Journal of Fluorine Chemistry 135 (2012) 285–291

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Investigation of superhalogen properties of RhF_n (n = 1–7) clusters using quantum chemical method

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ARTICLE INFO

Article history:
Received 23 August 2011
Received in revised form 9 November 2011
Accepted 18 December 2011
Available online 8 January 2012

Keywords:
Density functional theory
Superhalogen
Electron affinity
Dissociation energy
HOMO–LUMO gap

ABSTRACT

In this paper we have studied the interaction of Rhodium (Rh) atom with Fluorine (F) using density functional theory. Up to seven F atoms are bound to a single Rh atom which results in increase of electron affinities of the given molecule successively, reaching a peak value of 9.05 eV for RhF_7. By using HOMO–LUMO gap, molecular orbital analysis, binding energy of these clusters, we examined its stability and reactivity. It is found that energy required for dissociation of F_2 molecules are higher than energy required for dissociation of F atoms. The unusual properties are brought about by involvement of inner shell 4d-electrons, which not only allow RhF_n clusters to belong to the class of superhalogens but also show that its valence can exceed the nominal value of 1.

1. Introduction

In the periodic table, the seventh group elements are more electronegative than other elements. If somehow, we increase the electronegativity of any molecule beyond the values exhibited by halogen atoms, then such molecule may be termed as a superhalogen. A metal element which is surrounded by peripheral electronegative atoms, such as Cl, F, etc., increases the electronegativity. The concept of superhalogen was first developed for *sp* elements. In 1981, Gutsev and Boldyrev proposed a simple formula for superhalogens, $MX_{(n+1)/m}$, where n is the maximal formal valence of the central atom (M), and m is the normal valence of electronegative atom (X) [1]. According to this theory, LiF_2 should be a superhalogen and indeed its EA of 5.45 eV [2] is larger than that for F. Pioneering work of Gutsev and Boldyrev [3] through the theoretical investigation of electron affinities (EAs) of chemical compounds is also a milestone for the search of new superhalogen compounds. As part of their ongoing research on superhalogen, Gutsev and Boldyrev [4] also calculated the electronic structure of the 3d and 4d metal hexafluoride anions. They concluded that all the hexafluorides of 3d and 4d metals may be considered as superhalogens. Pradhan et al. [5] explained the way by which different halogen atoms (F, Cl and Br) interact with the 3d electrons of Mn atom. Using photoelectron spectroscopy experiments and density functional theory Wu et al. [6] showed a new class of magnetic magic clusters, whose stabilities are governed by the superhalogen behavior and a half-filled d shell. Pradhan et al. [7] showed a number of interesting features using density functional theory based study of the structure and spectroscopic properties of neutral and negatively charged MX_n clusters formed by a transition metal alom M (M = Sc, Ti, V) and up to seven halogen atoms X (X = F, Cl, Br). Koirala et al. [8] briefly reported the superhalogen properties of fluorinated coinage metal XF_n (X = Cu, Ag and Au; n = 1–7) clusters.

Wang et al. [9] reported a combined photoelectron spectroscopic and theoretical study of six superhalogen anions, which were given by the general formula MX_2^- (M = Li and Na; X = Cl, Br and I). They also tried to perform experiments on the corresponding fluoride superhalogens, LiF_2^- and NaF_2^-. But their electron binding energies appeared to be beyond the detachment laser photon energy (6.424 eV) and no spectra was obtained. The idea behind selection of these atoms is the difference between their electronegativities, which generates more charge at these atoms, however, these elements have fixed coordination number, which allows them to bind with a limited number of halogens. To overcome this difficulty of fixed valence, transition metal elements are used, since their valency varies due to the presence of d orbital electrons. For example, a transition metal element Manganese (Mn), which has an outer orbital configuration of $3d^5 4s^2$, has maximum formal valence of 7 and thus, according to this theory

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doi:10.1016/j.jfluchem.2011.12.009

MnO_4 can be termed as superhalogen. The EA of MnO_4 was predicted to be 5 eV, which was experimentally verified [10] and was much higher than the EA of Oxygen (O) which is only 1.42 eV. The oxidation state of a metal atom is defined as the number of electrons participating in chemical bonding. Similarly, other 3d transition metals also known to form superhalogens, such as FeO_4 and CrO_4 molecules have EAs of 3.8 eV and 4.96 eV, respectively [11].

The third row transition metals M are well known to form hexahalide molecules [12–15] and the EAs of MX_6 are larger than that of X (halogen atoms). These molecules can be used as important oxidizers and when combined with appropriate positive ions, MX_6 can form salts. One of the unique example in the transition metal series is gold (Au). Outer electronic configuration of Au is $5d^{10}6s^1$. According to this configuration, Au should only be monovalent, but its oxidation state is confirmed to be +5 and may even be as high as +7 [16,17]. The oxidation state of a metal atom is defined as the number of electrons that can be removed from it to participate in chemical bonding. AuF_6, with an estimated EA of about 10 eV [18], is the most powerful oxidizing hexafluoride of the third row transition series and is well known to form a stable $CsAuF_6$ salt [19]. On the other hand, silver (Ag) has the highest oxidation state of +3 and AgF^-_4 also forms a stable salt [20]. Rhodium (Rh) belongs to the same group as Cobalt which have ferromagnetic behavior like Iron. With its outer electron configuration of $4d^75s^1$, Rh is known to possess a normal valence of 1, but

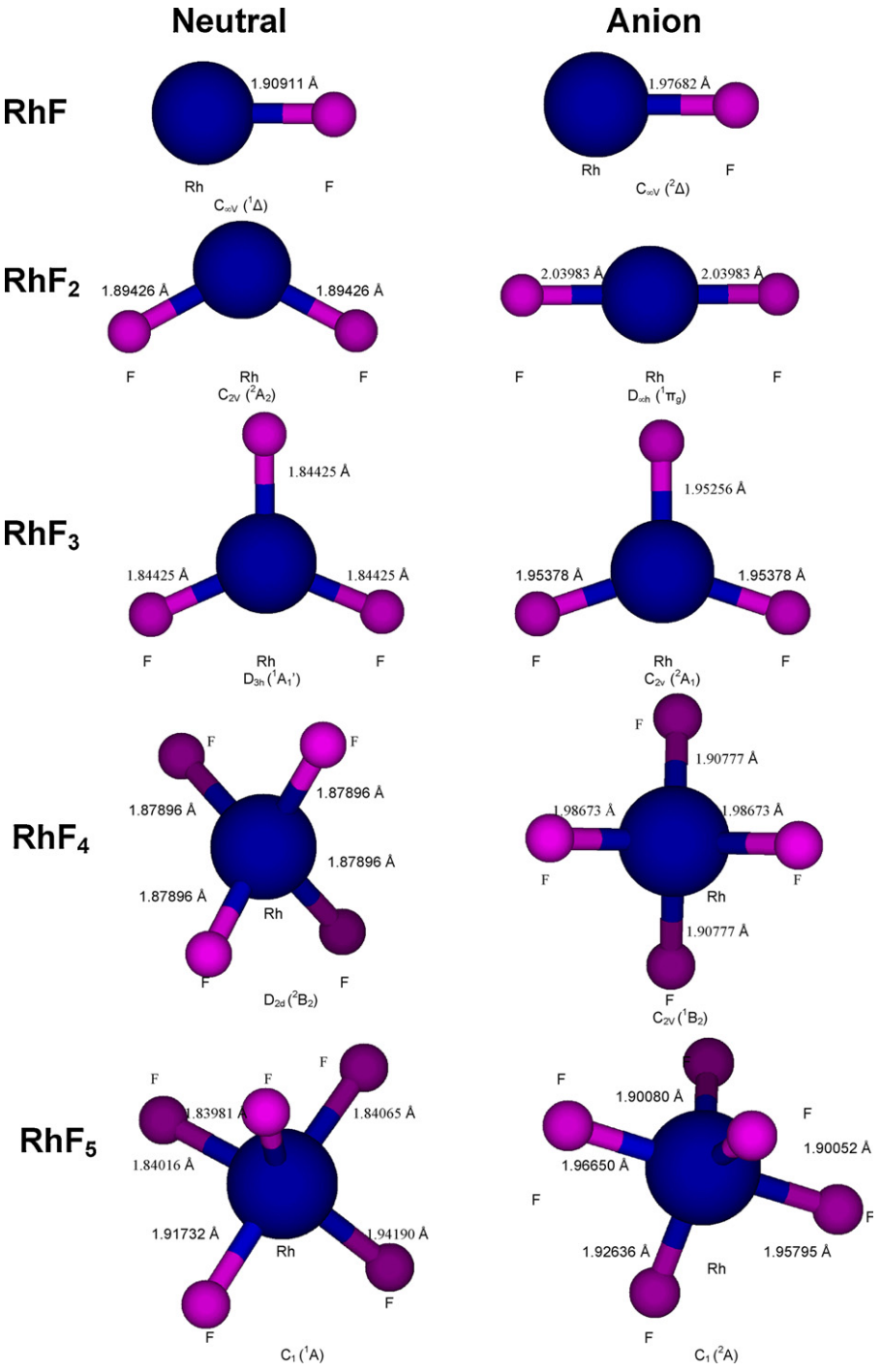

Fig. 1. Optimized geometries of RhF_n neutral and anionic clusters.

this can exceed up to 4 as exemplified by the existence of Rh_2O_3 and RhO_2. Actually Rh has partially filled 4d orbital as a result of which, it has variable coordination number, so it can bind with different numbers of F atoms. In this regard one can ask some questions. Can Rh also possess an oxidation state as high as +7? Can RhF_n clusters for $n \leq 7$ exist in gas phase? Do these clusters belong to the class of superhalogen? If yes, do these clusters form dimer as halogen atoms form F_2, Cl_2, etc. Is the binding of these clusters with an alkali metal stronger than that between F and alkali atoms?

In the present investigation, we have answered all these questions by using density functional theory (DFT) and molecular orbital approach. We find that Rh may also have oxidation number ranging from 1 to 7. However, RhF_7 cluster is not found to be stable, so the seventh atom of F is far away from the central Rh atom. Dissociation energy of the F_2 molecule is greater than the dissociation energy of F atom, hence, it is more common to find that Rh forms superhalogens with F_2. The EAs of RhF_n clusters increases continuously with increase in n, reaching a peak value of 9.05 eV for RhF_7. These values are much larger than the EA of Cl, namely, 3.62 eV [21], which is the most electronegative atom in the periodic table. We have also found that, the binding of RhF_7 superhalogens to an alkali atom is stronger than that between an alkali atom and F.

2. Results and discussion

In Fig. 1, RhF_n clusters in both neutral and anionic states of different sizes are shown. The structure of RhF_2 cluster in both anionic and neutral forms are different, since, the anionic form looks linear, while the neutral form appears to be somewhat triangular because the last electron is added to the lowest unoccupied molecular orbital (LUMO) of Rh. This added electron is delocalized over the whole molecule as a result of which, both F atoms are repelled by each other, making the structure linear. RhF_3 shows pyramidal structure in the case of its neutral form, however, in case of anion form, the last electron is added to LUMO of the central Rh atom, which increases the bond length between Rh and F. Hence, both the frontal F atoms are repelled by each other, which results in a distorted structure. In case of RhF_4, the structure is nearly the same in both anionic and neutral forms, except for the fact that, the bond length increases in the anionic form. More specifically, higher order structures are same in both cases, except that the there is an increase in bond length and hence, there is reduction in strain, leading to certain atoms being slightly displaced from their positions, which in turn leads to a deformed

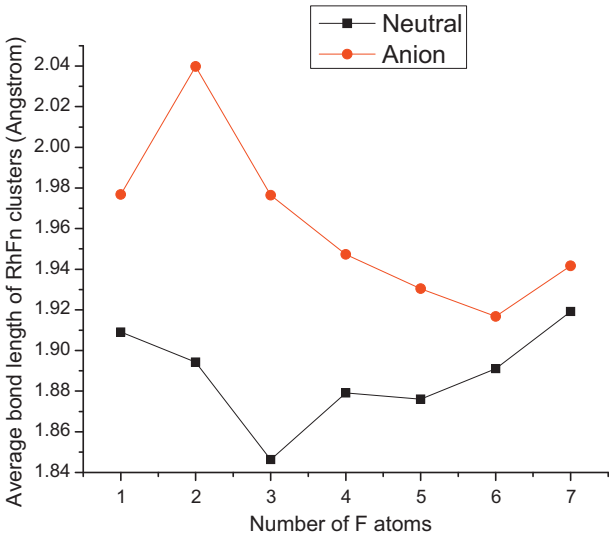

Fig. 2. Average bond length between Rh and F in neutral and anionic RhF_n clusters.

structure having higher stability. In the case of RhF_6, its shape is deformed in the anionic form, which becomes a distorted octahedron. Since, Rh has an outer electronic configuration [Kr] $4d^8 5s^1$, which implies that the coordination number of Rh could not exceed beyond 6, hence, it can combine with maximum six F atoms. In case of RhF_7, if Rh combines with a seventh F atom, then this atom will go far away from the central Rh atom, which results in an unstable structure. However, in case of anion, the last electron added to the LUMO of Rh and hence, coordination number increases to 7. So in case of anion, RhF_7 molecule will get little stability. Average bond length in both anionic and natural form with different number of F atoms is shown in Fig. 2. It is clear that in anionic form, the bond length is high, which implies that the bond strength is weak in accordance with the observations of other workers [22,23]. Hence, we can say that, these clusters are much more expected to be in the neutral form rather than in the anionic form.

The dissociation energies of F atom and F_2 molecule of neutral and anionic states are shown in Fig. 3(a) and (b), respectively. Table 1 shows the energy difference for different multiplicities of neutral and anionic RhF_n clusters. From Table 1, we can conclude that with the exception of anionic RhF_5 cluster, all other clusters, both in neutral and anionic form have the lowest possible spin state.

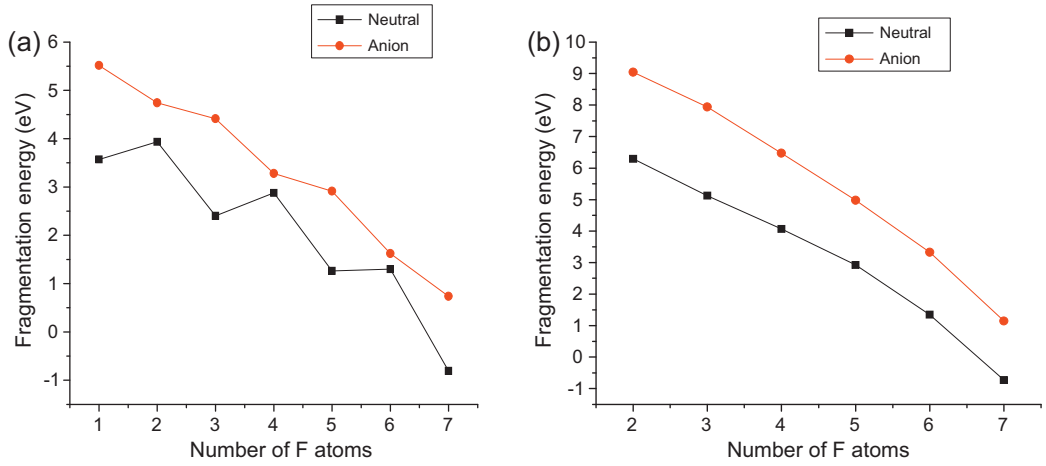

Fig. 3. (a) Fragmentation energies of neutral and anionic RhF_n clusters for fragmentation channel $RhF_n = RhF_{n-1} + F$ (b) Fragmentation energies of neutral and anionic RhF_n clusters for fragmentation channel $RhF_n = RhF_{n-2} + F_2$.

Table 1
Energy difference ΔE (in eV) between different multiplicities (M = 2S + 1) for neutral and anionic RhF_n clusters.

No. of F atoms	Neutral		Anion	
	M	ΔE	M	ΔE
1	1	0.00	2	0.00
	3	0.65	4	0.49
2	2	0.00	1	0.00
	4	0.97	3	1.14
3	1	0.00	2	0.00
	3	0.85	4	0.36
4	2	0.00	1	0.00
	4	0.60	3	0.93
5	1	0.00	2	0.02
	3	0.65	4	0.00
6	2	0.00	1	0.00
	4	1.01	3	1.12
7	1	0.00	2	0.00
	3	0.76	4	0.98

The relative stabilities of these clusters against fragmentation to F atom and F_2 molecule are studied by calculating the energy ΔE_n needed to dissociate these clusters into RhF_{n-1} + F, and RhF_{n-2} + F_2, namely,

$$\Delta E_n = -\{E[RhF_n] - E[RhF_{n-m}] - E[F_m]\}, \quad m = 1, 2 \tag{1}$$

$$\Delta E_n^- = -\{E[RhF_n^-] - E[RhF_{n-m}^-] - E[F_m]\}, \quad m = 1, 2 \tag{2}$$

The energy required to dissociate F atom and F_2 molecule decreases successively in both natural and anionic case as the number of F atoms increases. The calculated vibrational frequencies are positive for n = 1 to n = 6 in both neutral and anionic forms. So these molecules are stable in both neutral and anionic forms. This clearly indicates that the binding energy is sufficient for protection against dissociation and these molecules are at local minima. However, anionic forms are more stable against dissociation of F atom and F_2 molecule than the neutral forms. These clusters are also more stable against dissociation of F_2 molecule than F atom, which is more valuable for industrial purpose, since, F_2 molecules are easily available rather than atomic F to form these superhalogens. Neutral RhF_7 superhalogen clusters are unstable in both F and F_2 dissociation and lower order clusters are more stable than higher order ones.

In order to show reactivity of these clusters, we have plotted HOMO–LUMO gap against number of F atoms for both natural and anionic states in Fig. 4. This gap varies from 0.7 eV to 3.5 eV. Minimum HOMO–LUMO gap is found in case of anionic RhF_6 cluster. However, maximum HOMO–LUMO gap is found in case of

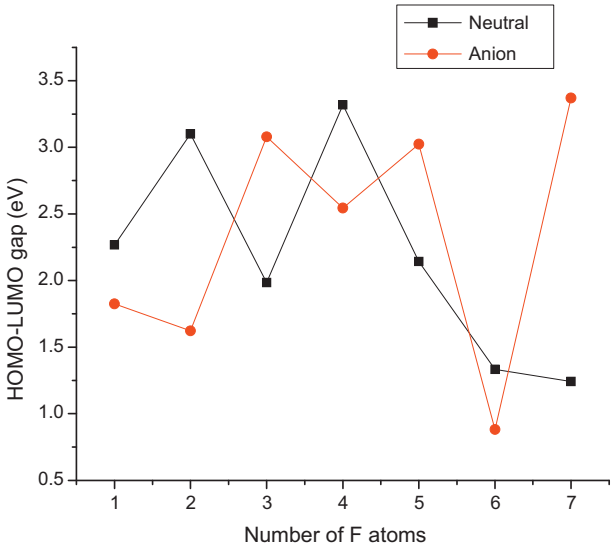

Fig. 4. HOMO–LUMO gap of neutral and anionic RhF_n clusters.

anionic RhF_7 cluster. We have already seen that anionic RhF_7 cluster is unstable against dissociation of F atom and F_2 molecule. HOMO–LUMO picture for RhF_7 cluster shown in Fig. 5(a) and (b), clearly shows that both HOMO and LUMO are situated over the whole molecule, so it is clear that the delocalized electron is situated over whole of RhF_7 cluster.

We already discussed that Rh atom has outer electronic configuration of [Kr] $4d^8 5s^1$, so its valence varies from 1 to 4. So the question arises how it can interact with different number of F atoms. To understand this mechanism, it is very important to know the contribution of 4d orbital of Rh atom, which interacts with the 2p orbital of F atom. The 4d orbitals are responsible for variation of coordination number. Hence, in this system whole electrons are not shifted towards the F atom. Fig. 6 shows the involvement of energy of 4d electrons in different order of molecules. The interaction between 4d orbital of Rh and 2p orbital of F makes perturbation in both 4d and 2p levels. As a result of this, perturbation of 4d level of Rh splits it into five different energy levels, however, 2p level of F splits in three different levels having nearly same energy. So bonding orbitals are of mix characteristics of p and d orbitals. These d orbital electrons are responsible for variation in the coordination number. From Fig. 6, it is clear that, as the number of F atoms increases, the energy of participating d electrons also increases in both anionic and neutral forms. This

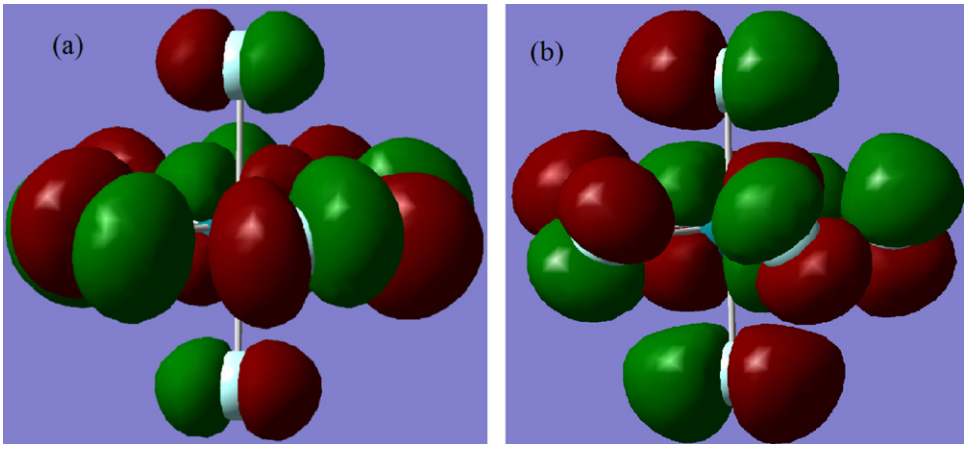

Fig. 5. (a) HOMO picture of RhF_7 cluster (b) LUMO picture of RhF_7 cluster.

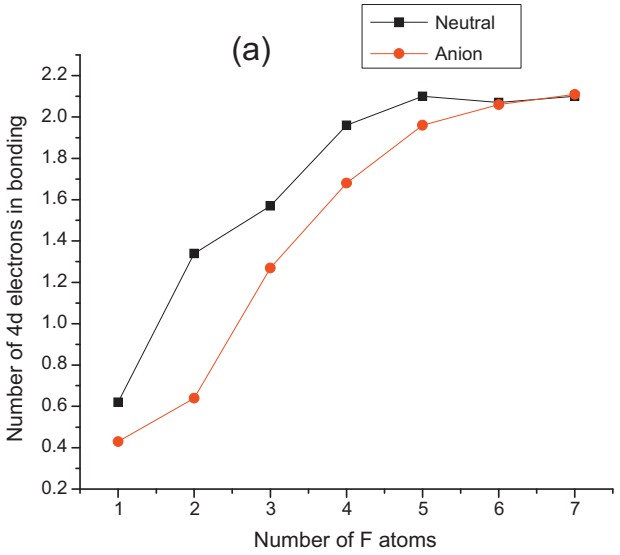

Fig. 6. Number of 4d electrons participating in bonding in neutral and anionic RhF_n clusters.

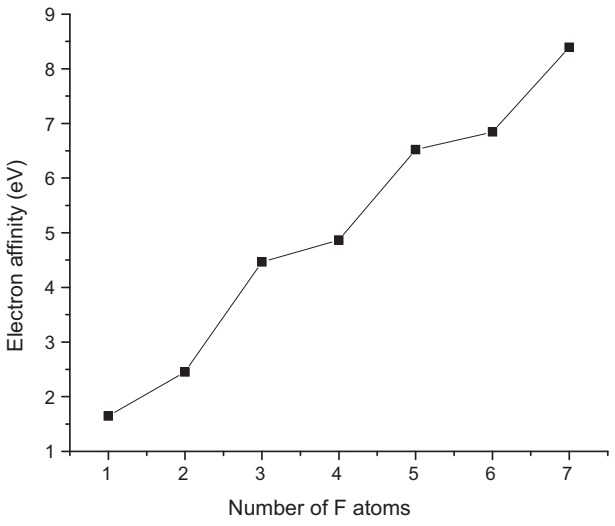

Fig. 7. Electron affinities of RhF_n clusters as a function of n.

clearly indicates that as the bonding energy of d electron increases, the possibility of formation of higher order clusters also increases. However, energy of d orbital for neutral form is greater as compared to the anionic form for $n < 6$.

Many years ago Gustev and Boldyrev [24,25] calculated the EAs of various chemical compounds and concluded that maximal EAs are enclosed within a range of 10–12 eV. However Sobczyk et al. [26] calculated the EAs of several anions and found that $Ta_3F_{16}^-$ has the EA of 12.63 eV. Recently Freza and Skurski [27] calculated the EA of $[H_{12}F_{13}]^-$ species as 13.87 eV, which is the largest EA reported so far in the literature. Fig. 7 shows a graph between EA and number of F atoms. These are calculated by taking the energy difference between the neutral and corresponding anionic forms of the cluster, both in their ground state configuration. EA rises from 1.5 eV to 9.0 eV as the number of halogen atoms increases from 1 to 7. The EA of RhF_7 (9.0 eV) is much higher than Cl atom, which has highest EA among all elements in the periodic table [21]. Hence, we can conclude that RhF_n ($n \geq 2$) clusters may be considered to be superhalogens.

Again a very important question arises. Is the polyvalent character of Rh a general characteristic or is this only confined with halogen? For this, we build different molecules of $Rh(O_2)_3$ and converge these geometries to the global minima to get the most stable structure. We find that the most stable structure for $Rh(O_3)_2$ has 2.76 eV binding energy per O_2, when the three O_2 molecules are bound in the superoxo form. The reason why Rh atom cannot dissociate three O_2 molecules while it can dissociate three F_2 molecules is that the binding energy of O_2 molecule, namely, 7.96 eV, is much larger than that for the F_2 molecule, namely, 1.37 eV. Thus, it appears that the polyvalent character of Rh may apply only in selected systems.

We need answers to the following questions to further understand the superhalogen behavior of RhF_n clusters. Upto what extent a superhalogen complex behaves like a halogen atom? As we know that halogen atoms form dimers. Does a superhalogen complex form a dimer? Second, a halogen atom interacting with an alkali atom forms an ionic compound, which is a salt. So, does a superhalogen bind more strongly to an alkali atom than a halogen atom? First of all we discuss the interaction between two RhF_4 units. In this case, Rh atom is positively charged while F atoms are negatively charged. We choose three initial possible geometries to study the formation of RhF_4 dimer. In first geometry, both the units are placed parallel to each other in such a way that the Rh atom of one unit is closer to two F atoms of other unit. In the other two geometries, both units are perpendicular to each other with Rh and F atoms close to each other. After geometry optimization, the third geometry which is of slightly distorted shape as compared to the second one is found to be most stable. After convergence to global minima, we checked the stability of this dimer by using frequency calculation, binding energy and HOMO–LUMO gap. We found that all the calculated frequencies were real, which clearly shows that the dimer is stable. Figs. 8(b) and (c) shows the HOMO and LUMO pictures of the most stable dimer. We can see that both HOMO and LUMO are situated over the whole molecule. The binding energy of

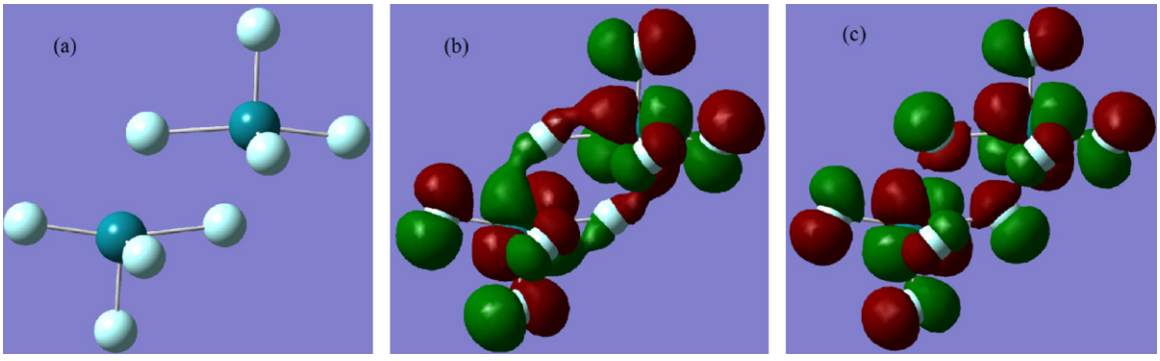

Fig. 8. (a) Optimized structure of RhF_4 dimer (b) HOMO picture of RhF_4 dimer (c) LUMO picture of RhF_4 dimer.

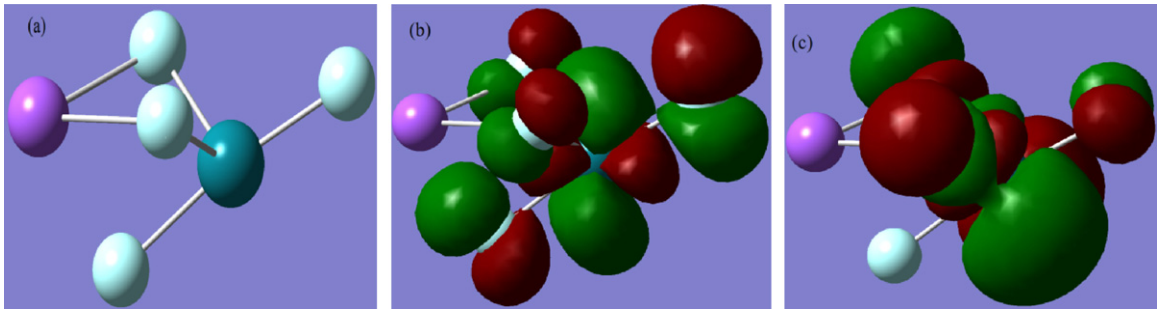

Fig. 9. (a) Optimized structure of RhF_4–Na complex (b) HOMO picture of RhF_4–Na complex (c) LUMO picture of RhF_4–Na complex.

most stable RhF_4 dimer is found to be 0.92 eV, which is slightly lower than binding energy of F_2 molecule, namely, 1.21 eV. The HOMO–LUMO gap for RhF_4 dimer is found to be 1.21 eV, which is quite small in comparison to the HOMO–LUMO gap of F_2 molecule, namely, 6.19 eV. These results clearly suggest that the RhF_4 dimer is chemically more reactive than F_2.

Now we discuss the interaction of RhF_4 superhalogen with an alkali atom of sodium (Na). We chose a structure in which a Na atom was placed at top of Rh atom and then optimized its geometry. After geometry optimization, we found that the Rh atom was slightly displaced in the molecular plane and it was bound to two F atoms [Fig. 9(a)]. After this, stability of this complex was confirmed by frequency and binding energy calculation. We found that all the frequencies were real, which implies that the resulting complex is stable. The binding energy of $NaRhF_4$ is found to be 5.16 eV. This is higher than the binding energy between a Na atom and a F atom, namely, 4.31 eV. Reactivity of this salt has been checked by the HOMO–LUMO gap, since, halogens when combined with an alkali metal form a more polar compound. Figs. 9(b) and (c) shows the HOMO and LUMO picture of RhF_4Na salt. From these figures it is clear that both HOMO and LUMO are situated over the whole molecule except Na atom. This is in contrast to NaF where the Na site does not contribute to HOMO, but contributes to LUMO. From this picture it is clear that bonding between Na atom and RhF_4 molecule is covalent in nature, which implies that bonding electrons are not shifted towards superhalogen side and hence, Na atom represents the inactive part of this molecule.

3. Conclusion

It has been shown that Rh binds with seven F atoms but neutral form of RhF_7 is not stable, however, in the anionic form RhF_7 is slightly stable and its HOMO–LUMO gap is found to be larger as compared to others. Energy needed to dissociate F_2 molecule is found higher than dissociation energy of atomic F. EA of RhF_n ($n \geq 2$) clusters is found more than Cl. It reached upto 7.00 eV for RhF_6 and 9.05 eV for RhF_7. The binding energy of $NaRhF_4$ is found higher than that for NaF, suggesting that a new class of salt can be synthesized by reacting RhF_4 with Na. The resulting supersalts with high oxidizing properties can have potential applications in combating biological agents.

4. Computational method

All the calculations have been done by the self consistent field technique using the linear combination of atomic orbital-molecular molecular approach. Total energies were calculated using DFT with B3PLY [28] method. We have chosen a complete set of Gaussian type orbitals and used the SDD basis set in our calculations. Various types of geometries were optimized using the *Gaussian 03W* program package [29]. Several molecular structures were build using the *GaussView 4.1* [30] program package and then optimization has been done to converge it to global minima. Normal mode frequencies were also calculated for all geometries to ensure that they belong to minima in the potential energy surface. After convergence the calculated data are well matched with experimental data. Such as the calculated bond length, EA and binding energy of F_2 are 1.461 Å, 3.480 eV and 1.37 eV, agree well with corresponding experimental values [31–33]. The lowest energy state geometries for $n \leq 4$ were re-optimized within actual symmetry constraints, if such obtained, in order to assign spectroscopic states. For higher n values, the C_1 structure was the lowest in energy at all levels. The structures of all the molecules shown in Fig. 1 have been prepared using the MOLDEN program [34].

Acknowledgement

Authors are thankful to the Deanship of Scientific Research, Najran University, Najran, Kingdom of Saudi Arabia for all financial support. Centre for Advanced Materials and Nano-Engineering (CAMNE), Najran University, Najran is highly acknowledged.

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