Benchmarking Density Functionals on First Row Transition Metal Fluorides (ScF−MnF)

Suresh Sampathkumar, Selvarengan Paranthaman

Abstract*: In this work, we have assessed the performances of ten density functionals for the bond length, vibrational frequency and bond dissociation energy values of first row transition metal fluorides (TMFs). The selected density functionals are, TPSSh, B3LYP, B97, PBE0, ωB97X, ωB97X-D, M05, M05-2X, M06 and M06-2X respectively. The obtained results are in agreement with the previous experimental or theoretical results. From this study, it is found that the mean deviation in the metal-fluoride bond length is in the range of 0.01−0.06 Å and the mean deviation in the metal-fluoride bond energy is in the range of 0.16−0.74 eV. Based on this study, we suggest that the B3LYP, TPSSh, B97 and PBE0 functionals can produce good results for selected metal fluoride systems and will be recommended for the above systems.

Keywords*: metal fluorides, benchmark study, density functionals, minnesota density functionals, bond dissociation energy.

I. INTRODUCTION

Density functional theory (DFT) is a very popular computer simulation method and is applied to all the major problems in physics, chemistry and material science etc., [1]−[4] Compare to the complicated wave function theory, DFT is much simple one since it defines the electronic structure of atoms and molecules into a 3-dimensional electron density of a system; while the former defines it as 3N-dimensional anti-symmetric wave function of a system which has a N electrons [1]. DFT has many exchange-correlation functionals which makes them as a successive one [5]. In a study, if the selected exchange-correlation functional was accurate then it exactly describes the quantum nature of material. Theoretical studies on structure and energetic calculations of transition metal compounds are difficult, because of its partially filled and near degenerate d orbitals [4], [6]. The above problem can be overcome with the use of coupled-cluster method (CCSD(T)) and multi-reference approaches (MRCI) [7].

Previous studies mentioned that theoretical studies on diatomic molecules are difficult as they possess the behavior of atom with the highest amount of correlation [8]. DFT has many exchange-correlation functionals and we do not know which one gives accurate result for any particular system. Therefore without doing benchmark calculations, it is difficult to find an accurate DFT functional for any specific transition metal systems. Because of these problems, many research groups are carried out DFT benchmark studies. Especially Truhlar et al. [8]−[12] and Dixon et al. [7], [13], [14] have studied most DFT benchmark calculations on metal containing complexes. Earlier, we have performed DFT benchmark studies on 3d-transition metal oxides (MOs) [15] and 3d-transition metal nitrides (MNs) [16]. The results from the above studies suggest that, the hybrid functionals performs well for MOs and MNs systems compare to the pure functionals. The pure functionals performs well in the case of structural properties, while their results are improper in the energetics of MOs and MNs. The reason for the above phenomena is that the pure functionals does not have Hartree-Fock (HF) exchange.

Similar to MOs and MNs, metal fluorides (MFs) are known as a mixture of transition metal atom and fluorine atom. These MFs receives huge interests from both experimentally and theoretically, because of their various applications [17]−[21]. Earlier, Koukounas et al. used *ab initio* methods to investigate the low-lying states of TiF−CuF molecules [22]−[24]. Later Furche et al. [25] and Zhao et al. [10] have performed assessment study on bond length and binding energies of ScF, TiF, CrF, FeF and CuF molecules with the use of few generalized gradient approximation (GGA) DFT functionals and few hybrid DFT functionals. Recently, Peng et al. studied the structure and electronic properties of vanadium fluoride clusters (VF_n, n=1−7) using DFT functionals [19]. Villa et al. have investigated copper substituted nickel fluoride (Cu supported NiF_2) as cathode material for Li-ion batteries [20]. Recently, transition metal fluorides are emerged as alternate cathode material for Li-ion batteries because of their relatively high voltage plateau and large theoretical capacities. Among the metal fluorides, iron fluoride and copper fluorides are popular due to their high theoretical capacity, high operating voltage, environmentally friendly and low-cost [21]. In order to understand the best DFT functionals for the first row transition metal fluorides (TMFs), in this work we have assess the performances of ten popular DFT functionals for the ScF, TiF, VF, CrF and MnF systems. The selected DFT functionals are evaluated by calculating structure (bond length) and energetic (bond dissociation energy) properties of the above selected systems. The results of the DFT functionals are compared and they are close to the previous experimental and highly accurate theoretical results.

From this study, we can select best DFT functional for the studies on metal fluoride complexes. Also, from this work we can develop new exchange-correlation functionals that will be useful for the metal fluoride complexes.

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II. METHODOLOGY

The selected TMFs (i.e. ScF, TiF, VF, CrF and MnF) are optimized using TPSSh [26], B3LYP [27], [28], B97 [29], PBE0 [30], ωB97X [31], ωB97X-D [32], M05 [33], M05-2X [34], M06 [9] and M06-2X [9] respectively. From the vibrational frequency calculations, it was confirmed that the optimized TMFs are in global minimum. Earlier, Xu et al. suggests that all electron (def2) basis set will provide good results in first row transition metal coordinated systems [11]. Therefore, we select the second generation default bases and triple zeta valence with polarized basis set (def2-TZVPP) for this assessment study [35]. The selected TMFs are also optimized using CCSD(T) [36] method. The bond dissociation energy (BDE) can be calculated using the following formula,

$$\text{i.e. } D_0 \text{ (TMFs)} = E \text{ (TMFs)} - [E \text{ (TM)} + E \text{ (F)}]$$

All the DFT calculations are performed with GAMESS (US) software [37]. The Gaussian09 software is used for the CCSD(T) calculations [38].

Table- I: The selected DFT functionals in this study.

DFT Functionals	Type	% HF Exchange	References
TPSSh	HmGGA	10	[26]
B3LYP	HGGA	20	[27], [28]
B97	HGGA	19.43	[29]
PBE0	HGGA	25	[30]
ωB97X	HGGA	15.77–100	[31]
ωB97X-D	HGGA	22.22–100	[32]
M05	HmGGA	28	[33]
M05-2X	HmGGA	56	[34]
M06	HmGGA	27	[9]
M06-2X	HmGGA	54	[9]

III. RESULTS AND DISCUSSION

The selected TMFs are optimized using ten popular DFT functionals which are listed in Table I. We only consider the hybrid and hybrid meta-generalized gradient approximation density functionals for this study. Because the hybrid and hybrid meta-generalized gradient approximation density functionals performs well in previous benchmark studies on transition metal coordinated systems [15], [16]. Like the previous study by Zhao et al. [10], in this study we calculate the electronic energy of each TMFs with different spin multiplicities to confirm the global minimum electronic structure for each TMFs.

The calculated bond length, vibrational frequency and BDE values are shown in Table II−IV respectively. The CCSD(T) results in this study are close to the experiment values except few cases. For example the experimental bond length of Sc-F is 1.788 Å [39], while the CCSD(T)/def2-TZVPP method overestimate this value to 1.854 Å. Similarly, the CCSD(T)/def2-TZVPP basis set overestimate the experimental BDE values of MnF and FeF. (Table IV) This may due to the selection of basis set; because previous studies show that the selection of basis set will majorly influence the results of these systems [15]. The mean unsigned deviation (MUSD) values in bond length, vibrational frequency and BDE are calculated and they are plotted as graph. (Fig.1.−Fig.3.)

Table- II: The optimized M-F bond distance (in Å) in selected metal monofluorides.

MF /DFT Functionals	ScF	TiF	VF	CrF	MnF
Electronic State	$^1\Sigma^+$	$^4\Sigma^-$	$^5\prod$	$^6\Sigma^+$	$^7\Sigma^+$
TPSSh	1.789	1.794	1.813	1.784	1.825
B3LYP	1.795	1.831	1.788	1.795	1.838
B97	1.793	1.825	1.821	1.797	1.836
PBE0	1.781	1.800	1.859	1.785	1.828
ωB97X	1.902	1.831	1.877	1.803	1.834
ωB97X-D	1.893	1.827	1.870	1.795	1.834
M05	1.800	1.788	1.868	1.810	1.837
M05-2X	1.905	1.843	1.891	1.823	1.844
M06	1.792	1.829	1.863	1.801	1.833
M06-2X	1.905	1.842	1.870	1.817	1.855
CCSD(T)	1.854	1.828	1.803	1.785	1.843
Expt.	1.788[a]	1.831[b]	1.776[c]	1.784[d]	1.839[e]

[a]reference [39]. [b]reference [40]. [c]reference [41]. [d]reference [42]. [e]reference [43].

A. *ScF*

The ScF has ground state in $^1\Sigma^+$ state. The calculated Sc-F bond length values shows that, the TPSSh functional produces good result. This functional almost reproduce the experimental value of 1.788 Å. The difference between experimental and TPSSh value is 0.001 Å. The results of other DFT functionals for Sc-F bond length is shown in Table II. The calculated results in this study improve the previous DFT result. Earlier Furche et al. [25] obtained the bond length of Sc-F using B3LYP (1.814 Å) and TPSSh (1.811 Å) functionals with QZVP basis set. In this study, the B3LYP and TPSSh functionals with the def2/TZVPP basis set gives 1.795 Å and 1.789 Å as bond length of Sc-F. This shows that the def2-TZVPP basis set provides closer result with the experimental value. In the vibrational frequency values, the PBE0 and TPSSh functionals provides good result. The difference between theoretical (PBE0 and TPSSh) and experimental result is less than 5 cm^{-1}. The differences between Minnesota functionals (M05 and M06) and experimental results is less than 10 cm^{-1}. In this study, the B3LYP (723 cm^{-1}) and TPSSh (731 cm^{-1}) functionals with def2-TZVPP basis set provides better results compare to the previous DFT study. In previous DFT study, the B3LYP and TPSSh functionals with QZVP basis set gives 686 cm^{-1} and 693 cm^{-1} as the vibrational frequency of ScF. The M05 and M06 functionals give accurate results in BDE of ScF. The differences between experimental and theoretical (M05 and M06) results are around 0.10 eV. From the above results, we find that the TPSSh functional perform well in bond length, vibrational frequency and BDE of ScF. Hence, we recommend this functional for the future studies on ScF molecules.

B. *TiF*

The TiF has ground state in $^4\Sigma^+$ state. The Ti-F bond length calculated by the B3LYP and ωB97X functionals reproduces the experimental value of 1.831 Å. The differences between experimental and theoretical (M06) result is 0.002 Å.

Earlier Furche et al. [25] obtained the bond length of Ti-F as 1.830 Å using B3LYP/QZVP method. In our study, the B3LYP/def2-TZVPP yields bond length of Ti-F as 1.831 Å. This shows that the def2-TZVPP basis set does not improve the previous results

produced by QZVP basis set.

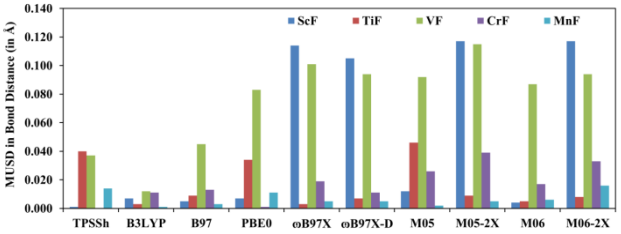

Fig.1. The Mean Unsigned Errors in the bond distance values of metal monofluorides (in Å).

The large deviation with experimental value in the Ti-F bond length is given by M05 functional (0.046 Å). The M05 functional produces 1.788 Å as the bond length of TiF. In the case of vibrational frequency, there are no experimental results found in the literature for $^4\Sigma^+$ state. Therefore, we compare the DFT results with our CCSD(T) result. The deviation between TPSSh and CCSD(T) result is only 2 cm^{-1}. The differences between CCSD(T) with PBE0 and M05-2X functionals are only around 20 cm^{-1}. Among the ten DFT functional, the M06 functional give large deviation (91 cm^{-1}) with the CCSD(T) result. The M06 functional overestimate the CCSD(T) value and gives 761 cm^{-1} as the harmonic vibrational frequency value of TiF. The calculated BDE value by B3LYP and M05 functionals are almost reproduces the experimental result. The difference between theoretical (B3LYP and M05) and experimental result is less than 0.10 eV. The experimental BDE value of TiF is 5.90 eV [40]. Earlier Furche et al. [25] obtained the bond length of TiF as 6.05 eV by using B3LYP/QZVP method. In our study, the B3LYP/def2-TZVPP yields BDE of TiF as 5.82 eV. This shows that the def2-TZVPP basis set improves the result compare to the QZVP basis set. The B97 functional gives deviation of 0.009 Å, 30 cm^{-1}, 0.22 eV in bond length, harmonic vibrational frequency and BDE values of TiF. Hence, we recommend B97 functional for further studies on TiF molecule.

Table- III: The calculated vibrational frequency values (in cm^{-1}) of selected metal monofluorides.

MF /DFT Functionals	ScF	TiF	VF	CrF	MnF
TPSSh	731	668	669	660	625
B3LYP	723	608	609	646	614
B97	709	640	546	637	605
PBE0	740	648	507	653	625
ωB97X	600	640	531	634	622
ωB97X-D	611	646	533	640	615
M05	726	702	668	634	630
M05-2X	599	648	711	614	632
M06	728	761	681	643	618
M06-2X	597	641	674	614	614
CCSD(T)	718	670	662	678	617
Expt.	736[a]	…	670[b]	664[c]	624[d]

[a]reference [39]. [b]reference [41]. [c]reference [42]. [d]reference [43].

C. *VF*

The VF has ground state in $^5\prod$ state. The previous *ab initio* study by Koukounas et al. [22] also results the $^5\prod$ state as the ground state of VF. In the case of bond length, all the selected DFT functionals overestimates the experimental bond length value of VF. (Table II) Among the ten DFT functionals, the B3LYP functional provide accurate result. The difference between B3LYP and experimental results is 0.012 Å. The calculated vibrational frequency value of VF is listed in Table III. The TPSSh and M05 functionals almost reproduces the experimental value of 670 cm^{-1}. The differences between the theoretical (TPSSh and M05) and experimental result is only 2 cm^{-1}. There are no experimental data found in the literature for the BDE of VF ($^5\prod$ state). Hence, we compare our DFT result with the CCSD(T) result. The BDE calculated by PBE0 and M06-2X functionals are in very close agreement with the CCSD(T) results. These functionals give 5.21 eV and 5.16 eV as the BDE of VF. (Table IV) Based on the above results, we recommend TPSSh and B3LYP functionals for the future studies on VF molecules.

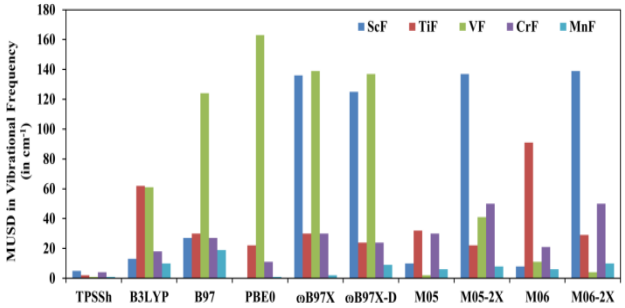

Fig. 2. The Mean Unsigned Errors in the vibrational frequency values of metal monofluorides (in cm-1).

D. *CrF*

The CrF has ground electronic state in $^6\Sigma^+$ state. The selected DFT functionals in this study successfully predict $^6\Sigma^+$ state as the ground state of CrF. The TPSSh functional reproduces the experimental bond distance (1.784 Å) value of CrF. The PBE0 functional also provides very accurate results. The deviation between experimental and theoretical (PBE0) results is only 0.001 Å respectively. Earlier, Furche et al. [25] have obtained bond length of Cr-F as 1.797 Å and 1.787 Å with the use of B3LYP and TPSSh functionals with QZVP basis set. In our study, the B3LYP and TPSSh functionals produces bond length of Cr-F as 1.795 Å and 1.784 Å by using def2-TZVPP basis set. This shows that, the selection of basis set is important for this study. All the selected DFT functionals underestimate the experimental vibrational frequency of CrF. (Table III) The TPSSh and PBE0 functionals show good performance in harmonic vibrational frequency value of CrF. The differences between theoretical (TPSSh and PBE0) and experimental result is only around 10 cm^{-1}. Earlier, Furche et al. [25] obtained 640 cm^{-1} and 653 cm^{-1} as the vibrational frequency of CrF by using B3LYP and TPSSh functionals with QZVP basis set. In our study, the above results are improvised. (Table III) In the case of BDE, all the selected DFT functionals overestimates the experimental value of 4.59 eV. The PBE0 functional shows better results compare to experimental results. The difference between experimental and PBE0 is 0.09 eV respectively. Earlier Furche et al. [25] obtained the BDE of CrF as 4.93 eV and 4.94 eV by using B3LYP and TPSSh functionals with QZVP basis set. Our calculations provide improved results than the previous results.

Both, B3LYP and TPSSh functionals provide 4.89 eV as the BDE of CrF. (Table IV) Based on the above results, we can find that the PBE0 functional performs well in the structure and energetics of CrF which will be useful for the future studies on CrF derivatives respectively.

Table- IV: The calculated bond dissociation energy values (in eV) of selected metal monofluorides.

MF /DFT Functionals	ScF	TiF	VF	CrF	MnF
TPSSh	6.03	6.08	5.98	4.89	4.96
B3LYP	6.00	5.82	5.83	4.89	4.53
B97	6.03	5.68	5.55	4.92	4.34
PBE0	5.93	6.13	5.21	4.68	4.79
ωB97X	6.47	5.56	4.92	5.14	4.32
ωB97X-D	6.49	5.69	4.97	4.90	4.48
M05	6.32	5.82	5.05	4.77	3.91
M05-2X	5.05	5.30	4.65	5.11	3.95
M06	6.33	5.59	4.69	4.80	4.04
M06-2X	6.00	5.41	5.16	5.12	4.12
CCSD(T)	5.85	5.28	5.32	4.73	6.67
Expt.	6.21 ± 0.395[a]	5.90[b]	…	4.59[c]	4.69[d]

[a]reference [39]. [b]reference [40]. [c]reference [44]. [d]reference [45].

E. *MnF*

The MnF has ground electronic state in $^7\Sigma^+$ state. The selected DFT functionals in this study successfully predict $^7\Sigma^+$ state as the ground state of MnF. All the selected functionals provides very good results in the bond length of MnF. (Table II) The difference between B3LYP and experimental result is only 0.001 Å. Similar to bond length results, the DFT functional show accurate results in the vibrational frequency of MnF. The TPSSh and PBE0 functionals give the deviation of only 1 cm^{-1} towards the vibrational frequency of MnF. In this work, the calculated results are improved compared to the previous study. Previously, Nhat et al. [17] calculated 611 cm^{-1} as the harmonic vibrational frequency of MnF by using B3LYP functional. They used 6-311++G(3df,2d) basis set for their calculation. In this work, the B3LYP (614 cm^{-1}) functional result is improvised towards the experimental value of 624 cm^{-1}. This results show that the def2-TZVPP basis set provides better result than the 6-311++G(3df,2d) basis set. In the case of BDE, the PBE0 functional result is close to the experimental value of 4.69 eV. The difference between theoretical (PBE0) and experimental result is 0.10 eV. The other functionals either overestimate or underestimate the experimental value. Our calculated results provide improved results over the previous DFT study. Previous DFT study by Nhat et al. [17] gives 5.03 eV as BDE of MnF, with the use of TPSSh/6-311++G(3df,2d). In our study, the results are improvised towards the experimental value (4.69 eV). (Table IV) Based on the above results, we recommend that the B3LYP and PBE0 functionals will be useful for the future studies on MnF complexes.

F. *Overall performances of selected DFT functionals*

To find the general/overall performances of selected DFT functionals, the MUSD errors in bond length, vibrational frequency and BDE of TMFs were calculated and plotted as graph. (Fig.1.−Fig.3.) The MUSD error is the deviation between experimental and our calculated DFT results. If there are no experimental results available, then we compare our DFT results with CCSD(T) result. Because earlier studies suggests that, the CCSD(T) values are highly accurate [7]. From the Fig.1, we find that the MUSD errors given by TPSSh, B3LYP, B97 and PBE0 functionals are less. These TPSSh, B3LYP, B97 and PBE0 functionals has minimum % of HF exchange compared to the other selected functionals in this study. From this, it was understood that the DFT functionals with minimum amount of % HF exchange produces good results in bond length values. The ωB97X, ωB97X-D, M05, M05-2X, M06 and M06-2X functionals have large MUSD errors in the bond lengths of ScF and VF systems.

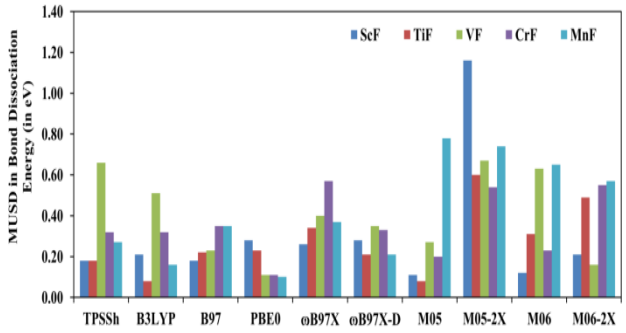

Fig. 3. The Mean Unsigned Errors in the bond dissociation energy values of metal monofluorides (in eV).

Similar to bond length results, the ωB97X, ωB97X-D, M05, M05-2X, M06 and M06-2X functionals have large MUSD errors in the vibrational frequency value of ScF. (Fig.2.) On the other hand, the B97, PBE0, ωB97X and ωB97X-D functionals have MUSD errors in vibrational frequency value of VF. The TPSSh functionals performs very well in the vibrational frequency values of all the selected metal fluorides. In the case of BDE values, the selected DFT functionals have MUSD error in the range of 0.10–1.20 eV. (Fig.3.) There is no variation in the performances of DFT functionals in the BDE values of metal fluorides. All the selected DFT functionals have the MUSD error of around 0.40 eV towards the BDE values of selected metal fluoride systems. The M05-2X functional performs worst in the BDE values of selected metal fluoride systems.

Table- V: The overall best performed DFT functionals in bond distance, vibrational frequency and bond dissociation energy values in selected metal monofluorides.

Property	Best Performed Functionals		
Bond Length	B3LYP	B97	TPSSh
Vibrational Frequency	TPSSh	M05	M06
Bond Dissociation Energy	PBE0	B3LYP	B97

The overall best performed DFT functionals in bond length, vibrational frequency and bond dissociation energy values of selected metal fluorides are tabulated in Table V.

IV. CONCLUSION

In this study, the performances of ten popular density functionals in the bond length, vibrational frequency and bond dissociation energy values of first row TMFs (i.e. ScF, TiF, VF, CrF and MnF) have been investigated. From this study, it is found that the selected density functionals produces mean deviation of 0.01−0.06 Å in the metal-fluoride bond length, 2−67 cm^{-1} in the vibrational frequency value and 0.16−0.74 eV in the metal-fluoride bond dissociation energy. The selected DFT functionals produces good results in bond length values of metal fluorides. Even though the calculated results are satisfied in the vibrational frequency values, the deviations in the bond dissociation energy values are high. Therefore, the density functionals needs further development to get accurate results in the energy values of metal fluorides. This study provides how the performances of traditional as well as the recently developed Minnesota functionals vary towards the metal fluoride systems. We hope that this work can be useful guidance for further development of density functionals that will be used for metal fluoride systems. Overall, we recommend B3LYP, TPSSh, B97 and PBE0 functionals for the future studies on 3d-TMFs.

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