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A survey of wave function effects on theoretical calculation of gas phase ^{19}F NMR chemical shifts using factorial design

H. Shaghaghi, H. Ebrahimi, M. Tafazzoli *, M. Jalali-Heravi

Department of Chemistry, Sharif University of Technology, P. O. Box 11155-9516, Tehran, Iran

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ABSTRACT

The wave functions for calculating gas phase ^{19}F chemical shifts were optimally selected using the factorial design as a multivariate technique. The effects of electron correlation, triple-ξ valance shell, diffuse function, and polarization function on calculated ^{19}F chemical shifts were discussed. It is shown that of the four factors, electron correlation and the polarization functions affect the results significantly. B3LYP/6-31 + G(df,p) wave functions have been proposed as the best and the most efficient level of theory for calculating ^{19}F chemical shifts. An additional series of fluoro compounds were used as a test set and their predicted ^{19}F chemical shifts values confirmed the validity of the approaches.

1. Introduction

^{19}F NMR is one of the most delicate and practical branches of nuclear magnetic resonance (NMR) spectroscopy. It has been widely used in many fields particularly in biological systems due to the fact that the F nucleus, as proved by experiments, enjoys the advantage of having a naturally occurring single isotope with one-half spin. As indicated in several recent investigations, the ^{19}F chemical shift is very sensitive to the environment and this facilitates the study of structure and dynamics in simple fluorine compounds [1–4] and biological systems [5–8].

The intermolecular effects present in condensed phases can be almost eliminated in gas phases [9]. Therefore, the gas phase properties can be considered as a zero point in many fields of research such as dynamics, solvent effects and hydrogen bonding studies. Although there are very limited reports on gas phase ^{19}F nuclear magnetic resonance properties [10–13], fortunately, the properties of molecules in dilute gases more closely resemble those obtained from the theoretical calculations for single molecules. The Gauge-independent atomic orbital (GIAO) method [14] has been successfully applied to the calculations performed for NMR parameters using ab initio computation methods. The simplest type of ab initio computation is Hartree–Fock (HF) scheme, in which the instantaneous coulombic electron–electron repulsion is not specifically taken into account and only its average effect (mean field) is included in the calculation [14,15]. There are methods such as density functional theory (DFT) and Moller–Plesset perturbation theory (Mpn) [14,15] in which correction for electron–electron repulsion is also included. Theoretical results of shielding constants are very sensitive to the selected calculation method as well as the basis sets. Fukaya and Ono [16] have calculated ^{19}F chemical shifts for different kinds of perfluoro compounds in different levels of theories, but they have compared their results with the experimental data of ^{19}F chemical shifts in solution phase. These researchers also have reported that B3LYP/6-31++G(d,p) with 10 ppm deviation is the best level for the ^{19}F chemical shifts calculation.

The factorial design has been utilized in many surveys as a multivariate method to find the best level of theory [17–22]. This statistical method allows discovering the most significant variables for a certain system with only few experiments [23,24]. In the present study, a factorial design was used for studying the effects of calculation methods and basis sets on ^{19}F chemical shifts. The main aim of the present contribution was developing a general optimum level of theory for calculating ^{19}F chemical shifts. This can be justified due to limited availability of experimental values for ^{19}F chemical shifts in gas phase. The results are promising and a level of theory with a minimum absolute deviation is proposed for each molecule.

2. Results and discussion

2.1. 2^4 factorial designs

In order to determine the optimum wave functions and calculational methods two 2^4 factorial designs were considered.

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* Corresponding author. Tel.: +98 21 66005718; fax: +98 21 66012983.
E-mail address: tafazzoli@sharif.edu (M. Tafazzoli).

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Based on preliminary experiences [17,18], for factors of electron correlation treatment (A), triple-ξ valance shell (B), diffuse function(C), and polarization function (D) were selected [14,15]. Each factor was considered at two levels, with (+) being denoted for inclusion (high level) and (−) for no inclusion (low level). Table 1 illustrates the two design matrices with different levels of theory. The only difference between the two designs I and II is the fact that in the former, density functional correlation (B3LYP) was used for the factor A, while second-order Møller–Plesset perturbation correction (MP2) was used as a high level in the latter. As illustrated in Table 1, there are 16 levels of theory for calculating the magnetic properties in each design. The structures of all selected compounds studied in this work were optimized using MP2/aug-cc-pVDZ level of theory. The magnetic properties were computed in 24 different levels of theory for each compound. GIAO method was applied to compute the shielding tensors. A total of 96 calculations was performed for these designs in addition to 24 calculations for tetrafluorosilane (SiF_4), which was considered as standard reference for the chemical shifts calculations. Chemical shifts for each fluorine nuclei, δ_i, were referred to SiF_4, for which the shielding was calculated at the same theoretical levels, using (Eq. (1)),

$$\delta_i = \sigma_{\text{standard}} - \sigma_i \tag{1}$$

where σ_i stands for the shielding tensor obtained using GIAO method. The Gaussian 98 package [25] was used to perform all the calculations. Experimental ^{19}F chemical shifts were obtained from Ref. [10]. For each compound, the calculated values were compared with the experimental ones and the absolute deviation (AD) was determined afterwards. In these designs, AD was considered as a response. This means that the best level of factors was chosen when AD has been minimized.

All the effects and interactions were plotted on a normal probability paper so that the most significant ones could be found. In the normal plot method, most of the negligible effects fall on a straight line, whereas the significant ones do not. Design Expert version 6.0.10 was used in this study to plot the effects. A complete description of the procedure for determining the effects and plots could be found in Refs. [23,24].

To assess the effect of polarization and diffuse functions on the results, more computations were performed for each compound with the polarization function factor at a (df,p) level and diffuse function at the ++ level. All 48 levels of theory were applied to

Table 1
2^4 factorial design.

Design I						Design II					
No.	Level of theory	A	B	C	D	No.	Level of theory	A	B	C	D
1	HF/6-31G	−	−	−	−	1	HF/6-31G	−	−	−	−
2	B3LYP/6-31G	+	−	−	−	2	MP2/6-31G	+	−	−	−
3	HF/6-311G	−	+	−	−	3	HF/6-311G	−	+	−	−
4	B3LYP/6-311G	+	+	−	−	4	MP2/6-311G	+	+	−	−
5	HF/6-31+G	−	−	+	−	5	HF/6-31+G	−	−	+	−
6	B3LYP/6-31+G	+	−	+	−	6	MP2/6-31+G	+	−	+	−
7	HF/6-311+G	−	+	+	−	7	HF/6-311+G	−	+	+	−
8	B3LYP/6-311+G	+	+	+	−	8	MP2/6-311+G	+	+	+	−
9	HF/6-31G(d,p)	−	−	−	+	9	HF/6-31G(d,p)	−	−	−	+
10	B3LYP/6-31G(d,p)	+	−	−	+	10	MP2/6-31G(d,p)	+	−	−	+
11	HF/6-311G(d,p)	−	+	−	+	11	HF/6-311G(d,p)	−	+	−	+
12	B3LYP/6-311G(d,p)	+	+	−	+	12	MP2/6-311G(d,p)	+	+	−	+
13	HF/6-31+G(d,p)	−	−	+	+	13	HF/6-31+G(d,p)	−	−	+	+
14	B3LYP/6-31+G(d,p)	+	−	+	+	14	MP2/6-31+G(d,p)	+	−	+	+
15	HF/6-311+G(d,p)	−	+	+	+	15	HF/6-311+G(d,p)	−	+	+	+
16	B3LYP/6-311+G(d,p)	+	+	+	+	16	MP2/6-311+G(d,p)	+	+	+	+

Table 2
Theoretical values of ^{19}F chemical shifts of fluoromethane using different basis sets together with their absolute deviation values.

Basis set	HF		B3LYP		MP2	
	CS[a]	AD[b]	CS[a]	AD[b]	CS[a]	AD[b]
6-31G	−93.93	13.78	−101.48	6.23	−91.78	15.93
6-311G	−92.19	15.52	−102.62	5.09	−91.61	16.10
6-31+G	−92.09	15.62	−103.90	3.81	−94.52	13.19
6-311+G	−86.80	20.91	−101.49	6.22	−81.96	25.75
6-31G(d,p)	−106.60	1.11	−109.35	1.64	−104.10	3.61
6-311G(d,p)	−109.30	1.59	−118.34	10.63	−109.79	2.08
6-31+G(d,p)	−102.24	5.47	−109.18	1.47	−103.36	4.35
6-311+G(d,p)	−102.00	5.71	−115.81	8.10	−101.24	6.47
6-31G(df,p)	−104.52	3.19	−105.88	1.83	−98.92	8.79
6-311G(df,p)	−107.96	0.25	−115.07	7.36	−103.16	4.55
6-31+G(df,p)	−101.09	6.62	−105.74	1.97	−98.30	9.41
6-311+G(df,p)	−103.77	3.94	−113.80	6.09	–	–
6-31++G	−92.18	15.53	−103.69	4.02	−94.03	13.68
6-311++G	−86.40	21.31	−100.90	6.81	−90.29	17.42
6-31++G(d,p)	−102.53	5.18	−109.32	1.61	−103.51	4.2
6-311++G(d,p)	−100.60	7.11	−114.81	7.1	–	–

[a] CS = ^{19}F chemical shift.

[b] AD = the absolute deviation from −107.71 (experimental value [10]).

compute the ^{19}F chemical shifts for a set of 15 molecules; accordingly, the level with the minimum absolute deviation was determined.

2.2. Plots analysis

The ^{19}F nuclear magnetic chemical shifts of fluoromethane (CH_3F) were calculated as a sample, using 46 different levels of theory and the results are given in Table 2. These calculations were performed using GIAO method. Deviations from the experimental values for these chemical shifts demonstrate that ^{19}F nuclear magnetic chemical shifts are very sensitive to the method of calculation and also to the basis set. The absolute deviation varies from 25.75 ppm for MP2/6-311+G level to 0.25 ppm for HF/6-311G(df,p) level. As illustrated in this table, there is no correlation between the minimum AD and the highest level of theory. We were not able to calculate the shielding constant for SiF_4 at the MP2/6-311+G(df,p) and MP2/6-311++G(d,p) levels of theory. It seems that applying a high MP2 computational level for molecules has been restricted by the number of fluorine nuclei and the size of the molecule and calculation ^{19}F chemical shifts of CF3CF3 and CF_3CF_2Cl stopped at MP2/6-31G(d,p) level.

The absolute deviation of ^{19}F chemical shifts of four typical fluoro compounds was obtained using 32 different levels of theory based on two 2^4 factorial designs given in Table 1. To have a straight line in the normal plots, the following points have been taken into account: the model should be a significant one; there should be as many points as possible located on the line; and the model should have the least residuals. In these plots, the points located along a straight line have no significant effects while the

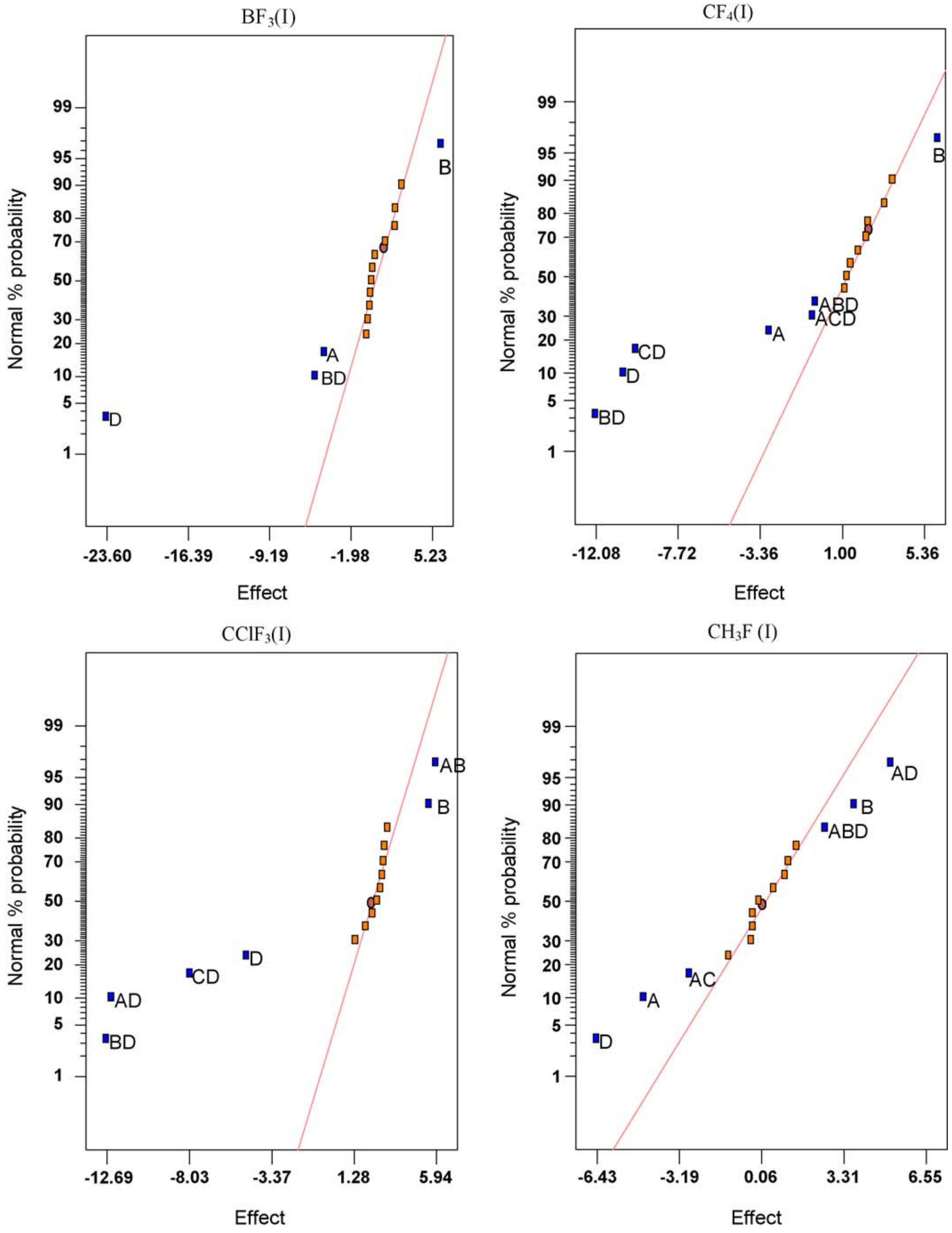

Fig. 1. Normal plots for ^{19}F chemical shift values using GIAO based on design I given in Table 1.

ones off the line correspond to the factors affecting the calculated ^{19}F chemical shifts most significantly. A detailed description of how to analyze the normal plots could be found elsewhere [23,24].

2.2.1. Design I

Fig. 1 shows four normal plots of ^{19}F chemical shifts based on the 2^4 factorial design I given in Table 1. We may well notice that factor D (polarization function), as indicated in Fig. 1, decreases the absolute deviation in all trifluoroborane (BF_3), tetrafluoromethane (CF_4), chloro-trifluoro-methane ($CClF_3$), and fluoromethane (CH_3F) molecules. Electron correlation factor (factor A) also decreases the absolute deviation in BF_3, CF_4, and CH_3F. As for the $CClF_3$ molecule, despite the fact that factor A is located along the straight line, its interaction with polarization function (factor AD) has led into a large reduction in the absolute deviation. Therefore, the inclusion of polarization function and electron correlation factors is necessary for having a correct calculation of ^{19}F chemical shifts. Similarly, although the diffuse function factor (factor C) is located along the straight line in all four molecules, the analyses of its interaction with factor D in CF_4 and $CClF_3$ molecules and with factor AC in CH_3F molecule produce a significant effect on decreasing the absolute deviation. Moreover, there is no interaction for diffuse function factor, the absolute deviation increases. Therefore, one may conclude that it is important to use a diffuse function in order to have a reliable calculation of ^{19}F chemical shifts. Triple-ξ valence shell (factor B) has a complex behavior and it increases the absolute deviation in all four molecules. However, the change is not considerable. Also, the interaction factor BD reduces the absolute deviation in BF_3, CF_4, and $CClF_3$ molecules. According to what was mentioned above, two levels of B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p) can be considered in calculating ^{19}F chemical shifts. Table 3 presents the experimental values of ^{19}F chemical shifts for BF_3, CF_4, $CClF_3$, and CH_3F along with the values calculated using B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p) levels of theory. Comparison of root mean square errors (RMS) for these two levels illustrates that triple-ξ valence shell factor increases the absolute deviation. Therefore, 6-31G should be considered for calculating ^{19}F chemical shifts. Accordingly, B3LYP/6-31+G (d,p) would be recommended as an optimum level of theory.

Since the factors of polarization and diffuse functions had a significant effect on reducing the absolute deviation, ^{19}F chemical shifts were calculated at B3LYP/6-31+G(df,p) and B3LYP/6-31++G(d,p) levels. The values calculated for BF_3, CF_4, $CClF_3$, and CH_3F molecules using these levels are given in Table 3. When polarization function level being promoted from (d,p) to (df,p), the RMS values illustrate a significant decrease; but using a higher level for diffuse function factor does not lead to a considerable change in the RMS error.

To assess the reliability of the wave functions and the method itself, the ^{19}F chemical shifts for 6 molecules were calculated using B3LYP/6-31+G(d,p) and B3LYP/6-31+G(df,p) levels, and the results, as presented in Table 4, were compared with the experimental values. The absolute deviations vary from 2.13 to 7.16 for CF_2Cl_2 and CF_3CF_3 respectively at B3LYP/6-31+G(d,p) level and from 0.49 to 5.44 for these molecules at B3LYP/6-31+G(df,p) level of theory. With (df,p) level being used for polarization function (factor D), the total RMS error decreases from 5.08 for B3LYP/6-31+G(d,p) to 3.8 for B3LYP/6-31+G(df,p).

2.2.2. Design II

Fig. 2 shows four normal plots of ^{19}F chemical shifts based on the 2^4 factorial design II given in Table 1. This figure demonstrates that polarization function (factor D) decreases the absolute deviation for all four molecules, as it does in design I. Factor A (electron correlation) also decreases the absolute deviation in CF_4

Table 3
Comparison of results of three different levels of theory obtained from design I and two levels of theory obtained from design II.

No.	Molecule	Calc.[a]	Calc.[b]	Calc.[c]	Calc.[d]	Calc.[e]	Calc.[f]	Exp.[g]
1	BF_3	44.03	32.18	34.88	32.18	41.52	47.15	36.02
2	CF_4	113.90	97.78	98.52	97.78	98.06	117.55	104.21
3	CF_3Cl	151.72	133.70	134.83	133.70	137.36	153.93	138.77
4	CH_3F	−115.81	−109.18	−105.74	−109.32	−109.79	−101.24	−107.71
RMS error	9.89	4.58	3.64	4.60	4.30	12.00		

[a] B3LYP/6-311+G(d,p).
[b] B3LYP/6-31+G(d,p).
[c] B3LYP/6-31+G(df,p).
[d] B3LYP/6-31++G(d,p).
[e] MP2/6-311G(d,p).
[f] MP2/6-311+G(d,p).
[g] Ref. [10].

Table 4
Experimental and theoretical ^{19}F chemical shifts values for the test molecules.

No.	Molecule	Calc.[a]		Calc.[b]		Calc.[c]		Exp.[d]
		CS[e]	AD[f]	CS[e]	AD[f]	CS[e]	AD[f]	
1	CF_3Br	145.52	3.79	146.01	3.30	147.07	2.24	149.31
2	CF_2Cl_2	158.40	2.13	160.04	0.49	158.08	2.45	160.53
3	CF_3H	82.33	6.73	83.92	5.14	81.73	7.33	89.06
4	CF_2ClH	91.59	4.29	93.69	2.19	90.34	5.54	95.88
5	$\mathrm{C}\mathit{F}_3\mathrm{CF_2Cl}$	74.18	7.07	75.77	5.48	–	–	81.25
6	$\mathrm{CF_3C}\mathit{F}_2\mathrm{Cl}$	89.37	4.08	91.50	1.95	–	–	93.45
7	CF_3CF_3	73.04	7.16	74.76	5.44	–	–	80.2

[a] B3LYP/6-31+G(d,p).
[b] B3LYP/6-31+G(df,p).
[c] MP2/6-311G(d,p).
[d] Ref. [10].
[e] CS = ^{19}F chemical shift.
[f] AD = the absolute deviation from the experiment.

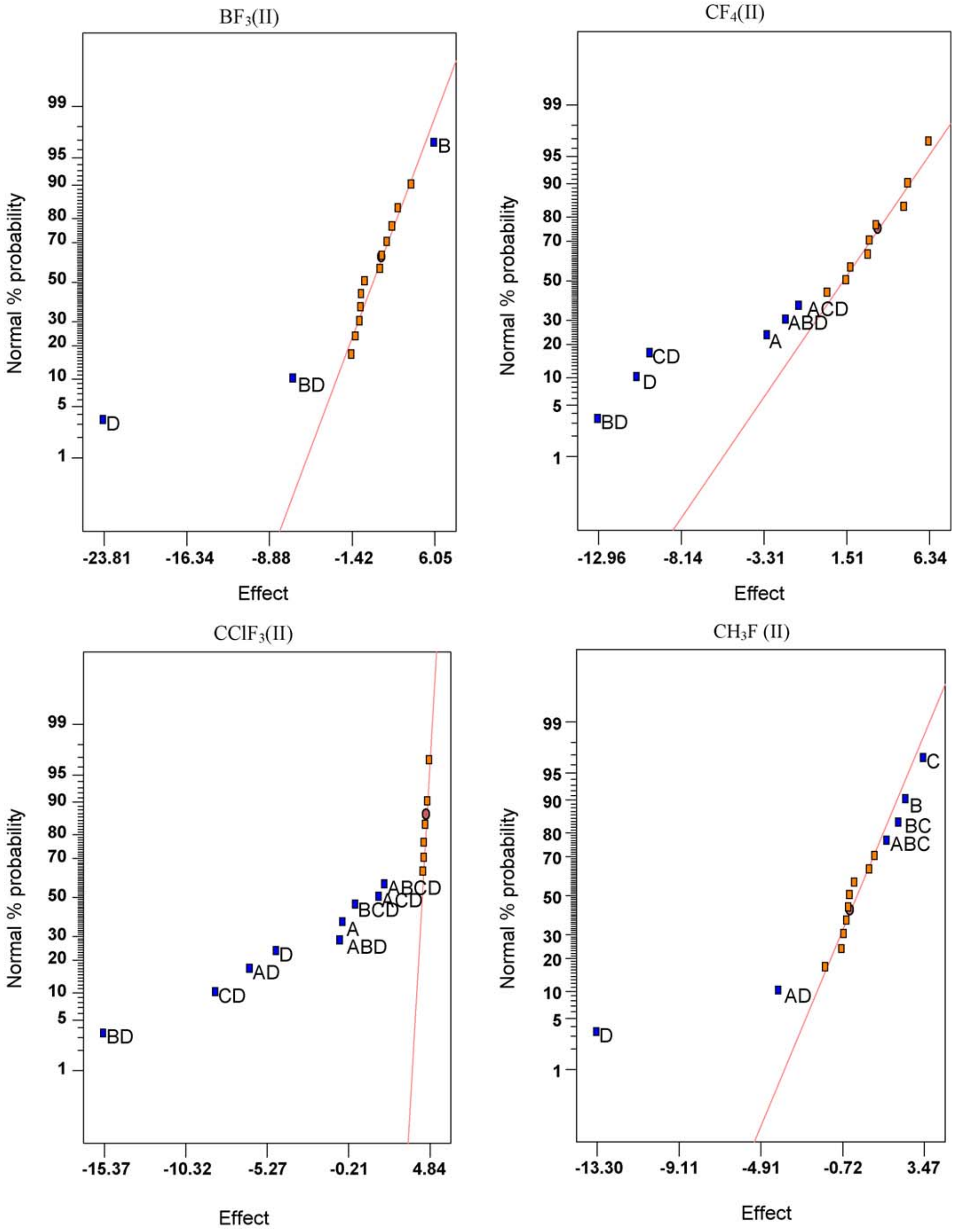

Fig. 2. Normal plots for ^{19}F chemical shift values using GIAO based on design II given in Table 1.

and $CClF_3$ molecules, and its interaction (factor) with factor D (AD) in $CClF_3$ and CH_3F reduces the absolute deviation. Although electron correlation has no significant effect on ^{19}F chemical shifts BF_3 molecule, no interaction factor increases the absolute deviation. Therefore, it is necessary to include both polarization function and electron correlation factors in order to have a reliable calculation of ^{19}F chemical shifts. As for the compounds BF_3 and CH_3F, triple-ξ valence shell (factor B) shows a small deviation from the straight line, but the analysis of interaction factor BD for BF_3, CF_4, and $CClF_3$ molecules demonstrates that the minimum absolute deviation for factor B obtained at high level of theory.

The diffuse function factor (factor C) is located along the straight line for the molecules of BF_3, CF_4, and $CClF_3$ and shows a small deviation from the straight line in CH_3F normal plot. The interaction factor CD reduces the absolute deviation in the cases of CF_4 and $CClF_3$, which is increased by the interaction factor BC in CH_3F molecule. Due to such complex behavior, the results of calculations at MP2/6-311G(d,p) and MP2/6-311+G(d,p) levels were compared with one another as presented in Table 3. RMS error has increased from 4.30 for MP2/6-311G(d,p) to 12.00 for MP2/6-311+G(d,p); thus by considering the RMS values one may conclude that the diffuse function factor should be considered at its low level. Therefore, MP2/6-311G(d,p) can be recommended as most appropriate wave function for calculating the ^{19}F chemical shifts. Table 4 demonstrates the theoretical values for the four compounds which were used to test the recommended level of theory based on design II.

Comparing the two designs applied, one can notice that the polarization function is an effective factor in both designs, whereas the effects of using triple-ξ valence shell and diffuse function

Table 5
Theoretical and experimental values of the ^{19}F chemical shifts and their level of theory.

No.	Molecule	Level of theory	Calc.	Exp.[a]	AD[b]
1	BF_3	HF/6-311G(df,p)	36.49	36.02	0.47
2	CF_4	HF/6-311+G(df,p)	103.87	104.21	0.34
3	CF_3Cl	B3LYP/6-311G(df,p)	139.07	138.77	0.30
4	CH_3F	HF/6-311G(df,p)	−107.96	−107.71	0.25
5	CF_3Br	HF/6-31G	149.67	149.31	0.36
6	CF_2Cl_2	MP2/6-31G	160.72	160.53	0.19
7	CF_3H	HF/6-31G	88.40	89.06	0.66
8	CF_2ClH	MP2/6-31G	95.93	95.88	0.05
9	CF_3CH_3	B3LYP/6-311G	104.66	104.49	0.17
10	$C\mathit{F}_3CF_2Cl$	MP2/6-31G	80.29	81.25	0.96
11	$CF_3C\mathit{F}_2Cl$	B3LYP/6-31+G(df,p)	91.50	93.45	1.95
12	CF_3CF_3	MP2/6-311G	78.63	80.2	1.57
13	PF_3	B3LYP/6-31+G(df,p)	140.87	134.83	6.04
14	POF_3	HF/6-31G(df,p)	74.98	74.94	0.04
15	COF_2	B3LYP/6-31G(d,p)	141.83	141.5	0.33
16	SF_6	MP2/6-311G(d,p)	228.83	223.57	5.26

[a] Experimental values are taken from Ref. [10].
[b] AD = the absolute deviation from experiment.

depend on whether MP2 or B3LYP level of correlation function has been used. The total RMS error values for the calculated ^{19}F chemical shifts at B3LYP/6-31+G(d,p), B3LYP/6-31+G(df,p), and MP2/6-311G(d,p) levels are 5.10, 3.80, and 4.60, respectively. The RMS values revealed that the B3LYP/6-31+G(df,p) is the most reliable level of theory for calculating ^{19}F chemical shifts. Although using second-order Møller–Plesset perturbation correction leads to ^{19}F chemical shifts with a reasonable RMS error, the calculation of ^{19}F chemical shifts at this level is not always possible.

The absolute deviations for ^{19}F chemical shifts of 15 molecules were calculated using 46 different levels of theory as feasible. The theoretical values with the minimum deviation from the experimental ones are illustrated in Table 5. Inspection of the results revealed that the absolute deviation values for majority of molecules are less than 1 ppm. However, no certain procedure can be traced in the best level of theory even for the molecules with similar structures such as CF_3Cl and CF_3Br.

3. Conclusion

The main goal of the present study was to develop a theoretical method for predicting the ^{19}F chemical shifts in gas phase. The effect of four factors, namely, electron correlation, triple-ξ valence shell, diffuse function, polarization function, as well as their interactions were assessed using a 2^4 factorial design. Polarization function and electron correlation were the most effective factors, therefore using high levels of these factors could improve the results. The most appropriate wave functions were proposed, and it was observed that a level of theory having the minimum absolute deviation could not be considered as a general tool for calculating ^{19}F chemical shifts.

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