Theoretical study on cooperative and extra-additive behavior of hydrogen-bonded clusters

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Abstract The stabilization energy $\triangle E(n)$ and four typical properties of hydrogen bond F—H···F in chain-like and cyclic (HF)_n clusters (n = 1—5) have been calculated using MP2 and three DF levels of theory with the Gaussian 98 program, and 6-31++G^{**} bases set. The results demonstrate that the extra-additive or cooperative behavior in (HF)_n clusters is very obvious. In addition, we studied much larger chain-like (HF)_n (n = 6, 9, 12, 18, 24) clusters using one of these DF methods.

Keywords: hydrogen-bonded, DF methods, non-additive or cooperative behavior.

Hydrogen-bonded clusters play an important role in many progresses of chemistry and biochemistry^[1,2]. In the past two decades, hydrogen-bonded clusters have received much attention both theoretically and experimentally^[3–5]. (HF)_n cluster is the simplest hydrogen-bonded cluster system. So that it is very useful to make the (HF)_n clusters as the model clusters for the study of the hydrogen-bonded clusters. Recently the non-additive or cooperative behavior in (HF)_n clusters is most interesting for all the investigators^[2,6]. In general, the larger the (HF)_n clusters, the more obvious the non-additive behavior of the hydrogen-bonded clusters. However, because of the limit of the computational capabilities, it is very difficult to compute larger (HF)_n (n > 6) clusters with the *ab initio* methods such as MP2. Fortunately, in recent years DF methods were confirmed very useful in the field of hydrogen-bonded clusters^[7–9].

In the present paper, we report computed results using *ab initio*/MP2 and three DF methods. Through the use of all these four methods, we studied the extra-additive or cooperative behavior in chain-like and ring-like (HF)_n (n = 1—5) clusters. The results demonstrate that DF methods are very useful in the field of hydrogen-bonded clusters. Then we computed much larger chain-like (HF)_n (n = 6, 9, 12, 18, 24) clusters using one of these DF methods.

1 Computational details

The three DF methods are (i) hybrid-B3LYP (B3 (Becke's three-parameter) + LYP (Lee-Yang-Parr)), (ii) the BLYP(B (Becke's 1988) + LYP) method, and (iii) the hybrid-B3P86(B + P86(Perdew, 1986)). The *ab initio* calculations were performed at the MP2 levels of theory. The Gaussian 98 program and $6-31++G^{**}$ bases were used in each of these methods.

2 Results and discussion

Generally, the formation of a hydrogen bond A—H····B is accompanied by the following trends^[2]: (i) The intermolecular distance R (A····B) is much shorter than the sum of the van der Waals radii of A and B; (ii) R (A-H) is longer in the complex than that in the monomer; (iii) The fundamental frequency v (A-H) is smaller in the complex than that in the monomer; (iv) The infrared intensity of v (A-H) is larger in the complex than that in the monomer. In addition, proton NMR chemical shifts are significantly smaller in the complex than that in the monomer.

The extent to which these trends are actually observable depends on the strength of the hydrogen bond.

Before all, it must be indicated that in this paper the structures of chain-like $(HF)_n$ clusters are zigzag lines. Fig. 1 shows the structures of chain-like and cyclic $(HF)_4$ clusters.



Fig. 1. The structures of chain-like and cyclic (HF)₄ clusters.

Because the averaged stabilization energy reflects the strength of the hydrogen bond directly, at first we study the averaged stabilization energy. There are two methods to define the averaged stabilization energy per hydrogen bond $\Delta E(n)$:

$$\Delta E_{a}(n) = E(n) - E(n-1) - E \tag{1}$$

or

$$\Delta E_{\rm b}(n) = (E(n) - n^* E(1))/m, \tag{2}$$

where E(n) is the total energy of the *n*-mer, m = n for cyclic clusters, and m = n - 1 for linear clusters. Here, the latter is adopted.

Fig. 2 shows the computed stabilization energy of cyclic and chain-like clusters obtained with the four computational levels. All these results excellently agree with the previously published theoretical studies^[2]. The three DF variants deliver interaction energy that is in quite good



Fig. 2. Stabilization energy of chain-like and cyclic hydrogen fluoride clusters plotted versus n. \checkmark , MP2; \blacktriangle , BLYP; \blacksquare , B3LYP; \bigcirc , B3P86.

agreement with the MP2 data. The good agreement indicates that, as far as the interaction energy is concerned, the much cheaper DF variants reproduce reliable values.

Compared with the chain-like (HF)_n clusters, the C_{nh}-symmetric structures are more stable for n = 4, 5. However, larger rings will tend to become less stable. Therefore, for eventual extrapolations to the solid, the analysis of the chain-like structures appears to be more appropriate. The increase in the stabilization energy of the clusters takes place upon enlarging the size of the chain-like (HF)_n clusters. This is always called non-additive behavior. Fig. 2 indicates that the averaged stabilization energy per hydrogen bond increases straightly while the clusters become larger. In other words, the larger the cluster, the more obvious the non-additive behavior in chain-like (HF)_n clusters. We call this extra-additive behavior.

However, the increase in the averaged stabilization energy per hydrogen bond is not unlimited. In fact, the increase becomes slower as the size of the chain-like (HF)_n clusters becomes larger (from n = 2 to 5). In order to obtain the limit in the averaged stabilization energy per hydrogen bond, larger chain-like (HF)_n clusters have to be investigated. So that larger chain-like (HF)_n clusters (n = 6,9,12,18,24) were investigated using one of the DF methods and the results obtained with this method are illustrated in fig. 2. From fig. 2 we can see distinctly that the limit is around -34 kJ • mol⁻¹.

The *R* (H-F) and *R* (F···F) distances are important structural parameters, and the characteristic structural parameters of the shortest hydrogen bond in each of the clusters are depicted in fig. 3. It can be obviously seen that the *R* (H-F) elongates while the *R* (F···F) reduces with enlarging the size of (HF)_n clusters. Results obtained with all the three DF methods are in qualitative agreement with the previous SCF investigations applying the same basis set^[6]. On the other hand, there are some quantitative differences between MP2 and DF results, in particular for the *R* (F···F) contractions.

However, we can see from fig. 3 that the results computed with all the four methods have the same trend and converge slowly. So that larger chain-like $(HF)_n$ clusters (n = 6, 9, 12, 18, 24) are computed with one of the DF methods and the results are shown in fig. 3. From fig. 3 we can see that while the $(HF)_n$ clusters are larger than $(HF)_{12}$, the computed results converge rapidly and the results (the *R* (H-F) distance is 0.094 nm and the *R* (F···F) distance is 0.25 nm) of $(HF)_{24}$ cluster are very close to the limit. The *R* (H-F) distances are quite difficult to determine experimentally and hence only rather approximate crystal values of 0.095—0.097 nm^[10] are available. The experimentally derived *R* (F···H) distances of about 0.253 nm for $(HF)_6$ from electron diffraction^[11] and of about 0.250 nm from neutron diffraction of solid HF appear more reliable.

The harmonic ν (H-F) vibrational frequencies were also computed. The frequency of the most intense ν (H-F) infrared mode of each cluster is shown in fig. 4. The strongest infrared active mode in the chains is always the lowest within the group of F-H stretching. In the rings, the corresponding in-phase mode is optically forbidden, and the strongly infrared active mode is always the second lowest and doubly degenerates. Because of the too large elongations of *R* (H-F) com-

puted with the DF methods, the corresponding shifts of the ν (H-F) vibrational frequencies are considerably too large. This trend is already visible in case of the cyclic trimer. The experimental shift of the vibrationally allowed, and doubly degenerated F-H stretching mode with respect to the monomer^[12] is -249 cm⁻¹, being in excellent agreement with the MP2 shift of -246 cm⁻¹. The computed MP2 shifts for the strongly infrared active F-H stretching mode of cyclic tetramer, pentamer and hexamer are also in excellent agreement with the experimental data^[13].



Fig. 3. (a) and (b) Computed *R* (F-H) distances of chain-like and cyclic hydrogen fluoride clusters, (c) and (d) computed R (F···F) distances of chain-like and cyclic hydrogen fluoride clusters. \checkmark , MP2; \blacktriangle , BLYP; \blacksquare , B3LYP; \blacklozenge , B3P86.



Fig. 4. Calculated ν (H-F) vibrational frequencies in chain-like and cyclic hydrogen fluoride clusters plotted versus n. \checkmark , MP2; \blacktriangle , BLYP; \blacksquare , B3LYP; \blacklozenge , B3P86.

Experimentally, the in-phase k = 0, F-H stretching frequency in the hydrogen fluoride crystal is shifted by -896 cm⁻¹ relative to the monomer frequency^[14]. It is more difficult to extrapolate the infinite chain limit in the case of hydrogen fluoride, because the optimal structure is not the fully linear arrangement, and the non-additive contributions are of greater importance to the interaction energy, which cause also a slower decay of the two edge effects at both sides of the chains. Hence, chain-like clusters approach the bulk limit considerably slow. As shown in fig. 4, the lowest v (H-F) frequencies of chain-like clusters converge slowly, and actually larger clusters should be treated. So that we computed larger chain-like (HF)_n clusters (n = 6, 9, 12, 18, 24) using one of the DF methods. The results obtained with the DF method are shown in fig. 4. From fig. 4, it is very obvious that while the chain-like (HF)_n clusters are larger than (HF)₉, the computed results converge rapidly and the v (H-F) vibrational frequency in (HF)₂₄ approaches the bulk limit (the F-H stretching frequency is shifted by -1014 cm⁻¹ relative to the monomer frequency).

The results of computed infrared intensities of the ν (H-F) modes are shown in fig. 5. The methodical trends upon chain length elongation or upon increasing the ring size parallel those already observed for the frequencies, with the MP2 and B3P86 intensities as the limiting cases. When the structural parameters and the vibrational frequencies are used, the computed infrared intensities of the chain-like clusters allow, in combination with an analysis of the normal modes, a nice separation of the convergence to edge and bulk properties, respectively. An indication for this behavior can be found in fig. 5 by inspecting the intensities of the two highest-lying modes up to the chain-like hexamer, corresponding to localized F-H stretches at non-hydrogen-bonded and hydrogen-bonded edges, respectively. The results in larger chain-like (HF)_n clusters (n = 6, 9, 12, 18, 24) obtained as one of the DF methods are illustrated in fig. 5, and the trends in the infrared intensities of the ν (H-F) modes also parallel those already observed for the frequencies.



Fig. 5. Calculated infrared intensities A (F-H) of the v (H-F) vibrational frequencies in chain-like and cyclic hydrogen fluoride clusters plotted versus *n*. \checkmark , MP2; \blacktriangle , BLYP; \blacksquare , B3LYP; \blacklozenge , B3P86.

3 Conclusion

In summary, we have investigated the stabilization energy ΔE (n) and four typical properties

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for hydrogen bond F—H···F in $(HF)_n$ clusters with MP2 and three DF methods. The good agreement with the results of MP2 and DF methods confirm that DF methods is very useful in the field of hydrogen-bonded clusters. In addition, we studied much larger chain-like $(HF)_n$ (n = 6, 9, 12, 18, 24) clusters using one of these DF methods, and the non-additive or cooperative behavior in $(HF)_n$ clusters was obviously observed.

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