGT		GIAO		CSGT	
basis set	$Al(H_2O)_6^{3+}$	$Al(OH)_4^-$	$Al(H_2O)_6^{3+}$	$Al(OH)_4^-$	$Al(H_2O)_6^{3+}$	$Al(OH)_4^-$	$Al(H_2O)_6^{3+}$	$Al(OH)_4^-$
3-21G	709.2	577.5	610.6	520.9	673.8	525.8	551.3	458.4
3-21G**	696.0	582.4	584.1	504.8	663.2	539.6	544.1	460.6
3-21+G**	630.0	602.0	599.4	519.3	594.8	563.7	563.0	477.3
6-31G	646.6	562.2	601.5	516.2	615.7	513.4	550.3	452.1
6-31G(d,p)	636.3	554.6	596.4	515.4	609.0	516.3	557.5	470.8
6-31+G(d,p)	632.3	560.4	603.5	521.7	609.6	528.7	566.5	480.2
6-311G	623.0	531.3	630.4	544.1	582.5	482.5	584.0	484.7
6-311G(d,p)	617.6	530.3	607.5	519.3	578.9	486.2	567.2	474.8
6-311+G(d,p)	616.0	531.0	612.8	523.3	576.4	487.1	572.1	475.5

TABLE 4: GIAO and CSGT ^{27}Al Chemical Shifts of $P-Al(OH)_4^-\cdot 12H_2O$ Relative to $P-Al(H_2O)_6^{3+}\cdot 12H_2O$ at HF, DFT, and MP2 Levels of Theory Using the 6-311+G(d,p) Basis

	GIAO			CSGT		
method	δ(ppm)	SE[a]	UE[b]	δ(ppm)	SE[a]	UE[b]
Pure DFT or Meta DFT						
BB95				93.6	13.6	13.6
BLYP	87.8	7.8	7.8	91.5	11.5	10.3
BP86	86.9	6.9	6.9	90.3	10.3	10.3
LSDA	91.2	11.2	11.2	94.7	14.7	14.7
mPWKCIS	86.7	6.7	6.7	90.3	10.3	10.3
mPWLYP	88.0	8.0	8.0	91.8	11.8	11.8
mPWPW91	86.9	6.9	6.9	90.3	10.3	10.3
PBE	87.1	7.1	7.1	90.4	10.4	10.4
TPSS				86.0	6.0	6.0
TPSSKCIS				90.3	10.3	10.3
VSXC				81.7	1.7	1.7
Hybrid DFT						
B3LYP	86.4	6.4	6.4	89.9	9.9	9.9
B97−1	84.5	4.5	4.5	87.6	7.6	7.6
B97−2				85.7	5.7	5.7
B98	84.3	4.3	4.3	87.6	7.6	7.6
BHandHLYP	84.2	4.2	4.2	87.4	7.4	7.4
MPW1K	112.9	32.9	32.9	113.9	33.9	33.9
mPW1PW91	85.1	5.1	5.1	88.2	8.2	8.2
O3LYP	83.0	3.0	3.0	85.9	5.9	5.9
PBE1PBE	85.2	5.2	5.2	88.3	8.3	8.3
X3LYP	86.5	6.5	6.5	90.0	10.0	10.0
Hybrid Meta DFT						
B1B95				91.2	11.2	11.2
BB1K				89.8	9.8	9.8
MPW1B95				91.0	11.0	11.0
MPW1KCIS	85.6	5.6	5.6	89.0	9.0	9.0
MPWB1K				89.8	9.8	9.8
MPWKCIS1K	83.7	3.7	3.7	86.7	6.7	6.7
TPSS1KCIS				86.2	6.2	6.2
TPSSh				85.4	5.4	5.4
Ab Initio WFT						
HF	79.7	−0.3	0.3	82.3	2.3	2.3
MP2	79.7	−0.3	0.3			

[a] SE denotes signed error. [b] UE denotes unsigned error.

of the prediction on the gas-phase species is the largest, up to approximately 6 ppm, and the values calculated on the supermolecular and PCM species are close to the experimental data, which underscores the importance of solvent effects. Comparing the calculated values of chemical shifts on supermolecular speices and PCM species, one can note that prediction on PCM species is more accurate than that on supermolecular species. Because the calculations of PCM species considered both explicit solvent effect and bulk solvent effect, the prediction of ^{27}Al NMR on the PCM species is the most accurate.

TABLE 5: Comparison of GIAO and CSGT Chemical Shifts (δ, in ppm) Calculated at HF/6-311+G(d,p) Level for Gas-Phase, Supermolecular and PCM Species

complex	GIAO	CSGT	exptl. data[a]
$Al(OH)_4^-$	85.0	89.5	80.0
$Al(OH)_4^-\cdot 12H_2O$	80.8	83.5	
$P-Al(OH)_4^-\cdot 12H_2O$	79.7	82.3	

[a] From ref 50.

3.4. Application to Large Polyoxocation Al_{13}. For confirmation of the tested results on monomeric aluminum species,

TABLE 6: Relative Chemical Shifts (δ, in ppm) of ^{27}Al for Al_{13} Calculated with Selected Methods

	GIAO			CSGT			
method	HF	O3LYP	MPWKCIS1K	HF	VSXC	calcd. data[a]	exptl. data[b]
$\delta_{Al(tetra)}$	60.1	62.3	63.9	62.4	59.9	56	63
$\delta_{Al(octa)}$	11.7	15.1	14.3	14.1	12.2	20	12

[a] From ref 10. [b] From ref 51.

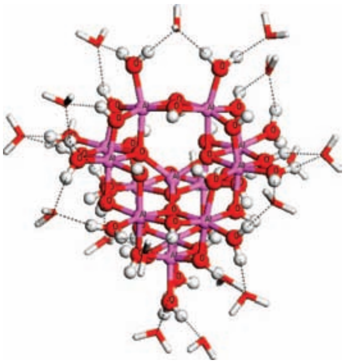


Figure 2. Optimized structure of P−Al_{13}•18H_2O.

the selected more accurate methods were applied to large polyoxocation $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13}). P−Al_{13}•18H_2O species was selected for the model species, and its structure is shown in Figure 2. The more accurate methods HF, O3LYP, MPWKCIS1K, and VXSC methods were employed to calculate the chemical shifts of tetrahedral and octahedral aluminums in Al_{13}. As shown in Table 6, in the GIAO calculations, the predicted values of the ^{27}Al NMR of tetrahedral aluminum used by HF, O3LYP and MPWKCIS1K methods are 60.1, 62.3, and 63.9 ppm respectively, close to the experimental data 63 ppm,[51] and O3LYP is the most accurate among them. For the prediction of ^{27}Al NMR of octahedral aluminum with GIAO method, HF method is the most accurate with the chemical shift of 11.7 ppm. In the CSGT calculations, HF predicts more accurately than VXSC for ^{27}Al NMR of tetrahedral aluminum, whereas VXSC performs better than HF for prediction of ^{27}Al NMR of octahedral aluminum, and all of the calculated values are consistent with the corresponding experimental data.[51] Compared to the data calculated by HF with GIAO method at 6-31G(d) level,[10] one can note that all of the data in the present article are more accurate, which indicates that enough large basis set is required for accurate prediction of chemical shifts. In summary, all the methods HF, O3LYP, MPWKCIS1K, and VXSC selected on the base of monomeric aluminum species also perform well on the calculations of ^{27}Al NMR of large polyoxocation Al_{13}.

3.5. Analytical Remarks. Although the purpose of this study is to provide tests and possible validations of theoretical methods including Hartree−Fock, MP2, and density functionals, and not to analyze the functionals theoretically, it is helpful to add a few theoretical analyses. Wave function theory, such as MP2, can account for the electron-correlation effects systematically, and thereby MP2 can give the best performance for prediction of ^{27}Al NMR. However, its computational cost is too demanding to be applied to large molecules or condensed-phase systems.[52] Although electron−electron interactions are treated only in an average mean-field way in HF theory, HF calculations also can give good results because the aluminum system studied here does not include significant electron correlation effects. Density functional theory is more robust than correlated WFT due to its excellent performance-to-cost ratio,[53] but many different density functionals developed for different purposes are not tested for prediction of ^{27}Al NMR. Pure DFT, meta DFT, hybrid DFT, and hybrid meta DFT are distinguished in the present article, and Hartree−Fock exchange is only involved in the hybrid DFT and hybrid meta DFT.[44] Table 4 shows that HF exchange is needed for density functionals in GIAO calculations to obtain accurate chemical shifts of ^{27}Al NMR for the inorganic aluminum systems. In CSGT calculations, meta DFT VSXC functional gives the best performance, which is consistent with the finding on prediction of ^{13}C chemical shifts.[52] Except VSXC and TPSS, the other functionals with better performance all involve HF exchange. The optimum amount of Hartree−Fock exchange depends on the molecule or reaction, depends on the property of interest for that molecule or reaction, and also depends on the choice of GGA because different GGAs are designed for different purposes.[44]

4. Concluding Remarks

In this article, we assessed the accuracy of 29 DFT methods, HF, and MP2 methods to predict the ^{27}Al chemical shifts on aquated Al(III) species. Among all of the tested methods, HF and MP2 give the best performance for the calculations of chemical shifts. Among all the DFT methods with GIAO calculations, O3LYP and MPWKCIS1K are the most accurate models for calculations of chemical shifts, with an unsigned error below 4 ppm, and the very popular B3LYP method overestimates largely the chemical shifts with an unsigned error of 6.4 ppm. Some other methods with unsigned error below 6 ppm in the GIAO calculations are BHandHLYP, B98, B97−1, mPW1PW91, PBE1PBE, and MPW1KCIS. Among all of the DFT methods with CSGT calculations, VSXC is the best method for the prediction of chemical shifts with an unsigned error of only 1.7 ppm, and the popular B3LYP method overestimates largely the chemical shifts with an unsigned error of 9.9 ppm. Some other methods with unsigned error below 6 ppm in the CSGT calculations are TPSSh, B97−2, O3LYP, TPSS, TPSS1KCIS, MPWKCIS1K, BHandHLYP, B97−1, and B98. The calculations about effects of solvent on accuracy of prediction of chemical shifts indicate that calculations of ^{27}Al NMR with inclusion of solvent effects would be more accurate than calculations on the gas-phase species for aquated Al(III) species.

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