Asymmetrically solvated anion with both kinetic and thermodynamic stabilities: Theoretical studies on the cluster anions (HF)\textsuperscript{n} (n=3–6)

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(Received 19 December 2006; accepted 28 February 2007; published online 17 April 2007)

At the level of MP2 with the aug-cc-pVDZ and aug-cc-pVTZ basis sets supplemented with diffuse bond functions, the authors searched the potential energy surfaces of (HF)\textsuperscript{n} (n=3–6). In accordance with the literature, they found that the symmetrically solvated-electron anion (3(FH)\textsubscript{(e)}) possesses the largest vertical detachment energy (VDE), while the dipole-bound anion ((FH)\textsubscript{(e)}) is the lowest isomer in energy for (HF)\textsubscript{n}. Their calculations demonstrated that, with the increase of the cluster size, the asymmetric (FH)\textsubscript{(e)}(HF)\textsubscript{n} cluster is stabilized with a simultaneously increased VDE. Thus they predicted that, for (HF)\textsubscript{n}, the (FH)\textsubscript{(e)}(HF)\textsubscript{2} cluster is both kinetically and thermodynamically most stable, possessing the largest VDE and being the global minimum at the same time. © 2007 American Institute of Physics. [DOI: 10.1063/1.2718953]

I. INTRODUCTION

The issue of binding an excess electron to a polar molecule or a cluster of polar molecules has long been a fascinating problem. Due to extensive theoretical studies,\textsuperscript{1–14} it is now well established that an excess electron can be bound by the dipole field of a neutral molecule or a neutral cluster to form a dipole-bound anion if the dipole moment of the neutral system is larger than ~2.5 D. Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive end of the dipole.\textsuperscript{9} This binding picture was confirmed by the subsequent studies.\textsuperscript{15,16} For a dipole-bound anion, it was found that the electron binding energy comes not only from the static Coulomb interaction but also from the electron correlation interaction between the loosely bound electron and the neutral molecular hosts. In fact, in many cases, correlation energy dominates the electron binding energy. Although higher order correlation effects can also be significant,\textsuperscript{4–8} the dispersion interaction was proved to be crucial to stabilize the dipole-bound anion.\textsuperscript{2–7}

The electron capture by biological molecules is of many important biologic consequences.\textsuperscript{17–23} For example, if the electron is attached to the valence orbital of a cell molecule, considerable geometric changes may occur, which may ultimately lead to the damage of the cell material.\textsuperscript{24} Less geometric change is expected in a dipole-bound anion, but recently it is found that the dipole-bound anion can serve as a precursor to the formation of valence-like anion.\textsuperscript{25–27} In the case of uracil, the comparison of the photoelectron spectra of the uracil and uracil-(H\textsubscript{2}O) anions demonstrated that although the uracil anion is a dipole-bound system, the complexation with just a single water molecule will favor the formation of the valence-type anion state over the dipole-bound state.\textsuperscript{28–30} Thus people have raised the possibility that a dipole-bound anion could act as a doorway state for electron capture by biologic molecules in the biological media.\textsuperscript{25,31,32}

Other than the dipole-bound state, an excess electron may also be trapped inside a molecular cluster. This kind of species is very often referred to as a solvated electron. This binding picture has been put forward since 1864 when it was first observed in liquid ammonia. Many systems containing solvated electrons have been studied, e.g., (NaCl)\textsubscript{n} (n=2,3,4), (HF)\textsubscript{n} (n=2,3,4), \textsuperscript{33} etc. As contrast to the normal (D-H⋯A) hydrogen bond, the concepts of electron-hydrogen (e⋯H) bond\textsuperscript{35} and the monoelectron dihydrogen (H⋯e⋯H) bond\textsuperscript{36} have been proposed in the corresponding studies.

There are several important differences between a solvated electron system and a dipole-bound anion. In the former, the extra electron is localized primarily inside a cluster of polar molecules whose dipoles are directing towards the excess electron.\textsuperscript{37} Such systems usually possess relatively large vertical electron detachment energies (VDEs), because the positive ends of the dipoles are pointing to each other at the moment when the excess electron is detached. This kind of neutral systems is unstable, which should undergo a larger geometrical rearrangement.\textsuperscript{33,34,37} In fact, some solvated electron systems may correspond to positive adiabatic electron affinities with respect to the ground state neutral system.\textsuperscript{38} Hence, such solvated electron systems would be considered as only kinetically stabilized. In the latter, the excess electron is localized outside the molecular framework and the dipoles are aligned constructively. There should accompany a smaller geometrical rearrangement upon electron detachment. A dipole-bound system would be thermodynamically stable, which has always been considered as the state of global minimum energy for the small anionic clusters.\textsuperscript{19,50} Then it comes a question: Is there an anionic...
structure which possesses the global minimum energy and the largest VDE at the same time? And we may further ask ourselves at what size and in what condition this anion can be formed.

In a recent research, Gutowski et al. have studied the (HF)$_2^-$ anion both theoretically and experimentally. They claimed that one of the peaks in the photoelectron spectra corresponds to a (HF)$_2^-$[(HF)$(e)$] cluster. This cluster was called an asymmetrically solvated electron, in which the dipole-bound anion of (HF)$_2$ was solvated by one HF monomer at the other side of the excess electron. It was found that this cluster is the second most stable structure in the potential energy surface of (HF)$_2^-$ and possesses the second largest VDE. The symmetric and asymmetric cluster anions of (HF)$_n^-$[(HF)$_b$] have been further examined by Hao et al. and a concept of monoelectron bimolecular bond (FHH$^*$[$e*...HF$]) has been put forward to explain the binding structure changes in the larger (HF)$_n^-$[(HF)$_b$] clusters. In this contribution, we focus on how a (HF)$_n^-$[(HF)$_b$] cluster can be both kinetically and thermodynamically most stable, possessing the largest VDE and being the global minimum at the same time.

II. COMPUTATIONAL DETAILS

Our calculations were performed by using the second order Møller-Plesset (MP2) method based on an unrestricted Hartree-Fock (UHF) starting point. The calculated expectation values ($S^2$) (<0.7501) for all anions studied here suggested that spin contamination is not an issue to significantly affect our findings, in accordance with the literature. The basis sets used were aug-cc-pVDZ and aug-cc-pVTZ of Dunning, supplemented with diffuse $s$ and $p$ bond functions (BFs). The lowest exponent of the five term $sp$ basis set in the BFs was set to be 4.5 ($a_u$) with a geometric progression ratio of 5.0. We assigned a ghost atom (labeled as Bq as it is in the Gaussian program package) with zero nuclear charge and zero number of electrons. We put the BFs on this ghost atom. The position of the ghost atom was chosen to be at the positive end of the molecular dipole of the cluster or the point where the dipole vector of each constituent (HF)$_n^-$, joined, as shown in Figs. 1–5. Moving around the Bq position by about 0.5 Å in the dipole bound (HF)$_3^-$ led to about 0.02 kcal/mol change in the total energy (~301.0 a.u.). So the reasonable Bq position will hardly affect the final energetics. In the literature, there are other ways in putting these diffuse functions. All of them are equally successful. Test calculations showed that adding a set of $d$ functions in the BFs brought only about 0.05 kcal/mol lower in the total energies in our cases, which were therefore not reported here. The methods used here have been proven to give reliable description of dipole-bound anions and the solvated electrons.

In this work, we carried out geometry optimizations for each isomer of (HF)$_n^-$(n=3–6). Analytical frequencies were calculated to confirm that each geometry was a true local minimum. Zero-point vibrational energy (ZPE) was calculated at the MP2/aug-cc-pVQZ+BF level with a scaling factor of 0.9830. VDEs were calculated by subtracting the energy of each isomer of (HF)$_n^-$ from that of the corresponding neutral one with the same structure. Counterpoise procedure was employed to remove the basis-set superposition error (BSSE) in energy decomposition analysis. We used the whole basis set, including BF, for the entire system as well as the constituent parts.

III. RESULTS AND DISCUSSION

The optimized structures at the MP2/aug-cc-pVTZ+BF level for the isomers of (HF)$_3^-$ are shown in Fig. 1. Structures at the MP2/aug-cc-pVDZ+BF level are very similar and hence are not shown. The calculated energies at both levels are listed in Table I. The open zigzag structure [denoted as (HF)$_3^-(e)$, Fig. 1(a)] corresponds to the dipole-bound anion. This is the global minimum in the potential energy surface of (HF)$_3^-$, but it possesses the smallest VDE (0.183 eV, Table I). The trigonal structure [denoted as 3(FH)[$e$], Fig. 1(c)] corresponds to the symmetrically sol-
vated anion. It is the least stable, being 7.0 and 4.9 kcal/mol higher in energy with respect to the dipole-bound state with and without the ZPE corrections, respectively. This structure has the largest VDE (0.658 eV). Photoelectron spectra of (HF)$_4^-$ have revealed the coexistence of two anionic isomers with VDEs of 0.24 and 0.43 eV.\cite{38} \textit{Ab initio} calculations at the coupled cluster level of theory with iterative single, double, and noniterative triple excitations [CCSD(T)] showed that the 0.24 eV peak corresponds to the dipole-bound state, and the 0.43 eV peak comes from an asymmetrical (FH)$_2^-(e)$ (HF) cluster.\cite{38} Our calculations also locate this state [Fig. 1(b)] and calculate its stability as in between the dipole-bound state and the symmetrically solvated anion (Table I). For this state, our calculations give VDE of 0.440 eV, in excellent agreement with the experimental value. But our calculations underestimate the first peak at 0.24 eV by 0.057 eV.

The trends appear in the stability and VDE for (HF)$_2^-$ is understandable. From the dipole-bound state [Fig. 1(a)] to the solvated electron state [Fig. 1(c)], the traditional hydrogen bonds are successively replaced by the electron-hydrogen bonds. Hence a significant reorganization energy is required for the neutral cluster to adopt the solvated state structure.\cite{34} This leads to a higher energy for the solvated electron clusters as compared to the thermodynamically stable dipole-bound anion. Since all the electron-hydrogen bonds will be broken when the excess electrons are removed, the solvated electron clusters obviously have a larger VDE. The solvated electron state possesses an energy higher than the ground state of the neutral system,\cite{38} and, in this sense, is only kinetically stable.

Figure 2 displays the optimized geometries at the TZ level for the isomers of (HF)$_3^-$. Table II summarizes the calculated energies at both DZ and TZ levels. The most interesting finding here is that, after ZPE corrections, the global minimum is the 2(FH)$_2^-(e)$ cluster (structure c in Fig. 2), instead of the dipole-bound state (FH)$_4^-(e)$ (structure a in Fig. 2). The 2(FH)$_2^-(e)$ cluster, which has a monoelectron dihydrogen (H...e...H) bond, is 0.58 kcal/mol thermodynamically more stable than the dipole-bound cluster anion (FH)$_4^-(e)$ at the level of MP2/aug-cc-pVTZ+BF.

Qualitatively, we may understand this difference by doing an energy decomposition analysis, as shown in Fig. 3. From the cluster anion (FH)$_4^-(e)$ to 2(FH)$_2^-(e)$, we see that the traditional hydrogen bond HB1 in (FH)$_4^-(e)$ changes to bond EHB2 as it is in the H...e...H bond. We may estimate the bond energies step by step. We may first remove the excess electron from the dipole-bound cluster anion (FH)$_4^-(e)$ to calculate the energy of electron-hydrogen bond, EHB1. The energy of bond HB1 is then calculated by separating the two (HF)$_2^-$(e) in (HF)$_3^-$. For the 2(FH)$_2^-(e)$ cluster anion, we first break bond EHB2 in the H...e...H bond to form a neutral (HF)$_2^-$ and a dipole-bound (FH)$_2^-(e)$. The excess electron is then removed from (FH)$_2^-(e)$ to calculate the energy of the second electron-hydrogen bond, EHB2'. We find that the

<table>
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<tr>
<th>Structure</th>
<th>Basis set</th>
<th>TE</th>
<th>TE(+ZPE)</th>
<th>TE(−e)</th>
<th>VDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(FH)$_4^-(e)$</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.061 935 2</td>
<td>−0.018 051 1</td>
<td>−0.049 935 5</td>
<td>0.327</td>
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<td>aug-cc-pVTZ+BF</td>
<td>−0.402 646 1</td>
<td>−0.358 762 0</td>
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<td>2(FH)$_2^-(e)$</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.059 718 6</td>
<td>−0.018 723 1</td>
<td>−0.021 040 1</td>
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<td>aug-cc-pVTZ+BF</td>
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<tr>
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<td>−0.017 046 9</td>
<td>−0.028 699 7</td>
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<td></td>
<td>aug-cc-pVTZ+BF</td>
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<td>−0.358 006 1</td>
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<tr>
<td>(FH)$_2^-(e)$(2HF)</td>
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<td>−0.015 149 4</td>
<td>−0.008 573 5</td>
<td>1.272</td>
</tr>
<tr>
<td></td>
<td>aug-cc-pVTZ+BF</td>
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<td>−0.356 167 9</td>
<td>−0.347 286 6</td>
<td>1.335</td>
</tr>
<tr>
<td>4(FH)$_4^-$</td>
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<td>−0.050 982 2</td>
<td>−0.011 216 8</td>
<td>0.002 917 3</td>
<td>1.467</td>
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<tr>
<td></td>
<td>aug-cc-pVTZ+BF</td>
<td>−0.391 829 8</td>
<td>−0.352 064 4</td>
<td>−0.335 835</td>
<td>1.524</td>
</tr>
</tbody>
</table>

FIG. 2. Optimized geometries for the (HF)$_3^-$ anions at the level of MP2/aug-cc-pVTZ+BF. Bq schematically labels where the excess electron is localized.
bond energies of EHB1 and HB1 in the dipole-bound cluster anion (FH)₄ₑ is 339 and 412 meV, respectively. The sum of them gives 751 meV. On the other hand, the bond energies of EHB2 and EHB2' in the 2(FH)₂ₑ cluster anion are calculated to be 730 and 67 meV, respectively. The sum of them leads to 797 meV. Comparison between bond energies of HB1, EHB1, EHB2, and EHB2' reveals some important information. (1) The strength of a normal hydrogen bond as bond HB1 is normally stronger than an electron-hydrogen (e···H) bond such as bonds EHB1 and EHB2'. (2) Bond EHB1 is stronger than bond EHB2' as the dipole moment of (HF)₄ (9.22 D) is larger than that of (HF)₂ (4.23 D). (3) The H···e···H bond as bond EHB2 is the strongest. We would like to emphasize that the EHB strengths between H···e···H and H···e are very different. The existence of one EHB greatly enhances the strength of the other. Clearly, the final stability of (FH)₂ₑ(FH)₂ comes from a collective contribution of both EHB2 and EHB2'. A good monoelectron dihydrogen (H···e···H) bonding demands that each part has its dipole large enough to bind the excess electron alone.

The results in Table II show that the energy gap between the 2(FH)₂ₑ cluster anion and its dipole-bound state isomer (FH)₂ₑ is only 0.42 kcal/mol at the MP2/aug-cc-pVDZ + BF level. When the larger basis set is enlarged to aug-cc-pVTZ+BF, the gap increases to 0.58 kcal/mol. We anticipate that even a larger basis set will further enhance the stability of the 2(FH)₂ₑ cluster anion over the dipole-bound isomer (FH)₂ₑ.

The importance of the monoelectron dihydrogen (H···e···H) bond is reinforced by the data of the (HF)₂ cluster anions, as shown in Table III. We see that the asymmetric cluster anion (FH)₃ₑ(HF)₂ (structure b in Fig. 4) is the absolute winner, being thermodynamically the most stable structure regardless of considering or not considering the ZPE corrections. At the level of MP2/aug-cc-pVDZ+BF, it is more stable than its dipole-bound state isomer (FH)₂ₑ (structure a in Fig. 4) by 5.10 kcal/mol. This number is increased to 6.0 kcal/mol when aug-cc-pVTZ+BF basis set is used instead.

There are other structures which can compete with the dipole-bound state in energy for (HF)₂ₑ. With the ZPE correction, isomers (FH)₃ₑ(HF) (structure c in Fig. 4) and 2(FH)₂ₑ(HF) (structure d in Fig. 4) are more stable than the dipole-bound state (HF)₃ₑ by 1.11 and 1.60 kcal/mol, respectively, at the level of MP2/aug-cc-pVTZ+BF. In these structures, the excess electron was solvated by three parts. Hence we get a strong implication that the dipole-bound anion can no longer be the thermodynamically most stable isomer in larger anionic systems. The H···e···H bond is very important to stabilize (HF)₂ₑ. But here the excess electron seems to prefer to be solvated by only two parts.

Inspection of VDEs in Table III reveals some new information. While the dipole-bound state (FH)₃ₑ remains to be the isomer with the lowest VDE, the symmetrically solvated electron state 5(FH)ₑ (structure f in Fig. 4) no longer possesses the largest VDE. The isomer (FH)₃ₑ(HF) (structure e in Fig. 4) wins over 5(FH)ₑ to be the one with the largest VDE at the level of MP2/aug-cc-pVTZ+BF. Indeed 2(FH)₂ₑ(HF) (structure d in Fig. 4) also competes with 5(FH)ₑ to have a comparable VDE.

Generally, the DZ results agree with the TZ results. But there is a significant exception. The (FH)₃ₑ(HF)₂ isomer is predicted to have an extraordinarily large VDE at the MP2/aug-cc-pVDZ+BF level. Comparison between the optimized geometries using DZ (structure b' in Fig. 4) and TZ (structure b in Fig. 4) gives us an important clue. The monoelectron dihydrogen (H···e···H) bond evolves into the monoelectron bimolecular bond (FH-e-HF), as described in detail by Hao et al. 41

![FIG. 3. Energy decomposition analysis for a comparison of bondings between (FH)₄ₑ and 2(FH)₂ₑ.](image)

**TABLE III.** Total energies (TEs) [in hartree, with respect to −501.0 for (HF)₂ₑ] and vertical electron detachment energies (VDEs) [in eV] at the MP2 level. Basis sets are aug-cc-pVDZ+BF for the first row and aug-cc-pVTZ+BF for the second in italics. Zero-point vibration energies (ZPEs) are calculated at the MP2/aug-cc-pVDZ+BF level with a scaling factor of 0.9675. The numbers in bold correspond to the lowest energies after ZPE correction.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Basis set</th>
<th>TE</th>
<th>TE(+ZPE)</th>
<th>TE(−e)</th>
<th>VDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(FH)₃ₑₑ</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.333 096</td>
<td>−0.277 487</td>
<td>−0.316 742</td>
<td>0.445</td>
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<td></td>
<td>aug-cc-pVTZ+BF</td>
<td>−0.759 208</td>
<td>−0.703 598</td>
<td>−0.704 087</td>
<td>0.467</td>
</tr>
<tr>
<td>(FH)₃ₑₑ(HF)₂</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.333 749</td>
<td>−0.285 613</td>
<td>−0.191 343</td>
<td>3.875</td>
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<tr>
<td></td>
<td>aug-cc-pVTZ+BF</td>
<td>−0.761 293</td>
<td>−0.713 156</td>
<td>−0.699 210</td>
<td>1.689</td>
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<tr>
<td>(FH)₃ₑₑ₂(HF)</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.330 390</td>
<td>−0.278 937</td>
<td>−0.265 266</td>
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<td>aug-cc-pVTZ+BF</td>
<td>−0.756 824</td>
<td>−0.705 871</td>
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<tr>
<td>2(FH)₂ₑₑ(HF)</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.331 132</td>
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<td>aug-cc-pVTZ+BF</td>
<td>−0.757 537</td>
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<td>(FH)₂ₑₑ₃(HF)</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.326 471</td>
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<td>aug-cc-pVTZ+BF</td>
<td>−0.752 609</td>
<td>−0.701 475</td>
<td>−0.673 487</td>
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<tr>
<td>5(FH)ₑₑ</td>
<td>aug-cc-pVDZ+BF</td>
<td>−0.318 431</td>
<td>−0.268 087</td>
<td>−0.241 658</td>
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<td></td>
<td>aug-cc-pVTZ+BF</td>
<td>−0.744 094</td>
<td>−0.693 749</td>
<td>−0.665 924</td>
<td>2.127</td>
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The energetics of (HF)$_n^-$ are summarized in Table IV and the optimized geometries are displayed in Fig. 5. Most importantly, we find that the asymmetric (HF)$_6^-[e](HF)_2$ cluster (structure $c$ in Fig. 5) is the global minimum and possesses the largest VDE at the same time. At the level of MP2/aug-cc-pVTZ+BF (without $f$ functions), its energy is 7.74 kcal/mol lower than that of the dipole-bound isomer (HF)$_6^-[e]$ (structure $a$ in Fig. 5), and its VDE is 5.287 eV larger than that of the 6(FH)$_6^-[e]$ (structure $e$ in Fig. 5). Table IV also shows that the symmetric 2(FH)$_3^-[e]$ (structure $b$ in Fig. 5) and 3(FH)$_2^-[e]$ (structure $d$ in Fig. 5) clusters are 6.05 and 3.69 kcal/mol, respectively, lower in energy than the dipole-bound isomer (HF)$_6^-[e]$. The energy sequence from low to high in Fig. 5 is $c < b < d < a < e$, and the VDE from large to small is $c > e > d > b > a$.

### Table IV: Total Energies (TEs) [in hartree, with respect to $-601.0$ for (HF)$_6^-$] and vertical electron detachment energies (VDEs) (in eV) at the MP2 level.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Basis set</th>
<th>TE</th>
<th>TE(+ZPE)</th>
<th>TE($-e$)</th>
<th>VDE</th>
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<td>(HF)$_6^-[e]$</td>
<td>aug-cc-pVDZ+BF</td>
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<td>$-0.905401$</td>
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<td>3(FH)$_3^-[e]$</td>
<td>aug-cc-pVDZ+BF</td>
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<td>aug-cc-pVTZ($-f$)+BF</td>
<td>$-0.980910$</td>
<td>$-0.915036$</td>
<td>$-0.902282$</td>
<td>2.140</td>
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<tr>
<td>(FH)$_4^-[e]$(HF)$_2$</td>
<td>aug-cc-pVDZ+BF</td>
<td>$-0.612707$</td>
<td>$-0.553642$</td>
<td>$-0.300733$</td>
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<td>aug-cc-pVTZ($-f$)+BF</td>
<td>$-0.979658$</td>
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<td>3(FH)$_2^-[e]$</td>
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<tr>
<td></td>
<td>aug-cc-pVTZ($-f$)+BF</td>
<td>$-0.954614$</td>
<td>$-0.891904$</td>
<td>$-0.857403$</td>
<td>2.645</td>
</tr>
</tbody>
</table>
We may conclude that the structures of $c=(\text{FH})_4[e] \times (\text{HF})_2$ and $b=2(\text{FH})_3[e]$, where the excess electron is surrounded by just two parts, are thermodynamically more stable than the isomers of the other kinds. The asymmetric structure $(\text{FH})_4[e](\text{HF})_2$ is also most kinetically stable. In accordance with the previous work, bond rearrangement occurs when the dipole moment difference between these two parts becomes too large. Figure 5(c) suggests that one H–F molecule in $(\text{FH})_4$ is ionized, giving a new structure of $(\text{FH}–\text{F–HF})^+ \cdots \text{H}^+$. Finally, it would be very interesting to determine the absolute thermodynamic stability of $(\text{FH})_4[e](\text{HF})_2$. It was claimed that the global minimum for $(\text{HF})_n$ is a cyclic non-polar structure. So we have optimized this structure at the TZ level as we do for $(\text{FH})_4[e](\text{HF})_2$. We obtain the total energies of $-601.8915182$ a.u. after ZPE correction for $(\text{HF})_n$. Using the corresponding numbers in Table IV, we arrive at an adiabatic ionization energy of $(\text{FH})_4[e](\text{HF})_2$ 0.713 eV. So $(\text{FH})_4[e](\text{HF})_2$ is a stable anion with respect to its neutral global minimum of $(\text{HF})_n$ and should be observed experimentally.

IV. CONCLUSION

In this contribution, we have searched the potential energy surfaces of $(\text{HF})_n (n=3–6)$. We focused on how a $(\text{FH})_4[e](\text{HF})_2$ cluster can be both kinetically and thermodynamically most stable, possessing the largest VDE and being the global minimum at the same time. We conclude the following:

(i) The dipole-bound anion cluster $(A)$ is always associated with the lowest VDE. It may present to be the global minimum for small cluster [in case of $(\text{HF})_n$, $n=3$]. If $A$ can be divided into two parts $(B$ and $C)$ and each part has a dipole large enough to bind an excess electron alone, the solvated state $(B)[e](C)$ has a great potential to be the global minimum [e.g., $2(\text{FH})_2[e], (\text{FH})_3[e](\text{HF})_2$, and $(\text{FH})_4[e](\text{HF})_2$].

(ii) The excess electron would rather form a bridge to connect just two parts besides it than to connect three or more parts in $(\text{HF})_n$, $n=4–6$. In all the solvated states studied here, the structure that one excess electron connects only two parts gives lower energy than the other kinds [e.g., $(\text{FH})_3[e](\text{HF})_2$ is lower in energy than $(\text{FH})_4[e](\text{HF})_2$].

(iii) In the cluster anions $(B)[e](C)$, the asymmetric structure is more stable than the symmetric isomers. This suggests that the maintenance of a dipole moment difference between parts $(B$ and $C)$ is good to stabilize the whole system. But if the dipole moment difference becomes too large, a bond rearrangement will happen in the part which has the relatively larger dipole moment [e.g., $(\text{FH})_4[e](\text{HF})_2$ vs $(\text{FH})_3[e](\text{HF})_3$].

(iv) An anionic cluster can be the global minimum and possess the largest VDE at the same time. It can be found in an asymmetrically solvated $(B)[e](C)$ state for some larger cluster anions [e.g., $(\text{FH})_4[e](\text{HF})_2$].

ACKNOWLEDGMENTS

This work is supported by NSFC (20525311, 20533030, and 20423002), the Ministry of Science and Technology (2004CB719902), and TRAPOYT from the Ministry of Education.

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