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Theoretical Studies of Group 1 Metal Complexes with Hydrogen Fluoride, $M(HF)_n$, M = Li, Na, and K: A New Type of Electrides†

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Small clusters of group 1 metal complexes with hydrogen fluoride molecules $M(HF)_n$, M = Li, Na, and K, are studied with the ab initio molecular orbital method. The trimer $M(HF)_3$ forms a C_{3v} cluster, in which the metal atom is ionized and the ejected electron is trapped on the top of three equivalent HF molecules. The optimized geometric structure of $Li(HF)_3$ is almost identical with that of the ion pair $Li^+(HF)_3Cl^-$ by replacing a Cl^- anion with an ejected electron $\{e^-\}$; thus $Li(HF)_3$ can be described as $Li^+(HF)_3\{e^-\}$. The entity $\{e^-\}$ is trapped under the electrostatic field created by three HF bond dipoles; and at the same time, the HF bonds are polarized and weakened. A triplet anion $\{e^-\}(HF)_3Li^+(HF)_3\{e^-\}$ is stable and is a possible anion unit of electrides.

1. Introduction

More than a decade ago, Fuke and co-workers[1] and Hertel and co-workers[2] studied the size dependence of the ionization threshold energy (ITE) of group 1 metal atom complexes with water molecules, $M(H_2O)_n$. Their remarkable findings are the convergence of ITE to a nearly equal energy at $n = 4$ for all of M = Li, Na, and Cs; the converged values are almost independent of the metals. Hashimoto and co-workers,[3−5] and Tsurusawa and Iwata[6,7] studied the clusters with the ab initio molecular orbital methods. In these computational works, it was concluded that the electron is ejected from the metal atom in the clusters of $n \geq 4$ and is surrounded by a few OH bonds of water molecules, although it was not possible to definitively identify the isomers of the clusters experimentally observed. Iwata and Tsurusawa reviewed both experimental and theoretical studies[8] in which they emphasized the similarity in the structure of the electron ejected from the metal in the clusters $n \geq 4$ with that of the excess electron in some of the small water cluster anions.[9,10] Both an ejected electron in the metal−water complexes and an excess electron in the water anions are stabilized by the surrounding OH bonds, in most cases more than two OH bonds of two or three (or more) water molecules. The electron is trapped in the electrostatic field created by a few OH bond dipole moments. Their structures can be denoted as $(OH)_r\{e^-\}(OH)_t$. The interesting characteristics found are that the OH bonds directing to the electron $\{e^-\}$ are lengthened, and their calculated harmonic frequencies are downward shifted, as the OH bonds in the hydrogen bonding system. Because of this similarity, Iwata and Tsurusawa called the bond between the OH and the $\{e^-\}$ an electron−hydrogen bond. In these clusters, in most cases, the water molecules form the hydrogen bond networks which mostly determine the geometric structure of the cluster; and as a result, the OH bonds surrounding the electron $\{e^-\}$ are not equivalent to each other.

There are numerous theoretical papers for the water anions; one of them includes extensive works for hexamer anion isomers by Kim's group.[11,12] Among various types of water anion clusters reported, some simple but interesting isomers are found for a water dimer anion of D_{2h}[9] and for a water trimer anion of D_{3h}.[10] In the D_{2h} dimer anion, the electron is trapped between two nonhydrogen bonded water molecules as $(OH_2)\{e^-\}(H_2O)$; four of the OH bonds of the two water molecules are equivalent. The D_{3h} trimer anion has a similar structure except that six OH bonds of three water molecules equivalently surround the electron $\{e^-\}$. The trimer anion of $(OH_2)\{e^-\}(HOHOH_2)$ is also found.[9] In these anions, the electron $\{e^-\}$ plays a role of glue to hold the water molecules. These dimer and trimer anions are much less stable than the linear dimer and trimer anions of the dipole bound type; and they are expected not to be detected in the normal experimental conditions. In 2002, Bowen and co-workers observed two isomers of hydrogen fluoride trimer anions $(HF)_3{}^{-1}$ [13] in the photoelectron spectra. With help of the computational study, they assigned the band at 0.24 eV to a linear chain dipole bound anion, and the band at 0.43 eV was assigned to an isomer of $(FH)\{e^-\}(HFHF)$, where the electron is trapped between an HF molecule and a dimer $(HF)_2$. In their calculations, they also found the D_{3h} trimer anion, and excluded it from the candidates because of less stability. The electronic structure and the nature of the excess electron $\{e^-\}$ in these clusters surrounded by water molecules or by hydrogen fluoride molecules are the same. The electron $\{e^-\}$ is trapped in an electrostatic field created by the surrounding multi-bond dipoles (OH or FH), and at the same time, the localized electron glues those dipoles by polarizing the OH or FH bonds. In retrospect, before our work on $(OH_2)\{e^-\}(H_2O)$, Gutowski and Skurski first reported such anion of $(FH)\{e^-\}(HF)$ and discussed the interaction in terms of the dispersion force.[14] After the paper of Bowen and co-workers, the computational studies for larger $(HF)_r\{e^-\}(HF)_t$ are reported.[15,16] In addition, although the authors are not aware of the similarity, the linear hydrogen halide anions of $XH\{e^-\}HX$ (X = Cl, Br) studied by Rauk and Armstrong[17] have the similar electronic structure; and two hydrogen halide molecules are glued by the excess electron $\{e^-\}$.

In these clusters, the entity denoted above by $\{e^-\}$ has no central positive charges at all. The crystal called electrides has such an entity as a unit of the crystal lattices.[18−20] A typical

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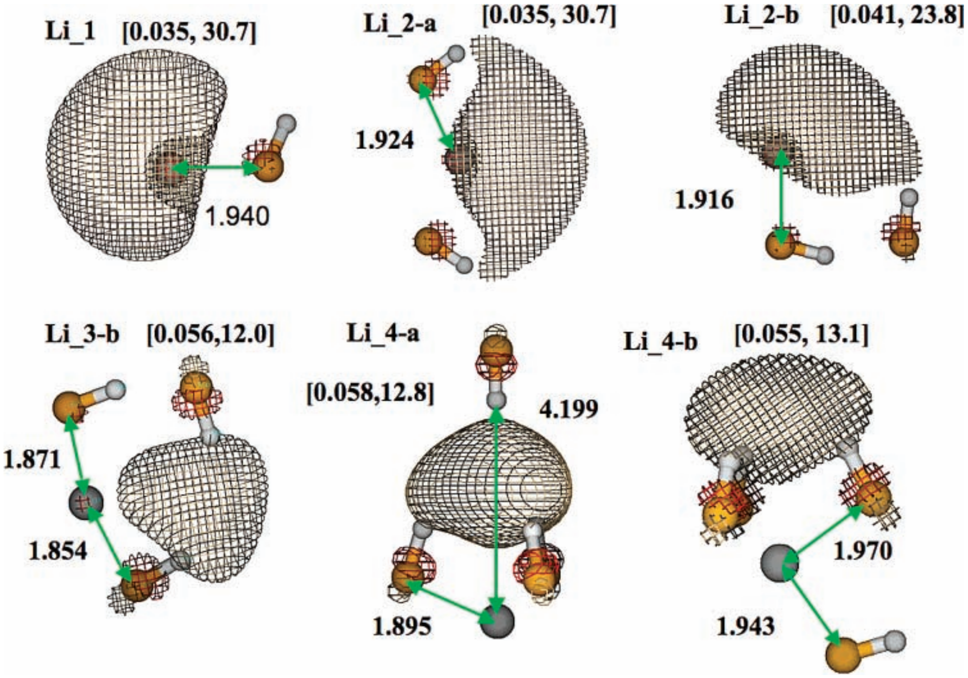

Figure 1. Geometric structures and the singly occupied molecular orbital (SOMO) of Li(HF)$_n$. See text on the boundary of SOMO. The numbers in the square brackets are [*IsoSurf*(0.5), *IsoVol*(0.5)/Å^3]. For a free Li atom, they are [0.039, 30.2].

organic electride is $Cs^+(15\text{-crown-}5)_2\{e^-\}$ reported by Dys.[18] Hosono and co-workers found a more complex inorganic electride $[Ca_{24}Al_{28}O_{64}]\{e^-\}_4$, which has unique electric and magnetic properties.[20] The F center in the alkali halide crystals is known to be such entities as defects.[21]

In the present paper, we show a new type of neutral clusters M(HF)$_n$, M = Li, Na and K, which have a similar structural entity of the excess electron $\{e^-\}$ ejected from a metal atom. It is demonstrated that the trimer $M^+(HF)_3\{e^-\}$ is a good candidate of a part of the unit of new electride crystals.

In our literature search, no papers for the clusters M(HF)$_n$ were found, except for a paper of an accurate ab initio study of a Li−HF complex,[22] which only discusses the nature of the weak molecular interaction.

2. Computational Methods

The geometry optimization was carried out with the UHF MP2/6-311++(d,p) level of calculations. The harmonic frequencies were also evaluated with the same level. Gaussian 03[23] was used in the calculations. All of the structures shown in the figures are confirmed to be at the local minimum by evaluating the harmonic frequencies. After the spin projection, the expectation value of S^2 is 0.750 for most of the clusters.

To determine a proper value for drawing the iso-value surface of molecular orbital (MO) ϕ_j, a program, *IsoMOSurf*, is developed.[24] For a given x_e ($1 > x_e > 0$), Function *IsoMOSurf*(x_e, ϕ_j) returns a value *IsoSurf*(x_e), which is determined to satisfy the condition

$$x_e = \int^{\text{inside of surface}} \mathrm{d}\boldsymbol{r}|\phi_j|^2 \simeq \sum_{k}^{\text{inside of surface}} |\phi_j(\boldsymbol{r}_k)|^2 v \qquad (1)$$

where the volume integral is approximated by a sum of the densities $|\phi_j(\boldsymbol{r}_k)|^2$ at the kth cube $\boldsymbol{r}_k$ times the volume of cube v, and the sum is taken from the largest value of $|\phi_j(\boldsymbol{r}_k)|^2$. To draw the MO surface, *IsoSurf*(x_e) is input to MOLDEN or to the other utility programs. The volume *IsoVol*($\boldsymbol{x}_e$) inside of the surface can be easily evaluated by counting the number of cubes taken in the sum. Previously, we called *IsoVol*(0.5) for the singly occupied MO SEM (singly occupied MO, SOMO, extension measure).[6] MOLDEN was used to draw the iso-value surface in the figures.[25]

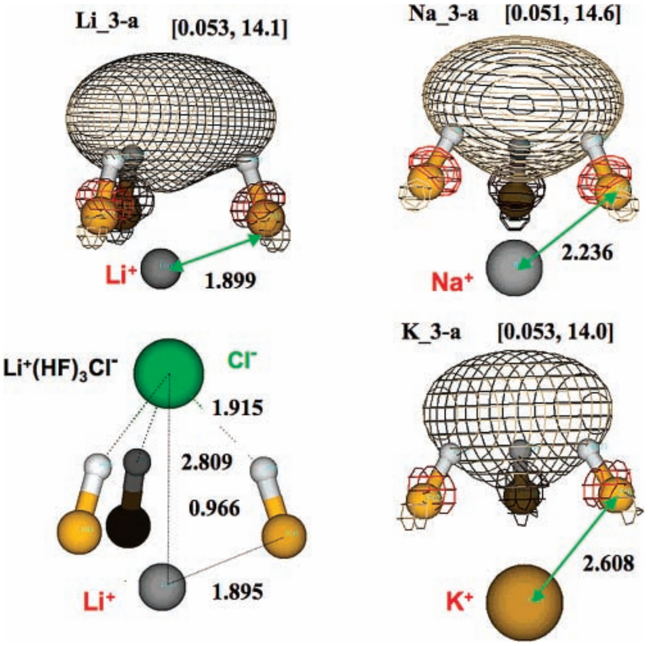

Figure 2. Comparison of geometric structures of C_{3v} isomers of Li(HF)$_3$, Na(HF)$_3$, and K(HF)$_3$ and of ion $Li^+(HF)_3Cl^-$. The numbers in the square brackets are [*IsoSurf*(0.5), *IsoVol*(0.5)/Å^3].

3. Results and Discussion

3.1. C_{3v} Form Isomer of M(HF)$_3$, M = Li, Na, and K. Figures 1 and 2 show the optimized structures of M(HF)$_n$ and the SOMOs. The metal−F distances and [*IsoSurf*(0.5), *IsoVol*(0.5)] for SOMO are given in the figures. The surfaces of SOMO show the characteristics of the electronic structure of the clusters. The Fermi contact terms of the nuclei also are a

TABLE 1: Characteristics of Some of the Clusters $Li(HF)_n$ and $K(HF)_n$

	ratio of Fermi contact term $F_{\text{in cluster}}{}^{a}/F_{\text{atom}}$	ΔVIE/eV^{b} $\text{IE}_{\text{cluster}} - \text{IE}_{\text{atom}}$	$\Delta R_{\text{HF}}^{\text{Max}}$/Å^{c} $R_{\text{HF}}^{\text{cluster}} - R_{\text{HF}}^{\text{isol}}$	$\Delta\nu_{\text{HF}}^{\text{Max}}$/cm$^{-1\ d}$ $\nu_{\text{HF}}^{\text{cluster}} - \nu_{\text{HF}}^{\text{isol}}$	*BE*/kJ mol^{-1} CP corr^{e} (uncorr.)
Li_1	0.704	−0.60	0.012	−236	−15.73 (−21.55)
Li_2-a	0.397	−0.81	0.016	−355	−41.11 (−55.15)
Li_2-b	0.638	−0.29	0.024	−518	−43.23 (−55.66)
Li_3-a	0.045	+0.41	0.044	−1068	−83.34 (−107.75)
Li_3-b	0.142	+0.15	0.063	−1353	−76.93 (−101.22)
Li_4-a	0.032	+0.55	0.038	−921	−104.08 (−129.95)
Li_4-b	0.027	−0.12	0.052	−1204	−124.40 (−158.77)
K_1	0.823	−0.40	0.004	−81	
K_2-a	0.613	−0.66	0.005	−108	
K_2-b	0.760	−0.16	0.013	−283	
K_3-a	0.070	+0.43	0.038	−916	
K_3-b	0.284	+0.34	0.038	−902	

[a] Calculated Fermi contact term for an isolated atom: 0.227 for Li and 0.865 for K. [b] Ionization energy (IE) for an isolated atom: 5.34 eV (515.2 kJ/mol) for Li and 4.24 eV (409.1 kJ/mol) for K. [c] $R_{\text{HF}}^{\text{isol}} = 0.917$ [d] $\nu_{\text{HF}}^{\text{isol}} = 4191.6$ cm^{-1} [e] Counterpoise corrected binding energy. See text.

good measure of the character of SOMO, and in Table 1, the ratio $F_{\text{in cluster}}/F_{\text{atom}}$ is given for Li and K complexes. The SOMOs of Li(HF)[Li_1] and of $Li(HF)_2$[Li_2-a and Li_2-b] are characterized as the sp hybridized orbital, and the reduction of the Fermi contact terms on the Li atom can be explained by the hybridization. For M = Na and K, the similar clusters to [Li_1], [Li_2-a], and [Li_2-b] are found. Because of the larger size of the metal atoms, the Na−F (K−F) distances are 2.388 (2.752) Å for [M_1] and 2.341 (2.736) Å for [M_2-a].

A drastic change in the electronic structure is found in $Li(HF)_3$[Li_3-a], shown in Figure 2. There is almost no electron on the Li atom, as seen in Figure 2 and in the ratio of the Fermi contact term given in Table 1. The cluster [M_3-a] has C_{3v} symmetry for M = Li, Na, and K. The SOMO electron is located outside of the framework of the cluster $Li^+(HF)_3$, and the cluster can be described as $Li^+(HF)_3\{e^-\}$, where the sign $\{e^-\}$ denotes that the electron in the SOMO is separated far away from the atomic nuclei; the electron $\{e^-\}$ forms a nearly isolated entity. The large coefficients of SOMO are found on the diffuse basis functions of all of the constituent atoms. In the previous works for the $M(H_2O)_n$ clusters,[7] we confirmed that the basis sets used can describe the ejected electron $\{e^-\}$. As is seen in Figure 2, $Na^+(HF)_3\{e^-\}$[Na_3-a] and $K^+(HF)_3\{e^-\}$[K_3-a] have the similar geometric and electronic structures with $Li^+(HF)_3\{e^-\}$, except for the metal−F distances. In the $M(HF)_n$ clusters, the group 1 metal atom is ionized at $n = 3$, which is in contrast to the $M(H_2O)_n$ clusters, in which the metal atom is ionized for $n \geq 4$.[5−7] The other difference from the $M(H_2O)_n$ clusters is the symmetric structure of $M(HF)_3$; three HF molecules are equivalent to each other. In most cases of the $M(H_2O)_n$ clusters, two OH bonds of a water molecule do not interact equivalently with the $\{e^-\}$ because of the hydrogen bond network among water molecules.

3.2. Electron−Hydrogen Bond. The structure of the C_{3v} isomer [M_3-a] clearly indicates that three equivalent HF molecules support the electron $\{e^-\}$ ejected from the metal atom. The interaction between the $\{e^-\}$ and the HF molecules is the electron−hydrogen bond, similar to the ion−hydrogen bond in halogen−water clusters $X^-(H_2O)_n$ (X = F, Cl, Br, and I).[26−28] So the entity $\{e^-\}$ in $Li^+(HF)_3\{e^-\}$ can be replaced with a halogen anion; in Figure 2, the optimized structure of $Li^+(HF)_3Cl^-$ is shown for comparison. The remarkable similarity between the structures of $Li^+(HF)_3\{e^-\}$ and $Li^+(HF)_3Cl^-$ can be noticed; for $Li^+(HF)_3\{e^-\}$, R(Li−F) = 1.899 Å, R(H−F) = 0.961 Å, angle(H−F−Li) = 97.1°, and the corresponding values for $Li^+(HF)_3Cl^-$ are 1.895 Å, 0.966 Å, and 94.5°.

In the C_{3v} isomer $M^+(HF)_3\{e^-\}$, an electron $\{e^-\}$ is captured by a strong electrostatic field created by the three equivalent FH bonds. We may call this type of electron "an electron bound by the surrounding multi-dipole moments", which should be differentiated from the dipole bound electron. The electron is much more tightly bound under the electrostatic field of the surrounding multi-dipole moments than the well-known dipole bound electron, so that it behaves similar to the halogen anion as shown in Figure 2.

The structure surrounding the entity $\{e^-\}$ also resembles the structures found computationally in the anions of $(OH_2)\{e^-\}(H_2O)$ of D_{2h}, $\substack{(OH_2)\\(OH_2)}\{e^-\}(H_2O)$ of D_{3h},[9,10] $(FH)\{e^-\}(HF)$ of $D_{\infty h}$[14], and $\substack{(FH)\\(FH)}\{e^-\}(HF)$ of D_{3h}.[13] In these anion clusters, no hydrogen bonds exist between water molecules and between hydrogen fluoride molecules. The excess electron $\{e^-\}$ glues the surrounding water molecules and hydrogen fluoride molecules. Similarly, the ejected electron $\{e^-\}$ in $Li^+(HF)_3\{e^-\}$ glues the hydrogen fluoride molecules; if the electron is removed (ionized), the remaining cation becomes a planar D_3 ion $Li^+(HF)_3$. The interaction between the electron $\{e^-\}$ and the H of HF and of H_2O is so strong that it can be called a 'bond'. So, we first used electron−hydrogen bond for such bonds between $\{e^-\}$ and H−O in $M(H_2O)_n$[6,7] and later in water cluster anions $(H_2O)_n^-$.[9,10]

As in the ordinal hydrogen bond, the O−H and F−H bonds directing to the electron $\{e^-\}$ are lengthened, and the harmonic force constants of the bonds become smaller.[7] The fourth and fifth columns of Table 1 show the largest changes among the bond lengths and among the harmonic frequencies in each cluster. We may compare them with the changes in the planer cation $Li^+(HF)_3$ from a free FH, where $\Delta R_{\text{HF}} = 0.009$ Å and $\Delta\nu_{\text{HF}} = -125$ cm^{-1}. The large lengthening of R_{HF} and the extreme downward shift of ν_{HF} in $Li^+(HF)_3\{e^-\}$ imply that the antibonding orbital σ^*_{HF} does have a contribution to the SOMO, which can also be seen in Figure 2.

Among 12 intermolecular vibrational modes, the highest 3 modes (747, 747, and 635 cm^{-1} for $Li^+(HF)_3\{e^-\}$) exhibit the unique motions; the metal atom and three F atoms do not move at all, and only three hydrogen atoms move to change the angles Li−F−H. It seems that three FH molecules are bending against the electron $\{e^-\}$. They have a relatively large transition dipole moment for the infra-red absorption spectrum. The similar modes are found in $Li^+(HF)_3Cl^-$; the corresponding frequencies are 1028, 882, and 882 cm^{-1}.

3.3. Other Isomers of $M(HF)_n$, $n = 2$, 3, and 4. In Figure 1, the structures of isomers $Li(HF)_2$, $Li(HF)_3$, and $Li(HF)_4$ are shown. The similar isomers are found for Na and K clusters. The difference in the geometry is for the metal−F distances. The calculated binding energies are compared in Table 1. They

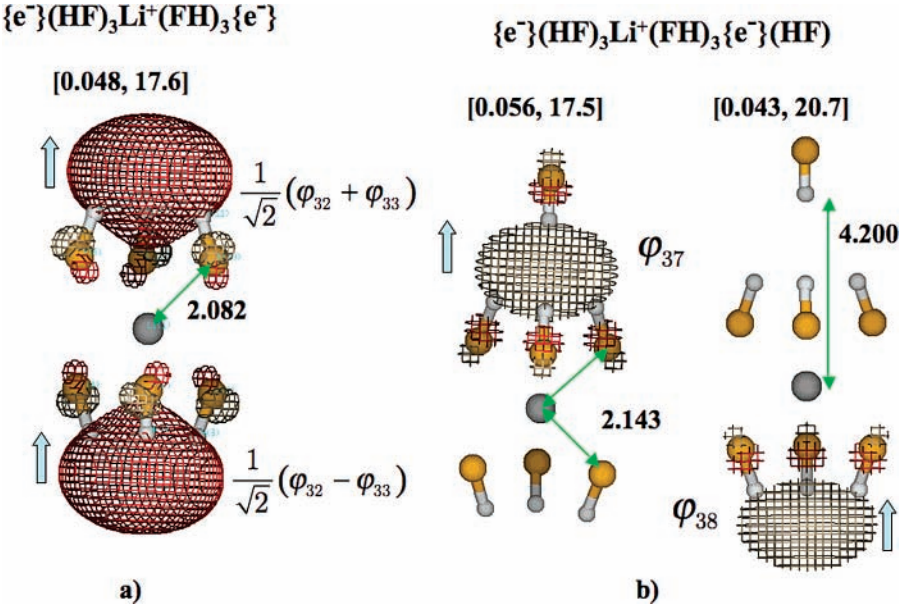

Figure 3. Geometric structures and two SOMOs for the triplet anion $\{e^-\}(HF)_3Li^+(HF)_3\{e^-\}$ and $\{e^-\}(HF)_3Li^+(HF)_3\{e^-\}$ HF. The numbers in the square brackets are [*IsoSurf*(0.5), *IsoVol*(0.5)/Å^3].

are evaluated with the counterpoise (CP) correction[29] to remove a part of the basis set superposition error (BSSE). In applying the traditional CP correction to the present systems, there are two problems. (1) Except for Li(HF), the clusters consist of more than two molecular units. As discussed by Valiron and Mayer,[30] the proper counterpoise procedure for the clusters requires the evaluation of the many-body BSSE. (2) To evaluate the CP correction, we have to identify the monomer units. What are the proper monomers in $Li^+(HF)_3\{e^-\}$? In the present study, simply a Li atom and a HF molecule are assumed to be monomer units. In the table, the uncorrected energies are also given.

For $Li(HF)_2$, the asymmetric isomer [Li_2-b] is slightly more stable than the symmetric [Li_2-a], and *IsoVol*(0.5) of [Li_2-b] is substantially smaller than that of [Li_2-a]. The changes ΔR_{HF} and $\Delta\nu_{HF}$ given in Table 1 for [Li_2-b] are for one of the FH bonds, which interacts with the electron entity $\{e^-\}$. Although the ratio $F_{\text{in cluster}}/F_{\text{atom}}$ suggests that the odd electron resides on the metal's orbital, one of the FH molecules forms the electron−hydrogen bond, which contributes to stabilizing the cluster and to shrinking the electron entity $\{e^-\}$.

For $Li(HF)_3$, the symmetric C_{3v} isomer [Li_3-a] in Figure 2 is definitely more stable than the 2 + 1 type isomer [Li_3-b]. Similar to the C_{3v} isomer [Li_3-a], the hydrogen atoms of two FH molecules in the isomer [Li_3-b] strongly interact with the ejected electron; one of the HF molecules is simultaneously hydrogen bonded to the other FH which is coordinated to the metal. It is the FH bond of this molecule that is the longest and weakest in Table 1. The ratio $F_{\text{in cluster}}/F_{\text{atom}}$ indicates that there is a part of the odd electron on the metal, but at the same time, *IsoVol*(0.5) is the smallest in Figures 1 and 2. Two dipole moments of the separately located HF molecules create the strong electrostatic field to trap the electron.

Because a HF molecule has only a single hydrogen donor site and a single hydrogen acceptor site, the number of possible isomers for $M(HF)_n$ is limited, which is contrasted with the clusters $M(H_2O)_n$. Because a water molecule has two sites of hydrogen donor and acceptor, the possible choices of hydrogen bond networks increase with n. No other forms of the isomers of $M(HF)_n$ are found $n \leq 3$.

As shown in Figure 1, two isomers are found for $Li(HF)_4$. In [Li_4-a], an isolated FH molecule caps on the top of [Li_3-a], forming a C_{3v} cluster. It is confirmed that the cluster is stable by evaluating the harmonic frequencies. The isomer [Li_4-b] is more stable than [Li_4-a], because of the strong Li^+ interaction with a FH molecule located at the other side of $(HF)_3\{e^-\}$.

The other isomer of $M^+(HF)_4\{e^-\}$, in which four HF are equivalently coordinated to the metal ion, was looked for in vain for M═Na and K. The initial model structure of C_{4v} collapses to a structure similar to [Li_4-b].

3.4. Ionization Energy. In Table 1, the changes in the ionization energy are given. For n = 1 and 2, the ionization energy decreases with n, similar to the water−group 1 metal clusters $M(H_2O)_n$.[1,2] But for the clusters having the ejected electron $\{e^-\}$, the ionization energies increase from a free metal atom: 5.75 eV for $Li(HF)_3$ [Li_3-a] from 5.34 eV of a Li atom and 4.67 eV for [K_3-a] from 4.24 eV of a K atom, calculated with the same level of theory. This is contrasted with the experimentally and theoretically found facts for the water−group 1 metal clusters $M(H_2O)_n$, in which the ionization threshold energies (ITE) for $n \geq 4$ are nearly the same values for the group 1 metals.[1,2] The increase of the ionization energy in $M^+(HF)_3\{e^-\}$ might result from the stong electrostatic field from the three HF molecules and the metal ion. The tightness (or diffuseness) of the electron cloud $\{e^-\}$ is a good measure of the electrostatic field where the electron is trapped. The volume *IsoVol*(0.5) for $M^+(HF)_3\{e^-\}$ is 14 Å^3 while the smallest for the clusters $M(H_2O)_n$ ($n \leq 6$, M = Li and Na) examined in the previous work[6] is 26 Å^3 with the same level of approximation. From the experimental point of view, the increase of the ionization energy is unfavorable for detecting these clusters. Because the clusters are neutral, to mass-select the clusters, the ionization is required; and as was for $M(H_2O)_n$, the measurement of the ITE is the best suited experiments. But if the ionization energy for the cluster is larger than the reference atom, it might be difficult to identify the cluster. Photoelectron spectroscopy might be a possible way with an electron−ion coincidence technique, because the ion $M^+(HF)_3$ is very stable, not dissociated after the photoionization.

3.5. Anions for Electrides. Because the electron {e^-} behaves like an halogen anion, a larger cluster having more than one {e^-} might be possible. Figure 3 shows the geometry of a triplet anion {e^-} $(HF)_3M^+(HF)_3${e^-}. The unrestricted Hartree−Fock MP2 was used in optimizing the geometry, and the S^2 value is 2.0015 before the spin projection and 2.0000 after the projection. In the figure, the sum and difference of two nearly degenerate SOMO (φ_{32} and φ_{33}) are shown; the orbital energy difference between two SOMO is 0.30 eV. The crystal having such a localized electron {e^-} as a constituent unit is called an electride.[18] The molecular anion, {e^-}$(HF)_3M^+(HF)_3${e^-}, might be possibly such a unit in the crystal. To examine the stability of the larger anion, another HF is added on the top of {e^-}, as in [Li_4-a]; another triplet anion {e^-}$(HF)_3M^+(HF)_3${e^-}HF is found as shown in Figure 3. Two SOMOs are drawn in the figure, and the orbital energy difference is 0.88 eV.

4. Concluding Remarks

It is interesting to design the electrides and molecular assemblies having a {e^-}$(HF)_3M^+(HF)_3${e^-} as an anion unit. One of the keys in the design is the search for the proper counter cations. The collaborative works with organic and inorganic chemists are essential. It is expected that these electrides and assemblies have the unique optical, magnetic, and electric properties.

In recent years many experimental[31,32] and computational works[33] of water cluster anions are reported. In this paper, we demonstrated a mechanism to localize the excess electron and to create the entity {e^-}. It is characterized by an “electron bound by the surrounding multi-dipole moments” and by the “electron−hydrogen bond”. These characteristics might help us to understand the structures and dynamics of the water cluster anions.

To evaluate the accurate binding energy of $M(HF)_n$, the BSSE has to be removed, but the ordinal CP method is not suitable to estimate it for the clusters studied in this work. It is because the electronic structure of the constituent units changes with the geometry and the size of the clusters and because the many-body terms are expected to be large. The simplest way to avoid the BSSE is to use the extensive basis set having both diffuse and high angular momentum functions, but it requires the large computer resources. As an alternative way, we have developed the perturbation theory (PT) based on the locally projected molecular orbital (LP MO),[34,35] which gives the binding energy close to the CP corrected HF energy for large clusters for a cost of a single supermolecule calculation. At this moment, the code for LP MO is only for the closed shell clusters. To apply this method to the clusters $M(HF)_n$, the theory and code for the open shell system have to be developed.[36]

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References and Notes

(1) Misaizu, F; Tsukamoto, K.; Sanekata, M.; Fuke, K. *Chem. Phys. Lett.* **1992**, *188*, 241.

(2) Hertel, I. V.; Haglin Nitsch, C.; Schulz, C. P. *Phys. Rev. Lett.* **1991**, *67*, 1767.

(3) Hashimoto, K.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11436.

(4) Hashimoto, K.; Kamitomo, T. *J. Am. Chem. Soc.* **1998**, *120*, 3560.

(5) Schulz, C. P.; Bobbert, C.; Shimosato, T.; Daigoku, K.; Miura, N.; Hashimoto, K. *J. Chem. Phys.* **2003,** *119*, 11620.

(6) Tsurusawa, T.; Iwata, S. *J. Phys. Chem. A* **1999**, *103*, 6134−6141.

(7) Tsurusawa, T.; Iwata, S. *J. Chem. Phys.* **2000**, *112*, 5705−5710.

(8) Iwata, S.; Tsurusawa, T. *Adv. Met. Semicond. Clusters* **2001**, *5*, 39.

(9) Tsurusawa, T.; Iwata, S. *Chem. Phys. Lett.* **1998**, *287*, 553.

(10) Tsurusawa, T.; Iwata, S. *Chem. Phys. Lett.* **2000**, *315*, 433.

(11) Lee, S.; Lee, S. J.; Lee, J. Y.; Kim, J.; Kim, K. S.; Park, I.; Cho, K.; Joannopoulos, J. D. *Chem. Phys. Lett.* **1996**, *254*, 128.

(12) Kim, K. S.; Lee, S.; Kim, J.; Lee, J. Y. *J. Am. Chem. Soc.* **1997**, *119*, 9329.

(13) Gutowski, M.; Hall, C. S.; Adamowicz, L.; Hendrick, J. H.; de Clercq, H. L.; Lyapustina, S. A.; Nilles, J. M.; Xu, S.-J.; Bowen, K. H., Jr. *Phys. Rev. Lett.* **2002**, *88*, 143001.

(14) Gutowski, M.; Skurski, P. *J. Phys. Chem. B* **1997**, *101*, 9143−9146.

(15) Hao, X.-Y.; Li, Z.-R.; Wu, D.; Li, Z.-S.; Sun, C.-C. *J. Chem. Phys.* **2003**, *118*, 10939.

(16) Hao, X.-Y.; Li, Z.-R.; Wu, D.; Li, Z.-S.; Sun, C.-C. *J. Chem. Phys.* **2003**, *118*, 83.

(17) Rauk, A.; Armstrong, D. A. *J. Phys. Chem. A* **2002**, *106*, 400.

(18) Dys, J. L. *Inorg. Chem.* **1997**, *36*, 3816.

(19) Dys, J. L. *Science* **2003**, *301*, 607.

(20) Matsuishi, S.; Toda, Y.; Miyakawa, M.; Hayashi, K.; Kamiya, T.; Hirano, M.; Tanaka, I.; Hosono, H. *Science* **2003**, *301*, 626.

(21) Kittel, C. *Introduction to Solid State Physics*; John Wiley and Sons: New York, 2005; Chapter 13.

(22) Lukes, V.; Bittererova, M.; Biskupic, S.; Laurine, V. *Theor. Chem. Acc.* **2003**, *109*, 316.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2006.

(24) Iwata, S. The algorithm is based on Tsurusawa’s. The code and manual can be downloaded from http://www.nabit.hiroshima-u.ac.jp/iwatasue/indexe.htm, **2007**.

(25) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, 123.

(26) Fuke, K.; Hashimoto, K.; Iwata, S. *Adv. Chem. Phys.* **1999**, *110*, 431.

(27) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J.; Xantheas, S. S. *J. Chem. Phys.* **1999**, *110*, 5.

(28) Choi, J. -H.; Kuwata, K. T.; Cao, Y. B.; Okumura, M. *J. Phys. Chem.* **1998**, *A102*, 503.

(29) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(30) Valiron, P.; Mayer, I. *Chem. Phys. Lett.* **1997**, *275*, 46.

(31) Hammer, N. I.; Shin, J.-W.; Headrick, J. M.; Diken, E. G.; Roscioli, J. R.; Weddle, G. H.; Johnson, M. A. *Science* **2004**, *306*, 675.

(32) Verlet, J. R. R.; Bragg, A. E.; Kammrath, A.; Cheshnovsky, O.; Neumark, D. M. *Science* **2005,** *307*, 93.

(33) Herbert, J. M.; Head-Gordon, M. *Proc. Natl Acad. Sci. U.S.A.* **2006**, *103*, 14282.

(34) Iwata, S.; Nagata, T. *Theor. Chem. Acc.* **2007**, *117*, 137.

(35) Iwata, S. *Chem. Phys. Lett.* **2006**, *431*, 204.

(36) Iwata, S. *J. Theor. Comp. Chem.* **2006**, *5*, 819.