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Superhalogen properties of CuF_n clusters

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A first-principles calculation based on gradient corrected density functional theory reveals unusual properties of a Cu atom interacting with F. Up to six F atoms are bound to a single Cu atom with electron affinities steadily rising as successive F atoms are attached, reaching a peak value of 7.2 eV in CuF_5. The large energy gaps between the highest occupied and lowest unoccupied molecular orbitals, both in neutral and anionic form, provide further evidence of their stability. These unusual properties brought about by involvement of inner shell 3*d*-electrons not only allow CuF_n to belong to the class of superhalogens but also show that its valence can exceed the nominal value of 1 and 2. © *2009 American Institute of Physics*. [doi:10.1063/1.3236576]

I. INTRODUCTION

A superhalogen consists of a metal atom at the center surrounded by peripheral electronegative atoms such as fluorine, chlorine, and oxygen. As the number of these electronegative atoms increases, the added electron is delocalized over these atoms and consequently electron affinity (EA) increases. Indeed, the EA of a superhalogen is much larger than that of any electronegative atom in the periodic table. The concept of superhalogens was initially developed for *sp* elements. According to Gutsev and Boldyrev,[1] superhalogens obey the formula $MX_{(n+1)/m}$, where n is the maximal formal valence of the central atom (M), and m is the normal valence of X. Thus LiF_2 should be a superhalogen and indeed its EA of 5.45 eV (Ref. 2) is larger than that of F. Many superhalogens have been known over the years and some of these even belong to the 3*d* transition metal series. While the valence of *sp* elements is fixed, the valence of transition metal elements can vary over a wide range and thus provides the possibility of discovering an entirely new class of superhalogens. For example, the maximum formal valence of Mn, which has an outer orbital configuration of $3d^54s^2$, is 7 and MnO_4 can be a superhalogen. Indeed, the EA of MnO_4 was predicted to be 5 eV, which was experimentally verified.[3] In comparison, the EA of O is only 1.42 eV. Similarly, other 3*d* transition metal atoms are also known to form superhalogens, and FeO_4 and CrO_4 clusters have electron affinities of 3.8 and 4.96 eV, respectively.[4]

The third row transition metals M are known to form hexafluoride molecules in salts[5] and the electron affinities of MF_6 are larger than that of F. These molecules can serve as important oxidizers and when combined with appropriate positive ions, MF_6 molecules can form salts. Gold provides a unique example in this series. Although it has an outer electron configuration of $5d^{10}6s^1$ and should only be monovalent, its highest oxidation state is confirmed to be +5 and may even be as high as +7.[6] 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 10 ± 0.5 eV,[7] is the most powerful oxidizing hexafluoride of the third row transition series and is known to form a stable $CsAuF_6$ salt.[8] Ag, on the other hand, has the highest oxidation state of +3 and AgF_4^- also forms a stable salt.[9] Cu belongs to the same group as Ag and Au. With its outer electron configuration of $3d^{10}4s^1$ Cu is known to possess a valence of 1 and 2 as exemplified by the existence of Cu_2O and CuO. In this contribution we ask the following questions. Can Cu, which belongs to the same group as Ag and Au, also possess an oxidation state as high as +6? Can CuF_n clusters for $n \leq 6$ exist in the gas phase? Do these clusters belong to the class of superhalogens? If so, do CuF_n superhalogens form dimers as halogen atoms do, e.g., F_2, Cl_2? Is the binding of CuF_n superhalogens with an alkali metal stronger than that between F and alkali atoms?

Using density functional theory (DFT) we show that Cu can indeed have oxidation states ranging from +1 to +4, and possibly +5. Neutral CuF_n clusters are stable in the gas phase against dissociation to F and F_2 for $n \leq 4$ while anion clusters are stable against dissociation to all possible channels for $n \leq 5$. The vibrational frequencies of CuF_6 cluster, both in the anionic and neutral forms, are positive which implies that these clusters are at a local minimum and can be stabilized if atomic F is used in their synthesis. The electron affinities of CuF_n clusters increase steadily with n reaching a peak value of 7.2 eV for CuF_5. CuF_6 has an EA of 7 eV. These values are much larger than the EA of F, namely, 3.40 eV.[10] The highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) gaps of these CuF_n clusters range between 1 and 5 eV. For comparison, we note that the HOMO-LUMO gap of C_{60} is only 1.6 eV. Based upon these observations CuF_n clusters can be expected to form the building blocks of a new class of salts with potential applications. Indeed a new salt containing CuF_6 octahedrons was

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recently synthesized.[11] We also find that the binding of CuF$_n$ superhalogens to an alkali atom is stronger than that between an alkali atom and F.

II. COMPUTATIONAL METHOD

Our calculations are carried out using the self-consistent field-linear combination of atomic orbital-molecular orbital approach. The total energies are calculated using DFT and generalized gradient approximation (GGA) for exchange-correlation potential (B3LYP).[12] While a number of GGA functionals are available, our choice of B3LYP functional was motivated by the recent work of Kolboe and Svelle,[13] where the authors showed that B3LYP functional confirmed the existence of a complex between the benzenium ion and ethane, in agreement with higher level calculations such as CCSD and QCISD. The atomic orbitals are represented by a Gaussian basis. We have used 6-311+G* basis set for F, and triple-zeta nonrelativistic all-electron basis set (cc-pVTZ-NR) for Cu.[14] Structures were optimized without any symmetry constraint using the GAUSSIAN 03 code.[15] Normal mode frequencies were calculated for all structures to ensure that they belong to minima in the potential energy surface. Several initial geometries were also used to confirm the ground state structure. Calculations were also repeated for higher spin states to determine the preferred spin multiplicity of the neutral and anionic clusters. The convergence for energy and force was set to 0.000 01 eV and 0.001 eV/Å. This numerical procedure yielded an EA for the F atom and an ionization potential for the Cu atom as 3.485 and 7.98 eV, respectively, which agree very well with corresponding experimental values of 3.40 (Ref. 10) and 7.72 eV.[16] The calculated bond length and binding energy of F$_2$ of 1.409 Å and 1.38 eV also agree very well with corresponding experimental values of 1.412 Å (Ref. 17) and 1.399 eV.[18]

III. RESULTS AND DISCUSSIONS

In Fig. 1 we plot the equilibrium geometries of neutral and anionic CuF$_n$ ($n=1-6$) clusters. The geometries of neutral CuF$_n$ clusters are similar to those of their anions and are planar up to CuF$_4$. The geometry of CuF$_6^-$ has octahedral symmetry. While the structures of these clusters in the gas phase have not been verified experimentally, in salts CuF$_6^-$ is a distorted octahedron.[11] The average bond lengths $\langle R \rangle$ between Cu–F in these clusters are given in Fig. 2. In anionic CuF$_n$ clusters for $n>2$, $\langle R \rangle$ is smaller than that in their neutral counterparts. This is in contrast to most anionic clusters where interatomic distances are larger than those in their neutrals. We will show in the following that this trend is consistent with the increasing stability and electronegativity of CuF$_n$ clusters for $n>2$.

In Table I we list the relative energies for two lowest spin multiplicities of CuF$_n$ neutral and anionic clusters. With the exception of neutral CuF$_3$ and CuF$_5$, all clusters, both anionic and neutral, have the lowest possible spin state. The relative stabilities of these clusters against fragmentation to F atom or F$_2$ molecule are studied by calculating the energy ΔE_n needed to dissociate these clusters into CuF$_{n-1}$+F and Cu$_{n-2}$+F$_2$, namely,

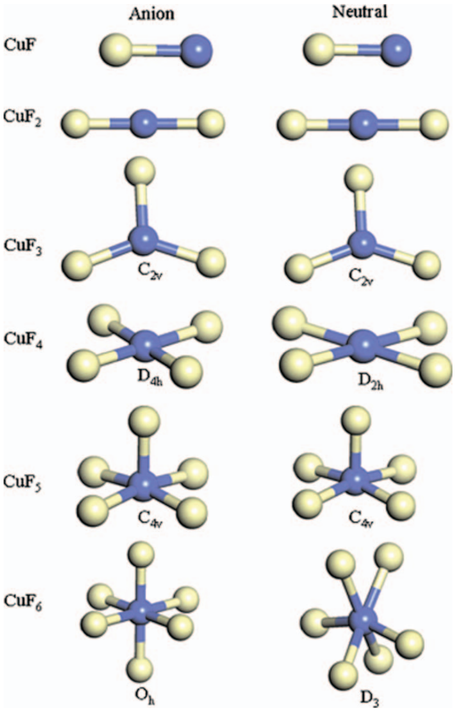

FIG. 1. Optimized geometries of CuF$_n$ neutral and anionic clusters.

$$\Delta E_n = -\{E[\mathrm{CuF}_n] - E[\mathrm{CuF}_{n-m}] - E[\mathrm{F}_m]\}, \quad m=1,2, \tag{1}$$

$$\Delta E_n^- = -\{E[\mathrm{CuF}_n^-] - E[\mathrm{CuF}_{n-m}{}^-] - E[\mathrm{F}_m]\}, \quad m=1,2. \tag{2}$$

The ΔE_n and $\Delta E_n{}^-$ values are plotted in Figs. 3(a) and 3(b). The energy costs decrease as successive F atoms and F$_2$ molecules are detached. The vibrational frequencies of all the CuF$_n$ clusters studied here are positive irrespective of their charge state. This implies that all these clusters are, at least, at local minima and are protected by energy barriers. More importantly, all these clusters are stable against dissociation to CuF$_{n-1}$+F. Thus, neutral and anionic clusters up to CuF$_6$ can be formed if atomic F is used in the experimental synthesis. However, neutral CuF$_5$ and CuF$_6$ clusters are unstable against dissociation to a F$_2$ molecule. On the contrary, CuF$_n{}^-$

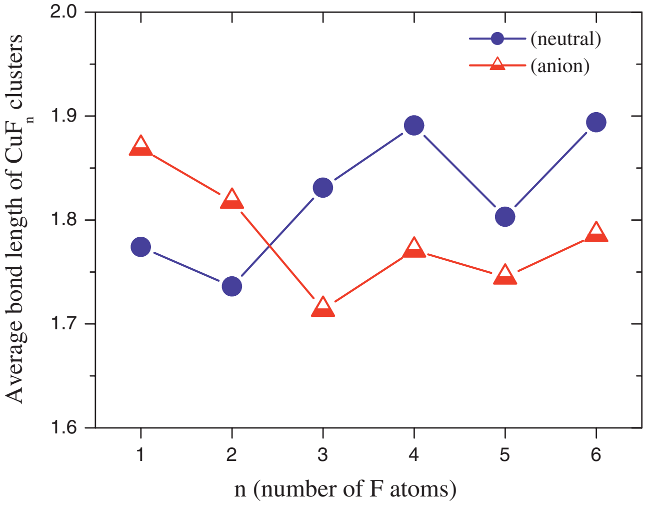

FIG. 2. Average bond length (angstrom) between Cu and F in neutral and anionic CuF$_n$ clusters.

TABLE I. EA (in eV) and energy difference ΔE (in eV) between different multiplicities ($M=2S+1$) for anion and neutral CuF_n clusters.

	Anion		Neutral		
n	M	ΔE	M	ΔE	EA
1	2	0.00	1	0.00	1.30
	4	3.80	3	1.78	
2	1	0.00	2	0.00	3.63
	3	3.21	4	1.12	
3	2	0.00	1	0.74	5.48
	4	4.60	3	0.00	
4	1	0.00	2	0.00	6.75
	3	1.54	4	0.54	
5	2	0.00	1	0.82	7.17
	4	0.24	3	0.00	
6	1	0.00	2	0.00	6.97
	3	1.07	4	0.52	

clusters up to $n=5$ are stable against all dissociation channels. The stability of these clusters is further established by examining their HOMO-LUMO gaps and vibrational frequencies. In Fig. 4 we show these HOMO-LUMO gaps along with maximum IR intensities as a function of number of F atoms. Note that the HOMO-LUMO gaps range between 1 and 5 eV in the neutral and anionic clusters. In comparison the HOMO-LUMO gap of C_{60} is only 1.6 eV.

To understand how a Cu atom which has a nominal valence of 1 or 2 can bind to as many as six F atoms, we have analyzed the HOMO and LUMO as well as the possible involvement of the inner shell 3d-electrons in bonding (Fig. 5). The latter was studied by using the natural bond analysis. The d-characteristics of the HOMO and LUMO are clearly seen confirming their involvement in bonding. In Fig. 6(a) we plot the number of 3d electrons participating in bonding in CuF_n clusters as a function of n. We see that this number increases with n in both neutral and anionic clusters. The involvement of 3d electrons is in terms of hybridization between Cu 3d and F 2p states rather than a complete charge transfer from the Cu to the F atoms. This is in agreement with the experimental finding of the existence of Cu 3d–F 2p hybridization in A_2CuF_4 (A=K, Cs).[19]

In Fig. 6(b) we plot the adiabatic electron affinities of the CuF_n clusters, which are calculated by taking the energy difference between the neutral and corresponding anionic clusters, both in their ground state configurations. These rise steadily as the number of F atoms increases reaching a peak value of 7.2 eV in CuF_5 cluster. This is more than a factor of

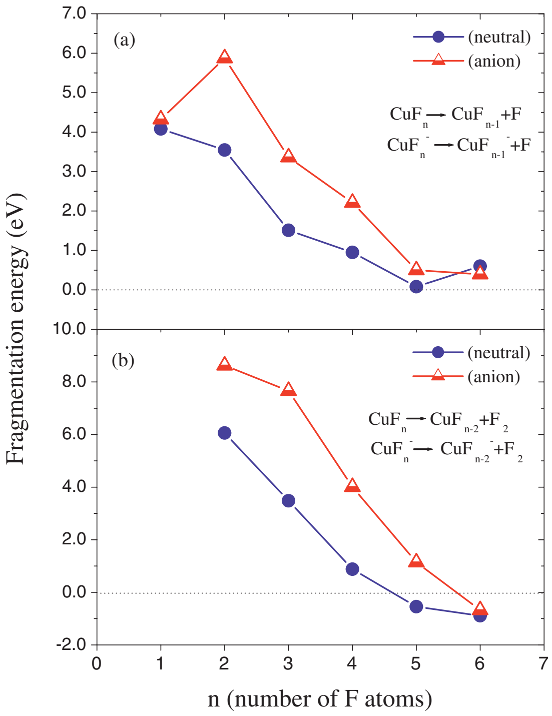

FIG. 3. Fragmentation energies (eV) for different channels [see Eqs. (1) and (2)].

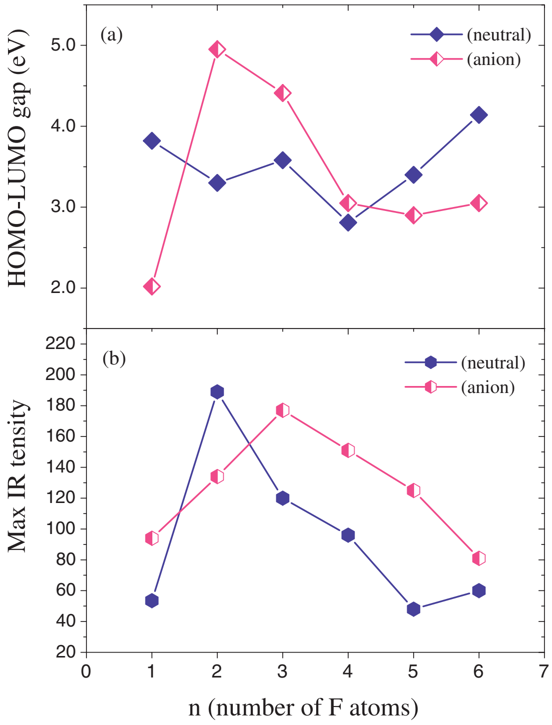

FIG. 4. (a) HOMO-LUMO gaps and (b) maximum IR intensities of neutral and anionic CuF_n clusters.

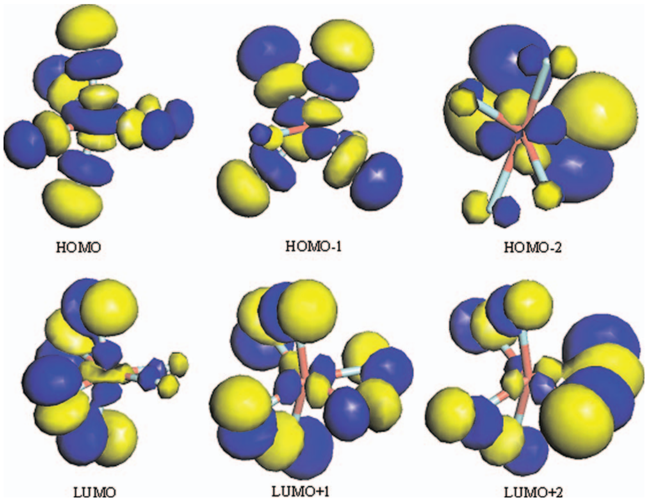

FIG. 5. HOMO and LUMO of CuF_6 clusters.

2 larger than the EA of the F atom. The EA of CuF_6 is 7 eV. Note that Scheller *et al.*[5] provided a calculated value of about 6 eV for the EA of CuF_6, although no details of this calculation are given. Hence, CuF_n $(n \geq 2)$ clusters can be termed as superhalogens.

According to the superhalogen theory, Cu with a maximal valence of 2 can permit CuF_3 to behave as a superhalogen. The fact that CuF_n $(n > 3)$ clusters are superhalogens is further evidence that inner shell electrons contribute to its valence, as has been discussed above. Thus, we see that CuF_6 has similar properties as AuF_6, even though most of the unique properties of Au are attributed to relativistic effects. Calculations based on quantum chemical techniques[20] have also found large EA of AuF_6. It should be pointed out that in the above calculation[20] the neutral and anionic clusters were constrained to have octahedral symmetry. While this is expected to be the case for the anionic clusters due to its filled HOMO, the neutral cluster will undergo Jahn–Teller distortion as observed here for CuF_6 (see Fig. 1) and the energy of AuF_6 can be further lowered. Hence, the calculated EA, namely, 9.56 eV (Ref. 20) of AuF_6, can only be an upper limit.

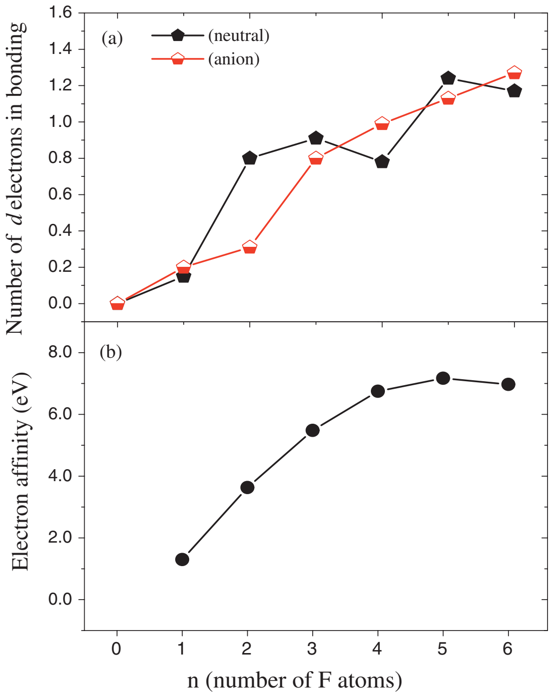

FIG. 6. (a) Number of 3*d* electrons participating in bonding in neutral and anionic CuF_n clusters obtained from a natural bond analysis and (b) EA of CuF_n clusters.

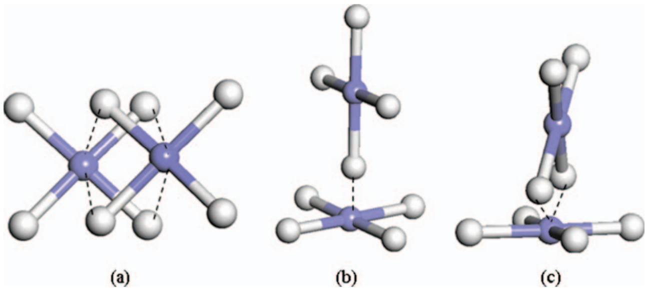

FIG. 7. Three initial configurations for determining the structure of CuF_4 dimers.

The question then arises. Is the polyvalent character of Cu a general characteristic or is it only confined to its interactions with halogens such as F? To answer this we have computed the equilibrium geometry and binding energy of Cu interacting with O_2 molecules. We found that $Cu(O_2)_3$ is stable with a binding energy of 0.95 eV per O_2. However, the three O_2 molecules are bound in the superoxo form where the O atoms remain molecular. This result is in agreement with earlier theoretical calculations[21] and consistent with photoelectron spectroscopy measurements.[22] The reason why Cu 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, 5.12 eV, is much larger than that of the F_2 molecule, namely, 1.399 eV. Thus, it appears that the polyvalent character of Cu may apply only in selected systems.

To further understand the superhalogen behavior of CuF_n complexes, we sought answers to the following questions. To what extent does a superhalogen complex behave like a halogen atom? Note that halogen atoms such as F and Cl form F_2 and Cl_2 molecules. Does a superhalogen complex form a dimer? Second, a halogen atom interacting with an alkali atom forms an ionic compound, a salt. Does a superhalogen bind more strongly to an alkali atom than a halogen atom? We answer these questions by concentrating on CuF_4 and its interaction with K.

We first discuss the interaction between two CuF_4 superhalogens. Based on the charge distribution in CuF_4, where Cu is positively charged while F is negatively charged, we chose three possible initial configurations to study the formation of CuF_4 dimer. These are given in Fig. 7. In the first configuration, the two units are placed parallel to each other but shifted so that the Cu site in one unit can be closer to two F sites in the other. In the second and third configurations, these two complexes are placed perpendicular to each other with Cu and F sites close to each other to promote interaction. However, after full optimization, we have found that these two units do not bind to form a stable dimer, suggest-

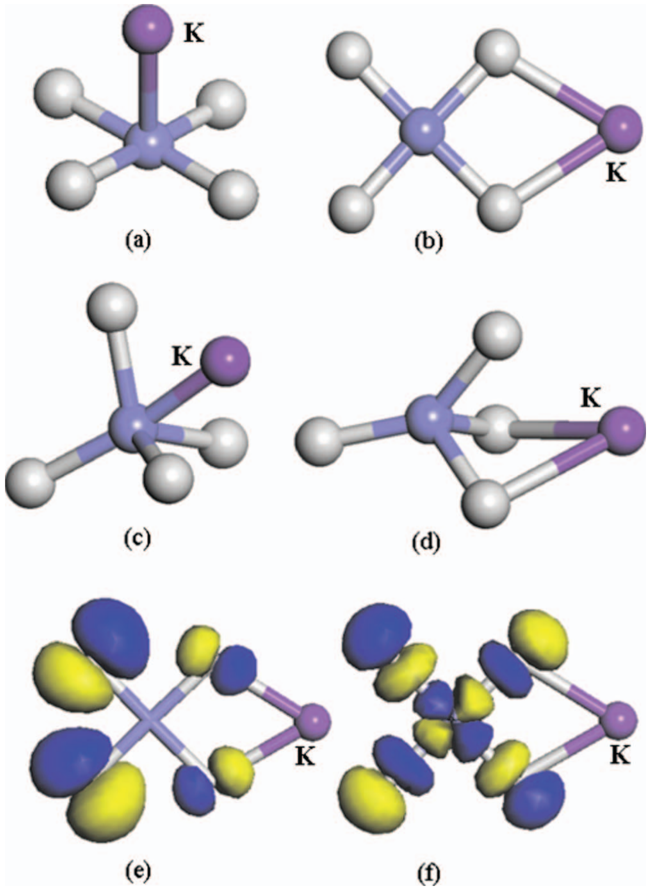

FIG. 8. [(a) and (c)] Initial and [(b) and (d)] final geometries. (e) HOMO and (f) LUMO of CuF_4–K complex.

ing that the superhalogen CuF_4 complex itself is very stable. Note that an earlier study has found that two CuF clusters bind.[23]

CuF_n superhalogens, when counterbalanced by appropriate positive ions, can form a new class of supersalts. Note that K_3CuF_6 has been synthesized[24] and in this compound Cu can be regarded to exist in an oxidation state of +3. Tetravalent Cu is also known. After numerous unsuccessful attempts, Harnischmacher and Hoppe[25] were successful in synthesizing the first known compound of Cu^{IV} (cesium hexafluorocuprate, Cs_2CuF_6). This orange-red solid undergoes vigorous decomposition with water. We are not aware of synthesis of any salt where Cu exists in the +5 or +6 oxidation state. As pointed out earlier, Jahn–Teller distorted CuF_6 octahedra have been seen in single crystal structure of copper usovites ($Ba_2CaCuCr_2F_{14}$).[11] Salts with CuF_5^- and CuF_6^- as building blocks may be useful in storing a large amount of F atoms safely and their controlled release may have beneficial effects in combating biological agents due to the oxidizing property of F. In addition, the varying HOMO-LUMO gaps of CuF_n clusters may permit their salts to have interesting optical properties.

Next we discuss the interaction of CuF_4 with a K atom. Initially we put the K atom on top of Cu [Fig. 8(a)]. After optimization we found a structure where the K atom binds with two F ions forming a planar structure [see Fig. 8(b)]. The binding energy of $KCuF_4$ is found to be 6.77 eV. This is higher than the binding between an F atom and a K atom, namely, 5.263 eV. The binding with K atom reduces the HOMO-LUMO gap (0.42 eV) and increases the chemical reactivity. The kinetic stability of the planar complex of CuF_4–K is confirmed by frequency calculations, as all the frequencies are real. To further check the thermodynamic stability of the planar structure, we calculated one isomer [Fig. 8(c)], where CuF_4 forms a tetrahedron, and the K atom is capped to the top site of Cu having the freedom to bind with three F ions. In the optimized structure, K atom is shifted to bind with two F ions [Fig. 8(d)]; however, the energy is 0.34 eV higher than that of the planar structure [Fig. 8(b)]. Therefore the planar geometry in Fig. 8(b) is the ground state. Figures 8(e) and 8(f) show the HOMO and LUMO, where the main contributions are from CuF_4. This is in contrast to KF molecule where the K site does not contribute to HOMO but to LUMO.

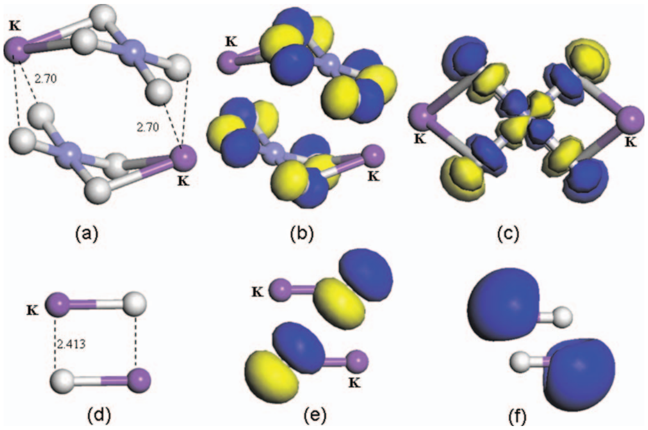

FIG. 9. (a) Geometry, (b) HOMO, and (c) LUMO of CuF_4–K dimer. For comparison, the corresponding geometry of $(KF)_2$ dimer is given.

We have seen that CuF_4 is stable and does not aggregate to form a dimer due to the large HOMO-LOMO gap. But once a K atom is introduced, strong binding occurs and the HOMO-LUMO gap is reduced to 0.42 eV. Thus we can expect the aggregation between two CuF_4–K complexes. Based on the charge distributions, the most stable geometry is given in Fig. 9(a), where the binding takes place between K site and F site with the distance of 2.7 Å, larger than the distance between two KF dimers [Fig. 9(d)]. The interaction energy is found to be 1.55 eV, which is 0.5 eV weaker than KF–KF dimer. From the geometry we can see that in CuF_4–K dimer the distortions occur in K sites while the planar structure of CuF_4 is still kept. This stability of CuF_4 allows it to be a building block of new salts. In fact, the planar geometry of CuF_4 is 0.63 eV lower in energy than that of tetrahedron where the Cu is in the center. Moreover, the main contributions to HOMO [Fig. 9(b)] and LUMO [Fig. 9(c)] in CuF_4–K dimer are from CuF_4, which are different from KF–KF dimer [Figs. 9(e) and 9(f)]. These results illustrate the similarities and differences between a superhalogen complex and a halogen atom.

IV. CONCLUSIONS

In summary, we have shown that a Cu atom can bind up to six F atoms if atomic F is used in their synthesis. CuF_n

(CuF_n^-) clusters for $n \leq 4$ ($n \leq 5$) are stable against *all* dissociation channels, ensuring that Cu can exist in a tetravalent state, at least in gas phase reactions. It has the possibility of existing in a hexavalent state, *albeit* in a metastable form. The electron affinities of these CuF_n clusters are higher than the most electronegative atom F in the periodic table and can reach a value as high as 7.2 eV. The interaction of superhalogens with an alkali atom is modeled by considering CuF_4 and K. The binding energy of $KCuF_4$ is larger than that of KF suggesting that a new class of salts can be synthesized by reacting CuF_n superhalogens with appropriate metal cations. The resulting salts with high oxidizing properties can have potential applications in combating biological agents.

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