

# Computational Studies of 3d-Metal Monofluorides Using Density Functional Theory Calculations Method

Abdulsamad Abdulkadir Marghilanai<sup>1</sup> Abdel Aziz Qasem Mohammad Jbarah<sup>2\*</sup>

1. Northern Borders University, Deanship of Scientific Research, ArAr campus, Saudi Arabia
2. Northern Borders University, Faculty of Arts and Science, Chemistry Department, Rafha campus, Saudi Arabia

\* E-mail of the corresponding author: [jbr.abed@yahoo.com](mailto:jbr.abed@yahoo.com)

## Abstract

Bond distances, vibrational frequencies, electron affinities, ionization potentials and dissociation energies of 3d transition metal monofluorides in neutral, positively and negatively charged ions were studied by the use of density functional method (B3LYP). The basis set used 6-311++ G(3df). The calculated results were compared with previously reported theoretical studies. Ground states for each molecule were determined. For some molecules it was found that low-lying state is much close to the ground state. In this case, further studies both experimentally and theoretically are necessary in order to find the true global minimum. Dipole moments for the neutral form of 3d transition metal monofluorides are obtained. A comparison was made between the electron affinities, ionization potentials and dipole moments of 3d transition metal monofluorides with those reported previously for 3d transition metal monoborides and for 3d transition metal monolithides.

**Keywords:** density functional theory; electron affinity; ionization potential; transition metals

## 1. Introduction

Knowing the nature of chemical bonds in mixed clusters between transition metals and main group elements is one of great interest in many areas of science such as surface chemistry, catalysis, astrophysics and organometallic chemistry. This is because compounds that containing 3d-metal atoms are theoretically one of the most interesting electronic systems. Therefore, several studies that focused on the diatomic molecules of 3d metal with the main group elements are reported recently. For example, similarities and differences in the structure of 3d-metal monocarbides and monoxides were studied by diverse density functional methods (DFT) (Gutsev et al. 2003). The electronic Structures of 3d-Metal Monolithides were investigated (Wang & Wu 2005). Density functional study of 3d-metal monoborides were reported (Wu 2005). An excellent review paper for diatomics of 3d metal with main group elements H, Li, B, C, N, O and F, were reported somewhere else (Harrison 2000).

For a long time, minor attention has been paid to the use of metal fluorides due to their well-known poor electronic conductivity arising from the highly ionic character of the metal halogen bond. However, as a result of recent developments, several investigations have been suggested about the use of metal fluorides either in primary or in secondary Li batteries (Amatucci & Pereira 2007). Transition element fluorides MF<sub>2</sub> and MF<sub>3</sub> compounds (with M = Ti, V, Fe, Mn, Ni...) have been studied as positive materials (Arai et al. 1997, Badway et al. 2003, Makimura et al. 2006, Li et al. 2004).

In the present work, we focus on the 3d transition metal monofluorides, TMF (TM=Sc–Zn), in neutral, positively and negatively charged ions. For TMF, we are unaware of any systematic studies both experimentally and theoretically. Limited studies were only available for specific species (Langhoff et al. 1988, Carlson & Moser 1967, Harrison 1983, Scott & Richards 1974, Harrison & Hutchison 1999, Steimle & Brazier 1982, Schwerdtfeger et al. 1990, Hayashi et al. 2008, Moravec et al. 2001, Boldyrev & Simons 1998, Sheridan et al. 2003, Ram et al. 1996, Katoh et al. 2004, Okabayashi & Tanimoto 1996, Sheridan & Ziurys 2003, Pouilly & Schamps 1978). The systematic study of 3d-metal monofluorides will allow us to extract the changes of properties and bonding nature across the 3d metal series. We will also compare our results with those reported previously (Langhoff et al. 1988, Carlson & Moser 1967, Harrison 1983, Scott & Richards 1974, Harrison & Hutchison 1999, Steimle & Brazier 1982, Schwerdtfeger et al. 1990, Hayashi et al. 2008, Moravec et al. 2001, Boldyrev & Simons 1998, Sheridan et al. 2003, Ram et al. 1996, Katoh et al. 2004, Okabayashi & Tanimoto 1996, Sheridan & Ziurys 2003, Pouilly & Schamps 1978). It is also hoped that our computational results will stimulate further experimental studies on these 3d metal monofluorides.

## 2. Computational Details

Optimization of the geometries were conducted by the use of Gaussian03 program (Frisch et al. 2003). Ionization potential (IP), bond distance, vibrational frequency, dissociation energy, and electron affinity (EA) were determined for the TMF molecules by use of density functional method B3LYP (Becke 1993, Lee et al. 1988). This hybrid functional consists of a mixture of a traditional Hartree–Fock-like exchange energy, the Slater exchange functional, with gradient corrections due to Becke (1993), and the correlation potential of Vosko, Wilk, and Nusair, with gradient corrections due to Lee et al. (1988). The basis set used is 6-311++ G(3df) in which diffuse functions (++) , 3 sets of d functions and one set of f functions (3df) are included. The population analyses were done by natural bonding orbitals (NBO) schemes. To avoid trapping at local minima of the potential energy surface, a number of different initial geometries (bond distances) are used. The calculation of energies were corrected by the zero-point vibrational energies. The dissociation energy was computed as the difference in the total energies  $E_{tot}$  of the diatomic TMF (TM=3d element) and its constituent atoms, e.g. for neutral species, it is  $D_e(TMf)=E_{tot}(TM)+E_{tot}(F)-E_{tot}(TMf)$ , and similar definitions for cations and anions.

## 3. Result and Discussion

Since the total energies of F and 3d-metal atoms and their ions are required to compute the dissociation energies, it is appropriate to investigate them before we proceed the calculations on the title molecules. The IP and EA of F atom were studied by use of exactly the same method and basis set as in the TMF molecules. Our calculated EA value of F atom is 3.46 eV. This value is agree with the previously obtained experimental values 3.34 (Atkins & Paula 2006) and 3.57 eV (Moiseiwitsch 1954). Our computed IP of F atom (21.39 eV) is larger than that previously reported (Lide 2004). A comparison of the IP and EA of 3d-metal atoms obtained by different methods was published recently (Wu 2005). Also a more details concerning the DFT description of neutral 3d-metal atoms and their anions is given elsewhere (Pouilly et al. 1978).

### 3.1 Ground States and Spectroscopic constants of TMF molecules

The theoretically obtained results for the title molecules were listed in Tables 1-4. In order to find the global minimum or ground state for each TMF molecule in neutral, cation and anion forms, the molecules were calculated at various possible spin multiplicities. The obtained results were given in Table 1. EA, IP, dipole moment of the neutral species and dissociation energy from the ground state of the TMF molecules were collected in Table 2

For neutral ScF molecule,  $^3\Delta$  is the ground state. This result is different from the assignment that based on ab initio methods (Carlson & Moser 1967, Harrison 1983), in which  $^1\Sigma^+$  is the ground state. However, The second lowest conformer is singlet state and 0.16 eV higher than the ground state. The calculated bond distance, vibrational frequency and dissociation energy are 1.854 Å, 646  $\text{cm}^{-1}$  and 6.23 eV (Table 1 and 2), respectively. Our calculated bond distance is very close to that reported in previous work (Harrison 1983). Also for this molecule it is notable from Table 1 that the triplet state of ScF has the longest bond length as compared to the other studied TMF molecules. The electron affinity and ionization potential is 0.99 and 7.04 eV, respectively. For cation form of ScF molecule,  $^2\Sigma^+$  is the ground state. The bond distance of the cation is shorter by 0.089 Å than that of neutral one. For the anion form of ScF molecule,  $^2\Delta$  is the is the ground state and its bond distance is longer by 0.045 Å than that of neutral one.

For the neutral TiF  $^4\Sigma^-$  is the ground state (Table 3). Doublet state is found to be the second lowest conformer and it has 0.274 eV higher than the ground state (Table 1). A previous theoretical study based on CCSD(T)/6-311++G(2d,2f) method on the quartet and doublet states of TiF has been reported (Boldyrev & Simons 1998). The result of this study supports a quartet ground state of TiF which is in agreement with our result. Also the pure rotational spectrum of TiF in its quartet ground state has been studied using millimeter/sub-millimeter wave direct absorption techniques (Sheridan 2003). Our calculated bond distance 1.786 Å and vibrational frequency 688  $\text{cm}^{-1}$  (Table 1) are close to the result of CCSD(T) study (1.832 Å, 638  $\text{cm}^{-1}$ ) (Boldyrev & Simons 1998). It should be mentioned that the TiF molecule has the highest vibration frequency value than the other studied TMF molecules. The electron affinity, ionization potential and dissociation energy are 0.95, 7.16 and 7.56 eV (Table 2), respectively. The  $^3\Delta$  ground state of the cation species of TiF has a shorter bond length by 0.036 Å and higher vibrational frequency by 27  $\text{cm}^{-1}$  than those of neutral one. The opposite situation

was observed in the case of  $^3\Sigma^-$  ground state of the anion form ( $\text{TlF}^-$ ). For  $\text{TlF}^-$  the bond length is 1.829 Å and vibrational frequency is 613  $\text{cm}^{-1}$ .

For neutral VF molecule  $^5\Pi$  is the ground state which is 0.755 eV lower in energy than the triplet. The calculated bond distance, vibrational frequency and dissociation energy are 1.793 Å, 655  $\text{cm}^{-1}$  and 7.61 eV (Table 1 and 2), respectively. The electron affinity and ionization potential is 0.95 and 7.51 eV, respectively. For the cation and anion species the ground state were found to be  $^4\Sigma^-$  and  $^4\Delta$ , respectively. The obtained bond length and vibrational frequencies are 1.731 Å and 766  $\text{cm}^{-1}$  for the  $\text{VF}^+$  molecule and 1.840 Å and 574  $\text{cm}^{-1}$  for the  $\text{VF}^-$ .

For neutral CrF  $^6\Sigma^+$  is the ground state (Table 3). This result is in agreement with both experiment (Kato et al. 2004, Okabayashi & Tanimoto 1996) and previous assignments of multi-reference configuration interaction (MRCI) and coupled cluster with perturbative triples (RCCSD(T) methods (Harrison 1999)). The calculated bond distance, vibrational frequency and dissociation energy are found 1.801 Å, 635  $\text{cm}^{-1}$  and 10.36 eV (Table 1 and 2), respectively. Among all the TMF molecules under study the CrF molecule has the highest dissociation energy. This results indicates that this molecule is the most stable one as compared to the other TMF molecules. The next lowest spin-state is a quartet and is 0.981 eV higher in energy than the ground state. For  $\text{CrF}^+$ ,  $^5\Sigma^-$  gives the lowest conformer.  $^5\Delta$  is the ground state for the  $\text{CrF}^-$ . The CrF bond length shortened in cation form of CrF by 0.078 Å, whereas it is longer by 0.045 Å in anion one.

Table 1. Calculated bond distances  $d$  (Å), vibrational frequency  $\omega_e$  ( $\text{cm}^{-1}$ ) and relative stability  $\Delta E$  (eV) of neutral diatomic TMF and charged species  $\text{TMF}^+$ ,  $\text{TMF}^-$  (TM=3d transition metal element) at possible spin multiplicities S.

S	ScF			VF			MnF			CoF			CuF		
	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$
1	1.79	71	0.160	1.72	70	2.056	1.76	64	4.26	1.73	64	2.102	1.77	60	0.000
	2	4		9	1		7	0	9	8	1		2	0	
3	1.85	64	0.000	1.77	64	0.755	1.74	66	2.31	1.75	62	0.000	1.78	59	2.192
	4	6		1	9		4	7	1	4	1		3	1	
5	3.27	26	7.656	1.79	65	0.000	1.78	60	1.36	1.79	61	0.272	1.79	51	10.47
	8			3	5		6	1	0	7	6		8	0	9
7	2.88	19	20.79	3.47	27	5.682	1.84	61	0.00	1.83	50	7.782	2.31	73	21.58
	5	7	4	2			3	1	0	0	8		5		3
9	-	-	-	-	-	-	2.97	67	7.09	2.34	17	15.31	2.98	18	31.98
							0		7	7	1	7	7	0	3
	TiF			CrF			FeF			NiF			ZnF		
	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$
2	1.77	64	0.274	1.73	68	3.356	1.74	63	2.84	1.75	62	0.000	1.79	58	0.000
	5	5		9	4		0	5	5	9	1		8	7	
4	1.78	68	0.000	1.77	68	0.981	1.75	66	0.04	1.76	64	1.025	2.76	59	7.013
	6	8		9	1		9	1	5	6	2		2		
6	4.31	17	6.094	1.80	63	0.000	1.79	65	0.00	1.81	61	8.632	2.81	84	18.66
	4			1	5		1	0	0	3	7		0		7
8	2.80	19	20.37	4.18	16	4.971	1.75	69	5.46	2.58	12	17.26	2.96	18	31.48
	1	5	7	5			9	1	5	0	7	0	4	9	1
	$\text{ScF}^+$			$\text{VF}^+$			$\text{MnF}^+$			$\text{CoF}^+$			$\text{CuF}^+$		
	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$
2	1.76	73	0.000	1.66	85	2.014	1.69	71	4.47	1.70	60	2.068	1.74	60	0.000
	5	8		8	0		6	6	1	8	1		8	1	
4	2.42	19	5.345	1.73	76	0.000	1.67	81	2.16	1.72	73	0.000	1.78	49	4.927
	2	9		1	6		4	1	6	0	5		9	5	
6	3.89	10	17.95	-	-	-	1.74	73	0.00	1.68	74	2.998	-	-	-
	5	2	8				3	4	0	8	1				
8	2.85	26	40.21	-	-	-	2.67	11	4.02	2.26	20	12.71	-	-	-
	5	0	8				9	6	6	8	5	3			
	$\text{TiF}^+$			$\text{CrF}^+$			$\text{FeF}^+$			$\text{NiF}^+$			$\text{ZnF}^+$		
	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$	$d$	$\omega_e$	$\Delta E$
1	1.72	80	0.713	1.73	73	4.001	1.67	77	3.33	1.70	72	1.952	1.72	72	0.000
	1	2		3	0		9	5	3	0	3		0	2	
3	1.75	71	0.000	1.72	74	1.864	1.73	65	1.64	1.69	74	0.000	2.45	14	2.625
	0	5		9	3		0	7	2	5	9		2	4	
5	2.43	17	5.324	1.72	77	0.000	1.74	71	0.00	1.77	57	4.472	-	-	-
	6	4		3	5		5	8	0	8	9				
7	3.60	10	16.13	2.39	16	3.569	1.71	75	1.84	-	-	-	-	-	-

	7			8			5			9			5			8			1			6		
	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$	<i>d</i>	$\omega_g$	$\Delta E$
9	2.80	25	39.96	3.44	10	12.26	2.31	23	9.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	8	3	9	0	7	1	4	1	1															
	<b>ScF<sup>-</sup></b>			<b>VF<sup>-</sup></b>			<b>MnF<sup>-</sup></b>			<b>CoF<sup>-</sup></b>			<b>CuF<sup>-</sup></b>											
2	1.89	57	0.000	1.77	61	1.987	1.82	55	2.79	1.85	48	0.140	1.86	45	0.000									
4	1.86	59	1.465	1.84	57	0.000	1.83	52	1.70	1.82	52	0.000	1.83	51	4.268									
6	3.91	21	8.430	1.91	49	0.453	1.90	49	0.00	1.85	51	2.344	1.82	48	11.88									
8	3.00	17	21.40	3.42	31	7.207	1.89	51	1.80	1.75	64	7.773	2.88	12	22.59									
	8	8	9	5	5		9	8	3	0	4		2	4	1									
	<b>TiF<sup>-</sup></b>			<b>CrF<sup>-</sup></b>			<b>FeF<sup>-</sup></b>			<b>NiF<sup>-</sup></b>			<b>ZnF<sup>-</sup></b>											
1	1.81	63	0.799	1.71	68	4.992	1.79	55	3.40	1.75	60	0.533	1.94	38	0.000									
3	1.82	61	0.000	1.84	54	1.935	1.83	50	1.87	1.83	49	0.000	1.86	48	2.705									
5	1.91	48	0.759	1.84	55	0.000	1.84	54	0.00	1.81	54	3.210	3.72	27	9.255									
7	-	-	-	1.95	44	0.297	1.84	56	2.17	1.83	52	9.947	3.40	70	20.36									
9	-	-	-	4	0		0	1	5	3	0		5	70	2									
				4.28	18	4.747	1.79	62	4.85	-	-	-	3.03	16	30.98									
				6	6		5	8	2				0	6	6									

For neutral MnF the ground state is  ${}^7\Sigma^+$  which is 1.360 eV lower in energy than the next lowest spin state quintet (Table 1). The calculated bond length 1.843 Å, are very close to that reported experimentally by Sheridan and Ziurys (2003). They concluded also that among all 3d transition metal fluorides, MnF has the longest bond distance. However, according to our calculation MnF has the second longest bond distance (see Table 1).  ${}^6\Sigma^+$  and  ${}^6\Delta$  is the ground states for  $\text{MnF}^+$  and  $\text{MnF}^-$ , respectively. The bond length shortened in cation form by 0.1 Å, whereas it is longer by 0.059 Å in anion one. The calculated vibrational frequencies for MnF,  $\text{MnF}^+$ , and anion  $\text{MnF}^-$  are 611, 734, and 499  $\text{cm}^{-1}$ , respectively. The calculated dissociation energy of the neutral MnF molecule is 8.45 eV.

For neutral FeF,  ${}^6\Delta$  has the lowest energy state with a bond length of 1.791 Å and a vibrational frequency of 650  $\text{cm}^{-1}$ . It is also seen from Table 1 that quartet state is only 0.045eV higher than the lowest energy structure, suggesting that it is a strong competitive candidate for the ground state. However,  ${}^6\Delta$  ground state of FeF is in agreement with both experimental and previous ab initio SCF-CI results [Pouilly & Schamps 1978]. The calculated dissociation energy for the neutral FeF is 8.25 eV (Table 2).  ${}^5\Sigma^-$  and  ${}^5\Delta$  are the ground state for  $\text{FeF}^+$  and  $\text{FeF}^-$ , respectively. The bond length of the cation and anion forms of FeF are 1.745 Å and 1.845 Å, respectively.

The lowest spin state of the neutral CoF molecule is triplet ( ${}^3\Sigma^-$ ) and is 0.272 eV lower in energy than the second lowest spin state quintet (Table 1). Thus, quintet state is a strong competitive candidate for the ground state. The calculated bond length, vibrational frequency and dissociation energy for this molecule are 1.754 Å, 621  $\text{cm}^{-1}$  and 4.47 eV, respectively (Table 1 and 2). The cation and anion forms of CoF has the same lowest ground state, which is  ${}^4\Sigma^-$ . The calculated bond distance is 1.720 and 1.821 Å for  $\text{CoF}^+$  and  $\text{CoF}^-$ , respectively. The vibrational frequency of the neutral, cation and anion forms of CoF are 621, 735 and 524  $\text{cm}^{-1}$  (Table 1), respectively.

For neutral NiF,  ${}^2\Sigma^+$  state is the ground state (Table 3). The second lowest spin state is the quartet, which is higher in energy by 1.025 eV than that of ground state. The calculated bond distance, vibrational frequency and dissociation energy are 1.759 Å, 621  $\text{cm}^{-1}$  and 5.69 eV (Table 1 and 2), respectively.  ${}^3\Pi$  state is the ground state for  $\text{NiF}^+$  and its calculated bond distance and vibrational frequencies are 1.695 Å and 749  $\text{cm}^{-1}$ , respectively.  ${}^3\Sigma^-$  is the ground state for  $\text{NiF}^-$  with a bond length of 1.839 Å and and vibrational frequency of 497  $\text{cm}^{-1}$ .

${}^1\Sigma^+$  is the lowest ground state for the neutral CuF molecule with bond distance of 1.772 Å and vibrational frequency of 600  $\text{cm}^{-1}$  (Table 1 and 3). These values are very close with the conclusion of configuration interaction with single and double excitations study (CISD) (Schwerdtfeger et al. 1990). The calculated

dissociation energy for the neutral CuF is 4.07 eV (Table 2). The second lowest spin state for CuF molecule is the triplet, which is 2.192 eV higher in energy than the singlet ground state.  $^2\Sigma^+$  is the lowest ground state for the anion and cation forms of the CuF molecule. The bond distance and vibrational frequencies in the cation form of CuF is 1.748 Å and 601  $\text{cm}^{-1}$ , respectively. These values are very close to that of neutral one. The corresponding bond length and vibrational frequencies of the  $\text{CuF}^-$  are 1.862 Å and 451  $\text{cm}^{-1}$ , respectively, which are in agreement with the conclusion of MP2 study (1.876 Å, 450  $\text{cm}^{-1}$ ) (Schwerdtfeger et al. 1990).

For neutral ZnF molecule,  $^2\Sigma^+$  is the ground state. The second lowest spin state for ZnF molecule is the quartet, which is 7.013 eV higher in energy than the singlet ground state. The neutral ZnF has the smallest dissociation energy (2.95 eV) due to the close shell of Zn ( $3d^{10}4s^2$ ). For both cation and anion forms of ZnF molecule,  $^1\Sigma^+$  is the ground state. The ground state obtained in our study of neutral and anion forms of the ZnF molecule is in perfect agreement with the previous experimental results and Ab initio calculations (Hayashi et al. 2008, Moravec et al. 2001). The bond distance, vibrational frequency and EA of neutral form of ZnF molecule are found to be 1.798 Å, 587  $\text{cm}^{-1}$  and 2.04 eV, respectively. The experimentally reported vibrational frequency and EA values are 620  $\text{cm}^{-1}$  and 1.974 eV [18], which are very close to our calculated values. The ZnF bond length is shortened by 0.078 Å in the cation form, whereas is longer by 0.146 Å in anion one (Table 1).

### 3.2 Dissociation energy and ionization potential of TMF molecules

In order to calculate the dissociation energy of charged species of the TMF molecules, we chose two channels for the cation forms and two channels for the anion one. The two channels for the cation are  $\text{TMF}^+ \rightarrow \text{TM}^+ + \text{F}$  and  $\text{TMF}^+ \rightarrow \text{TM} + \text{F}^+$  and the two channels for the anion are  $\text{TMF}^- \rightarrow \text{TM} + \text{F}^-$  and  $\text{TMF}^- \rightarrow \text{TM}^- + \text{F}$ . For the cation forms of all TMF, channel  $\text{TMF}^+ \rightarrow \text{TM}^+ + \text{F}$  gives lower dissociation energy than that of  $\text{TMF}^+ \rightarrow \text{TM} + \text{F}^+$  (Table 2) and is, therefore, preferred. It is not surprising to get such a result. This is because F atom has larger IP compared with all metal atoms. The calculated IP value in our study of F atom is 21.39 eV and the reported IP values of the 3d metal atom in a previous study [3] that used same of our calculation method are 6.56, 6.40, 6.74, 7.03, 7.52, 7.79, 7.72, 7.91, 8.04 and 9.43 eV for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, respectively. From Table 2 one can note also that the channel  $\text{TMF}^- \rightarrow \text{TM} + \text{F}^-$  gives lower dissociation energy than that of  $\text{TMF}^- \rightarrow \text{TM}^- + \text{F}$ . This result indicated that the channel  $\text{TMF}^- \rightarrow \text{TM} + \text{F}^-$  is the preferred one for all the anion forms of TMF molecules. This is a logically conclusion since our calculated EA value of 3.46 eV for F atom is larger than that of all 3d metals. It should be mentioned that the reported EA values of the 3d metal atom in a previous study (Wu 2005) that used same of our calculation method are -0.16, 0.68, 0.68, 0.64, -0.53, 0.41, 1.03, 1.14, 1.21 and -1.03 eV for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, respectively.

Table 2. Calculated dipole moment (Debye (D)) of the neutral species, ionization potential IP (eV), electron affinity EA (eV) and dissociation energy  $D_e$ ,  $D_{e11}$ ,  $D_{e12}$ ,  $D_{e21}$  and  $D_{e22}$  (eV) from ground state geometry.

	ScF	TiF	VF	CrF	MnF	FeF	CoF	NiF	CuF	ZnF
$\mu$	3.02	3.20	3.35	4.16	2.58	2.20	4.92	4.88	5.13	3.13
IP	7.04	7.16	7.51	8.19	7.99	9.17	8.84	9.63	10.78	9.54
EA	0.99	0.95	0.95	0.93	1.34	1.58	1.46	1.42	1.35	2.04
	<b>Channel <math>\text{TMF} \rightarrow \text{TM} + \text{F}</math></b>									
$D_e$	6.23	7.56	7.61	10.36	8.45	8.25	4.47	5.69	4.07	2.95
	<b>Channel <math>\text{TMF}^+ \rightarrow \text{TM}^+ + \text{F}</math></b>									
$D_{e11}$	7.30	6.15	7.46	7.72	8.54	5.53	5.64	2.57	1.33	2.84
	<b>Channel <math>\text{TMF}^+ \rightarrow \text{TM} + \text{F}^+</math></b>									
$D_{e12}$	20.58	21.80	21.49	23.57	21.85	20.47	17.03	17.45	14.69	14.81
	<b>Channel <math>\text{TMF}^- \rightarrow \text{TM} + \text{F}^-</math></b>									
$D_{e21}$	3.77	5.06	5.11	7.84	6.33	6.38	2.47	3.65	1.96	1.54
	<b>Channel <math>\text{TMF}^- \rightarrow \text{TM}^- + \text{F}</math></b>									
$D_{e22}$	7.39	6.96	8.89	9.00	9.60	7.75	7.14	4.60	4.21	6.03

Figure 1 compare the EA values of TMF molecules with those previously reported for 3d-metal monoborides (TMB) (Wu 2005) and 3d-Metal Monolithides (TMLi) (Wang & Wu 2005). As can be seen in Figure 1, EA energies for neutral TMF molecules are higher than that all molecules of TMLi and TMB except the case of ScB

and TiB. In comparing the range of electron affinity, it is wider for TMF molecules (1.11 eV) than that for TMB (0.91 eV) and TMLi (0.62 eV) molecules.

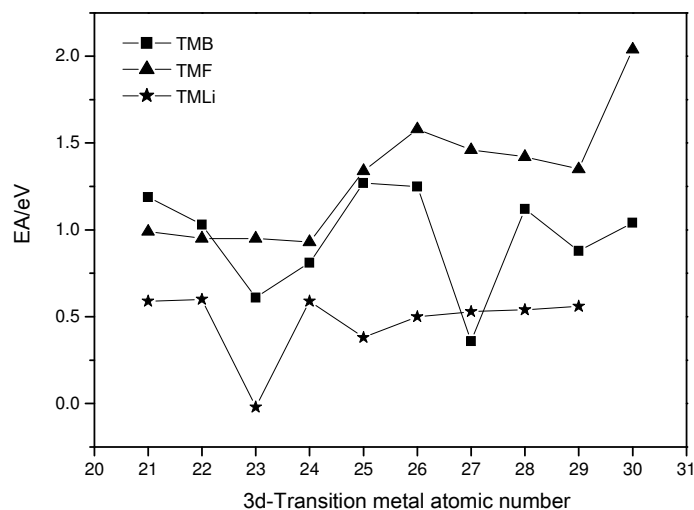


Figure 1. EA value of the TMF, TMB and TMLi molecules versus atomic number of the corresponding 3d-transition metal (Sc-Zn). EA values of TMLi and TMB molecules are obtained from the references (Wu 2005) and (Wang & Wu 2005), respectively.

Figure 2 compare the IP values, of TMF molecules with that previously reported for 3d-metal monoborides (TMB) (Wu 2005) and 3d-Metal Monolithides (TMLi) (Wang & Wu 2005). As shown in Figure 2, the IP energies of TMF molecules are higher than those of TMLi and TMB molecules. Also, the range of IP energies of TMF molecules (3.74 eV) is wider than that for TMB (1.44 eV) and TMLi (1.99 eV) molecules.

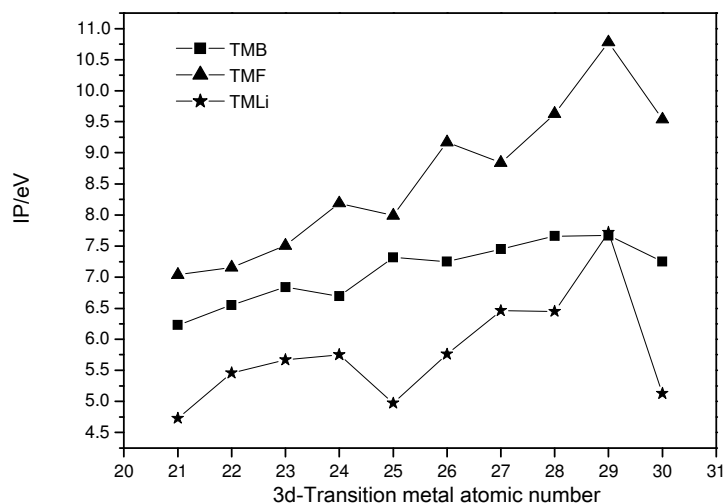


Figure 2. IP value of the TMF, TMB and TMLi molecules versus atomic number of the corresponding 3d-transition metal (Sc-Zn). IP values of TMLi and TMB molecules are obtained from the references (Wu 2005) and (Wang & Wu 2005), respectively.



### 3.3 Bonding Analysis of TMF molecules

The bonding types are complex for these systems which are included covalent, ionic and dative components. If the bonding were purely ionic, the dipole moment of ScF would be 8.89 D, but it is 3.02 D (Table 2), which shows that other components of the bonding are dominant. Therefore, besides ionic component, covalent bonds are formed between the transition metal 3d orbitals and the fluorine 2p orbitals. From Table 2, it is seen that the dipole moment of the neutral molecules increases from ScF to CrF, and then decreases sharply to its minimum value (2.20 D) which is for FeF molecule. From FeF to CuF the dipole moment increases again to its maximum value (5.13 D) which is for CrF molecule and then decreases again to the value of 3.13 D in the case of ZnF molecule. This results suggest that the covalent or ionic character of the bond are varied across the series. This phenomenon was also observed in neutral TMLi molecules (Wang & Wu 2005) as shown in the comparable Figure 3. Figure 3 shows also that covalent or ionic character across the series of the bonds for neutral TMB molecules (Wu 2005) are different from those of TMF and TMLi. The reported dipole moment for neutral TMB molecules (Wu 2005) suggests the increase of the covalent bond across the series from ScB to ZnB. It is also notable from Figure 3 that the values of the dipole moment of the TiF, MnF and FeF are very close to those of TiB, MnB and FeB, respectively.

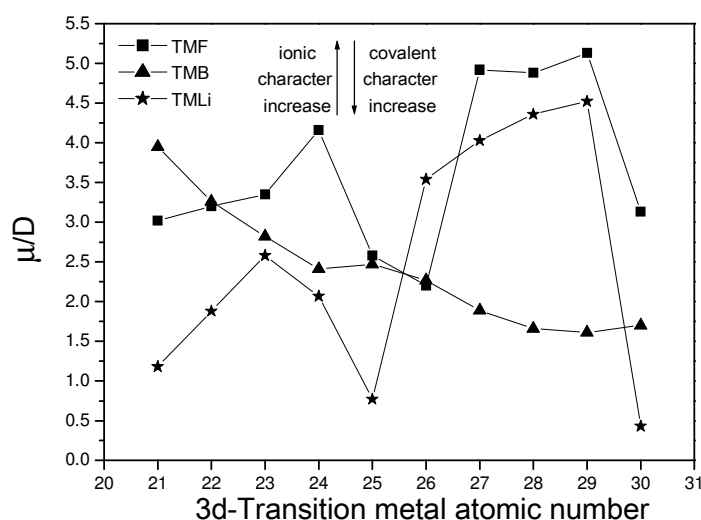


Figure 3.  $\mu$  value of the TMF, TMB and TMLi molecules versus atomic number of the corresponding 3d-transition metal (Sc-Zn).  $\mu$  values of TMLi and TMB molecules are obtained from the references (Wu 2005) and (Wang & Wu 2005), respectively.

From Table 3, it can also be seen that the spin multiplicity is very regular for neutral, anion and cation species from ScF to FeF. For these molecules and ZnF molecule, we also noted that the spin multiplicity of anion and cation is obtained by -1 compared with the corresponding neutral one. For CoF, NiF and CuF the spin multiplicity of the anion and cation is obtained by +1 compared with the corresponding neutral species. It is notable also that the spin multiplicity is regular for neutral, anion and cation species from CoF to ZnF.

Table 3. Ground state occupations of the neutral and charged 3d-metal monofluorides

Neutral		Cation		Anion				
State	Electronic configuration	State	Electronic configuration	State	Electronic configuration			
ScF	${}^3\Delta$	$8\sigma^2 9\sigma^1 3\pi^4 \delta^1$	ScF <sup>+</sup>	${}^2\Sigma^+$	$8\sigma^2 9\sigma^1 3\pi^4$	ScF <sup>-</sup>	${}^2\Delta$	$8\sigma^2 9\sigma^2 3\pi^4 \delta^1$
TiF	${}^4\Sigma^-$	$8\sigma^2 9\sigma^1 3\pi^4 \delta^2$	TiF <sup>+</sup>	${}^3\Delta$	$8\sigma^2 9\sigma^1 3\pi^4 \delta^1$	TiF <sup>-</sup>	${}^3\Sigma^-$	$8\sigma^2 9\sigma^2 3\pi^4 \delta^2$
VF	${}^5\Pi$	$8\sigma^2 9\sigma^1 4\pi^1 \delta^2$	VF <sup>+</sup>	${}^4\Sigma^-$	$8\sigma^2 9\sigma^1 3\pi^4 \delta^2$	VF <sup>-</sup>	${}^4\Delta$	$8\sigma^2 9\sigma^2 4\pi^2 \delta^1$
CrF	${}^6\Sigma^+$	$8\sigma^2 9\sigma^1 4\pi^2 \delta^2$	CrF <sup>+</sup>	${}^5\Sigma^-$	$8\sigma^2 4\pi^2 \delta^2$	CrF <sup>-</sup>	${}^5\Delta$	$8\sigma^2 9\sigma^1 4\pi^2 \delta^3$
MnF	${}^7\Sigma^+$	$8\sigma^2 9\sigma^1 10\sigma^1 4\pi^2 \delta^2$	MnF <sup>+</sup>	${}^6\Sigma^+$	$8\sigma^2 9\sigma^1 4\pi^2 \delta^2$	MnF <sup>-</sup>	${}^6\Delta$	$8\sigma^2 9\sigma^1 10\sigma^1 4\pi^2 \delta^3$
FeF	${}^6\Delta$	$8\sigma^2 9\sigma^1 10\sigma^1 4\pi^2 \delta^3$	FeF <sup>+</sup>	${}^5\Sigma^-$	$8\sigma^1 9\sigma^1 4\pi^2 \delta^4$	FeF <sup>-</sup>	${}^5\Delta$	$8\sigma^2 9\sigma^1 10\sigma^1 4\pi^2 \delta^3$
CoF	${}^3\Sigma^-$	$8\sigma^2 9\sigma^2 4\pi^4 \delta^2$	CoF <sup>+</sup>	${}^4\Sigma^-$	$8\sigma^2 9\sigma^1 4\pi^2 \delta^4$	CoF <sup>-</sup>	${}^4\Sigma^-$	$8\sigma^2 9\sigma^2 10\sigma^1 4\pi^4 \delta^2$
NiF	${}^2\Sigma^+$	$8\sigma^2 9\sigma^1 4\pi^4 \delta^4$	NiF <sup>+</sup>	${}^3\Pi$	$8\sigma^2 9\sigma^1 4\pi^3 \delta^4$	NiF <sup>-</sup>	${}^3\Sigma^-$	$8\sigma^2 9\sigma^1 10\sigma^1 4\pi^4 \delta^4$
CuF	${}^1\Sigma^+$	$8\sigma^2 9\sigma^2 4\pi^4 \delta^4$	CuF <sup>+</sup>	${}^2\Sigma^-$	$8\sigma^2 9\sigma^1 4\pi^4 \delta^4$	CuF <sup>-</sup>	${}^2\Sigma^+$	$8\sigma^2 9\sigma^2 10\sigma^1 4\pi^4 \delta^4$
ZnF	${}^2\Sigma^+$	$8\sigma^2 9\sigma^2 10\sigma^1 4\pi^4 \delta^4$	ZnF <sup>+</sup>	${}^1\Sigma^+$	$8\sigma^2 9\sigma^2 4\pi^4 \delta^4$	ZnF <sup>-</sup>	${}^1\Sigma^+$	$8\sigma^2 9\sigma^2 10\sigma^2 4\pi^4 \delta^4$

### 3.4 Mulliken and Natural Orbital Population Analyses Charges

The calculated atomic charges from Mulliken and natural orbital population analysis are collected along with natural orbital electron configurations in Table 4. In all the neutral molecules, the charge on metal atom is positive and that on the fluorine atom is negative. For all TMF molecules studied here, Mulliken as well as natural orbital population analysis charges show that when an electron is removed from the neutral dimer to generate cation, most of the total positive charge localized on transition metal atom. Similarly, when an electron is added to the neutral molecule to form anion, most of the negative charge localized on fluorine atom.

The natural orbital electronic configuration for neutral molecules in Table 4, it can be said that for ScF, TiF, VF, MnF, FeF, CoF and NiF molecules, electrons originally localized on 4s atomic orbitals of transition metal atoms have been transferred to the 3d orbital of the corresponding transition metal atoms and to the 2p orbitals of the fluorine atoms. For CrF and CuF molecules, the electrons originally localized on the 4s and 3d orbitals of these transition metal atoms have been transferred to the 2p orbitals of fluorine atoms. For the ZnF molecule, electrons originally localized on the 4s orbitals of Zn have been transferred to the 2p orbitals of fluorine.



Table 4. Atomic charges from Mulliken and natural orbital population analysis and natural orbital electronic configuration of first-row transition metal monofluorides at B3LYP/6-311++ G(3df) level.

	Atom	Mulliken	Natural	Natural orbital electronic configuration
ScF	Sc	0.553	0.843	[core] 4s <sup>0.90</sup> 3d <sup>1.19</sup> 4p <sup>0.06</sup>
	F	-0.553	-0.843	[core] 2s <sup>1.99</sup> 2p <sup>5.84</sup> 3s <sup>0.01</sup>
ScF <sup>+</sup>	Sc	1.427	1.744	[core] 4s <sup>0.27</sup> 3d <sup>0.98</sup>
	F	-0.427	-1.744	[core] 2s <sup>1.99</sup> 2p <sup>5.74</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
ScF <sup>-</sup>	Sc	-0.360	-0.075	[core] 4s <sup>1.82</sup> 3d <sup>1.16</sup> 4p <sup>0.10</sup>
	F	-0.640	-0.925	[core] 2s <sup>1.99</sup> 2p <sup>5.88</sup> 3s <sup>0.04</sup>
TiF	Ti	0.489	0.597	[core] 4s <sup>0.87</sup> 3d <sup>2.50</sup> 4p <sup>0.02</sup> 4d <sup>0.01</sup>
	F	-0.489	-0.597	[core] 2s <sup>1.95</sup> 2p <sup>5.62</sup> 3s <sup>0.02</sup> 3d <sup>0.01</sup>
TiF <sup>+</sup>	Ti	1.315	1.506	[core] 4s <sup>0.46</sup> 3d <sup>2.03</sup>
	F	-0.315	-0.506	[core] 2s <sup>1.96</sup> 2p <sup>5.53</sup> 3d <sup>0.01</sup>
TiF <sup>-</sup>	Ti	-0.396	-0.331	[core] 4s <sup>1.81</sup> 3d <sup>2.45</sup> 4p <sup>0.05</sup> 5s <sup>0.01</sup> 4d <sup>0.01</sup>
	F	-0.604	-0.669	[core] 2s <sup>1.96</sup> 2p <sup>5.66</sup> 3s <sup>0.05</sup> 3d <sup>0.01</sup>
VF	V	0.511	0.474	[core] 4s <sup>0.86</sup> 3d <sup>3.59</sup> 4p <sup>0.09</sup>
	F	-0.511	-0.474	[core] 2s <sup>1.92</sup> 2p <sup>5.51</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
VF <sup>+</sup>	V	1.349	1.309	[core] 4s <sup>0.46</sup> 3d <sup>3.24</sup>
	F	-0.349	-0.309	[core] 2s <sup>1.94</sup> 2p <sup>5.35</sup> 3d <sup>0.01</sup>
VF <sup>-</sup>	V	-0.360	-0.476	[core] 4s <sup>1.81</sup> 3d <sup>3.52</sup> 4p <sup>0.13</sup> 5s <sup>0.02</sup> 4d <sup>0.01</sup>
	F	-0.640	-0.524	[core] 2s <sup>1.93</sup> 2p <sup>5.54</sup> 3s <sup>0.02</sup> 3p <sup>0.03</sup> 3d <sup>0.01</sup>
CrF	Cr	0.551	0.821	[core] 4s <sup>0.46</sup> 3d <sup>4.69</sup> 4p <sup>0.03</sup>
	F	-0.551	-0.821	[core] 2s <sup>1.99</sup> 2p <sup>5.82</sup> 3p <sup>0.01</sup>
CrF <sup>+</sup>	Cr	1.359	1.607	[core] 4s <sup>0.04</sup> 3d <sup>4.34</sup> 4p <sup>0.01</sup>
	F	-0.359	-0.607	[core] 2s <sup>2.00</sup> 2p <sup>5.60</sup> 3d <sup>0.01</sup>
CrF <sup>-</sup>	Cr	-0.322	-0.104	[core] 4s <sup>1.44</sup> 3d <sup>4.53</sup> 4p <sup>0.10</sup> 5s <sup>0.02</sup>
	F	-0.678	-0.896	[core] 2s <sup>1.98</sup> 2p <sup>5.88</sup> 3s <sup>0.03</sup>
MnF	Mn	0.542	0.837	[core] 4s <sup>0.94</sup> 3d <sup>5.12</sup> 4p <sup>0.10</sup>
	F	-0.542	-0.837	[core] 2s <sup>1.98</sup> 2p <sup>5.81</sup> 3s <sup>0.03</sup> 3d <sup>0.01</sup>
MnF <sup>+</sup>	Mn	1.360	1.687	[core] 4s <sup>0.12</sup> 3d <sup>5.18</sup> 4p <sup>0.02</sup>
	F	-0.360	-0.687	[core] 2s <sup>1.99</sup> 2p <sup>5.68</sup> 3d <sup>0.01</sup>
MnF <sup>-</sup>	Mn	-0.323	-0.081	[core] 4s <sup>1.83</sup> 3d <sup>5.16</sup> 4p <sup>0.08</sup> 5s <sup>0.01</sup>
	F	-0.677	-0.919	[core] 2s <sup>1.99</sup> 2p <sup>5.86</sup> 3s <sup>0.06</sup> 3d <sup>0.01</sup>
FeF	Fe	0.495	0.808	[core] 4s <sup>0.95</sup> 3d <sup>6.14</sup> 4p <sup>0.09</sup>
	F	-0.495	-0.808	[core] 2s <sup>1.99</sup> 2p <sup>5.79</sup> 3s <sup>0.02</sup> 3d <sup>0.01</sup>
FeF <sup>+</sup>	Fe	1.320	1.672	[core] 4s <sup>0.21</sup> 3d <sup>6.09</sup> 4p <sup>0.01</sup> 4d <sup>0.01</sup>
	F	-0.320	-0.672	[core] 2s <sup>1.99</sup> 2p <sup>5.65</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
FeF <sup>-</sup>	Fe	-0.341	-0.096	[core] 4s <sup>1.72</sup> 3d <sup>6.27</sup> 4p <sup>0.08</sup> 5s <sup>0.01</sup> 4d <sup>0.01</sup>
	F	-0.659	-0.904	[core] 2s <sup>1.98</sup> 2p <sup>5.86</sup> 3s <sup>0.05</sup> 3d <sup>0.01</sup>
CoF	Co	0.582	0.752	[core] 4s <sup>0.45</sup> 3d <sup>7.78</sup> 4p <sup>0.01</sup> 4d <sup>0.01</sup>
	F	-0.582	-0.752	[core] 2s <sup>1.98</sup> 2p <sup>5.76</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>
CoF <sup>+</sup>	Co	1.289	1.612	[core] 4s <sup>0.18</sup> 3d <sup>7.19</sup> 4p <sup>0.01</sup>
	F	-0.289	-0.612	[core] 2s <sup>1.99</sup> 2p <sup>5.59</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
CoF <sup>-</sup>	Co	-0.302	-0.145	[core] 4s <sup>1.43</sup> 3d <sup>7.60</sup> 4p <sup>0.10</sup> 5s <sup>0.01</sup> 4d <sup>0.01</sup>
	F	-0.698	-0.855	[core] 2s <sup>1.97</sup> 2p <sup>5.82</sup> 3s <sup>0.05</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>
NiF	Ni	0.582	0.816	[core] 4s <sup>0.30</sup> 3d <sup>8.86</sup> 4p <sup>0.02</sup>
	F	-0.582	-0.816	[core] 2s <sup>1.99</sup> 2p <sup>5.81</sup> 3d <sup>0.01</sup>
NiF <sup>+</sup>	Ni	1.242	1.527	[core] 4s <sup>0.12</sup> 3d <sup>8.34</sup> 4p <sup>0.01</sup>
	F	-0.242	-0.527	[core] 2s <sup>2.00</sup> 2p <sup>5.51</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
NiF <sup>-</sup>	Ni	-0.296	-0.095	[core] 4s <sup>1.32</sup> 3d <sup>8.66</sup> 4p <sup>0.09</sup> 5s <sup>0.01</sup>
	F	-0.704	-0.905	[core] 2s <sup>1.98</sup> 2p <sup>5.88</sup> 3s <sup>0.03</sup>
CuF	Cu	0.580	0.835	[core] 4s <sup>0.23</sup> 3d <sup>9.92</sup> 4p <sup>0.02</sup>
	F	-0.850	-0.835	[core] 2s <sup>1.99</sup> 2p <sup>5.83</sup>
CuF <sup>+</sup>	Cu	1.164	1.265	[core] 4s <sup>0.07</sup> 3d <sup>9.66</sup> 4p <sup>0.01</sup>
	F	-0.164	-0.265	[core] 2s <sup>2.00</sup> 2p <sup>5.26</sup> 3d <sup>0.01</sup>
CuF <sup>-</sup>	Cu	-0.287	-0.074	[core] 4s <sup>1.09</sup> 3d <sup>9.87</sup> 4p <sup>0.10</sup> 5s <sup>0.01</sup>
	F	-0.713	-0.926	[core] 2s <sup>1.99</sup> 2p <sup>5.91</sup> 3s <sup>0.02</sup>
ZnF	Zn	0.520	0.504	[core] 4s <sup>1.48</sup> 3d <sup>10.00</sup> 4p <sup>0.02</sup>
	F	-0.520	-0.504	[core] 2s <sup>2.00</sup> 2p <sup>5.50</sup>
ZnF <sup>+</sup>	Zn	1.315	1.720	[core] 4s <sup>0.27</sup> 3d <sup>9.98</sup> 4p <sup>0.02</sup>
	F	-0.315	-0.720	[core] 2s <sup>1.99</sup> 2p <sup>5.71</sup> 3d <sup>0.02</sup>
ZnF <sup>-</sup>	Zn	-0.331	-0.013	[core] 4s <sup>1.92</sup> 3d <sup>10.00</sup> 4p <sup>0.09</sup> 5s <sup>0.01</sup>
	F	-0.669	-0.987	[core] 2s <sup>2.00</sup> 2p <sup>5.95</sup> 3s <sup>0.03</sup>

## 5. Conclusion

Density functional method B3LYP was used to compute the spectroscopic constants of 3d-metal monofluorides. Part of our calculated results are in reasonable agreement with previous theoretical and experimental studies. For ScF, TiF, FeF and CoF, competitive candidate for the ground state was found, in particular for FeF (0.045 eV higher than the ground state). This indicates that both experimental study and advanced computations are necessary in order to locate the global minimum. Weak bonding was obtained for neutral ZnF because of the closed-shell metal Zn. The population analyses appear to be a very useful in understanding the trends of the chemical bonding of the neutral species and the behavior of the dipole moment for the neutral series. Our calculated electron affinity energies for the neutral 3d-metal monofluorides molecules are higher than that reported for all molecules of 3d transition metal monoborides and for 3d transition metal monolithides except the cases ScF and TiF. Also our calculated ionization potential energies for the neutral 3d-metal monofluorides molecules are higher than that reported 3d transition metal monoborides and for 3d transition metal monolithides molecules.

## References

- Gutsev, G. L., Andrews, L. & Bauschlicher Jr., C. W. (2003). Similarities and differences in the structure of 3d-metal monocarbides and monoxides. *Theoretical Chemistry Accounts*, 109, 298-308
- Wang, M. Y. & Wu, Z. J. (2005). Electronic structures of 3d-metal monolithides. *Journal of Cluster Science*, 16, 547-558
- Wu, Z. (2005). Density functional study of 3d-metal monoborides. *Journal of Molecular Structure: THEOCHEM*, 728, 167-172
- Harrison, J. F. (2000). Electronic structure of diatomic molecules composed of a first-row transition metal and main-group element (H-F). *Chemical Reviews*, 100, 679-716
- Amatucci, G. G. & Pereira N. (2007). Fluoride based electrode materials for advanced energy storage devices. *Journal of Fluorine Chemistry*, 128, 243-262
- Arai, H., Okada, S., Sakurai, Y. & Yamaki J. (1997). Cathode performance and voltage estimation of metal trihalides. *Journal of Power Sources*, 68, 716-719
- Badway, F., Cosandey, F., Pereira, N. & Amatucci, G. G. (2003). Carbon metal fluoride nanocomposites: high-capacity reversible metal fluoride conversion materials as rechargeable positive electrodes for Li batteries. *Journal of The Electrochemical Society*, 150, A1318-A1327
- Makimura, Y., Rougier, A. & Tarascon J. (2006). Pulsed laser deposited iron fluoride thin films, for lithium-ion batteries. *Applied Surface Science*, 252, 4587-4592
- Li, H., Balaya, P. & Maier, J. (2004). Li-storage via heterogeneous reaction in selected binary metal fluorides and oxides. *Journal of The Electrochemical Society*, 151, A1878- A1885
- Langhoff, S. R., Bauschlicher, C. W. & Partridge H. (1988). Theoretical study of the scandium and yttrium halides. *Journal of Chemical Physics*, 89, 396-407
- Carlson, K. D. & Moser, C. (1967). Electronic Structure and Ground State of Scandium Monofluoride. *Journal of Chemical Physics*, 46, 35-46
- Harrison, J. F. (1983). Electronic structure of scandium fluoride. A low-resolution ab initio study, *The Journal of Physical Chemistry*, 87, 1312-1322
- Scott, P. R. & Richards W.G. (1974). A reassignment of molecular orbital configurations of the electronic states of ScF. *Chemical Physics Letters*, 28,101-103
- Harrison, J. F. & Hutchison, J. H. (1999). The electronic structure of the low lying sextet and quartet states of CrF and CrCl. *Molecular Physics*, 97, 1009-1027
- Steimle, T. C., Brazier, C. R. & Brown, J. M. (1982). Rotational and hyperfine structure in the yellow system of CuF. *Journal of Molecular Spectroscopy*, 91, 137-149
- Schwerdtfeger, P., Boyd, P. D. W., Bowmaker G. A. & Aldridge, L. P. (1990). Theoretical studies on CuF<sup>+</sup>, CuF, CuF<sup>-</sup>, CuF<sub>2</sub>, and CuF<sub>2</sub><sup>-</sup>. *Structural Chemistry*, 1, 405-415
- Hayashi, S., Léonard, C. & Chambaud, G. (2008). Ab initio study of the low lying electronic states of ZnF and ZnF<sup>-</sup>. *Journal of Chemical Physics*, 129, 44313-44321
- Moravec, V. D., Klopcic, Chatterjee, S. A., B. & Jarrold, C. C. (2001). The electronic structure of ZnO and ZnF determined by anion photoelectron spectroscopy. *Chemical Physics Letters*, 341, 313-318
- Boldyrev, A. I. & Simons, J. (1998). On the ground electronic states of TiF and TiCl. *Journal of Molecular Spectroscopy*, 188, 138-141
- Sheridan, P. M., McLamarrah, S. K. & Ziurys, L. M. (2003). The pure rotational spectrum of TiF (X<sup>4</sup>Φ<sub>r</sub>): 3d transition metal fluorides revisited. *Journal of Chemical Physics*, 119, 9496-9504

- Ram, R. S., Bernath, P. F. & Davis, S. P. (1996). Fourier Transform Emission Spectroscopy of the  $g^4\Delta-a^4\Delta$  System of FeF. *Journal of Molecular Spectroscopy*, 179, 282-298
- Katoh, K., Okabayashi, T., Tanimoto, M., Sumiyoshi, Y. & Endo, Y. (2004). Electronic properties of CrF and CrCl in the  $X^6\Sigma^+$  state: Observation of the halogen hyperfine structure by Fourier, transform microwave spectroscopy. *Journal of Chemical Physics*, 120, 7927-7932
- Okabayashi, T. & Tanimoto M. (1996). The rotational spectrum of the CrF radical in the  $X^6\Sigma^+$  state. *Journal of Chemical Physics*, 105, 7421-7424
- Ram, R. S., Bernath, P. F. & Davis S. P. (1996). The low-lying electronic states of CoF. *Journal of Chemical Physics*, 104, 6949-6955
- Sheridan, P. M. & Ziurys, L. M. (2003). Molecules in high spin states II: the pure rotational spectrum of MnF ( $X^7\Sigma^+$ ). *Chemical Physics Letters*, 380, 632-646
- Pouilly, B. & Schamps, J. (1978). Electronic states of the FeF molecule. II. Ab initio calculations. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 11, 2289-2300
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A., Stratmann, Jr., R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G. A., Ayala, P. Y., Cui, Q., Morokuma, K., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Cioslowski, J., Ortiz, J. V., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Andres, J. L., Gonzalez, C., Head-Gordon, M., Replogle, E. S. & Pople, J. A. (2003). *Gaussian, Inc.*, Pitts-burgh.
- Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *Journal of Chemical Physics*, 98, 5648-5652
- Lee, C., Yang, W. & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37, 785-789
- Atkins P. & Paula J. D. (2006). *Atkins' Physical Chemistry*. 8th Ed., Oxford University Press, New York, pp. 1010
- Moiseiwitsch, B. L. (1954). On the electron affinities of atomic fluorine, oxygen and lithium. *Proceedings of the Physical Society A*, 67, 25-32
- Lide, D. R. (2004). *CRC Handbook of Chemistry and Physics*, 84th Ed., CRC Press LLC, pp. 10-178
- Bauschlicher, C. W. & Gutsev, G. L. (2002). The electron affinities of transition metal atoms at the CCSD(T) and density functional levels of theory. *Theoretical Chemistry Accounts*, 108, 27-30
- Pouilly, B., Schamps, J., Lumley, D. J. W. & Barrow, R. F. (1978). Electronic states of the FeF molecule. I. Analysis of rotational structure. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 11, 2281-2288

This academic article was published by The International Institute for Science, Technology and Education (IISTE). The IISTE is a pioneer in the Open Access Publishing service based in the U.S. and Europe. The aim of the institute is Accelerating Global Knowledge Sharing.

More information about the publisher can be found in the IISTE's homepage:

<http://www.iiste.org>

## CALL FOR JOURNAL PAPERS

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. There's no deadline for submission. **Prospective authors of IISTE journals can find the submission instruction on the following page:** <http://www.iiste.org/journals/> The IISTE editorial team promises to review and publish all the qualified submissions in a **fast** manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

## MORE RESOURCES

Book publication information: <http://www.iiste.org/book/>

Recent conferences: <http://www.iiste.org/conference/>

## IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digital Library, NewJour, Google Scholar

