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Theoretical Investigation of ^{19}F NMR Chemical Shielding of Alkaline-Earth-Metal and Alkali-Metal Fluorides

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The ^{19}F NMR chemical shieldings of solid-state alkaline-earth-metal fluorides MF_2 (M = Be, Mg, Ca, Sr, Ba) and alkali-metal fluorides MF (M = Li, Na, K, Rb, Cs) were systematically studied by the gauge-independent atomic orbital (GIAO) method at the level of density functional theory (DFT). The 6-311+G(d) basis set was used for the inspected fluoride ion. The performance of the effective core potentials (ECP) of LanL2DZ and CRENBL basis sets for metal atoms were compared to 3-21G all-electron basis set. The role of d polarization functions for metal atoms is investigated. The results show that the clusters $[FMg_3F_9]^{4-}$, $[FM_4F_6]^{+}$ (M = Ca, Sr, Ba), and $[FM_6]^{5+}$ (M = Li, Na, K, Rb, Cs) used to model the bulk solids are reasonable. The electrons in the next outermost shell of metal atoms have significant influence on the ^{19}F NMR calculations and should be treated as valence electrons together with the electrons in the outermost shell, while the remaining electrons can be represented by the ECP of CRENBL basis set. When the CRENBL basis set (with ECP for core electrons) supplemented with two sets of d polarization functions was used for the metal atoms, the approach of locally dense basis sets can be used to successfully reproduce the ^{19}F shielding values. Since only the inspected resonant fluorine atom needs a high-grade all-electron basis set, it is a relatively inexpensive means of obtaining reliable shielding properties for the inspected species. In addition, the different exchange-correlation functional implemented in hybrid DFT method has a minor influence on the calculated shielding. Although all the calculated results are somewhat overestimated, the correlation coefficients and the slopes of the fitting lines between the theoretical predictions and experimental observations are close to unity, indicating the good agreement of the theoretical results to the experimental values.

1. Introduction

By virtue of high signal sensitivity, large range of chemical shift, and large value of spin coupling constant, fluorine is an ideal nucleus for NMR investigation. Information concerning local geometry, chemical environment, intermolecular bonding, and dynamic processes of some fluorine atoms in fluorides may be extracted from ^{19}F NMR spectra. One kind of fluoride in which NMR researchers are interested is inorganic fluoride acting as important catalyst and/or supported reagent. Since a catalyst in the practical case is normally used in solid state and its activity is closely related to its local structure, solid-state NMR techniques are required in order to provide relevant information. This is particularly important for ionic species because the change of their local structures is likely great on going from solid state to solution state. The development of NMR techniques has made it possible to obtain isotropic chemical shift of compounds in solid state as well as in liquid state.[1,2] A lot of solid state ^{19}F NMR data have been reported for inorganic fluorides.[1−3] On the other hand, theoretical and computational chemistry plays an important role in understanding, explaining, and predicting experimental results. A comparison between experimental and calculated data may be helpful in making correct assignments and understanding the relationship between chemical shielding and molecular structure. The area of theoretical and computational chemistry dealing with NMR properties is blossoming, allowing the investigations of the influence of environment on the NMR properties of inspected resonant nucleus from first principles.[4−6] Recently, more and more theoretical studies on ^{19}F NMR properties have been performed, and generally satisfactory results have been achieved [see, for examples, refs 7−16]. However, most of these studies have been concentrated on metal-free organic fluorides. To date, only a few ab initio calculations have been carried out on metal fluorides, owning to the greater computational challenges of metal fluorides.[7,9,12] Since metal fluorides are important materials in practical application, they are worth to investigate not only experimentally but also theoretically. In our previous paper, we performed an ab initio computational study on the ^{19}F chemical shielding of alkali-metal fluorides MF (M = Li, Na, K, Rb) and obtained favorable results.[9] In this paper, we extend our study of ^{19}F chemical shielding to a more complicated series: alkaline-earth-metal fluorides MF_2 (M = Be, Mg, Ca, Sr, Ba), which has not been investigated theoretically from first principles yet.

As there is not a good all-electron basis set for barium, the effective core potential (ECP) is applied in order to take the whole series into account. Compared to all-electron basis set, ECP accounts for relativistic effects to some extent. It is believed that relativistic effects will become important for the elements from the fourth row of the periodic table. Therefore, ECP may

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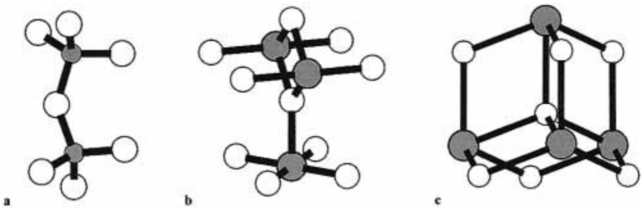

Figure 1. Cluster models of BeF_2 (a), MgF_2 (b), and MF_2 (M = Ca, Sr, Ba) (c) used in calculations. F^-, empty spheres; M^{2+}, filled spheres.

provide better result than all-electron basis set does when nonrelativistic calculation is performed for heavy metal compounds. Though ECP has been used widely for transition metal compounds in the investigation of NMR properties,[5] little experience has been gained about alkali-metal and alkaline-earth-metal compounds. Does ECP (with valence basis set) work well in describing the first two columns of the periodic table when NMR properties are concerned? Are there any differences resulting from different ECPs? We will find the answer in this work by exploring the influence of different basis set combinations, including basis set of all-electron and basis set with ECP, on the calculated ^{19}F shielding values of metal fluorides. Additionally, the employment of ECP implies the application of the approach of locally dense basis set. The approach of locally dense basis set means that the inspected resonant atom (and its neighboring atoms if necessary) is represented by a large number of basis functions, while the remaining atoms are represented by smaller basis sets. This method has been successfully used in the calculations of NMR shielding constants and chemical shifts of resonant nuclei such as ^{13}C, ^{15}N, ^{17}O, and ^{31}P in organic compounds at the levels of Hartree−Fock (HF) and the second-order Møller−Plesset (MP2) perturbation theories, respectively.[17,18] However, organic or inorganic fluorides have not yet been studied by this approach at density functional theory (DFT) level.[19] As methods based on DFT have shown their advantages in theoretical computations, e.g., they yield close results to those of MP2 with significant reduction of CPU time, the another purpose of this work is to see whether the approach of the locally dense basis set is valid at DFT level for fluorides in this work. In addition, we will discuss the effect of different hybrid DFT methods on the calculated results. On the basis of the results of MF_2, some new calculations will be performed for alkali-metal fluorides MF (M = Li, Na, K, Rb, Cs).

2. Computational Method

BeF_2 is reported to crystallize in the structure of α-quartz with space group $P3_221$ at room temperature.[19] The model cluster adopted is $[FBe_2F_6]^{3-}$ as shown in Figure 1a. Seven F^- atoms form two slightly distorted tetrahedra sharing an apex, and each Be atom lies near one of the centers of the tetrahedra. The average Be−F distance is 0.1543 nm. A $[FMg_3F_9]^{4-}$ cluster as shown in Figure 1b was used to represent the fluoride ion and its environment in solid-state MgF_2, which has the tetragonal rutile structure. The interionic distances were taken from its bulk solid with the lattice parameters $a = b = 0.4623$ nm and $c = 0.3052$ nm. The central F^- ion locates near the center of the triangle formed by three coordinated Mg^{2+} ions. The line connecting the central F^- ion and its nearest neighboring F^- ion bisects the shorter edge of the triangle. This FMg_3F cluster is of a planar structure. The remaining eight F^- ions are divided into two groups. Each group forms a plane perpendicular to the plane of FMg_3F. For cubic MF_2 (M = Ca, Sr, Ba) with CaF_2 structure type and lattice parameters 0.5463, 0.5800, and 0.6260 nm, respectively, a $[FM_4F_6]^+$ cluster shown in Figure 1c was employed as a model. The four nearest neighboring metal ions coordinated to the central F^- ion form a tetrahedron. The six outer fluoride ions are arranged to surround the central F^- ion in such a way that they form an octahedron. A $[FM_6]^{5+}$ cluster as described in our previous report[9] was used to model the alkali-metal fluorides. The six metal ions around the central F^- ion form an octahedron. The lattice parameters of MF (M = Li, Na, K, Rb, Cs) are 0.4018, 0.4614, 0.5328, 0.5630, and 0.6010 nm, respectively.

The method employed to calculate the ^{19}F NMR chemical shielding of the central fluorine atom is gauge-independent atomic orbital (GIAO)[20] as implemented in the Gaussian 98 package.[21] Our previous results[9] showed that B3LYP[22,23] gave better results than HF and was easier to converge than pure DFT method in self-consistent iteration. Therefore, B3LYP method was utilized in this study. In addition, using the $[FCa_4F_6]^+$ cluster, other hybrid DFT methods (B3P86,[22,24] B3PW91,[22,25] B1LYP,[23,26] and MPW1PW91[25,27]) were tested to study the influence of different hybrid schemes and approximate exchange-correlation functionals on the calculated result.

For the B3LYP study, the following basis set combinations were used: basis **I**, fluorine atoms 6-311+G(d) and metal atoms 3-21G; basis **II**, fluorine atoms 6-311+G(d) and metal atoms LanL2DZ (Be (10s,5p)/[3s,2p], Mg (3s,3p)/[2s,2p], Ca (8s,5p)/[3s,3p], and Sr and Ba (8s,6p)/[3s,3p], with ECP for core electrons except Be); basis **III**, except for the central fluorine atom to which 6-311+G(d) was applied, LanL2DZ was used for all other atoms (F (10s,5p)/[3s,2p] without ECP); basis **IV**, the same as basis **III**, but LanL2DZ of the metal atoms was replaced by CRENBL (Li and Be (4s,4p), Na and Mg (6s,4p), K and Ca (5s,4p), Rb and Sr (5s,5p), and Cs and Ba (5s,5p,4d), with ECP for core electrons except for Li and Be);[28−30] basis **V**, the same as basis **IV** except that two sets of d polarization functions were added to the valence basis sets of the metal atoms other than Ba for which no polarization functions are available,[31−33] i.e., Li and Be (4s,4p,2d), Na and Mg (6s,4p,2d), K and Ca (5s,4p,2d), Rb and Sr (5s,5p,2d), Cs (5s,5p,6d), and Ba (5s,5p,4d). The construction of two sets of d polarization functions from a single d function (for Rb, Sr, and Cs) was based on the even scaling rule suggested by Frisch and co-workers,[31] where the single exponent in the single d function was replaced by two exponents, one twice as large and one-half as large as the original exponent. Only basis **V** was used for other hybrid DFT calculations of CaF_2. For comparison, some new calculations were performed for the ^{19}F chemical shieldings of MF using basis **I**, **IV**, and **V**.

3. Results and Discussion

The calculated isotropic ^{19}F chemical shieldings of the alkaline-earth-metal fluorides using different basis set combinations were listed in Table 1. For a consistent comparison, all the experimental results were taken from the most recent measurements using magic-angle-spinning (MAS) technique at a spinning rate of 15 kHz and converted to the absolute shieldings by the conversion factor $\sigma_{C_6F_6} = 353$ ppm.[3] The theoretical results of ref 3 were also presented in Table 1 for comparison.

First, consider the results of MF_2 (M = Mg, Ca, Sr) obtained from basis **I** in the B3LYP scheme. For CaF_2 and SrF_2 (see Table 1), the discrepancies of absolute shieldings between the theoretical predictions and experimental observations, σ_{diff}, are almost the same and somewhat larger than those in the case of

TABLE 1: Experimental and Calculated Values of ^{19}F Chemical Shielding of Alkaline-Earth-Metal Fluorides (ppm)[a]

	α-BeF_2	MgF_2	CaF_2	SrF_2	BaF_2
			Exp.[3]		
σ_{exp}		382	295	272	200
			Basis **I**		
σ_{cal}	383	390	354	332	
σ_{diff}		8	59	60	
			Basis **II**		
σ_{cal}	381	415	352	336	306
σ_{diff}		33	57	64	106
			Basis **III**		
σ_{cal}	387	425	345	327	294
σ_{diff}		43	50	55	94
			Basis **IV**		
σ_{cal}	383	408	346	336	221
σ_{diff}		26	51	64	21
			Basis **V**		
σ_{cal}	380	392	303	299	221
σ_{diff}		10	8	27	21
			ref 3		
σ_{cal}		411	310	–	206
σ_{diff}		29	15	–	6

[a] See text for the definition of the basis sets and the clusters used to model bulk solid. Note that basis **V** used for BaF_2 is the same as basis **IV**. σ_{cal} and σ_{exp} represent the calculated and experimental absolute shieldings, respectively. The experimental values have been converted to absolute shieldings by using the conversion factor $\sigma_{C_6F_6} = 353$ ppm. $\sigma_{diff} = \sigma_{cal} - \sigma_{exp}$.

alkali-metal fluorides[9] (59 and 60 ppm, respectively, compared to 30−50 ppm of MF). For MgF_2, the σ_{diff} value is only 8 ppm, indicating a good agreement of the calculated absolute shielding to the experimental observation.

Because no 3-21G basis set exists for Ba, basis **II** was employed in order to investigate the chemical shieldings of the whole series. The results show that there are only minor changes in the absolute shieldings of CaF_2 and SrF_2 (change by −2 and 4 ppm, respectively). This implies that the LanL2DZ basis set (valence basis set with ECP) for Ca and Sr is comparable to the 3-21G all-electron basis set in the study of ^{19}F chemical shieldings of CaF_2 and SrF_2. However, the discrepancy of MgF_2 between the calculated absolute shielding and experimental measurement becomes large although its value (33 ppm) is still smaller than those of CaF_2 and SrF_2. Moreover, the result of BaF_2 is quite poor: the σ_{diff} value is more than 100 ppm, a 53% overestimate of the shielding.

If the larger basis set, 6-311+G(d), for all the next-nearest F atoms was replaced by a smaller one, LanL2DZ, i.e., basis **III** is used, the variation of ^{19}F absolute shieldings from basis **II** is in the range of 7−12 ppm. Except for MgF_2, the results from basis **III** are even slightly better than those from basis **II**. Therefore, the grade of the basis set for the next-nearest fluoride ions can be lowered from 6-311+G(d) to LanL2DZ with little loss of accuracy. For the sake of time saving, the smaller basis set, LanL2DZ, was used for outer fluorine atoms in the following study.

Compared to the results of MgF_2 from basis **I**, the results from basis **II** and **III** became poor. Undoubtedly, this is due to the LanL2DZ basis set of Mg. Analyzing the LanL2DZ basis set carefully, we found that only the two outermost electrons of Mg atom are treated as valence electrons while the remaining 10 electrons in inner shells are described by ECP. However, there are 10 valence electrons beyond ECP for the other alkaline-earth-metal atoms. Fewer valence electrons for Mg in the LanL2DZ basis set may make it less suitable to describe the interactions between Mg^{2+} and F^-, as pointed out by Schreckenbach and Ziegler in the study of the frozen-core approximation.[34] A basis set of Mg in which ECP represents two 1s electrons only may be helpful for improving the results. To verify this point, we tried the basis set CRENBL that satisfies this requirement. Using CRENBL instead of LanL2DZ in basis **III** (i.e., basis **IV**), we obtain a $\sigma_{diff} = 26$ ppm for MgF_2, which is a better than $\sigma_{diff} = 43$ ppm that produced by basis **III**. This indicates the importance of the definition of the core electron number. On the other hand, both the results of CaF_2 and SrF_2 from basis **IV** are close to those from basis **III**, demonstrating little influence of basis set variation. Interestingly, the calculated result of BaF_2 is remarkably improved (decrease by 73 ppm compared to basis **III**) and thus in the best agreement with the experimental value among the alkaline-earth-metal fluorides. What is the reason?

After examining the difference between the components of the LanL2DZ and CRENBL basis sets of these metal atoms, we supposed that the d functions in the CRENBL basis set of Ba may play an important role in improving the calculated results. On the basis of this assumption, a Huzinaga single d polarization function was added to the valence basis set of Ca in basis **IV**. The calculated ^{19}F shielding of CaF_2 is 346 ppm. It seems that d function makes little contribution to the shielding. However, by adding two sets of Pople d polarization functions to the valence basis set of Ca (basis **V**), the ^{19}F shielding value becomes 303 ppm, which is only 8 ppm larger than the experimental observation and much less than the 346 ppm of basis **IV**. The σ_{diff} value of MgF_2 is also reduced to 10 ppm when basis **V** is employed. The larger reduction of the calculated shielding of CaF_2 than that of MgF_2 implies the greater effect of d functions on the heavier metal atom. As there are no Pople double d polarization functions available for Sr, we constructed two sets of d polarization functions from the exponent of Huzinaga d polarization function.[31] The result was remarkably improved as well. All these results illustrate the importance of d functions in proper representations of the valence wave functions of the metal atoms. At least two sets of d polarization functions are desired for the metal atoms to describe the NMR properties of MF_2 and MF (see following discussion) accurately. Naturally, f functions may be helpful for further improvement of the theoretical results of BaF_2 as well as SrF_2.

To investigate whether d polarization functions have the same effect on the other basis sets, the same sets of d polarization functions were added to the 3-21G and LanL2DZ basis sets of Mg and Ca in basis **I** and **III**, respectively. The results show a similar effect as those in basis **V**. The calculated shieldings are 299 and 302 ppm for CaF_2 and 384 and 416 ppm for MgF_2, respectively. The larger shielding of MgF_2 from LanL2DZ (416 ppm) results from the fewer valence electrons described by the valence basis set, as we have discussed above. These results demonstrate that the influence of the augmented d polarization functions is independent of the basis set used. Moreover, they imply that an appropriate description of valence atomic orbits is very important for the atoms nearest to the inspected resonant nucleus.

The other accessible basis sets with ECP representing 46 core electrons of Ba: Hay-Wadt MB ($n + 1$) ECP,[34] Hay-Wadt VDZ ($n + 1$) ECP,[35] and Stuttgart RSC ECP,[36] were also examined when the basis sets of fluorine atoms were kept unchanged (i.e., in the frame of basis **IV**). The results show that the basis set with Stuttgart RSC ECP tends to underestimate the shielding ($\sigma_{cal} = 152$ ppm), while the other two basis sets yield the same result as the LanL2DZ basis set does. Therefore, the CRENBL basis set produces the most reasonable result for BaF_2 using the present model under our consideration.

As we have shown, d polarization functions play a significant role in properly describing the valence wave functions of the metal atoms. Does it hold for fluorine atom? In the frame of basis **V**, when the number of d polarization functions in the basis set of the central fluorine atom is either zero or two (6-311+G and 6-311+G(2d), respectively), the calculated shielding of CaF_2 is 303 ppm, the same as that of basis **V**. It means that the role of the d polarization functions of fluorine atoms can be left out in our calculations. In fact, diffuse function is more important for a correct description of the central fluorine atom. Using 6-311G(d) instead of 6-311+G(d) for the central fluorine atom, the calculated shielding increases to 328 ppm. However, the calculated shielding of the central fluorine atom is the same when the diffuse function was added to the LanL2DZ basis set of the outer fluorine atoms. These reveal that only the central fluorine atom requires a high-grade basis set and that the LanL2DZ basis set is qualified for outer fluorine atoms, as has been validated by the small variation of the calculated shieldings from basis **II** to **III**.

By now, we have not mentioned the results of BeF_2. To the best of our knowledge, no ^{19}F NMR experimental data for crystalline BeF_2 have been reported. Therefore, comparison can only be carried out among the theoretical results obtained from the different basis set combinations. Apparently, these results are close to each other (see Table 1). This is easy to understand. As we have discussed above, the qualities of the different basis set combinations mainly depend on the different settings of the number of electrons described by the valence basis sets (all electron, 2 or 10) and the number of d polarization functions in the valence basis sets (0 or 2) of the metal atoms. For BeF_2, all the calculations are actually all-electron ones, and the d polarization functions have little influence on the calculated results of fluorides containing the metal atoms belonging to the first row of the periodic table (see also LiF in the following section).

Considering all basis set combinations investigated, our results indicate that the approach of the locally dense basis set is suitable for the study of alkaline-earth-metal fluorides, i.e., one can use an appropriate large basis set for the fluorine atom of which the chemical shielding is investigated, while lowering the requirement for the basis sets describing the surrounding atoms. The basis set representing core electrons by ECP is a good choice for metal atoms. Besides saving CPU time, it supplements the shortage of good all-electron basis sets for heavier metal atoms and can be used in nonrelativistic calculations. However, care must be taken in determining the core electron number. On the other hand, additional proper sets of d polarization functions to the valence basis sets can improve the results notably. Among the five basis set combinations investigated, basis **V** gives the closest calculated results to the experimental measurements. Concerning the complexity in theoretical treatments of fluorine as well as heavy metal atoms, the calculated results from basis **V** are quite acceptable. The larger deviations between the theoretical and experimental shieldings for SrF_2 and BaF_2 may be partly due to spin−orbit coupling. The effects of spin−orbit coupling on NMR properties are supposed to become pronounced for light atoms bonded directly to heavy atoms.[4,5,37,38] In such a case, spin−orbit coupling on heavy atom is transferred to light atom through chemical bond. It depends strongly on the involvement of valence s orbitals of the inspected atom in bonding to the heavy atom.

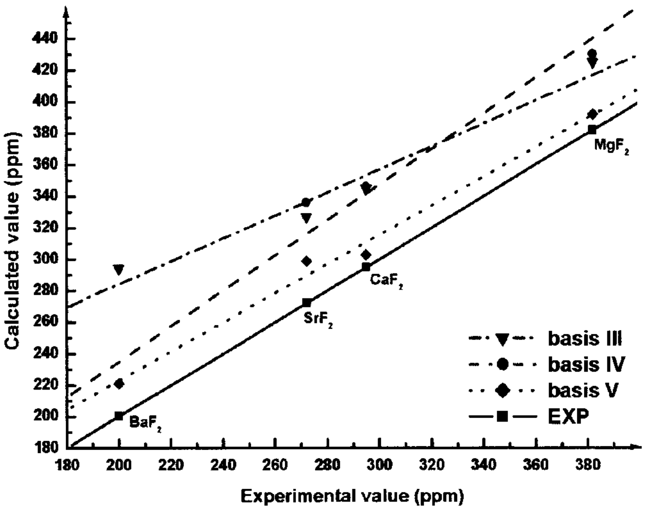

Figure 2. Comparison between theoretical and experimental results of ^{19}F chemical shielding for alkaline-earth-metal fluorides. The symbols indicate the experimental or theoretical values, and the lines represent the linear fitting of the data.

The relationships between the theoretical and experimental chemical shieldings can be seen easily from Figure 2, where the three sets of theoretical values obtained using basis **III**−**V** are linearly fitted to the experimental values. The linear regression equations can be expressed as

$$\text{Basis } \mathbf{III}: \quad \sigma_{\text{cal}} = 0.73\sigma_{\text{exp}} + 138.4 \tag{1}$$

$$\text{Basis } \mathbf{IV}: \quad \sigma_{\text{cal}} = 1.13\sigma_{\text{exp}} + 9.7 \tag{2}$$

$$\text{Basis } \mathbf{V}: \quad \sigma_{\text{cal}} = 0.93\sigma_{\text{exp}} + 37.5 \tag{3}$$

The experimental line in Figure 2, EXP: $\sigma_{\text{cal}} = \sigma_{\text{exp}}$, is represented by solid line. The correlation coefficients for eqs 1−3 are 0.982, 0.984, and 0.995, respectively. They are all close to unity. The correlation coefficient can be taken as an index to characterize the quality of the calculated results.[15] The near unity values indicate good correlativities between the theoretical and experimental results. On the other hand, the slopes of the fitting lines change from one case to another (0.73, 1.13, and 0.93, respectively). The closer to unity it is, the better the parallel relationship is between the fitting line and the experimental line, i.e., the more similar the variation trend is between the fitting shieldings and the experimental measurements. Obviously, basis **V** gives the best results whether judged from the correlation coefficients or the slopes of the fitting lines. On the basis of the good correlativity of our results, the ^{19}F NMR experimental shielding of crystalline BeF_2 predicted from eq 3 approximates 368 ppm. It is 14 ppm smaller than the experimental value of MgF_2, similar to the relationship between LiF and NaF. This prediction value needs experimental verification in future.

Recently, Bureau et al. presented an empirical calculation of ^{19}F chemical shieldings of a large number of inorganic fluorides based on Ramsey's theory using Löwdin molecular orbitals.[3] In their calculations, the ^{19}F chemical shielding was calculated as a summation of contributions over its surrounding cation neighbors, and some parameters used were determined by fitting to the experimental measurements. Their results for alkaline-earth-metal fluorides were listed in Table 1. The comparison shows that our results from basis **V** are slightly better than those

TABLE 2: Experimental and Calculated Values of ^{19}F Chemical Shielding of Alkali-Metal Fluorides (ppm)[a]

	LiF	NaF	KF	RbF	CsF
			Exp.[3]		
σ_{exp}	390	410	318	276	195
			Basis **I**		
σ_{cal}	433	446	364	309	236
σ_{diff}	43	36	46	33	41
			Basis **IV**		
σ_{cal}	405	442	359	316	195
σ_{diff}	15	32	41	40	0
			Basis **V**		
σ_{cal}	405	437	327	284	196
σ_{diff}	15	27	9	8	1
			ref 3		
σ_{cal}	411	395	303	269	214
σ_{diff}	21	−15	−15	−7	19
			ref 7		
σ_{cal}	422	396	380	393	359
σ_{diff}	32	−14	62	117	164

[a] All symbols and definitions are the same as those in Table 1.

in ref 3 except for BaF_2. Taking into account that their results were obtained by a rather crude method, the agreement is quite satisfactory. Although ab initio method is more time-consuming compared to empirical method, it avoids the introduction of some artificial factors and the dependence on empirical parameters. Considering the model used in ref 3, it would be interesting to see if the nearest cations are enough to account for the ^{19}F NMR shielding in our calculations. Replacing $[FMg_3F_9]^{4-}$ and $[FCa_4F_6]^{+}$ by $[FMg_3]^{5+}$ and $[FCa_4]^{7+}$, respectively, the results from basis **V** are 443 and 353 ppm. They are about 50 ppm larger than those obtained from the bigger clusters. This illustrates that the $[FMg_3]^{5+}$ and $[FCa_4]^{7+}$ clusters are too small to be used for proper descriptions of the shielding properties of central F^- ions in our calculations. Therefore, unlike ref 3, the contributions to the NMR shielding of the central F^- ion from the farther anions besides the nearest neighbor cations need to be considered to get better theoretical results with present method.

On the basis of the above discussion, we used basis **V** to calculate ^{19}F NMR shieldings of CaF_2 by other hybrid DFT methods. The calculated values using B3PW91, B3P86, B1LYP, and MPW1PW91 are 304, 306, 307, and 310 ppm, respectively. These results are at the same level of accuracy as that obtained by B3LYP. It implies that the selection of exchange-correlation functional is not crucial in the hybrid DFT scheme in this study.

Now consider the alkali-metal fluorides. The calculated and observed ^{19}F chemical shieldings of the alkali-metal fluorides are summarized in Table 2. Although the σ_{diff} values of basis **I** are somewhat large, they are close to each other within the series. Therefore, when relative chemical shifts are considered in this series, the results are acceptable. For example, taking KF as a reference, the maximum deviation of the theoretical shift from the measured one is only 13 ppm. For NaF, KF, and RbF, the calculated results obtained from basis **IV** are close to those obtained from basis **I**. For LiF, the calculated result obtained from basis **IV** is much better than that from basis **I**. The reason is still unclear. Excluding LiF for which the d polarization functions of the Li atoms show no effect on the calculated result, the addition of two sets of d polarization functions to the valence basis sets of the metal atoms analogously improves the results of basis **IV** as in the case of alkaline-earth-metal fluorides. As the CRENBL basis set of Cs already has four sets of d functions, the additional two sets of d polarization functions cause almost no change in calculated shielding (σ_{cal} only increases by 1 ppm). Similar result can be predicted for BaF_2. Like MF_2, basis **V** gives the best individual results and a correct overall pattern.

Table 2 also includes the theoretical results from two recent reports. In the ab initio calculations reported by Mortimer and co-workers,[7] the metal ions were replaced by protons with valence orbitals corresponding to those of the metal atoms, and the fluorine was described by 6-311+G(3d). Obviously, their σ_{diff} values are quite large for the heavier metal fluorides. The shielding value of CsF is overestimated by more than 80%. The absolute values of σ_{diff} in the empirical calculations are close to our results using basis **V**.[3] However, if the sign of σ_{diff} is concerned, a clear difference exists: our results are all overestimated, while there is not a definite regularity for the calculated results of ref 3 (and ref 7). Similar to the case of ref 7, the calculated shielding of LiF in ref 3 is greater than that of NaF, which is contrary to the pattern of the shieldings determined experimentally.

We have pointed out that the failure of ref 7 may be mainly caused by the neglect of the core electrons of the metal atoms,[8] i.e., by taking only one electron into account for the metal atoms. Our current work on MgF_2 has shown that the electrons in the next outer shell of the Mg atoms should be treated as valence electrons together with the outermost electrons. This can be further proved by LiF. In basis **V**, if the two 1s electrons of Li are represented by ECP, the calculated shielding of LiF is 470 ppm, significantly larger than 405 ppm when the 1s electrons are handled as valence electrons. Therefore, the metal ions cannot be simply replaced by protons with valence orbitals representing the metal atoms. Now a new question arises: is the shielding property of ^{19}F only related to the electrons in the two outermost shells of the metal atoms besides the contributions from the fluorine atom itself? Using Na^+ ions instead of protons to replace the metal ions according to the method of ref 7 (actually there are two more valence electrons than the expected number: nine), we obtained 332, 275, and 261 ppm for KF, RbF, and CsF, respectively, by basis **V** without ECP. The former two values are close to those obtained using basis **V** with ECP, which implies that the contribution to the ^{19}F shielding from the core electrons of the metal atoms is minor. However, the latter shielding value is remarkably different from 196 ppm obtained using basis **V** with ECP. This may be due to the relativistic effects of the heavy metal atom Cs which was completely ignored when ECP was omitted. Therefore, ECP needs to be taken into acoount for heavy atoms although their core electrons may have little contribution to the ^{19}F shielding.

Figure 3 illustrates the linear fitting of the calculated shieldings of the alkali-metal fluorides to the experimental shieldings. The experimental line is included as well. The linear regression equations are as follows:

$$\text{Basis } \mathbf{I}: \quad \sigma_{\mathrm{cal}} = 1.00\sigma_{\mathrm{exp}} + 39.6 \tag{4}$$

$$\text{Basis } \mathbf{V}: \quad \sigma_{\mathrm{cal}} = 1.10\sigma_{\mathrm{exp}} - 20.4 \tag{5}$$

$$\text{Ref 3}: \quad \sigma_{\mathrm{cal}} = 0.94\sigma_{\mathrm{exp}} + 20.5 \tag{6}$$

$$\text{Ref 7}: \quad \sigma_{\mathrm{cal}} = 0.23\sigma_{\mathrm{exp}} + 316.5 \tag{7}$$

The correlation coefficients of eqs 4−7 are 0.998, 0.999, 0.979, and 0.876, respectively. The corresponding slopes are 1.00, 1.10, 0.94, and 0.23, respectively. The correlation coefficients and slopes of the fitting lines based on our calculated results are close to unity, indicating the good linear relationships between the theoretical predictions and experimental observations.

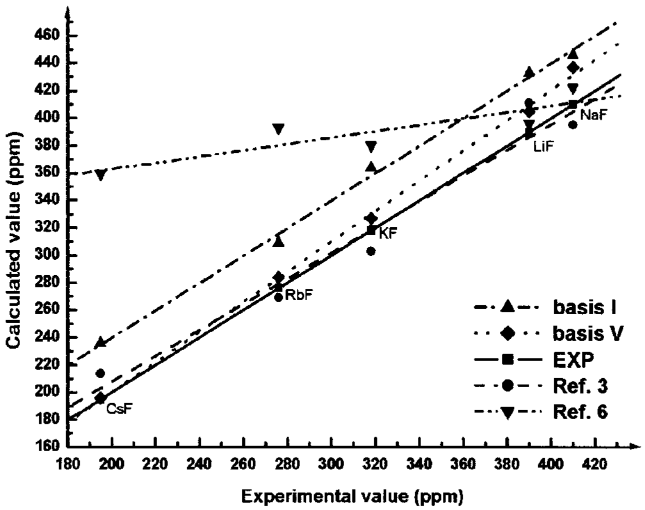

Figure 3. Comparison between theoretical and experimental results of ^{19}F chemical shielding for alkali-metal fluorides. The symbols indicate the experimental or theoretical values, and the lines represent the linear fitting of the data.

Compared to our results, the correlation coefficient and the slope of the fitting line based on the calculated results in ref 3 only somewhat deviate from unity. However, the correlation coefficient and the slope of the fitting line based on the calculated results in ref 7 obviously depart from unity, showing that the theoretical results of ref 7 are rather poor. When the whole series is concerned, the calculated results from basis **V** are the closest to the experimental ones judged from the best correlation coefficient, 0.999. The fitting line of the calculated results from basis **I** is parallel to the experimental line (slope 1.00) with good correlation coefficient 0.998. The average overestimation of the ^{19}F shieldings is 39.6 ppm by basis **I**. This value would be reduced by the addition of d polarization functions to the basis set of metal atoms.

4. Conclusions

The ^{19}F NMR chemical shieldings of solid state alkaline-earth-metal and alkali-metal fluorides are systematically studied by B3LYP method using various basis set combinations. It is the first successful effort to calculate the ^{19}F NMR chemical shieldings of alkaline-earth-metal fluorides from first principles. Our calculated results show that the models $[FMg_3F_9]^{4-}$, $[FM_4F_6]^{+}$ (M = Ca, Sr, Ba), and $[FM_6]^{5+}$ (M = Li, Na, K, Rb, Cs) can be used to reproduce the individual experimental results accurately as well as the overall patterns of the ^{19}F chemical shieldings in the same series correctly when the basis sets employed in the calculations are carefully selected. All the calculated shieldings are somewhat overestimated. The approach of locally dense basis set is adoptable in the study of these two series at DFT level, where only the central inspected fluorine atom calls for a high-grade basis set. The core electrons of the metal atoms can be well depicted by ECP including some relativistic effects for heavy atoms. Besides the advantage of saving computer resources compared to all-electron calculations, the utilization of the locally dense basis set method combined with ECP makes it possible to investigate the systems containing heavy atoms without high-level all-electron basis sets using nonrelativistic method with acceptable computational accuracy. However, the comparison of the theoretical results from the LanL2DZ and CRENBL basis sets for metal atoms show that attention must be paid to the definition of the core electron number. The electrons in the two outermost shells should be treated as valence electrons.[35] The d polarization functions of the metal atoms can significantly improve the calculated results no matter an all-electron basis set or a basis set with ECP is used. At least two sets of d functions are desired for the valence basis sets of the metal atoms to describe the phase space occupied by the valence electrons properly. Satisfying the above conditions, the CRENBL valence basis set augmented with two appropriate sets of d polarization functions plus ECP can well describe the alkaline-earth-metal and alkali-metal atoms nearest to the inspected fluorine nucleus. Using basis **V**, the predictions of the ^{19}F NMR chemical shieldings of alkaline-earth-metal and alkali-metal fluorides are satisfactory. The discrepancy of absolute shieldings between the theoretical calculations and experimental measurements are less than 30 ppm and may be partly caused by spin−orbit coupling in heavy metal fluorides. Good linear relationships exist between the theoretical and experimental results. In addition, the ^{19}F NMR shielding of crystalline BeF_2 was predicted to be roughly 368 ppm. This study will shed light on the future investigations of other complicated metal fluorides.

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