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ARTICLE

Coupled Clusters Calculation of Small Clusters (n=1-4) of Hydrogen Fluoride

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ABSTRACT

Hydrogen fluoride is one of the simplest heterodiatomic molecule, and have been a model molecule for computational calculation methods. However, the presence of hydrogen bond between the molecule can interfere with the simplified models in the calculations. This can be mitigated by replacing the single molecule calculation with clusters of molecules. Calculation results using CCSD(T)/LANDL2DZ showed that the cluster interaction get stronger as the number of hydrogen fluoride increase, with polygonal clusters tend to be more strongly interact than the other. H-F bond length tend to increase but not significantly with change within 2% or less. H-F vibrational frequency tend to decrease with polygonal structure tend to decrease quite significantly in comparison to the other geometry.

Keyword: Hydrogen Fluoride, Hydrogen Bonds, Molecular Cluster, Coupled Clusters.

ABSTRAK

Asam fluorida merupakan salah satu molekul heterodiatomik paling sederhana dan merupakan salah satu molekul yang paling umum untuk model perhitungan kimia komputasi. Namun adanya ikatan hidrogan antar molekul dapat mengganggu akurasi hasil perhitungan. Hal ini dapat diatasi dengan cara menggunakan klaster HF dalam perhitungan. Hasil perhitungan dengan menggunakan CCSD(T)/LANL2DZ menunjukkan bahwa interaksi dalam klaster cenderung meningkat seiring dengan meningkatnya jumlah asam fluorida, dengan klaster poligonal yang cenderung memiliki interaksi yang lebih kuat. Panjang ikatan H-F cenderung meningkat seiring bertambahnya molekul, namun peningkatannya umumnya di bawah 2%. Frekuensi vibrasi H-F cenderung berkurang dengan frekuensi pada struktur poligonal yang mengalami penurunan yang paling drastis.

Kata Kunci: *Asam Fluorida, Ikatan Hidrogen, Kluster Molekul, Coupled Clusters.*

INTRODUCTION

Hydrogen Fluoride (HF) is one of the simplest heterodiatomic molecule. Due to its simplicity, there have been several studies on it both experimentally and theoretically. While the simplicity of the molecule making it easier to study theoretically, both by using quantum mechanics methods and classical mechanics methods. Experimental study of the molecule however, it a bit more complicated due to its ability to form hydrogen bonds [1-12].

Hydrogen fluoride as a single molecule can be modeled using rotating harmonic oscillator, molecular interaction between the molecule is not negligible making the simple model failed to provide a satisfactory answer. The same perturbation also not included when in the LCAO-MO calculation. Some more pressing with this is the presence of hydrogen bonds between the molecule that can change the properties of the molecule between isolated single molecule to its gaseous state. The use of more than one molecule in the calculation is sometimes use to compensate for the correction from intermolecular interaction. There have been several studies on the clusters of HFs using several computational methods including Approximate Coupled Cluster Double substitution (ACCD), Restricted Hartree-Fock (RHF), Density Functional Theory (DFT), and 2nd order Moller-Plesset Perturbation Theory (MP2) [10-12].

In this study, we will revisit the study of HF clusters and compute its structure and properties using CCSD(T) due to its accuracy and reasonable calculation time for small molecules [13-14].

COMPUTATIONAL DETAILS

Computational methods used in this study is CCSD(T)/LANL2DZ [14-17]. The properties that were calculated in this study include optimized structure, relative energy levels,

All calculation was performed by Orca 4.2.1 while the visualizations are performed using Avogadro 1.2.0 [18-20].

Structure of the clusters are restricted to only that is symmetric with order of symmetry that is at least 3. This requirement only linear (n=1-4), polygonal (n=2-4), and polyhedral (n=4) are included. The structure from now on will be denoted as HFnx, with n as the number of hydrogen fluoride in the cluster and x is the geometry of the structure with x = a as linear, x = b as polygonal, and x = c as polyhedral.

Other structures while theoretically possible are not included. We also discard any transition state resulting from the calculation, as it is beyond the scope of this study.

RESULT AND DISCUSSION

Structure and Interaction

Due to the fact that any 2 bodies or more present within a localized space can interact with each other, any structure with 2 components ore more will necessarily have lower energy level than the sum of the components. In this study, the cluster interaction energy (ΔE) and cluster interaction energy per unit HF ((ΔE)̅) is calculated using these following equations:

$$\Delta E = E_{cluster} - nE_{HF} \qquad (eq.1)$$

$$\overline{\Delta E} = \frac{\Delta E}{n} = \frac{E_{cluster}}{n} - E_{HF} \qquad (eq.2)$$

Where E_cluster, E_HF, and n is the energy of the whole clusters, the energy of isolated HF molecule, and the number of HF in the clusters.

Table 1. Clusters energy levels in kcal/mol

Cluster	n	ΔE	$\overline{\Delta E}$
HF2a	2	-5.6730	-2.8365
HF2b	2	-4.2327	-2.1163
HF3a	3	-13.5322	-4.5107
HF3b	3	-15.8914	-5.2971
HF4a	4	-22.3497	-5.5874
HF4b	4	-29.5321	-7.3830
HF4c	4	-12.3659	-3.0915

The cluster interaction energy as the function of number of the HF in the clusters as shown in table 1 did not follow any apparent pattern until the structure of the cluster was taking into consideration.

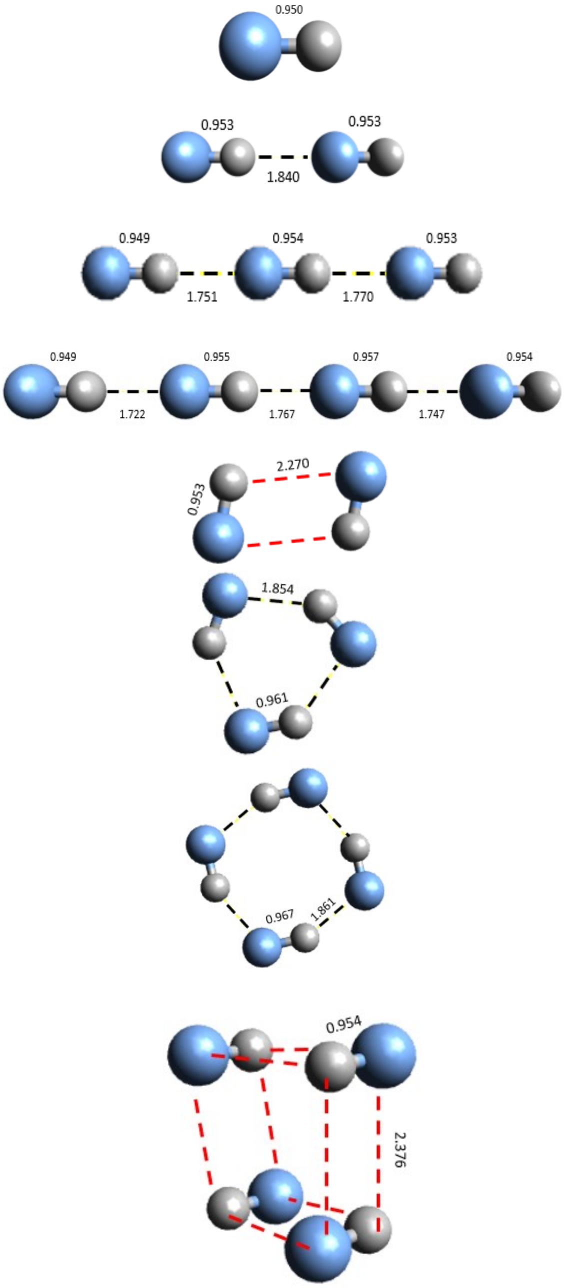

Figure 1. Structure of Linear, Polygonal, and Polyhedral Clusters

In figure 1, the hydrogen bond was represented as dashed black lines, while distance between adjacent hydrogen and fluorine atoms that are not connected by either covalent or hydrogen bond are represented as dashed red line, with the numbers adjacent with the bonds and/or lines are the distance in Angstrom.

By considering this information, it can be seen that linear HF2a, HF3a and HF4a all have hydrogen bonding, but the number of hydrogen bonding will be one less than

n, thus will tend to be less stable than HF2b, HF3b, and HF3b that has exactly n hydrogen bonding. The violation from this rule in HF2a and HF2b can also directly be explained by the fact that HF2a actually form hydrogen bond, while HF2b did not. This is mainly due to the restriction by the distance (2.270 Å) which longer than the usual hydrogen bond.

Cluster interaction energy per unit HF also change as the cluster size increase. This is due to the fact that while the between non adjacent atom exist. This interaction however decreases, as the function of distance which is why (ΔE)̅ in linear clusters decay at higher rate than the one in polygonal clusters. This structure also explained why HF3c has the lowest interaction energy, the structure did not form any hydrogen bond. Thus, any interaction between the HF unit is mainly in the form of van der Waals interaction.

The formation of clusters not only affect the energy, it also affected the structure of HF unit, albeit not significantly, with the largest deviation of 1.79% from the isolated structure.

Electron Distribution

Electron distribution within a cluster will also be affected by the structure of the cluster. This distribution will manifest as the partial charges of the atoms within the molecules in the clusters.

Table 2. Partial Charges of Hydrogen and Fluorine

n	Linear		Polygonal		Polyhedral	
	H	F	H	F	H	F
1	0.449	-0.449				
2	0.483	-0.466	0.490	-0.490		
	0.472	-0.489	0.490	-0.490		
3	0.494	-0.471	0.490	-0.490		
	0.509	-0.512	0.490	-0.490		
	0.480	-0.500	0.490	-0.490		
4	0.499	-0.473	0.504	-0.504	0.473	-0.473
	0.520	-0.518	0.504	-0.504	0.473	-0.473
	0.517	-0.524	0.504	-0.504	0.473	-0.473
	0.483	-0.505	0.504	-0.504	0.473	-0.473

The partial charges of the clusters as shown in table 2 include some interesting insight into the electron distribution throughout the clusters. Partial charges in polyhedral clusters behaved as expected, due to lack on hydrogen bonds between the structure any partial charge transfer will only occur within the molecule. Any charge transfer between the molecules is either nonexistent or very minimal. The partial charges within polygonal clusters also shows similar tendency, with partial charge of each unit actually sums to zero. This is due to the fact that the hydrogen atoms are indistinguishable with each other due to the symmetry of the structure. Thus, any charges transfer from a unit, will be received from the other unit.

The exception to unit neutrality within a cluster is only in linear clusters, which due to the fact that it is possible to excess charge in a unit to be neutralized by the adjacent unit. Because the structure actually has ends, it is the possible for a unit to be not neutral and being neutralized by other units, while not neutralizing others. While this allow partial charges within a unit, it still maintain neutrality within the whole clusters.

Vibrational Frequencies

The effect of cluster formation on the vibrational frequency of hydrogen fluoride can manifest in at least 3 ways, which are the shift in frequencies, number of vibrational modes, as well as types of vibrational modes. New types of vibrational modes can manifest into the calculation results as bending vibrations and not merely stretching vibration. This bending vibrational mode resulting from more than 2 atoms involved in the vibration in clusters. The use of clusters also increases the number of vibrational modes, even in the H-F stretching mode from 1 vibration in isolated HF to n vibrational modes in the clusters of size n. For simplicity, this study will consider only H-F stretching mode and neglect other vibrational modes. The vibrational frequencies of the H-F stretching is provided in table 3.

Table 3. HF Stretching Vibrational Frequency in cm-1

n	Linear	Polygonal	Polyhedral
1	3804		
2	3807	3771	
	3822	3773	
3	3754	3612	
	3790	3666	
	3822	3667	
4	3683	3426	3756
	3752	3535	3756
	3769	3535	3758
	3821	3578	3760

With the exception of HF2a, all the clusters vibrational frequencies decrease relative to the isolated HF. This decrease may be attributed to the constrained that was caused by the presence of other HF unit in the clusters. As HF2a are the least constrained of them it could possibly explained why the frequency increases.

From table 3, it can also be seen that compared to linear and polyhedral clusters, polygonal clusters tend to have very similar frequencies with each other as indicated by the very low relative standard deviation of 0.03%, 0.71%, and 1.68% for HF2b, HF3b, and HF4b respectively. Polygonal clusters also shifted the furthest from isolated HF with relative shift of 0.85%, 4.11%, and 7.52% for HF2b, HF3b, and HF4b. These phenomena are mainly caused by the structure of the clusters. Polygonal clusters are more strongly interacting then the other structure, restricting the motion, shifting the vibrational frequencies. Atoms in polygonal clusters also more equal to each other as every structure has rotational symmetry of order n, allowing the vibrational structure to be nearly degenerate to each other. Linear clusters on the other hand did not have rotational symmetry other than the one on the axis of the bonds, which is consistent with the results from partial charges.

Other Clusters

It is quite possible for other clusters to exist, especially for n≥4. For cluster with 3 or less unit, there are simply no other possible minima in the potential energy surface. This is mainly for the fact that any other distribution of hydrogen and fluorine atoms in 3D space will necessarily become either non-minima or optimized into one of the minima included here.

For n=4, it is possible that there are some configurations are not included in this manuscript. However, those configurations are likely to be less stable. Larger clusters while maybe plausible, it is currently beyond the reach of our computational resources by using CCSD(T)/LANDL2DZ. Other methods with lower complexity may provide acceptable results. For n=5,7, we cannot conceive symmetrical structures other than linear and polygonal, while for n=6,8, it may be possible by using symmetry from truncated tetrahedron, cubes, and octahedron. For n=6 in particular, utilizing the edges of truncated tetrahedron seems to be a plausible structure for a cluster. In the limit as n approaches a realistic number of molecules in everyday situation, the results of the calculation should become more accurate.

CONCLUSIONS

We investigate the structure and vibrational frequencies of hydrogen fluoride clusters. Our calculation showed that the structure of symmetrical hydrogen fluoride clusters with 4 units of HF or less can be categorized into 3 types, which are linear, polygonal, and polyhedral. Polygonal clusters tend to be the outliers with highest cluster interaction energy, and largest shift in vibrational frequencies. In term of partial charges however, the linear clusters are the outlier due to the fact that the clusters have ends that can be neutralized by other unit without neutralizing other.

AUTHOR CONTRIBUTION

HAA, HH, FK, and YS all involved in the conceptualization of the paper. HAA performed the calculation and writing.

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