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Negative ions of transition metal-halogen clusters

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A systematic density functional theory based study of the structure and spectroscopic properties of neutral and negatively charged MX_n clusters formed by a transition metal atom M (M=Sc, Ti, V) and up to seven halogen atoms X (X=F, Cl, Br) has revealed a number of interesting features: (1) Halogen atoms are bound chemically to Sc, Ti, and V for $n \leq n_{\max}$, where the maximal valence $n_{\max}$ equals to 3, 4, and 5 for Sc, Ti, and V, respectively. For $n > n_{\max}$, two halogen atoms became dimerized in the neutral species, while dimerization begins at $n=5$, 6, and 7 for negatively charged clusters containing Sc, Ti, and V. (2) Magnetic moments of the transition metal atoms depend strongly on the number of halogen atoms in a cluster and the cluster charge. (3) The number of halogen atoms that can be attached to a metal atom exceeds the maximal formal valence of the metal atom. (4) The electron affinities of the neutral clusters abruptly rise at $n=n_{\max}$, reaching values as high as 7 eV. The corresponding anions could be used in the synthesis of new salts, once appropriate counterions are identified. © *2010 American Institute of Physics*. [doi:10.1063/1.3489117]

I. INTRODUCTION

There is considerable interest in studying negative ions not only because they are among the best known oxidizing agents,[1] but also they play an important role in atmospheric chemistry by acting as nucleation centers.[2] Among the elements in the Periodic Table, halogen atoms are the most electronegative because they possess a hole in the outermost p-shell (ns^2np^5 electronic configuration), which can readily accommodate an electron in order to close the np shell. An extra electron attachment to a halogen atom results in the negatively charged ion whose total energy is significantly lower than that of the corresponding neutral. Consequently, the halogen atoms possess the highest electron affinities[3] (3.0–3.6 eV) among all the elements. It has been demonstrated that molecules consisting of a metal atom at the core surrounded by halogen atoms possess electron affinities that can be higher than those of the halogen atoms.[4–6] This was first brought into the focus by the pioneering experiments[7,8] of Bartlett half a century ago when he succeeded in synthesizing the $XePtF_6$ salt. The ability to ionize noble gas atoms by highly electronegative PtF_6 moiety ushered a new era in noble gas compounds and highlighted the importance of negative ions such as transition metal hexafluorides.[5,9]

In 1981, Gutsev and Boldyrev[10,11] introduced the term "superhalogen" to characterize the species with high electron affinities. A conventional superhalogen contains an atom (M) surrounded by electronegative ligand atoms (X) and has the formula $MX_{(n+1)/m}$ where n is the maximal formal valence of M and m is the normal valence of X. In 1999, the smallest superhalogen anions MX_2^- (M=Li, Na; X=Cl, Br, I) were first experimentally studied using photoelectron spectroscopy. The experimental findings were interpreted on the basis of *ab initio* calculations.[12] Larger superhalogen anions MX_3^- (M=Be, Mg, Ca; X=Cl, Br, F),[13–15] MX_4^- (M=B, Al; X=F, Cl, Br) (Refs. 16 and 17) were studied along with Na_xCl_{x+1} ($x=1-4$).[18] Examples of other superhalogens include LiF_2,[19] MnO_4,[6] and CrO_4 (Ref. 20) whose electron affinities are, respectively, 5.45, 5.0, and 4.96 eV. While several molecules involving transition metal atoms are known to possess high electron affinities,[23,29,30] many more are waiting to be discovered. Superhalogens to be found are expected to serve as building blocks of new energetic materials.[21–23]

In this paper, we have carried out a systematic study of the structure and electron affinities of MX_n clusters (M=Sc, Ti, V; X=F, Cl, Br; $n=1-7$). We have selected transition metal atoms as the core due to the following reasons: (1) Since d electrons of a transition metal atom are localized while outer s electrons are delocalized, it is not clear which maximal formal valence can be assigned to a particular transition metal atom and how many halogen atoms this metal atom can bind? For example, Mn with its outer electron configuration of $3d^54s^2$ exhibits oxidation states ranging from −3 to +7. In MnO_4, the maximal valence of Mn is 7 and consequently MnO_4 behaves as a superhalogen possessing the EA of 5 eV.[6] (2) Due to their unfilled d-shells, the transition metal atoms carry magnetic moments. For example, the magnetic moments of Sc, Ti, and V are 1, 2, and 3 μ_B, respectively. It is interesting to know how these moments change as halogen atoms are successively attached to these metal atoms and as the corresponding cluster charge state is altered.

Using hybrid density functional theory,[24,25] we have calculated the equilibrium geometries, electronic structure, and preferred spin states of both neutral and negatively charged MX_n clusters (M=Sc, Ti, V and X=F, Cl, Br and $n=1-7$). In negatively charged clusters, we found that the maximum number n of halogen atoms that can be attached to these

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early transition metal atoms can be at most six. Electron affinities are calculated as the differences between the total energies of the anions and their corresponding neutral parents at their respective ground state geometries. The vertical detachment energies, on the other hand, correspond to the difference in the total energy between the anion ground state and the neutral having the anion geometry. The results are compared with available experiments. In Sec. II we provide a brief description of our theoretical procedure. In Sec. III the role of different halogens F, Cl, and Br on the structure and spectroscopic properties of ScX_n clusters is studied. Interactions of Ti and V with F atoms are discussed in Sec. IV and the results are summarized in Sec. V.

II. COMPUTATIONAL METHOD

Our calculations are carried out using density functional theory and the Becke's three parameter hybrid exchange functional combined with the Lee–Yang–Par correlation functional (B3LYP).[24] The atomic orbitals are represented by Gaussian basis sets 6-311+G*.[26] The geometries are optimized without any symmetry constraint using GAUSSIAN 03 code. The effect of basis sets and hybrid exchange-correlation energy functional on calculated electron affinities is examined by using larger basis sets and outer valence greens function (OVGF) method. Different initial geometries with halogen atoms bound to the transition metal atoms both molecularly and chemically were used to determine the ground state geometries. All allowable spin multiplicities are tried to determine the total spin of the ground state. The convergence for total energy and force was set to 0.000 001 eV and 0.001 eV/Å, respectively. The vibrational frequencies of all the clusters studied are positive and the states at the corresponding geometries belong to minima at the potential energy surface. Calculations for all neutral $ScCl_n$ as well as MX_2 (M=Sc, Ti, V) clusters were repeated using Vienna *Ab initio* simulation package (VASP) (Ref. 27) and the PW91 (Ref. 28) form for the generalized gradient approximation for the exchange and correlation potential to confirm their geometries. The optimized geometries were same as those obtained using the GAUSSIAN 03 code. These results can be obtained from the authors.

III. ScX_n (X=F, Cl, Br; AND n=1–5)

A. Equilibrium geometries

We first discuss our results on Sc decorated with F, Cl, and Br to determine how the geometries, electronic structure, and spectroscopic properties of metal halide clusters depend on the type of halogen atoms. We display the ground state geometries of neutral and anion ScF_n (n=1–5) clusters in Fig. 1. The geometries of neutral clusters are similar to those of their corresponding anions for $n \leq 3$ where all F atoms are bound chemically. This is consistent with the maximal valence ($n_{\max}$) of Sc of three. However, there are significant differences between the geometries of neutral and anion clusters for $n \geq 4$. While ScF_4^- has a perfect tetrahedral geometry, in neutral ScF_4 two of F atoms are closer to each other and form a quasimolecular structure with a bond length of 2.02 Å. Note that the bond length of a F_2 molecule calculated at the same level theory used in this work is 1.41 Å. This is again consistent with the maximal valence of Sc of three. In the neutral ScF_4, four F atoms require four electrons to close their outermost electronic shells while Sc atom can only afford three electrons. Consequently, the second F_2 molecule does not split and the bond between the F atoms only stretch. A similar adduct-type structure was found for AlF_4 where Al has the valence of three.[17] In ScF_4^-, on the other hand, the fourth electron required to fill in the shells of four F atoms is supplied by the added electron. In neutral ScF_5 clusters, we find two pairs of F atoms are bound to Sc in a quasimolecular form with the distance of 2.00 Å between them. In contrast, only one pair of F atoms binds quasimolecularly to Sc atom in ScF_5^- and the distance between these two F atoms is 1.96 Å. For n=6, our calculations show that the anionic ScF_6 cluster dissociates into ScF_4 cluster and a F_2 molecule during optimization.

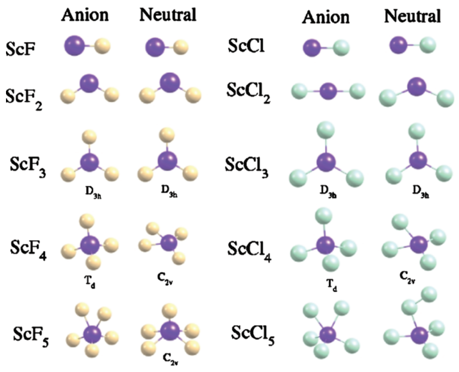

FIG. 1. Optimized geometries of the anionic and neutral of ScF_n and $ScCl_n$ clusters. The corresponding symmetries are listed.

The ground state equilibrium geometries of neutral and anion $ScCl_n$ clusters are also given in Fig. 1. These geometries are very similar to those of ScF_n clusters with the exception of n=2 and 5. Anionic $ScCl_2$ is linear while ScF_2 has a bent structure. In neutral $ScCl_5$, two Cl atoms bind quasimolecularly with only one of them bound to the Sc atom. The geometries of neutral and anionic $ScBr_n$ clusters are similar to those of $ScCl_n$ clusters and hence not shown in Fig. 1. The bond lengths between Cl and that between Br atoms in quasimolecular structures of $ScCl_4$ and $ScBr_4$ are 2.80 and 3.03 Å, respectively. Note that the calculated bond lengths of Cl_2 and Br_2 molecules are 2.05 and 2.33 Å, respectively. In both anion and neutral $ScCl_5$ clusters, the bond lengths between the Cl atoms forming quasimolecular structure are 2.68 and 2.09 Å, respectively, while in the anion and neutral $ScBr_n$ clusters, the corresponding bond lengths are 2.90 and 2.39 Å, respectively.

In Fig. 2(a) we display the average bond lengths, $\langle R \rangle$, between Sc and F atoms in neutral and anionic ScF_n clusters. In all cases, the average bond lengths of the anionic clusters are larger than those in the neutral clusters with the exception for n=4 where the two average bond lengths are nearly equal. The average bond lengths between Sc and Cl atoms in the neutral and charged $ScCl_n$ clusters and between Sc and Br in the $ScBr_n$ clusters are given in Figs. 2(b) and 2(c), respectively. The results are similar to those shown in Fig. 2(a) for ScF_n clusters.

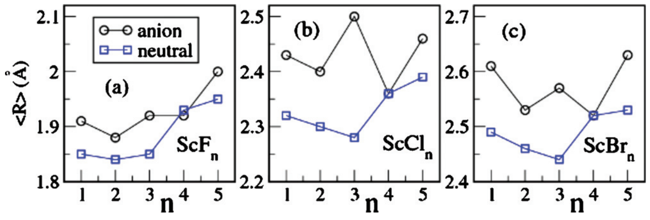

FIG. 2. The average Sc–F, Sc–Cl, and Sc–Br bond lengths (in angstrom) in the neutral and anionic clusters.

B. Stability and fragmentation energies

We define the fragmentation energies as

$$\Delta E_{\mathrm{neutral}} = E(\mathrm{Sc}X_n) - E(\mathrm{Sc}X_{n-m}) - E(X_m), \quad m = 1,2, \quad (1)$$

$$\Delta E^1{}_{\mathrm{anion}} = E(\mathrm{Sc}X_n{}^-) - E(\mathrm{Sc}X_{n-m}{}^-) - E(X_m), \quad m = 1,2, \quad (2)$$

$$\Delta E^2{}_{\mathrm{anion}} = E(\mathrm{Sc}X_n{}^-) - E(\mathrm{Sc}X_{n-m}) - E(X_m{}^-), \quad m = 1,2. \quad (3)$$

In Fig. 3(a) we display the fragmentation energies of neutral ScF_n clusters where F atom is a product. As is seen, the fragmentation energies increase slowly from $n=1$ to 3, but decreases abruptly at $n=4$. This is not surprising because $n=4$ exceeds the maximal formal valence of Sc by one. Fragmentation energies of the channels where F_2 is a product are shown in Fig. 3(b). Comparing Figs. 3(a) and 3(b), one notes that the preferable dissociation channel of the neutral ScF_5 is $\mathrm{ScF}_3+\mathrm{F}_2$.

Fragmentation energies of $\mathrm{ScF}_n{}^-$ clusters are shown in Figs. 3(c) and 3(d). As is seen from Fig. 3(c), the fragmentation energies increase slowly with n and drop sharply for $n=5$. The preferred dissociation channel yields a F atom for all values of n. The extra charge is carried by the F atoms for $n \leq 4$ and by ScF_4 for $n=5$. As will be discussed later, this is because the EA of F is larger than the electron affinities of ScF_n clusters for $n \leq 3$ while the EA of ScF_4 is larger than that of the F atom. The $\mathrm{ScF}_6{}^-$ anion does not exist and dissociates into $\mathrm{ScF}_4{}^-$ and F_2 molecule during optimization. The larger fragmentation energy for $n=4$ indicates an enhanced stability of the $\mathrm{ScF}_4{}^-$ anion.

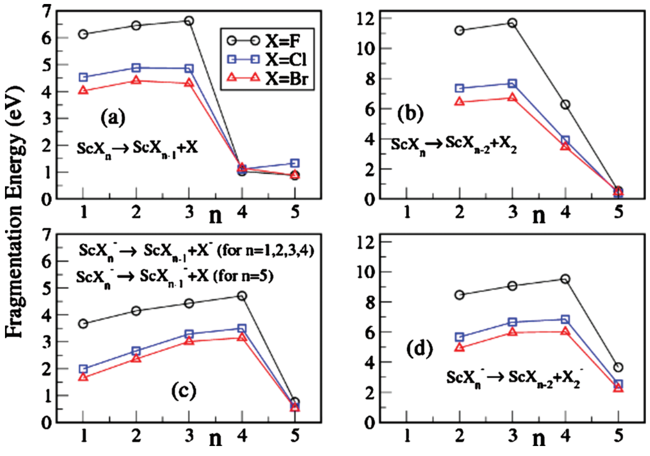

FIG. 3. Fragmentation energies (in eV) of ScF_n, ScCl_n, and ScBr_n clusters with respect to halogen atoms and molecules.

We also display the corresponding fragmentation energies for ScCl_n and ScBr_n clusters in Fig. 3. The trend is same as that in ScF_n clusters. The only difference is that the fragmentation energies of ScBr_n clusters are smaller than in the ScCl_n clusters which, in turn, are smaller than in the ScF_n clusters. The decreasing stability of $\mathrm{Sc}X_n$ clusters as X varies from F to Br is due to the increasing size of these halogen atoms that gives rise to a larger bond distance between Sc and the halogen atoms.

C. Magnetic moments

The magnetic moment of Sc atom in its ground state configuration ($3d^1 4s^2$) is 1 μ_B. Thus, the ground state spin multiplicities of neutral ScF_n clusters are expected to be either a singlet or a doublet depending upon whether n is odd or even. While this is the case for ScF_2, ScF_3, and ScF_4, the ground state spin multiplicities for neutral ScF and ScF_5 are both three. The reason why the ground state of ScF is a triplet is related to the fact that F is monovalent. The neutral ScF_5 cluster has two pairs of quasimolecular F_2 and possesses the same spin multiplicity as ScF. On the contrary, all charged $\mathrm{ScF}_n{}^-$ clusters have either singlet or doublet ground state. Except for $n=1$ the ground states of ScCl_n, $\mathrm{ScCl}_n{}^-$, ScBr_n, and $\mathrm{ScBr}_n{}^-$ clusters are also either singlets or doublets depending upon whether n is odd or even. The spin multiplicity of the neutral ScCl_5 or ScBr_5 clusters is different from that of ScF_5. This is consistent with the difference in their ground state geometries in Fig. 1. The ground state geometrical configurations of ScCl_5 (ScBr_5) clusters contain quasimolecular Cl_2 (Br_2) attached to the ScCl_3 (ScBr_3) cluster and the corresponding state has the same spin multiplicity as ScCl_3 (ScBr_3).

In all neutral MX_2 clusters, the transition metal atom retains its magnetic moment. As long as the $3d$ electrons are not participating in the interaction, valence shell electron pair repulsion (VSEPR) theory can be used to analyze the geometries. According to this theory, the geometries are bent when the central atom has one or two lone pairs of electrons while it is linear when there are three lone pairs of electrons in the central atom. Consequently, geometries of $\mathrm{Sc}X_2$ clusters are bent. In anionic MX_2 clusters, much of the extra electron goes to the transition metal (discussed later in the section) and the magnetic moment decreases by one in each case. Thus, the VSEPR theory does not hold good. Anionic ScF_2 is bent while $\mathrm{ScCl}_2{}^-$ and $\mathrm{ScBr}_2{}^-$ are linear. Since Cl is larger than F, $\mathrm{ScCl}_2{}^-$ becomes linear to minimize the repulsive force between Cl atoms. Similar is the case with $\mathrm{ScBr}_2{}^-$ cluster.

D. Vertical detachment energies and electron affinity

The calculated vertical detachment energies (VDE) of an extra electron from the $\mathrm{Sc}X_n{}^-$ anions and electron affinities (EAs) of the neutral $\mathrm{Sc}X_n$ clusters are given in Table I and

TABLE I. The EA and VDE (in eV) for Sc halide clusters together with the ground state magnetic moments of the neutral and anion clusters obtained at the B3LYP level of theory.

Cluster	Neutral μ (μ_B)	Anion μ (μ_B)	EA (eV)	VDE (eV)
ScF	2	1	1.02	1.05
ScF_2	1	0	1.18	1.22
ScF_3	0	1	1.28	1.49
ScF_4	1	0	7.16	7.74
ScF_5	2	1	7.05	7.95
ScCl	2	1	1.19	1.24
$ScCl_2$	1	0	1.50	1.61
$ScCl_3$	0	1	2.15	2.43
$ScCl_4$	1	0	6.11	6.35
$ScCl_5$	0	1	5.35	6.29
ScBr	2	1	1.23	1.30
$ScBr_2$	1	0	1.55	1.64
$ScBr_3$	0	1	2.30	2.70
$ScBr_4$	1	0	5.59	5.83
$ScBr_5$	0	1	4.80	5.71

Fig. 4. While the EA values of ScF, ScF_2, and ScF_3 are relatively small, ScF_4 has the EA of 7.16 eV and is a superhalogen. The EA and VDE values are rather close to each other in ScF, ScF_2, and ScF_3 which is consistent with small changes in the neutral geometries following an attachment of the extra electron (see Fig. 1). On the contrary, the VDE and EA values are very different in ScF_4 and ScF_5 due to dramatic differences between the corresponding neutral and anionic geometries.

The EA values of $ScCl_n$ and $ScBr_n$ are displayed in Figs. 4(b) and 4(c), respectively. There are significant differences with respect to the previous case of ScF_n. The EA values of $ScCl_4$ and $ScBr_4$ are less steep. It is seen from Table I that the EA values of ScF_n for $n \leq n_{\max}$ are smaller than those of $ScCl_n$ which in turn are smaller than those of $ScBr_n$. Reverse is the case for $n \geq n_{\max}$. This behavior is due to the combination of two effects: electronegativity and size of halogen atoms. We will discuss this in more detail in the following section. The experimental EA is available only for $ScCl_4$.[29,30] Our calculated EA value for $ScCl_4$ is approximately 0.7 eV smaller than the experimental value. In view of good agreement with experiment for other superhalogens mentioned in Sec. I, it is unclear what is the reason of this mismatch. To see if this difference is caused by limitations in the basis sets we calculated the EA for $ScCl_4$ using a larger basis set, namely, 6-311+G(3df).[31] The EA of $ScCl_4$ and VDE of $ScCl_4^-$ are calculated to be 5.96 and 6.31 eV, respectively, using 6-311+G(3df) basis set. These compare well with corresponding values of 6.11 and 6.38 eV obtained using 6-311+G* basis sets. Clearly, basis sets are not the cause for the large discrepancy between theory and experiment. In order to see if the disagreement is due to deficiency in the density functional theory, we used the OVGF/6-311+G(3df) (Refs. 32 and 33) method with the anionic $ScCl_4$ geometry obtained using the larger basis sets to calculate VDE. This yielded a value of 7.26 eV which is much closer to the experimental value of 7.14 eV. Recall that calculations using B3LYP+6-311+G* underestimated the VDE value by ~0.7 eV. However, the VDE values for $ScCl_n^-$ ($n=1,2,3$) obtained using the OVGF/6-311+G(3df) method are 1.15, 1.44, and 2.46 eV, respectively, for $n=1,2,3$ and match well with the VDE values in Table I. In a similar way, the VDE for anionic ScF_4 and $ScBr_4$ are calculated to be 9.74 and 6.60 eV, respectively, using the OVGF/6-311+G(3df) method.

E. Charge distribution

In order to understand the nature of bonding of halogen atoms to Sc, we analyzed charges on Sc and halogen atoms as a function of n for both neutral and anionic species using natural bond orbital analysis.[34] The results are displayed in Fig. 4. In all ScX_n clusters, the total charges on Sc atom are positive indicating charge transfer from Sc to the halogen atoms. The charges on the Sc atom for $n \leq n_{\max}$ steadily rise in both neutral and anionic clusters and the charge on Sc is

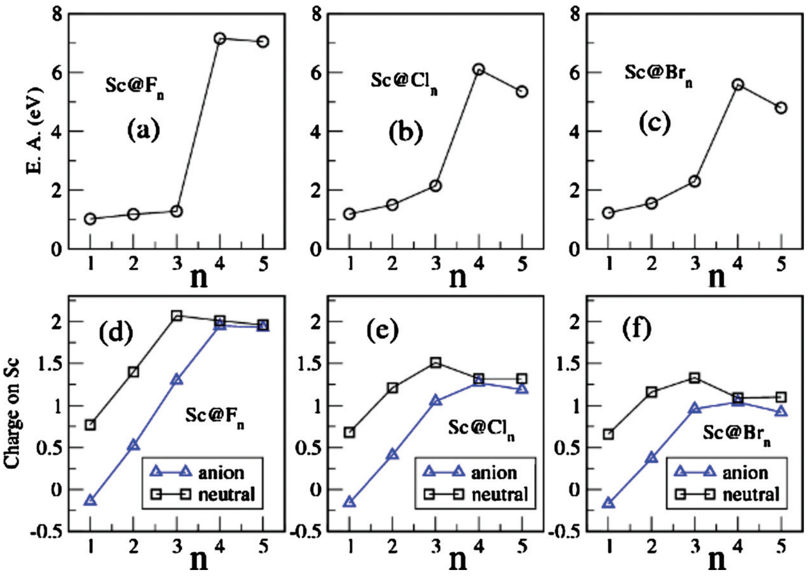

FIG. 4. Top panels: EA of ScF_n, $ScCl_n$, and $ScBr_n$ clusters. Bottom panels: the charge on Sc atom [in (e)] for anionic and neutral clusters.

smaller in the anions than in the neutral clusters. For $n \geq n_{\max}$, the charge on Sc is same irrespective of whether it is an anion or a neutral cluster.

Results in Figs. 4(d)–4(f) illustrate the nature of bonding between Sc and halogen atoms. In neutral ScX_n clusters for $n \leq n_{\max}$ Sc atom continues to transfer charge to X atoms since X atoms are electronegative. When the number of X atoms reaches the maximal valence of Sc, this transfer is no longer possible and subsequent X atoms bind to Sc in quasimolecular form. When the extra electron is added to ScX_n clusters, it prefers to go to the Sc atom which is already positively charged for $n \leq n_{\max}$. Hence the total charge on Sc reduces in ScX_n^- compared to that in ScX_n clusters. At $n > n_{\max}$, the extra electron in ScX_n^- goes to the X atoms and this causes the EA to rise sharply as seen in Table I and Fig. 4.

Electron counting shows that the neutral ScX_4 cluster has one electron less than what is necessary to satisfy the octet rule. Both factors, one electron less than necessary to close electronic shell in ScX_4 and the extra electron being distributed among all X atoms, give rise to large EA for ScX_4. Hence, ScX_4 is a superhalogen. When one more X atom is added and we move from $n=4$ to 5, we find the same charge on Sc, in both anionic and neutral clusters. Since two electrons are needed to close the shells in ScX_5^-, EA does not increase further.

We see from Table I and Fig. 4 that the EAs of ScX_n for $n \leq n_{\max}$ increase as one X goes from F to Br, but reverse happens for $n \geq n_{\max}$. To explain the former we note that the charge on Sc in ScF$_n$ clusters is larger than that in ScCl$_n$ clusters which in turn is larger than that in ScBr$_n$ clusters as shown in Figs. 4(d)–4(f). This is a reflection of the size of the X atoms: as the size increases from F to Br, the distance between Sc and X becomes larger and the bonding gets weaker. Correspondingly, the EAs of ScX_n increase from X=F to X=Br for $n \leq 3$.

For $n \geq n_{\max}$, the extra charge in the anion clusters goes to the halogen atoms. Since the electronegativity increases from Br to Cl to F, the EA of ScX_n for $n \geq 4$ increases from X=Br to X=F.

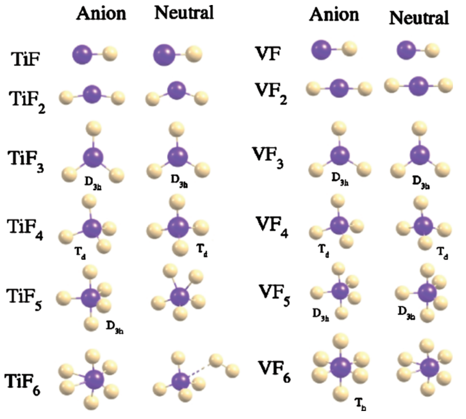

FIG. 5. Optimized geometries of the neutral and charged clusters of TiF$_n$ and VF$_n$ clusters. The corresponding symmetries are listed.

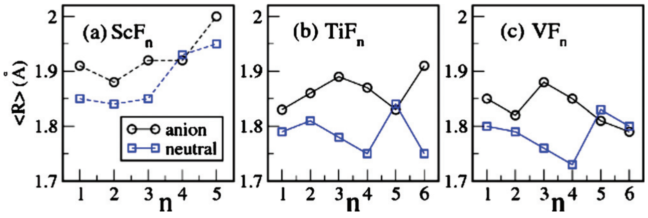

FIG. 6. The Sc–F, Ti–F, and V–F average bond lengths (in angstrom) in neutral and anionic clusters.

IV. TiF$_n$ AND VF$_n$

A. Equilibrium geometries

In order to understand how the spectroscopic properties will change as the occupancy of the 3d orbitals changes, we studied TiF$_n$ and VF$_n$ clusters. Since the electronic configurations of Ti and V atoms are $3d^2 4s^2$ and $3d^3 4s^2$, respectively, the maximal valence $n_{\max}$ of Ti and V is four and five, respectively. The geometries of neutral and anionic TiF$_n$ and VF$_n$ clusters were optimized following the same procedure as outlined before. The optimized geometries are given in Fig. 5. The ground state optimized geometries of the neutral and anionic clusters of TiF$_n$ are similar to those for ScF$_n$ for $n \leq 4$ with the exception that the neutral TiF$_4$ is a perfect tetrahedron because it is isoelectronic to ScF$_4^-$. Neutral ScF$_2$ is linear due to the presence one lone pair of electrons while TiF$_2$ is linear due to presence of two lone pairs of electrons. This is in accordance with the VSEPR theory discussed earlier. The equilibrium geometry of TiF$_2^-$ is a bent structure which can be explained similar to the bent structure of ScF$_2^-$ cluster. The ground state geometry of the neutral TiF$_5$ cluster is also similar to that of the ScF$_5^-$ cluster. The bond length in the quasimolecular F$_2$ in neutral TiF$_5$ is 1.96 Å. For $n=6$, we also found a pair of quasimolecular F$_2$'s in the anion cluster with the same bond length. The neutral TiF$_6$ cluster has an adduct type geometry TiF$_4^*$F$_2$, with positive vibrational frequencies. A similar adduct-type structure AuF$_5^*$F$_2$ was found for a AuF$_7$ species.[35] The average bond lengths for the neutral and charged clusters are given in Fig. 6. For $n=5$ we find that the average bond lengths for both the species are essentially the same.

Optimized ground state geometries in the VF$_n$ clusters are similar to those in TiF$_n$ for $n=1$, 3, and 4 (see Fig. 5), while we found linear geometries for both VF$_2$ and VF$_2^-$. VF$_2$ cluster is linear due to the presence of three lone pairs of electrons according to the VSEPR theory and the addition of an electron keeps the structure intact. The geometries of VF$_5$ are TiF$_5^-$ are very similar since they are isoelectronic. The VF$_7^-$ cluster dissociates into VF$_6^-$ and F while neutral VF$_7$ cluster dissociates into VF$_5$ and F$_2$. We found all frequencies to be positive. The average bond lengths for neutral and anion VF$_n$ clusters are displayed in Fig. 6. The average bond lengths for anion geometries are larger than for the corresponding neutral geometries except for $n=5$ and 6 when they are essentially the same for both the species.

B. Stability and fragmentation energies

The fragmentation energies are displayed in Fig. 7. The neutral TiF$_n$ clusters are very stable for $n \leq 4$ while the an-

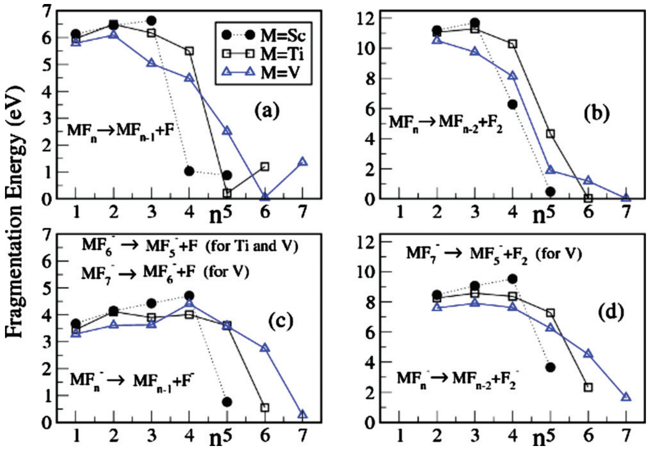

FIG. 7. Fragmentation energies (in eV) of TiF_n and VF_n clusters with respect to F and F_2. Fragmentation energies of ScF_n are shown for comparison.

ionic clusters are stable up to $n=5$. We did not find any noticeable peak at $n=5$ similar to the peak at $n=4$ for anionic ScF_n clusters in Fig. 3. The fragmentation energy decreases for $n>2$ in both neutral and anionic VF_n clusters. The stability for anionic cluster at $n=6$ is less than that at $n=5$ although it was expected to have a peak at $n=6$. So the fragmentation energies of VF_n clusters indicate that the F atoms are weakly attached to V atom even when the number of F atoms is smaller than the maximal formal valence of V atom.

C. Magnetic moments

The magnetic moments of TiF and VF are larger than that of Ti (V) atom by one. For larger n, the magnetic moments exhibit oscillations between 1 and 0 depending on whether the total number of electrons is odd or even. For the anion clusters, the magnetic moments of TiF and VF are same as those of the corresponding metal atoms and decrease by one as subsequent F atoms are attached. This trend continues up top $n \leq 4$ beyond which the magnetic moments oscillate between 0 and 1.

TABLE II. The EA and VDE (in eV) for Ti and V fluoride clusters along with the ground state magnetic moments of the neutral and anion clusters obtained at the B3LYP level of theory.

Cluster	Neutral μ (μ_B)	Anion μ (μ_B)	EA (eV)	VDE (eV)
TiF	3	2	0.98	1.01
TiF_2	2	1	1.11	1.18
TiF_3	1	2	1.22	1.72
TiF_4	0	1	1.99	2.32
TiF_5	1	0	6.87	7.89
TiF_6	0	1	6.22	7.50
VF	4	3	0.98	1.01
VF_2	3	2	1.01	1.03
VF_3	2	3	2.08	2.62
VF_4	1	2	3.41	4.22
VF_5	0	1	4.55	5.06
VF_6	1	0	7.26	8.29

D. VDE and EA

The calculated EA and VDE values of TiF_n and VF_n are given in Table II and Fig. 8. We found the EA and VDE values to be very close to each other for $n \leq 4$ and $n \leq 5$ in TiF_n and VF_n series, respectively, due to similarity in the corresponding neutral and anionic geometries. By analogy with ScF_n, we expect a jump in the EA for TiF_5 and VF_6 clusters. As seen from Fig. 8, there is a sharp rise in the EA value for TiF_5 but the rise in EA value for VF_6 is much less pronounced. The VDE values for anionic TiF_5 and VF_6 are calculated to be 9.63 and 9.83 eV, respectively, using the OVGF/6-311+G(3df) method.

E. Charge distribution

The charges on Ti atom for both neutral and anionic clusters are given in Fig. 8(e). As is seen, they increase steadily with the number of F atoms for both the neutral and anionic TiF_n. However, they assume the same value at $n=5$, the maximal valence of Ti. In the anionic TiF_5^- cluster, the extra electron is distributed among five F atoms and hence, there is a sharp increase in EA between $n=4$ and 5 as shown in Fig. 8(b). There is a drop in EA at $n=6$ which is expected because it has two electrons less than that required for the closed shell. For VF_n clusters, we expected a jump in the EA when we go from $n=5$ to $n=6$. But we see a completely different behavior in Fig. 8(c), though the EA for VF_6 is very high. We found the same charge on Ti in TiF_n clusters for $n \geq 5$ as on Sc in ScF_n clusters for $n \geq 4$. This is not a coincidence but reflects the fact that the valence of Ti is one more than that of Sc. The charges on V for neutral and anion clusters are very close to each other for $n \geq 4$ since the extra electron in VF_n is delocalized over F atoms for $n \geq 4$. Hence, all these clusters should have high EAs. In fact the EA for VF_4 is 3.41 eV which is close to the EA of F atom. But the electron counting indicates that VF_4 is three electrons less than what is required for closed shell. Therefore, the EAs continue to increase for $n=5$ and 6 as shown in Fig. 8(c). As VF_6 behaves like a superhalogen with one electron less than required for the closed shell, its EA is the largest. VF_7, on the other hand requires two electrons to close its shell and hence its EA falls below that of VF_6.

V. CONCLUSIONS

A systematic study based on density functional theory was carried out to understand the electronic structure and spectroscopic properties of early transition metal atoms M (Sc, Ti, and V) interacting with halogen atoms X (F, Cl, and Br). Several interesting observations are made:

(1) Transition metal atoms can bind more halogen atoms than their maximal formal valence $n_{\max}$ would allow. The number of halogen atoms that can bind chemically to the metal atom is $n_{\max}$. Once the number of halogen atoms is larger than $n_{\max}$, halogen atoms begin to bind in a quasimolecular X_2 form. The transition metal atoms can bind one more halogen atom chemically in the

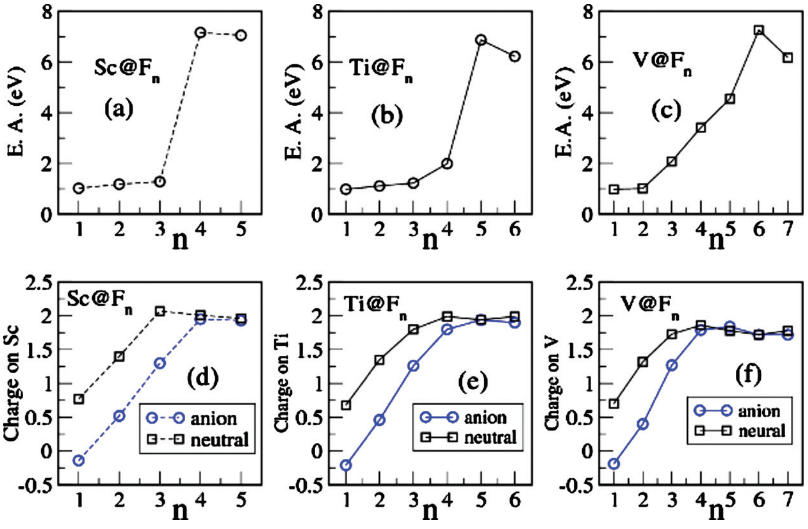

FIG. 8. EA (in eV), charges on Ti and V atoms in the neutral and charged TiF$_n$ and VF$_n$ clusters. The values of ScF$_n$ are presented for comparison.

anion than in the neutral cluster. That is, the extra electron serves as an additional valence for the central atom.

(2) The fragmentation energies of ScX_n increase slowly up to $n=3$ and decrease as n grows farther. A ScX_4 cluster behaves as a superhalogen since it has one electron less than required to close the valence shell. The binding energy in the ScX_4^- anion exceeds 4 eV and very high energy is required for the detachment of the extra electron. The electron affinities of a transition metal halide can be higher than 7 eV.

(3) The behavior of the TiF$_n$ ($n_{\max}=4$) clusters and their anions is similar to that found for the ScX_n series. The fragmentation energies of TiF$_n$ are large for $n\leq 4$ and decreases suddenly at $n=5$. Neutral TiF$_5$ has EA of 6.87 eV and satisfies the formula for a conventional superhalogen.

(4) VF$_n$ clusters behave slightly different from ScF$_n$ and TiF$_n$ clusters. The binding energy of VF$_n$ decreases beginning with $n=2$. This is in contrast to what one would have naively expected, namely, the binding energies to be large until the number of halogen atoms reaches $n_{\max}$. Consequently, the F atoms are weakly attached to V atom as compared to Sc or Ti atom. The EAs for ScF$_n$ and TiF$_n$ clusters are larger than the EA of F atom only if n is more than $n_{\max}$. On the contrary, the EAs of several VF$_n$ clusters are larger than the EA of F even if the number of F atoms attached is less than $n_{\max}$. The same charge on V for neutral and anion VF$_4$ clusters also confirms that the participation of d electrons decreases as we go from Sc to V. It will be interesting to study the interaction of F atoms with the transition metals having larger d electron occupancy than V.

(5) Experimental result of the VDE only exists for ScCl$_4$. We noted that B3LYP level of theory cannot quantitatively account for this experimental result. However, VDE calculation using OVGF method agrees very well with experiment. For $n\leq n_{\max}$, OVGF level of theory provides no significant improvement. It will be interesting to compare our results with experimental data on ScF$_4$ and ScBr$_4$ when available.

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