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Interactions of a Mn atom with halogen atoms and stability of its half-filled 3d-shell

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Using density functional theory with hybrid exchange-correlation potential, we have calculated the geometrical and electronic structure, relative stability, and electron affinities of MnXn compounds (n = 1–6) formed by a Mn atom and halogen atoms X = F, Cl, and Br. Our objective is to examine the extent to which the Mn–X interactions are similar and to elucidate if/how the half-filled 3d-shell of a Mn atom participates in chemical bonding as the number of halogen atoms increases. While the highest oxidation number of the Mn atom in fluorides is considered to be +4, the maximum number of halogen atoms that can be chemically attached in the MnXn− ions is 6 for X = F, 5 for X = Cl, and 4 for X = Br. The MnCln and MnBrn neutrals are superhalogens for n ≥ 3, while the superhalogen behavior of MnF2 begins with n = 4. These results are explained to be due to the way different halogen atoms interact with the 3d electrons of Mn atom. © 2011 American Institute of Physics. [doi:10.1063/1.3601753]

I. INTRODUCTION

Bartlett and Lohmann,1, 2 who found that PtF6 is capable of oxidizing both an O2 molecule and a Xe atom whose first ionization potentials are 12.22 eV and 12.17 eV, respectively, impressively demonstrated the high oxidative power of transition metal halides nearly half a century ago. This power is due to a very high electron affinity (EA) of the platinum hexafluoride, which was estimated to be 6.8 eV. The experimental findings helped to outline a class of species named as superhalogens,3 A typical superhalogen MXk+1 is composed of a central metal atom M and halogen atoms X, and k is the maximal formal valence of the central atom. It was found that such MXk+1 compounds possess4–6 the electron affinities that are larger than the EAs of the halogen atoms (F: 3.399 ± 0.003 eV; Cl: 3.617 ± 0.003 eV; Br: 3.365 ± 0.003 eV).7 The earlier work was mainly concentrated on sp-superhalogens, such as MX2 (M = Li, Na; X = Cl, Br, I),8 MX3 (M = Be, Mg, Ca; X = Cl, Br),9–11 MX4 (M = B, Al; X = F, Cl, Br),12, 13 and MX6 (M = 3d-5d metal atoms).14, 15 These studies have been extended to the superhalogens containing transition metal atoms16–18 as well as to the superhalogens containing oxygen19–21 and hydrogen22 as ligand atoms. Currently, there is a surge of interest in the superhalogens and their anions, because the anions play an important role in chemistry as oxidizing agents,23 nucleation center,24 biocatalysts, and building blocks of new energetic materials.25, 26

No exception was found to the superhalogen formula, if the central atom is an sp-element. However, it is not straightforward to apply the superhalogen MXk+1 concept to transition metal halides, because transition metal atoms exhibit multiple oxidation states. In particular, the oxidation state of Mn atom can vary from 0 [e.g., in Mn2(CO)10] to +7 [e.g., in MnO4−] or even be negative. Since the valence electronic configuration of the Mn atom is 3d54s2, the maximal formal valence of Mn is to be +7. If this is the case, MnO4− has to be a superhalogen because the sum of oxygen valencies is one more than 7. Indeed, MnO4 was found to possess the electron affinity of ∼5 eV in combined theoretical and experimental study.27 However, “the maximal formal valence” of Mn in halides is not clear because its highest oxidation state is +7 in oxides but +4 in fluorides.28 Therefore, it is interesting to study how the electron affinity of manganese halides depends on the number and type of halogen atoms.

The purpose of the present work is to perform a systematic study on the neutral and singly negatively charged manganese halides MnXn (X = F, Cl, Br) for all n values for which at least one species in a pair MnXn−–MnXn− is thermodynamically stable. The preferred oxidation state found for Mn is +2, which is indicative of the participation in the bonding of only 4s electrons. One could compare the properties of Mn trihalides with the properties of sp-halides whose central atom possesses an ns2 valence shell as only chemically active. For this purpose, we choose MgX2 halides because Mg has the valence electronic shell 3s2. We use density functional theory with a hybrid exchange-correlation functional in our calculations of the equilibrium geometries, electronic structure, and preferred spin multiplicities of neutral and anionic states. In Sec. II we provide a brief description of our theoretical procedure. In Sec. III we describe the structure and spectroscopic properties of MnXn and MnXn−, and Sec. IV provides a brief summary of the work.

II. COMPUTATIONAL DETAILS

Our computations are performed using the combination of Becke’s hybrid 3-parameter exchange functional and
correlation functional of Lee–Yang–Parr referred to as B3LYP.39 We use a spin-unrestricted version of the B3LYP method. This generally produces spin-contaminated states.30 It is quite common that spin contamination is large in low-spin states, but is negligible for high-spin states. Since all our Mn halides studied possess high-spin ground states (GS), the spin contamination is rather small and does not exceed 5%. The atomic orbitals are represented by Gaussian 6–311+G(3df) basis sets.31, 32 The choice of a proper method is critical in obtaining reliable results.33–36 and can be based on comparison of the results obtained using a particular method to experiment or on performance of the method for compounds closely related to those under study. As for the experimental data, the photoelectron spectra have been measured for MnCl3− and MnBr3−.37 Our B3LYP/6-311+G(3df) value of 5.05 eV for the vertical detachment energy (VDE) of an extra electron from MnCl3− is in fair agreement with the experimental values of 5.6 ± 0.2 eV (Ref. 37) and 5.50 ± 0.06 eV.17 Our B3LYP VDE value obtained for MnBr3− is 4.95 eV, which is also in fair agreement with the experimental value of 5.36 ± 0.06 eV.17

Comparison of dozens of different methods was performed using, as the reference, the results obtained by coupled-cluster method with singles and doubles and non-iterative triples [CCSD(T)] (Ref. 38) for hexafluorides of 4d and 5d transition metals.39, 40 It was found that the B3LYP provides the values which are quite close to the corresponding CCSD(T) values, and the B3LYP performance is better than the performance of pure DFT methods in the case of nd-metal halides.

Further support to the reliability of the B3LYP/6-311+G(3df) level is provided in Table I, where the results of our B3LYP calculations are compared to those of RCCSD(T) calculations performed earlier for MnF.41 As is seen, the B3LYP values of the bond length and dissociation energy are in excellent agreement with experiment42,43 and the RCCSD(T) values obtained using a 5-zeta basis set. The B3LYP values, obtained for MnF+ and MnF− are also close to the values obtained using the RCCSD(T) approach.

The geometries are first optimized without any symmetry constraint using GAUSSIAN 03 code.44 Various guess structures with halogen atoms bound to the metal atom both molecularly and chemically were used to determine the ground-state geometries. All possible spin multiplicity states. The convergence threshold for total energies was set to 0.000001 eV and for the forces to 0.001 eV/Å. The lowest energy state geometries were re-optimized within actual symmetry constraints, if such obtained, in order to assign spectroscopic states.

The vibrational frequencies of all cluster states discussed below are positive, which means that their geometries belong to the minima on the potential energy surfaces. Adiabatic electron affinities (EAad) are calculated as the differences between total energies of the anion and its neutral parent computed at the corresponding ground-state geometries. The VDEs are computed as the differences in total energies of an anion and its neutral parent at the anion ground-state geometry.

### III. RESULTS and DISCUSSION

We first discuss the structure of neutral and singly negatively charged Mn chlorides because there are experimental mass spectrometry data, followed by a discussion of our results on neutral and anionic series of Mn bromides and fluorides. Finally, we outline the structure and properties of Mg trihalides since Mg has the same oxidation state as Mn in its most thermodynamically stable halides.

#### A. MnClₙ clusters

The mass spectra of the MnClₙ− anions produced in a pulsed arc cluster ion source exhibit rather unusual features.37 Since Mn oxidation states of +2 and +7 are quite common (e.g., in MnCl₂, MnO, and MnO₄−), one could anticipate that the prominent peaks should correspond to MnCl₃− and MnCl₅−. However, only a MnCl₃− peak was observed in the spectra, which shows that the preferable interactions of Cl with Mn are likely divalent. In order to explore the character of Mn–Cl interactions, we optimized the lowest total energy state geometries of MnClₙ and MnClₙ− shown in Fig. 1 as a function of the Cl amount. The extra electron attachment is accompanied by significant geometry changes, namely, MnCl₂ is linear, while MnCl₃− is bent, the MnCl₃ and MnCl₄ geometries possess C₃ᵥ and D₂ᵥ symmetry, respectively, while the MnCl₅− and MnCl₆− geometries have D₃ᵥ and D₂ᵥ symmetry, respectively. In MnCl₃, 3 Cl atoms are bound dissociatively to the central atom, while 2 Cl atoms

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>rₑ (Å)</th>
<th>Dₑ (eV)</th>
<th>IE (eV)</th>
<th>rₑ (Å)</th>
<th>Dₑ (eV)</th>
<th>IE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnF, calc.</td>
<td>7 Σ⁺</td>
<td>1.843</td>
<td>4.65</td>
<td>7.99</td>
<td>1.840</td>
<td>4.68</td>
<td>8.0 ± 0.1</td>
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<tr>
<td>Expt.</td>
<td>1.838⁶</td>
<td>4.61 ± 0.08⁶</td>
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<tr>
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<td>1.750</td>
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<td></td>
<td></td>
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<tr>
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<td>1.34</td>
<td>1.908</td>
<td>2.51</td>
<td>1.13</td>
</tr>
</tbody>
</table>

⁶See Ref. 41. ⁷See Ref. 42. ⁸See Ref. 43. A Dₑ value, the zero point vibrational energy contribution taken from the B3LYP harmonic frequency calculations is ~0.04 eV.
are attached molecularly, and the geometry corresponds to a MnCl₃*Cl₂ adduct. The molecular nature of Cl₂ in this adduct can be confirmed by the bond length of 2.01 Å in the adduct’s Cl₂ dimer, which practically matches the equilibrium bond length of 2.00 Å in the free-standing Cl₂ dimer computed at the same level of theory. On the contrary, all Cl atoms are bound to the Mn atom chemically in the MnCl₅⁻ anion whose ground-state geometry has C₄ᵥ symmetry. In both MnCl₆ and MnCl₄⁺, four Cl atoms are bound chemically to the Mn atom, while two Cl atoms are bound molecularly, and these species possess the adduct MnCl₄⁺Cl₂ geometries. Our results obtained for the neutral and negatively charged Mn chlorides allow one to state that the highest oxidation state of Mn with respect to Cl is +4.

In neutral MnClₙ, the total magnetic moment decreases from 6 μₜ in MnCl to 3 μₜ in MnCl₄, i.e., each added Cl atom decreases the total magnetic moment by 1 μₜ in this series. Since MnCl₃ can be viewed as a MnCl₄⁺Cl₂ adduct, it has the same total magnetic moment as MnCl₃. By analogy, MnCl₅ has the same total magnetic moment as MnCl₄. Except for MnCl₅⁻ and MnCl₆⁻, the total magnetic moment of an anion is larger by 1 μₜ than the total magnetic moment of the corresponding neutral parent. The total magnetic moment of MnCl₅⁻ is smaller by 1 μₜ than that of the total magnetic moment of neutral MnCl₅ due to the increase in the number of chemically bound Cl atoms: three Cl atoms attached chemically to the Mn atom in MnCl₅ vs five atoms attached chemically in MnCl₅⁻. Both neutral and anionic MnCl₆ clusters have adduct-type AX₄*Y₂ geometries and, therefore, their total magnetic moments are the same as those of MnCl₄ and MnCl₄⁻, respectively.

Relative thermodynamic stabilities of MnClₙ clusters are estimated from the energies computed for different decay channels. The smallest dissociation energies of the neutral species are to be obtained according to the formula:

\[ \Delta E_{\text{neutral}} = E(\text{MnCl}_n) - E(\text{MnCl}_{n-m}) - E(\text{Cl}_m), \quad m = 1, 2. \] (1)

while for the anions, one have to estimate the energies of four decay channels according to the formulas:

\[ \Delta E_{\text{anion}}^1 = E(\text{MnCl}_{n}^-) - E(\text{MnCl}_{n-m}^-) - E(\text{Cl}_m), \quad m = 1, 2. \] (2a)

\[ \Delta E_{\text{anion}}^2 = E(\text{MnCl}_{n}^-) - E(\text{MnCl}_{n-m}^-) - E(\text{Cl}_m), \quad m = 1, 2. \] (2b)

Figure 2 presents the fragmentation energies of neutral and anionic MnClₙ clusters computed according to these formulas. For n = 1–3, neutral MnClₙ would likely prefer to dissociate into MnClₙ₋₁ + Cl, while the lowest energy fragmentation channel for larger n corresponds to the yield of Cl₂. As can be seen from Fig. 2, MnCl₂ is the most stable in the neutral series, which is consistent considering the preferred oxidation state of Mn atom to be +2. The lowest energy decay channel of MnCl₃ corresponds to dissociation into MnCl₁ + Cl₂, as it can be anticipated on the basis of the adduct geometry of MnCl₅ in Fig. 1. The fragmentation energy of MnCl₅ is only 0.11 eV and it decreases to 0.03 eV for MnCl₆, that is, both these neutrals are of the van der Waals type. Since MnCl₂ is thermodynamically the most stable species in the neutral series, it is not surprising that MnCl₅⁻ is the most stable species in the anion series [see Fig. 2(b)] in agreement with experiment. While the yield of molecular chlorine is energetically preferred in the neutral series beginning with MnCl₄, it is MnCl₅⁻ in the anion series.

As it was stated before, the highest oxidation state of Mn relative to Cl atoms is +4. According to our

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**FIG. 1.** Optimized geometries of neutral and singly negatively charged MnClₙ clusters. Bond lengths are in (Å).
computations of the thermodynamic stability of Mn chlorides, MnCl and MnCl are the most stable species in the neutral and anionic series, respectively. Therefore, one can conclude that the preferred oxidation state of Mn in chlorides is +2. This corresponds to the participation of only two 4s electrons in chemical bonding, whereas the half-filled 3d shell of Mn atom remains intact. The high total magnetic moment of MnCl is mostly due to the spins of 3d-electrons occupying localized atomic spin-orbitals of Mn.

The calculated VDEs of MnCl and the EA of neutral MnCl, are presented in Table II. As can be seen, the EA and VDE values are quite different for all Mn chlorides (except for MnCl) apparently due to significant distortions of the neutral geometries produced by the extra electron attachment. While the EA values of MnCl and MnCl are relatively small, MnCl has the EA of 4.50 eV and is a superhalogen. The EA and VDE values of MnCl are larger than the EA of a Cl atom for n ≥ 3, and, hence, all of them are superhalogens.

In order to gain insight into the nature of chemical bonding in the Mn chlorides, one can analyze the electronic distributions reflected in the charges on atoms computed using natural atomic orbitals (NAO). The Mn charge obtained from the NBO analysis is presented in Fig. 2(d) as a function of n. The charge is positive in all neutral MnCl, which indicates the anticipated metal-to-ligand charge transfer. As can be seen, the Mn charge increases at n = 2 and then decreases at n = 3 and 4. The Mn charges in MnCl and MnCl are nearly the same as in MnCl and MnCl, respectively, in accord with the adduct type of MnCl (MnCl*Cl2) and MnCl (MnCl*Cl2). In the MnCl anions, the Mn charge increases up to n = 3 and then decreases at n = 4 and 5. The Mn charge in MnCl is the same as it is in MnCl since the MnCl anion corresponds to a weakly bound MnCl*Cl2 complex. The Mn charges in neutral MnCl and MnCl are significantly larger than the Mn charges in the corresponding anions. This means that the extra electron is mostly localized on the Mn atom in these anions. However, the extra electron is delocalized over halide atoms in the MnCl anions for n ≥ 3 and the corresponding neutral species are superhalogens.

It is interesting to compare the properties of MnCl with the properties of MgCl and ZnCl, where Mg and Zn possess oxidation states of +2. Unlike the lowest total energy structure of MnCl, where all Cl atoms are bound dissociatively, the lowest total energy structure of MgCl contains non-dissociated quasi-molecular Cl2, as shown in Fig. 3. The computed MgCl EA of 5.43 eV is to be compared to

<table>
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<th>Cluster</th>
<th>Neutral GS μ (μB)</th>
<th>Anion GS μ (μB)</th>
<th>EA (eV)</th>
<th>VDE (eV)</th>
</tr>
</thead>
<tbody>
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<td>1.52</td>
<td>1.59</td>
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<td>6</td>
<td>1.10</td>
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<td>MnCl4</td>
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<td>MnCl5</td>
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<td>MnCl6</td>
<td>3</td>
<td>4</td>
<td>5.36</td>
<td>5.97</td>
</tr>
</tbody>
</table>

FIG. 3. Ground-state geometries of the neutral and anionic Mg trihalides.

The computed EA of ZnCl is 5.40 eV, which practically matches the MgCl EA value. Both neutral and anionic ZnCl geometries are similar to the MgCl geometries; therefore, one can assert that both Mg and Zn interact with three chlorine atoms in a similar way. The smaller value of the MnCl EA compared to the MgCl and ZnCl EA values can be related to the involvement of 3d electrons in the Mn–Cl interactions. Indeed, the ground-state total magnetic moment of MnCl is 4 μB and the total NAO occupation of spin-up 3d electrons is 4.58 e according to the results of the NBO analysis.

B. MnBr clusters

In order to examine how the involvement of the Mn 3d subshell in the bonding in Mn halides depends on the halide electronegativity, we calculated the properties of Mn bromides and fluorides. First we consider bromides whose optimized geometries are displayed in Fig. 4. The ground-state neutral and anionic geometries of MnBr are similar to those of MnCl for n ≤ 3 with the only exception of MnBr, which is linear, while MnCl is bent. For larger n, there are a number of differences between Mn chloride and bromide structures. In neutral MnBr, only two Br atoms are chemically attached to the Mn atom, while two other Br atoms are attached molecularly. The Br–Br distance in the dimer is 2.37 Å, which is close to the bond length of 2.31 Å in a free-standing Br2 molecule. All Br atoms are attached chemically to the Mn atom in the MnBr anion in the same way as in the MnCl anion. Both neutral MnBr and its MnBr anion contain a Br2 dimer bound to the MnBr core. We have not considered larger MnBr clusters because the binding energy of Br2 already in MnBr3 is very small.
The total magnetic moments of neutral MnBrₙ clusters are 
4 \( \mu_B \) for \( n = 3 \) and 5 \( \mu_B \) for \( n = 2 \) and 4, respectively. MnBr₃ has the same magnetic moment as MnBr₂ because it has a MnBr₂⁺Br₂ adduct-type geometry. Similarly, the ground-state geometrical structure of MnBr₃ can be described as MnBr₃⁺Br₂; therefore, the total magnetic moments of MnBr₃ and MnBr₅ match each other. The total magnetic moment of MnBr₂⁻ is 4 \( \mu_B \), while it is 6 \( \mu_B \) in MnCl₂⁻. The difference is reflected in the different ground-state geometries of MnBr₂⁻ and MnCl₂⁻.

The fragmentation energies of neutral and anionic MnBrₙ clusters calculated using Eqs. (1) and (2) are displayed in Figs. 5(a) and 5(b), respectively. Similar to the neutral MnClₙ chlorides, the neutral Mn bromides would dissociate to MnBrₙ₋₁ + Br for \( n \leq 3 \) and to MnBrₙ₋₂ + Br₂ for \( n = 4 \) and 5. The binding energies of MnBr₄ and MnBr₅ are very small which is consistent with their adduct-type geometries. Among the anionic Mn bromides, the yield of a Br₂ dimer is energetically preferred only for MnBr₃⁻. The MnBr₂ and MnBr₅⁻ species are the most thermodynamically stable in the neutral and anionic series, respectively. This allows the oxidation state of +2 to be considered as the preferred state in interactions between Mn and Br atoms. This number corresponds to the preferred oxidation state of Mn in chlorides; however, the maximum oxidation state of Mn relative to Br is +3, i.e., one less than relative to Cl.

The calculated VDEs of MnBrₙ⁻ and the EA_{ad} of neutral MnBrₙ are presented in Table III. While the EA_{ad} values of MnBr and MnBr₂ are smaller than 2 eV, the EA_{ad} of MnBr₃ is 4.58 eV, which makes this tribromide a superhalogen. The NAO charge of the Mn atom obtained for the neutral and anionic MnBrₙ series is plotted in Fig. 5(d) as a function of \( n \).

For the neutral species, the Mn charge oscillates between odd and even \( n \) values. In anions, the Mn charge increases up to \( n = 3 \), decreases at \( n = 4 \), and increases again at \( n = 5 \). According to this plot, the extra electron is mostly localized at Mn in MnBr⁻ and MnBr₂⁻. This can be related to the relatively low EA_{ad} values of their neutral parents. In MnBr₃⁻ cluster, the extra electron is delocalized over the ligand atoms, which is typical for superhalogens. There is no substantial increase in the EA_{ad} of MnBr₄ and MnBr₅ compared to the EA_{ad} of MnBr₃. The calculated VDE and EA_{ad} values of MnCl₃ and MnBr₃ clusters are underestimated with respect to the experimental values by about 0.5 eV, which is in agreement with the previously reported theoretical values. We also calculated the EA_{ad} values of MnCl₃ and MnBr₃ using the 6–311+ (3df) basis set and the second-order perturbation theory. The MP2 EA_{ad} values of 5.49 eV and 5.70 eV obtained for MnCl₃ and MnBr₃, respectively, are overestimated compared to the corresponding experimental values of 5.07 ± 0.06 eV and 5.03 ± 0.06 eV.

The total magnetic moment of the lowest total energy state of MnBr₃ is 4 \( \mu_B \) and the 3d shell occupation is 4.70 \( e^- \), which is to be compared to 4.58 \( e^- \) in MnCl₃. The larger occupation of 3d electrons in MnBr₃ indicates that Mn–Br interactions are weaker than the Mn–Cl interactions.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Neutral GS ( \mu_B )</th>
<th>Anion GS ( \mu_B )</th>
<th>EA (eV)</th>
<th>VDE (eV)</th>
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<td>MnBr</td>
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<td>MnBr₃</td>
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<td>4</td>
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<td>4.81</td>
<td>5.37</td>
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</table>
ently, it is due to a larger size of Br atoms compared to Cl atoms, which is reflected in longer Mn–Br bond lengths as compared to the Mn–Cl bond lengths.

We also computed the lowest total energy excited states (ES) of MnCl$_3$ and MnBr$_3$, which were found to possess the same total magnetic moment of 6 $\mu_B$. The excited state geometries are similar to the geometries of the corresponding ground states of MgCl$_3$ and MgBr$_3$ shown in Fig. 3. The 3$d$ subshell occupation in these isomers increases to 4.96 $e$, which means that the Mn 3$d$ electrons are chemically inserted in these excited states. The total energy difference between the ground and excited states of MnCl$_3$ is 0.90 eV and the difference reduces to 0.49 eV in MnBr$_3$. The larger 3$d$ electron occupation in ground-state MnBr$_3$ and smaller total energy difference in the ground-excited state in MnBr$_3$ compared to those of MnCl$_3$ confirm interactions of Mn 3$d$ electrons with Br electrons to be weaker than with Cl electrons.

C. MnF$_n$ clusters

Optimized geometries of the ground-state MnF$_n$ and MnF$_n^-$ series are shown in Fig. 6. As can be seen, fluorine atoms are attached dissociatively up to $n = 5$ and $n = 6$ in the neutral and anion series, respectively. This behavior is different from that found above for the MnCl$_n$ and MnBr$_n$ series. It is rather surprising that a Mn atom can chemically bind three Br atoms, four Cl atoms, and five F atoms (see Figs. 1, 4, and 6) despite these ligand atoms belong to the same group of halogens. The neutral MnF$_6$ geometry corresponds to a MnF$_4^*F_2$ adduct, while the MnF$_6^-$ geometry is nearly octahedral. Adding one more F atom to the structures of the hexafluorides results in thermodynamically metastable neutral and anionic MnF$_7$. Total energies of the MnF$_7$ and MnF$_7^-$ states shown in the bottom of Fig. 6 are higher than the dissociation limits MnF$_3 + F_2$ and MnF$_5^- + F_2$ by 1.34 eV and 0.23 eV, respectively.

In the neutral MnF$_n$ series, the total magnetic moment decreases monotonously from 6 $\mu_B$ of MnF to 2 $\mu_B$ of MnF$_5$. The smallest total magnetic moments found in the MnBr$_n$ and MnCl$_n$ series are 4 $\mu_B$ and 3 $\mu_B$, respectively. That is, the value of the smallest total magnetic moment decreases when the halogen size decreases. As anticipated, MnF$_6$ possesses the same total magnetic moment as Mn$_4^*F_2$ cluster because the hexafluoride has an adduct-type MnF$_4^*F_2$ geometry. The total magnetic moment of the MnF$_5^-$ anions is larger than that of the corresponding neutral clusters by 1 $\mu_B$ for $n = 3, 4, 5$.

Fragmentation energies of MnF$_n$ clusters are displayed in Fig. 7. The smallest energy dissociation channel of neutral MnF$_n$ corresponds to MnF$_{n-1} + F$ for $n \leq 5$, and the smallest energy decay channel of anionic MnF$_n$ corresponds to MnF$_{n-1}^- + F$ up to $n = 6$. The MnF$_5^-$ anion shown in Fig. 6 is metastable with respect to the MnF$_5^-$ + F$_2$ decay. Figure 7 shows MnF$_2$ to be the most thermodynamically stable in the neutral series. However, the thermodynamically most stable anion cluster in the MnF$_n^-$ series is MnF$_5^-$ but not MnF$_3^-$ as would follow from the analogy with the chlorine and bromine series. Judged by the ability of Mn to bind chemically up to 5 fluorine atoms in the neutral MnF$_n$ series, one could assign the maximum oxidation state of +5 to Mn relative to F. However, the maximum oxidation state of Mn relative to F was previously assigned as +4. This discrepancy can be ascribed to a lower thermodynamic stability of MnF$_5$ with respect to that of MnF$_4$ [see Fig. 3(c)].

Our calculated VDE and EA$_{ad}$ values of Mn fluorides are given in Table IV. As in the chlorine and bromine series, the EA$_{ad}$ values are relatively small in the beginning of the series and jump up to 3.42 eV at MnF$_3$, which is smaller than the EA of a Cl atom. Note that the EA$_{ad}$ values of both MnCl$_3$ and MnBr$_3$ are higher than the MnF$_3$ EA$_{ad}$ by about 1 eV. The EA$_{ad}$ of the next member in the series, MnF$_4$, is 5.07 eV and this tetrafluoride is a superhalogen. As in the preceding
chloride and bromide series, the VDE and EA \( \text{ad} \) values are rather different for \( n = 3–7 \) because an extra electron attachment results in large geometry changes.

The Mn NAO charge in the neutral and anionic MnF\(_2\) series is plotted in Fig. 7(d) as a function of \( n \). In the neutral series, the Mn charge increases up to \( n = 3 \) and then saturates. In the anion series, the Mn charge saturation occurs after \( n = 4 \). The extra electron is entirely delocalized over fluorine atoms in the MnF\(_4\) \(^{-}\) anion, and MnF\(_4\) is a superhalogen. This is not so in the MnF\(_3\) \(^{-}\) anion, where the extra electron is partially localized on the Mn atom, and, as a consequence, MnF\(_3\) is not a true superhalogen. This could be due to a rather large involvement of Mn 3d electrons in the chemical bonding, which is reflected in the Mn 3d population of 4.35 e. This is appreciably smaller than the 3d subshell occupation in the Mn tribromides and trichlorides. When moving from MnF\(_2\) to MnF\(_3\) and MnF\(_4\), a substantial increase in EA \( \text{ad} \) values is observed, and the Mn hexafluoride possesses the highest EA \( \text{ad} \) value in the considered Mn halide series, which exceeds the EA of a Cl atom nearly two times.

The interaction between Mn and F in MnF\(_3\) is different from that between Mn and Cl (Br) in MnCl\(_3\) (MnBr\(_3\)). This is reflected from the following results: (1) The occupancies of 3d electrons in the majority spin channel of Mn in MnF\(_3\) are 4.35 e while that in MnCl\(_3\) and MnBr\(_3\) are 4.58 e and 4.70 e, respectively. (2) The excited state of MnF\(_3\) lies 1.50 eV above the GS, while it is 0.90 eV for MnCl\(_3\) and 0.49 eV for MnBr\(_3\). (3) The magnetic moment of the ES of MnF\(_3\) is 2 \( \mu_B \), while that for MnCl\(_3\) and MnBr\(_3\) is 6 \( \mu_B \). The energy of the 6 \( \mu_B \) state in MnF\(_3\) is 2.53 eV higher than the GS. Note that the 6 \( \mu_B \) magnetic moment arises when 3d\(^{6}\) electrons behave as inert core. Clearly, this is not the case with the ES of MnF\(_3\).

Finally, we compare the trends in binding energies of MgX\(_3\) and MnX\(_3\) (X = F, Cl, Br). Figure 8 presents the differences in binding energies of the neutrals and its anions computed according to Eqs. (1) and (2). As can be seen, there are opposite trends in the Mg and Mn trihalide series. If the difference in the binding energies of a halogen atom in a neutral MgX\(_3\) cluster and its anion increases when moving from Br to F, then the reverse trend is observed for the Mn trihalides. These trends illustrate the role the Mn 3d-subshell plays during interactions with halogen atoms.

### IV. CONCLUSIONS

Using density functional theory, we performed a systematic study of interactions of halogen atoms with a single Mn atom. In order to gain insight into the role played by the Mn half-filled 3d-shell, we compared the properties of MnX\(_3\) and MgX\(_3\) trihalides. Our results can be summarized as follows:

(i) The interaction of Mn 3d electrons with halogen atoms is seen to differ from one halogen atom to another. While the geometries of neutral MnCl\(_n\) and MnBr\(_n\) bear some resemblance with each other, those of the MnF\(_n\) clusters are different. This demonstrates that the 3d\(^{6}\) subshell of Mn interacts more strongly with F than with Cl or Br. This is due to the larger electronegativity and smaller size of fluorine atoms that permit them come closer to the Mn atom.

(ii) By analogy to the classic MgCl\(_3\) sp-superhalogen, MnCl\(_3\) and MnBr\(_3\) are superhalogens as well, but not MnF\(_3\) whose adiabatic electron affinity nearly matches the EA of the F atom. This allows one to assign the preferred oxidation number of +2 for Mn interacting with Cl or Br, and +3 relative to F.

(iii) The adiabatic electron affinity of MgBr\(_3\) is larger than that of MgCl\(_3\), which, in turn, is larger than that of MnF\(_3\). The difference between the calculated electron affinities of MnCl\(_3\) and MnBr\(_3\) clusters is only 0.08 eV,
which is in good agreement with the experimental value of 0.04 eV.

(iv) In the anion series, MnCl$_3^-$, MnBr$_3^-$, and MnF$_4^-$ are thermodynamically the most stable species.

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