

Investigation of superhalogen behaviour of RuF_n ($n = 1-7$) clusters: density functional theory (DFT) study

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MS received 12 October 2011; revised 11 September 2012

Abstract. In the present investigation, interaction of ruthenium (Ru) atoms with fluorine (F) atoms was studied using the density functional theory utilizing B3LYP method. It was found that up to seven F atoms can bind to a single Ru atom which results in increase of electron affinities successively, reaching a peak value of 6.95 eV for RuF_6 . Its stability and reactivity were also examined by using HOMO–LUMO gap, molecular orbital analysis and binding energy of these clusters. 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 attributed to the involvement of inner shell 4d-electrons, which not only allow RuF_n clusters to belong to the class of superhalogens but also show that its valence can exceed the nominal value of 1. The interaction of RuF_4 superhalogen with an alkali atom lithium (Li) were also studied which suggests that a new class of salt can be synthesized by reacting RuF_4 with Li.

Keywords. Density functional theory; superhalogen; electron affinity; dissociation energy; HOMO–LUMO gap.

1. Introduction

Halogen atoms possess the highest EAs (3.0–3.6 eV) among all the atoms in periodic table (Hotop and Lineberger 1985). However, molecules may exceed this limit of 3.6 eV due to collective effects. There is a class of molecules known as superhalogens, that are especially important oxidizers. 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, $\text{MX}_{(n+1)/m}$, where n is the maximum formal valence of the central atom (M), and m is the normal valence of electronegative atom (X). Pioneering work of Gutsev and Boldyrev (1985) 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 (1984) also calculated the electronic structure of 3d and 4d metal hexafluoride anions. They concluded that all the hexafluorides of 3d and 4d metals may be considered as superhalogens.

According to this theory, LiF_2 should be a superhalogen and indeed its EA of 5.45 eV (Gutsev *et al* 1997) is larger than that of F. Wang *et al* (1999) reported a combined photoelectron spectroscopic and theoretical study of six superhalogen anions, which were given by the general formula, MX_2^- ($M = \text{Li}$ and Na ; $X = \text{Cl}$, 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 generate 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, MnO_4 can be termed as superhalogen. EA of MnO_4 was predicted to be 5 eV, which was experimentally verified (Gutsev *et al* 1999a, b) and was much higher than 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 are also known to form superhalogens, such as FeO_4 and CrO_4 molecules having EAs of 3.8 and 4.96 eV, respectively (Gutsev *et al* 1999a, b).

The third row transition metals, M , are well known to form hexahalide molecules (Compton and Reinhardt 1980; Scheller *et al* 1995; Lucier *et al* 1998a, b; Graudejus *et al* 1999) and 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

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be monovalent only, but its oxidation state is confirmed to be +5 and may even be as high as +7 (Riedel and Kaupp 2006; Himmel and Riedel 2007). AuF_6 with an estimated EA of about 10 eV (Compton 1978), is the most powerful oxidizing hexafluoride of the third row transition series and is well known to form a stable CsAuF_6 salt (Leary and Bartlett 1972). On the other hand, silver (Ag) has the highest oxidation state of +3 and AgF_4^- also forms a stable salt (Lucier *et al* 1998a, b). Ruthenium (Ru) belongs to the same group as iron which have ferromagnetic behaviour. With its outer electronic configuration of $4d^7 5s^1$, Ru is known to possess a normal valence of 1. Actually, Ru 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, many questions will arise. Can Ru also possess an oxidation state as high as +7? Can RuF_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, all of these questions are answered by using density functional theory (DFT) and molecular orbital approach. We find that Ru may also have oxidation number ranging from 1 to 7. Dissociation energy of F_2 molecule is greater than the dissociation energy of F atom, hence, it is more common to find that Ru forms superhalogens with F_2 . EAs of RuF_n clusters increase continuously with increase in n , reaching a peak value of 6.95 eV for RuF_6 . These values are much larger than EA of F, viz. 3.40 eV (Rienstra-Kiracofe *et al* 2002), which is the most electronegative atom in the periodic table. It is also found that the binding of RuF_n superhalogens to an alkali atom is almost equally stronger to that between an alkali atom and F.

2. Computational method

All the calculations have been done by the self-consistent field technique using the linear combination of atomic orbital–molecular orbital approach. Total energies were calculated using DFT with B3LYP (Becke 1993) method. A complete set of Gaussian type orbitals are chosen and SDD basis set is used in these calculations. Various types of geometries were optimized using Gaussian 03W program package (Frisch *et al* 2003). Several molecular structures were built using GaussView 4.1 (Frisch *et al* 2007) program package and then optimization was done to converge it to global minima. Normal mode frequencies were also calculated for all geometries to ensure that they belong to global minima in the potential energy surface. After convergence, the calculated data are well matched with experimental data. The calculated bond length, EA and binding energy of F_2 are 1.461 Å, 3.480 eV and 1.37 eV, respectively agree well with corresponding experimental values (Dibeler 1969; Pople *et al* 1989; Rienstra-Kiracofe *et al* 2002).

3. Results and discussion

In figure 1, RuF_n clusters in both neutral and anionic states of different sizes are shown. Structure of RuF_2 cluster in both anionic and neutral forms are different, as 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 Ru. 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. Similarly structural difference between neutral and anionic form of RuF_5 cluster can easily be seen as in case of anion, the last electron is added to LUMO of the central Ru atom, which increases the bond length between Ru and F. Hence, both the frontal F atoms are repelled by each other, which results in a distorted structure. All other structures are nearly same in both states, except that there

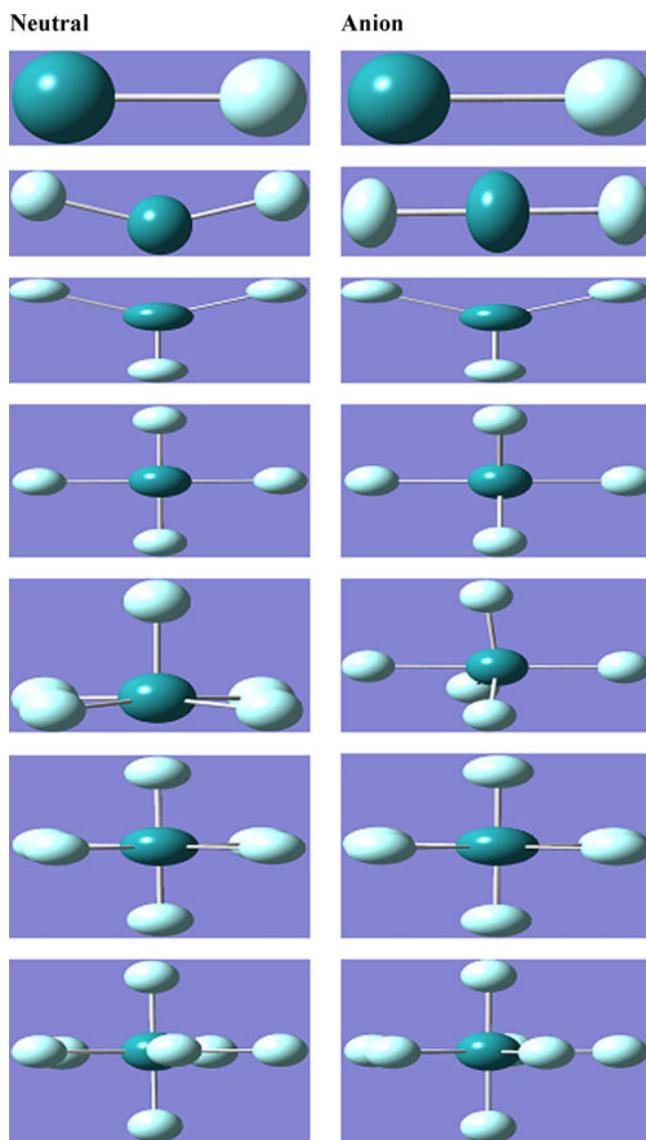


Figure 1. Optimized geometries of RuF_n neutral and anionic clusters.

is an increase in bond length in anionic form and hence, there is reduction in strain, leading to certain atoms being slightly displaced from their positions, which in turn leads to a deformed structure having higher stability. Average bond length in both anionic and neutral form with different number of F atoms are shown in figure 2. It is clear that in anionic form, the bond length is high, which implies that the bond strength is weak and this is in accordance with the observations of other workers (Costales *et al* 2003; Li and Gong 2006). Hence, we can say that these clusters are much more expected to be in the neutral form rather than in the anionic form. Another important inference may be made based on the nature of the graph in figure 2 at $n = 3$ value. In both the anionic and neutral forms, there is an observable dip in the graph at $n = 3$, which indicates the presence of important structural changes. Ruthenium is a rare-transition metal belonging to platinum group of the periodic table and its electronic configuration is given as $[\text{Kr}] 4d^7 5s^1$. As fluorine (F) atoms are combined with ruthenium (Ru) atom, $4d^7$ electrons of Ru interact with $2p$ electrons of F, leaving $5s^1$ half-filled shell untouched. In RuF_3 molecule, all the

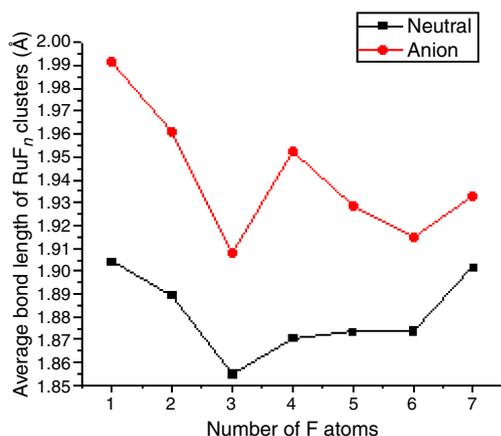


Figure 2. Average bond length between Ru and F in neutral and anionic RuF_n clusters.

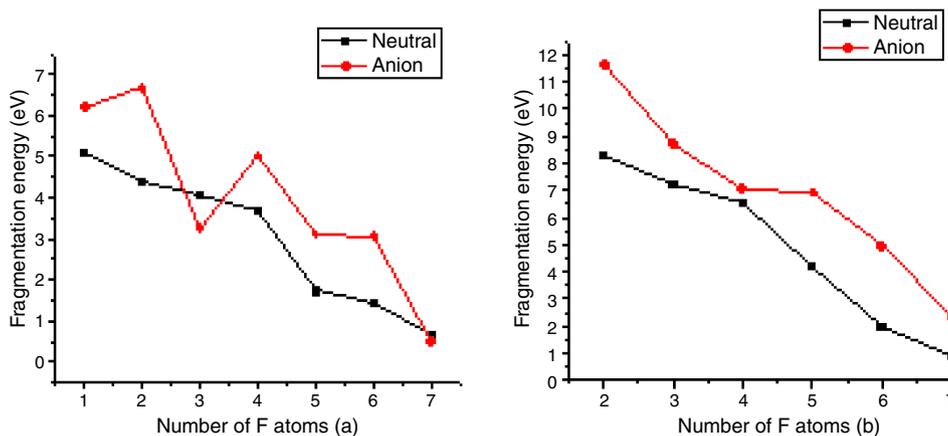


Figure 3. (a) Fragmentation energies of neutral and anionic RuF_n clusters for fragmentation channel $\text{RuF}_n = \text{RuF}_{n-1} + \text{F}$ and (b) fragmentation energies of neutral and anionic RuF_n clusters for fragmentation channel $\text{RuF}_n = \text{RuF}_{n-2} + \text{F}_2$.

d electrons are engaged leading to a more stable configuration and hence, a decrease in the average bond length and EA values are observed. As more F atoms are attached to Ru atom, its $5s^1$ electron begins to participate in the bonding and all $4d$ and $5s$ valence electrons of Ru hybridize and mix with ligand orbitals ($\text{F } 2p$) leading to an increase in the average bond lengths and EA values of RuF_n species when $n > 3$.

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 $\text{RuF}_{n-1} + \text{F}$ and $\text{RuF}_{n-2} + \text{F}_2$, viz.

$$\Delta E_n = - \{ E [\text{RuF}_n] - E [\text{RuF}_{n-m}] - E [\text{F}_m] \},$$

$$m = 1, 2, \quad (1)$$

$$\Delta E_n^- = - \{ E [\text{RuF}_n^-] - E [\text{RuF}_{n-m}^-] - E [\text{F}_m] \},$$

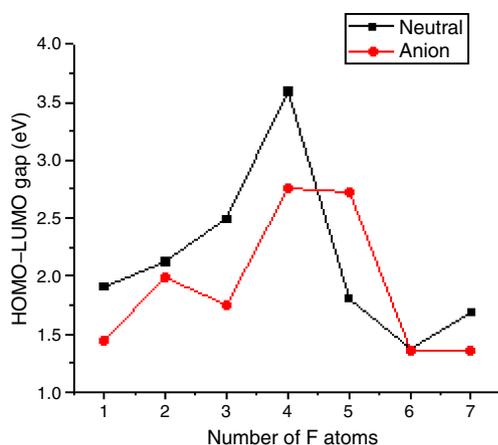
$$m = 1, 2. \quad (2)$$

The dissociation energies to F atom and F_2 molecule of neutral and anionic states are shown in figures 3(a) and (b), respectively. In both figures 3(a) and (b), a dip is observed at $n = 3$ for the anionic form, the deviation in figure 3(a) being more noticeable. In RuF_3^- , the extra electron would fill the lowest unoccupied molecular orbital LUMO which does not contain contributions from the central atom by symmetry at the anion ground state geometry. The resulting RuF_3^- anion, thus, has a closed-shell structure and should be thermodynamically and electronically very stable. Table 1 shows energy difference for different multiplicities of neutral and anionic RuF_n clusters. From table 1, we can conclude that with the exception of neutral RuF_4 cluster, all other clusters, both in neutral and anionic form, prefer higher spin state.

The energy required for dissociation to F atom and F_2 molecule decreases successively in both neutral and anionic cases as the number of F atoms increases. This clearly suggests that lower order clusters are more stable than higher order ones. All these neutral and anionic clusters up to ($n = 7$) are stable against dissociation to $\text{RuF}_{n-1} + \text{F}$ and

Table 1. Energy difference (in eV) between different multiplicities ($M = 2S + 1$) for anion and neutral RuF_n clusters.

Sl. no.	Neutral		Anion	
	M	ΔE	M	ΔE
1	2	0.84	1	1.46
	4	0.00	3	0.00
2	1	0.70	2	0.36
	3	0.00	4	0.00
3	2	0.92	1	1.29
	4	0.00	3	0.00
4	1	0.00	2	1.34
	3	0.45	4	0.00
5	2	1.13	1	0.79
	4	0.00	3	0.00
6	1	1.03	2	1.43
	3	0.00	4	0.00
7	2	0.34	1	1.05
	4	0.00	3	0.00

**Figure 4.** HOMO–LUMO gap of neutral and anionic RuF_n clusters.

$\text{RuF}_{n-2} + \text{F}_2$. The calculated vibrational frequencies are positive for $n = 1$ to $n = 7$ 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. Hence, all the neutral and anionic RuF_n clusters up to ($n = 7$) can be formed if atomic F or molecular F_2 are used in the synthesis. More specifically, 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.

In order to show reactivity of these clusters, we have plotted HOMO–LUMO gap against the number of F atoms for both neutral and anionic states in figure 4. For neutral RuF_n clusters, this gap varies from 1.36 to 3.60 eV, while for anionic clusters this gap varies from 1.35 to 2.75 eV. Minimum HOMO–LUMO gap is found in case of anionic RuF_7 cluster. However, maximum HOMO–LUMO gap is found in case of neutral RuF_4 cluster. HOMO–LUMO picture for RuF_4 and RuF_7 clusters is shown in figures 5(a) and (b), respectively.

We already discussed that Ru atom has an outer electronic configuration of $[\text{Kr}] 4d^7 5s^1$ and possesses a normal valence of 1. 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 Ru atom, which interacts with $2p$ orbital of F atom. $4d$ orbital is responsible for variation of coordination number. Hence, in this system whole electrons are not shifted toward F atom. Figure 6 shows involvement of $4d$ electrons in different order of clusters. The interaction between $4d$ orbital of Ru and $2p$ orbital of F makes perturbation in both $4d$ and $2p$ levels. As a result of this perturbation, $4d$ level of Ru splits into five different energy levels, however, $2p$ level of F splits into 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 figure 6, it is clear that as the number of F atoms increases, the participating d electrons also increase in both anionic and neutral forms.

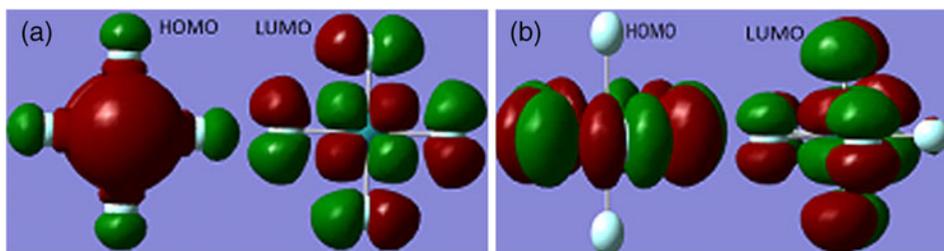
**Figure 5.** (a) HOMO and LUMO pictures of RuF_4 cluster and (b) HOMO and LUMO pictures of RuF_7 cluster.

Figure 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 1.10 to 6.95 eV as the number of halogen atoms increases from 1 to 7. EA of RuF₆ (6.95 eV) is much higher than F atom, which has the highest EA among all elements

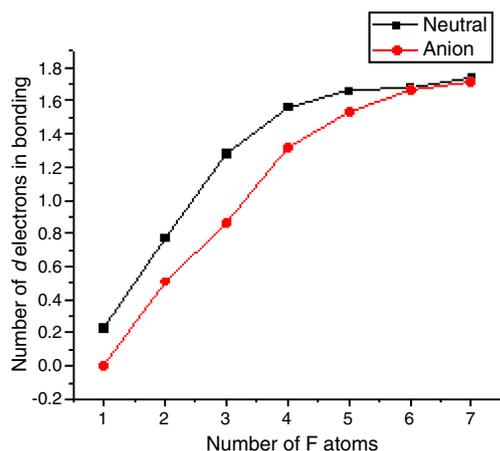


Figure 6. Number of 4d electrons participating in bonding in neutral and anionic RuF_n clusters.

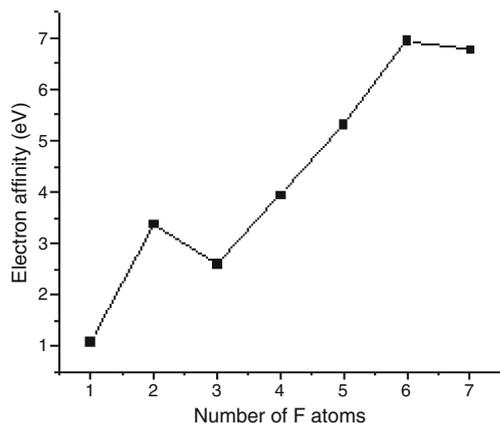


Figure 7. Electron affinities of RuF_n clusters as a function of *n*.

in the periodic table. Hence, we can conclude that RuF_n (*n* ≥ 4) clusters may be considered to be superhalogens.

Again a very important question arises. Is the polyvalent character of Ru a general characteristic or is this only confined with halogen? For this, we build different molecules of Ru(O₂)₃ and converge these geometries to the global minima to get the most stable structure. We find that the most stable structure for Ru(O₃)₂ has 3.84 eV binding energy per O₂, when the three O₂ molecules are bound in the super-oxo form. The reason why Ru atom cannot dissociate three O₂ molecules, while it can dissociate three F₂ molecules is that the binding energy of O₂ molecule, viz., 7.96 eV, is much larger than that for F₂ molecule, viz., 1.37 eV. Thus, it appears that the polyvalent character of Ru may apply only in selected systems.

We need answers to the following questions to further understand the superhalogen behaviour of RuF_n clusters. Up to 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 RuF₄ units. In this case, Ru atom is positively charged while F atoms are negatively charged. We choose three initial possible geometries to study the formation of RuF₄ dimer. In first geometry, both the units are placed parallel to each other in such a way that Ru 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 Ru and F atoms close to each other. After geometry optimization, the first geometry is found to be most stable. This optimized geometry is shown in figure 8(a). 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. Figures 8(b) and (c) show 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 most stable RuF₄ dimer is found to be 0.79 eV, which is less than binding energy of F₂

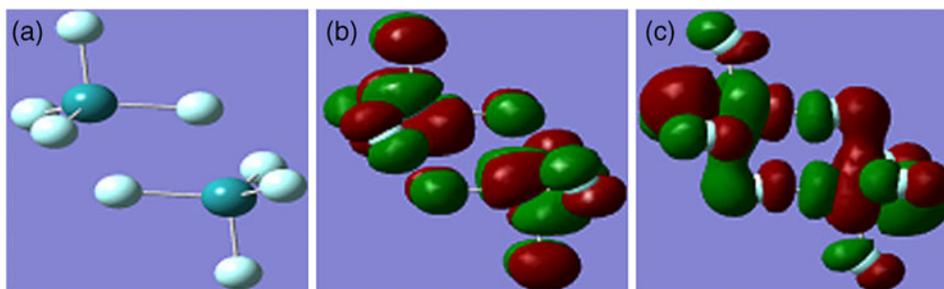


Figure 8. (a) Optimized structure of RuF₄ dimer, (b) HOMO picture of RuF₄ dimer and (c) LUMO picture of RuF₄ dimer.

molecule, viz., 1.21 eV. HOMO–LUMO gap for RuF_4 dimer is found to be 3.05 eV, which is quite small in comparison to HOMO–LUMO gap of F_2 molecule, viz., 6.19 eV. These results clearly suggest that RuF_4 dimer is chemically more reactive than F_2 .

Now we discuss the interaction of RuF_4 superhalogen with an alkali atom, lithium (Li). We chose a structure in which Li atom was placed on top of Ru atom and then optimized its geometry. After geometry optimization, we found that Li atom was slightly displaced in the molecular plane and it was bound to two F atoms (figure 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 LiRuF_4 is found to be 4.94 eV. This is a little bit lower than the binding energy between Li and F atoms, viz., 5.45 eV. Reactivity of this salt has been checked by HOMO–LUMO gap, since halogens when combined with an alkali metal form a more polar compound. The

binding of Li atom to RuF_4 decreases HOMO–LUMO gap by 0.12 eV. Figures 9(b) and (c) show HOMO and LUMO picture of LiRuF_4 salt. From these figures, it is clear that both HOMO and LUMO are situated over the whole molecule except Li atom. This is in contrast to LiF , where Li site does not contribute to HOMO, but contributes to LUMO. From this picture it is clear that bonding between Li atom and RuF_4 molecule is covalent in nature, which implies that bonding electrons are not shifted towards superhalogen side and hence, Li atom represents the inactive part of this molecule.

We have seen how RuF_4 forms dimer and from this it is clear that binding of Li in RuF_4 cluster decreases HOMO–LUMO gap by a small amount. We again checked whether RuF_4 –Li complex is able to form dimer like RuF_4 or not. Based on the charge distributions, the most stable geometry is given in figure 10(a). In RuF_4 –Li dimer, binding takes place between Li site and two F sites with a distance of 2.11 Å, which is greater than the distance between LiF dimer (1.76 Å) (figure 10(d)). The binding energy of

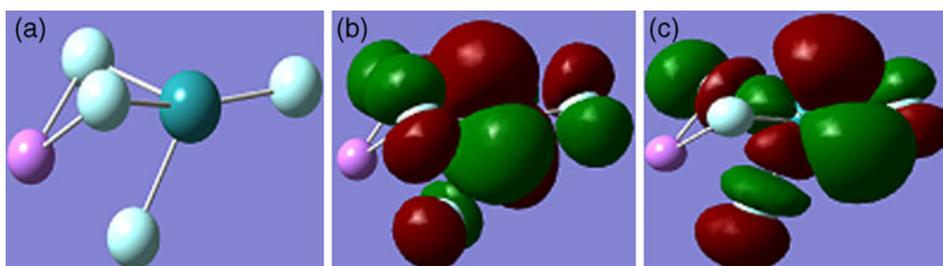


Figure 9. (a) Optimized structure of RuF_4 –Li complex, (b) HOMO picture of RuF_4 –Li complex and (c) LUMO picture of RuF_4 –Li complex.

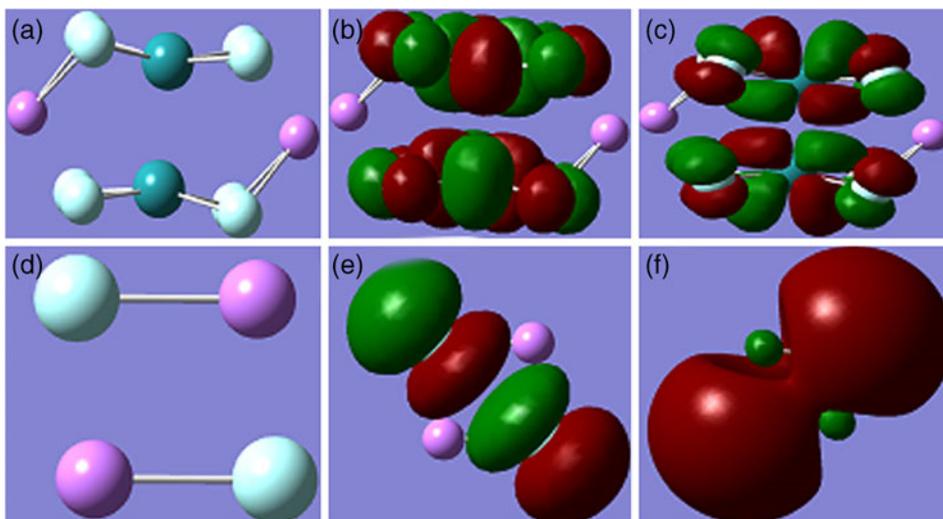


Figure 10. (a) Optimized structure of RuF_4 –Li dimer, (b) HOMO picture of RuF_4 –Li dimer, (c) LUMO picture of RuF_4 –Li dimer, (d) optimized structure of LiF dimer, (e) HOMO picture of LiF dimer and (f) LUMO picture of LiF dimer.

RuF₄-Li dimer is found to be 2.31 eV, which is a little bit lower than the binding energy of LiF dimer, viz., 2.95 eV. From the optimized geometry, we can see that in RuF₄-Li dimer, the distortions occur in Li sites, while the structures of RuF₄ are still kept intact. Thus, RuF₄ serves as the building blocks of new salts. Moreover, the main contributions to HOMO (figure 10(b)) and LUMO (figure 10(c)) in RuF₄-Li dimer are from RuF₄, which are different from LiF (figures 10(e) and (f)) dimer. These results illustrate the similarities and differences between superhalogen complex and halogen atom.

4. Conclusions

It has been shown that Ru atom can bind up to seven F atoms, if atomic F is used in their synthesis. RuF_n clusters in both neutral and anionic forms are stable against all dissociation channels, ensuring that Ru can exist in heptavalent state. Energy needed to dissociate F₂ molecule is found higher than dissociation energy of atomic F. EA of RuF_n ($n \geq 4$) clusters is found more than F. It reached up to 6.95 eV for RuF₆ cluster. The binding energy of LiRuF₄ is found little bit lower than that of LiF, suggesting that a new class of salt can be synthesized by reacting RuF₄ with Li. The resulting supersalts with high oxidizing properties can have potential applications in combating biological agents.

Acknowledgements

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

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