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Superhalogen properties of ZnF_n (n = 1 to 6) nanoclusters

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ABSTRACT

We perform density functional based calculations on the structures and stabilities of ZnF_n clusters up to n = 6. We find that Zn can bind successively to four F atoms, expanding its oxidation state to +4 from nominal value of +2. All these species are stable in their neutral as well as anionic states. Furthermore, the adiabatic electron affinities of these species suggest that ZnF_n behave as superhalogen for n > 2. Thus it may be possible, at least theoretically, to synthesize new class of compounds having predetermined oxidizing power utilizing ZnF_n superhalogen clusters.

Keywords: Superhalogen, Zinc fluorides, stability, electron affinity, DFT.

INTRODUCTION

The term 'superhalogen' refers to the molecular species whose electron affinities (EA) are larger than chlorine, a halogenic element with the highest EA (3.6 eV) in the periodic table. Such species conventionally consist of central metal atoms and highly electro-negative ligands. Collectively, it causes to increase the EA of system due to more positive charge delocalization over several ligand atoms. The pioneering work of Gutsev and Boldyrev [1] opened the route to the study of superhalogens. These species can be used for the oxidation of counterpart system with relatively high ionization potentials such as O_2, Xe [2] as well as synthesis of novel species with unusual chemical properties [3-5].

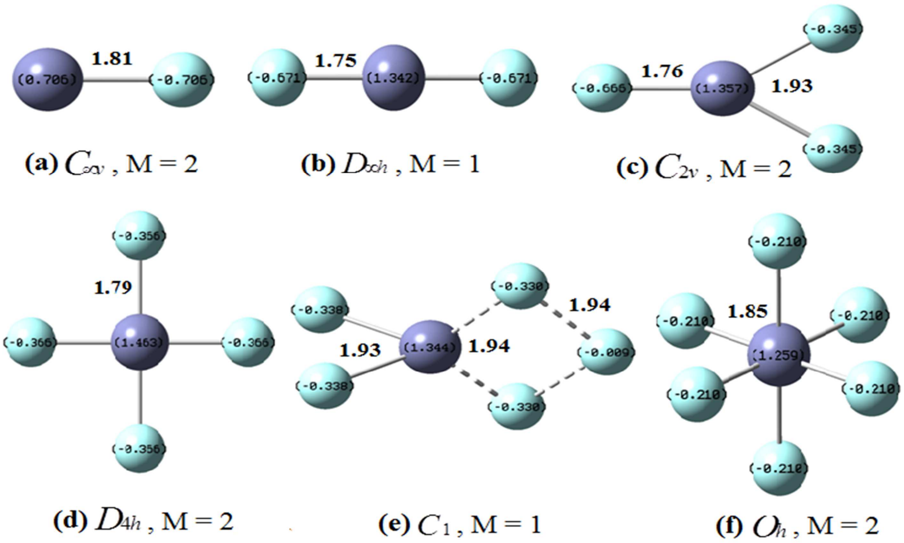
Historically, superhalogen species were given a general formula, ML_{k+1}, where k is the formal oxidation state of s block metal M and L represent electronegative ligands such as F, Cl or O. Due to their fixed valance, however, s block elements can bind only with a limited number of electro-negative atoms. Overcoming this limitation, d block transition metal elements came into play as they are known to show variable oxidation states. Even more interesting is the case of transition metal oxides. For example, the maximum oxidation state of manganese (Mn) can go up to +7. The stability of MnO4 and the existence of KMnO4, a well known oxidizing agent, support this fact. The EA of MnO4 was estimated to be 5 eV which is verified experimentally [6]. We have explored the superhalogen characteristics of a number of transition metal oxides [7-11]. Their EA values are quite larger than that of O atom which is only 1.42 eV. Recently, we have reported systematic studies on OsF_n [12], MF_n (M = Fe, Co & Ni) [13] and $AuCl_n$ [14] species.

We investigate here the superhalogen properties of ZnF_n clusters for n = 1 to 6 using density functional theory (DFT). We discuss the structures and stabilities of ZnF_n in their neutral as well as anionic forms. We calculate the EAs of neutral ZnF_n clusters and explain their origin.

MATERIALS AND METHODS

We have optimized the initial geometries of neutral and anionic ZnF_n clusters in which all F bind atomically to central Zn atom. Normal mode calculations are performed in order to ensure that all the optimized structures belong to a minimum in potential energy surface. The same calculations are repeated for higher spin multiplicity to obtain preferred spin states. Computations were carried out with Gaussian 09 program [15] at B3LYP level [16, 17] with SDD basis set for all atoms in the framework of DFT. This computational scheme has already been employed in some previous studies [7-14] and proven to provide reliable geometries and energetics of superhalogen species. Furthermore, we have noticed the superiority of B3LYP over MP2 method in a recent investigation [18].

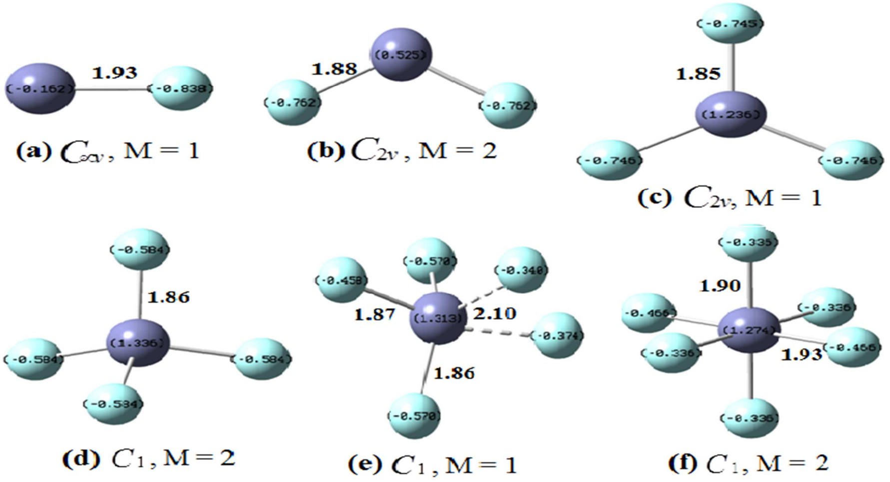
RESULTS AND DISCUSSION



(a) $C_{\infty v}$, M = 2 **(b)** $D_{\infty h}$, M = 1 **(c)** C_{2v}, M = 2

(d) D_{4h}, M = 2 **(e)** C_1, M = 1 **(f)** O_h, M = 2

Figure 1. Optimized geometries of neutral ZnF$_n$ nanoclusters (n = 1 to 6). Atoms are labelled with NBO charges (in e) and marked with respective bond-lengths (in A^o). Symmetries as well as spin multiplicities (M) are also given



(a) $C_{\infty v}$, M = 1 **(b)** C_{2v}, M = 2 **(c)** C_{2v}, M = 1

(d) C_1, M = 2 **(e)** C_1, M = 1 **(f)** C_1, M = 2

Figure 2. Optimized geometries of anionic ZnF$_n$ nanoclusters (n = 1 to 6). Atoms are labelled with NBO charges (in e) and marked with respective bond-lengths (in A^o). Symmetries as well as spin multiplicities (M) are also given

The equilibrium geometries of ZnF$_n$ (n = 1 to 6) neutral and anionic clusters are shown in Fig. 1 and Fig. 2. Atoms labelled with NBO charges, bond-lengths, symmetry as well as preferred spin multiplicity (M) of all species are also displayed. NBO charges are compared with atomic charges obtained with various other schemes and found to be more reliable [19]. All species are found to favour lower spin states energetically. The bond-lengths, Zn-F are higher in anions than in their neutral counterparts. Neutral ZnF$_2$ takes a linear $D_{\infty h}$ structure while its anion assumes a bent C_{2v} structure (Fig. 1b & Fig. 2b). The structure of neutral ZnF$_3$ closely resembles to that of its anion with planar C_{2v} geometry (Fig. 1c & Fig. 2c). In case of ZnF$_4$, a square planar D_{4h} geometry is favoured in neutral form while its anion takes a distorted tetrahedral C_1 structure (Fig. 1d & Fig. 2d). For n = 5, neutral ZnF$_n$ takes a structure in which two F atoms are very weakly bound and one F goes far away from centre (Fig. 1e) unlike its anion in which only two F atoms bind weakly but rest F bind strongly to central Zn (Fig. 2e). For n = 6, neutral ZnF$_n$ takes an octahedral (O_h) structure which becomes distorted in its anionic form (Fig. 1f & Fig. 2f). However, we will show later that ZnF_6 species are unstable and dissociate into various fragments.

Normal mode analysis reveals all real frequencies for structures given in Fig. 1 and Fig. 2. Thus they belong to at least a local minimum in potential energy surface implying that they are thermodynamically stable. In order to analyse further the stability of these structures, we have considered their fragmentation to F atom and F_2 molecule. The corresponding fragmentation energies for neutral as well as anions are calculated as follows,

ΔE ($ZnF_n \rightarrow ZnF_{n-1} + F$) = $E[F] + E[ZnF_{n-1}] - E[ZnF_n]$
ΔE ($ZnF_n \rightarrow ZnF_{n-2} + F_2$) = $E[F_2] + E[ZnF_{n-2}] - E[ZnF_n]$; $n = 1$ to 6

Where E[..] represents the electronic energy of respective species excluding zero point energy. The fragmentation energies are plotted in Fig. 3. All ZnF_n species up to $n = 5$ are found to be stable as ΔE is positive. ZnF_6 is unstable and dissociates into ZnF_5 + F fragments while its anion is unstable for both dissociation channels. On the other hand for $n = 5$, fragmentation energies are very small against dissociations either to F or to F_2 indicating that some F atoms are very weakly bound to Zn. For fragmentation to F_2 molecule, dissociation energy decreases continuously with the increase in F atoms up to $n = 5$. A similar trend is observed for dissociation to F atom with a discontinuity for neutral ZnF_2 and ZnF_3 anion. The higher fragmentation energies of these species as are in accordance with the smaller bond-length values compared to their neighbours.

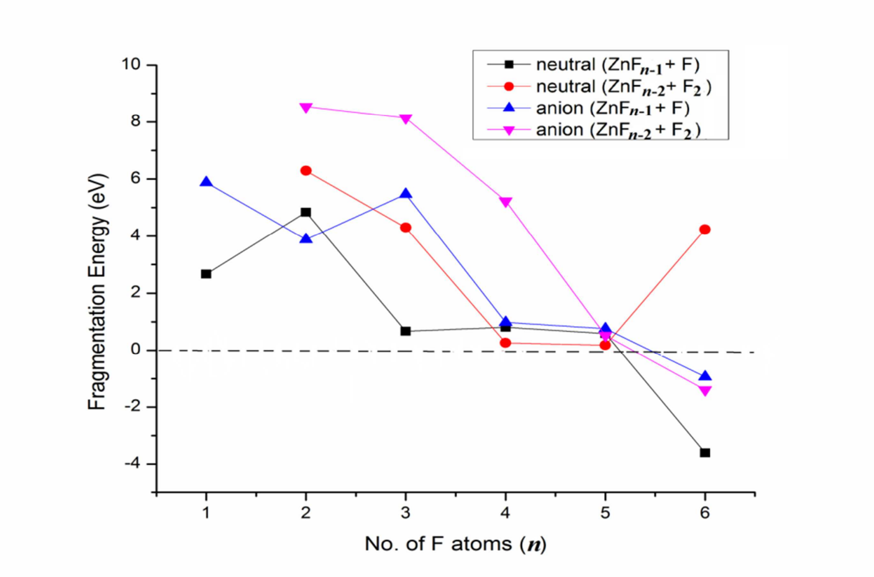


Figure 3. Fragmentation energies (ΔE) of neutral and anionic ZnF_n nanoclusters for F atom and F_2 molecule

Evidently Zn can bind with a maximum of four F atoms successively and form stable neutral and anionic ZnF_n species up to $n = 4$. Thus maximum oxidation state of Zn can be +4 as far as bonding with F atoms are concerned. Note that Zn possesses a main oxidation state of +2 which is reflected by the existence of ZnF_2. However, it is possible for Zn to exist in tetravalent state and form ZnF_4 due to involvement of inner shell 3d electrons in bonding.

In order to compare chemical reactivity of ZnF_n species, we have calculated the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO). These orbitals are responsible for chemical reaction and interaction with other species. In Fig. 4, we have plotted HOMO-LUMO gap as a function of n. The higher gap for ZnF_2 suggests that it is relatively more stable while smaller gap for ZnF_4 indicates that it is chemically more reactive or kinetically less stable. It may explain why it is not preferable for Zn to exist in ZnF_4 rather than ZnF_2. This further suggests that it is possible for ZnF_4 to react easily with appropriate metal atoms and form a complex compound with high oxidizing properties. As usual, an opposite trend of HOMO-LUMO gap is observed in case of ZnF_n anions.

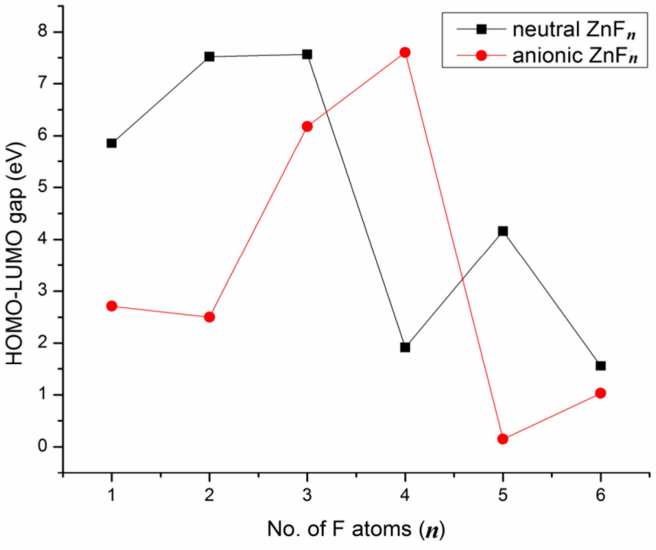


Figure 4. HOMO-LUMO gap of neutral and anionic ZnF$_n$ nanoclusters

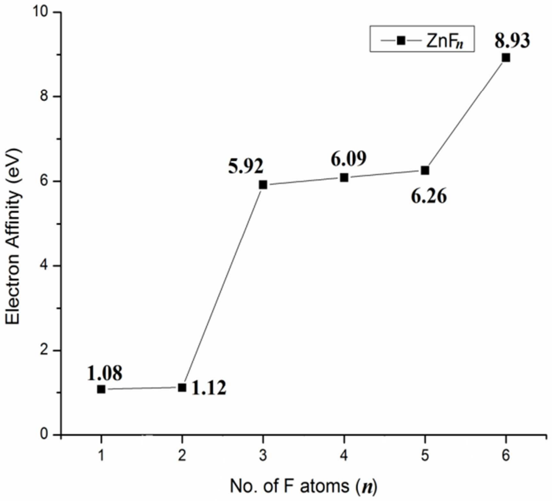


Figure 5. Adiabatic electron affinities of ZnF$_n$ for n = 1 to 6

Now we discuss EAs of these clusters and their origin. The adiabatic EA is calculated by difference of energies between neutral species and their anions both in their ground state configurations. The calculated EAs of all these clusters are plotted in Fig. 5 as a function of n. We can see that the EA value increases remarkably as the successive F atoms are attached to central metals and reaches at its maximum of 8.93 eV for n = 6. However, we didn't find any ZnF$_6$ as a stable structure so maximum EA of ZnF$_n$ species is limited to 6.09 eV for ZnF$_4$ in which all four F bind atomically to Zn. Thus large EAs ZnF$_3$ and ZnF$_4$ suggest that ZnF$_n$ clusters behave as superhalogens for all $n > 2$. These large EAs result due to more positive charge localization on Zn atom. We analyse the distribution of electrons in ZnF*n* clusters referring to NBO charges labelled on atoms in Fig. 1 and Fig. 2. In ZnF, charge concentrated on Zn is +0.71 e. As the number of F atoms increases, charge on Zn increases but saturates at +1.46 e on Zn in ZnF$_4$. Moreover, in ZnF$^-$, about 85% of extra negative charge is located on Zn. As successive F atoms are attached, extra charge starts to delocalise over several F atoms. Figure 6 plots the difference in NBO charges on Zn between neutral and anionic ZnF$_n$ clusters. Apparently, the charge difference decreases rapidly as the successive F atoms are attached. Furthermore, for $n > 2$, the charge difference is very small implying that positive charges on Zn in neutral and anion are almost equal. This explains the reason for high EA values of ZnF$_n$ species for $n > 2$.

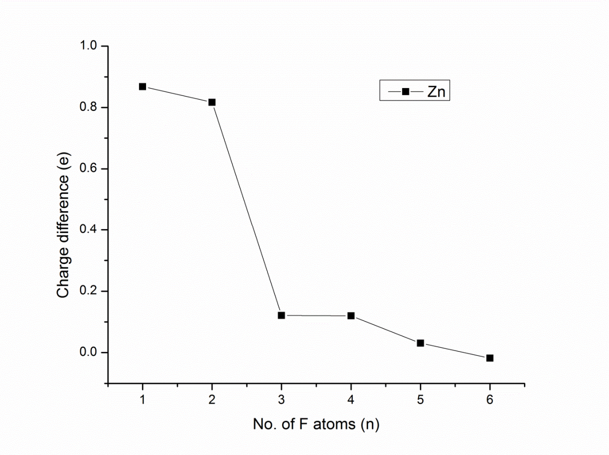


Figure 6. NBO charge difference for Zn in neutral and anionic ZnF_n nanoclusters

CONCLUSION

In summary, we have shown theoretically that Zn can bind dissociatively to four F atoms. All ZnF_n species are stable up to $n = 4$ irrespective of their charge and spin states. Thus maximum possible oxidation state of Zn can be as high as +4, at least in the case of bonding with F atoms. The electron affinity of ZnF_n species indicates that they behave as supe rhalogens for $n > 2$. The large electron affinity of ZnF_4 along with the enormous stability of its anion suggests the possibility of synthesis of an unusual compound by interaction with appropriate metals.

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