

A DFT study of temperature dependent dissociation mechanism of HF in HF(H₂O)₇ cluster

SWATANTRA K YADAV^a, HIRDYESH MISHRA^{a,*} and ASHWANI K TIWARI^{b,*}

^aDepartment of Physics, MMV, Banaras Hindu University, Varanasi 221 005, India

^bIndian Institute of Science Education and Research Kolkata, Mohanpur 741 246, India
e-mail: hmishra@bhu.ac.in; ashwani@iiserkol.ac.in

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Abstract. We report a Density Functional Theoretical (DFT) study of dissociation of Hydrogen Fluoride (HF) in HF(H₂O)₇ cluster, using B3LYP functional and empirical exchange correlation functional M06-2X along with 6-31+G(d,p) basis set. Dissociation constant, K_{RP} , of HF dissociation and pK_a values of HF in cluster at various temperatures have been reported. It has been found that both K_{RP} and pK_a are highly dependent on temperature. The variation of pK_a with temperature suggests that HF is strong acid at lower temperatures. Our study also reveals that HF is a stronger acid in water cluster than in bulk water. Further, the results obtained by DFT calculations have been compared with the earlier reported results obtained from Monte Carlo (MC) simulation. It is found that DFT results are qualitatively consistent with the results of MC simulation but quantitatively different.

Keywords. Acid -water cluster; DFT; M06-2X; Thermochemistry.

1. Introduction

Proton transfer in acids inside water cluster has been extensively studied to understand many phenomena in environmental and atmospheric chemistry.^{1–3} Extensive research, including theoretical^{4–8} as well as experimental,⁹ have been carried out to find the stable conformers of acid-water clusters.¹⁰ The most stable structure of water cluster, cubic (H₂O)₈, provided the idea of cubic HF(H₂O)₇ cluster. Kuo *et al.*¹¹ performed a series of studies on water cluster by means of graph theory and *ab initio* methods and found that cubic structure of HF(H₂O)₇ is more stable in comparison with any other topology.

Electronic structure calculations of a number of acids in water clusters, with 4 or 7 solvent molecules have been carried out by Smith *et al.* to identify stationary structures on the potential energy surfaces. The relative energetics and stationary structures of HF have shown ionization to be more favourable in the larger clusters.¹² Re *et al.*¹³ investigated the stability of HF acid-water clusters [HF-(H₂O)_n] employing DFT method and found that more than seven molecules of H₂O are needed to stabilize the acid-water cluster system.

An extensive study has been performed by Kisiel *et al.* to understand the acidity of weak acids in water

cluster.^{14,15} During the dissociation process of acid in water cluster, the system quickly crosses a transition state. Dissociation of acid in water cluster involves the formation of two kinds of ions, namely Eigen ions and Zundel ions.¹⁶ Eigen ion is basically hydronium ion surrounded by three H₂O molecules and Zundel ion is H ion connected with two H₂O molecules. The existence of these ions has been observed by mass spectroscopy¹⁷ and infrared spectroscopy.¹⁸

Initial computational work related to this topic were performed at 0 K, but the study at 0 K does not provide information about acidity of HF at room temperature. Recently, some theoretical studies have been reported on the temperature dependence of rate constant of dissociation K_{RP} and pK_a values for many acids in acid-water cluster.¹⁹ Elena *et al.*¹⁹ performed a Restrained Monte-Carlo (RMC) simulation on a cubic cluster of HF(H₂O)₇ in the temperature range of 25–300 K to understand the mechanism of proton transfer in the system. It was found that the mechanism of proton transfer in the cluster is highly temperature dependent and at higher temperature causes the formation of an intermediate metastable state between reactant and product.

Effect of temperature in the calculation was included with the help of Temperature Accelerated Monte-Carlo (TAMC)²⁰ approach. These calculations showed that HF is a stronger acid in the water cluster compared

*For correspondence

to that of in bulk water. It was also reported that the pK_a value for HF in water cluster strongly depends on temperature. Its acidity increases at low temperatures. According to their study, this behavior has the entropic origin. They also performed temperature dependent study of rate constant (K_{RP}) and found that it strongly depends on temperature in lower temperature range (25–150 K), but remains nearly constant at higher temperatures.

We performed a systematic DFT study in order to understand the dissociation process and its temperature dependence at the molecular level. The purpose of this study is to compare the DFT results with Monte-Carlo studies. Structural properties of cluster such as bond length and IR stretching frequency provide useful information regarding transfer of proton from acid to the nearest water molecule and ionization process in acid-water cluster. Nearly all the acid-water clusters have tendency to ionize, which can be identified by A-H (A-acid) stretching frequency.¹⁶ Therefore, we have reported all these additional information for the system. The computational details are given in section 2, results are presented and discussed in section 3, followed by conclusion in section 4.

2. Computational

All the calculations have been carried out using Gaussian 09²¹ suite of programs. Thermochemical parameters were estimated at different temperatures by mean of DFT. Becke's three parameter hybrid exchange functional were used with gradient corrected, Lee-Yang-Parr correlation (B3LYP)²² along with 6-31+G(d,p) basis set. We have also employed highly parameterized empirical M06-2X functional of Zhao and Truhlar^{23–26} with the same basis set. M06-2X functional has been found to be extremely useful for non-covalent interactions.²⁷ In order to compute free energy, enthalpy and other thermo chemical quantities at different temperatures, frequency calculations were also performed. Harmonic approximation was followed during frequency calculation at low temperature but at higher temperatures, *viz.* at 225 K and 300 K, where anharmonicity has significant value, anharmonic corrections have been made. QST3²⁸ approach was used to obtain transition state for H-F dissociation. QST3 needs three input geometries *viz.* reactant, product and a guessed reasonable transition state geometry to search the true transition state. All the optimized geometries of reactant

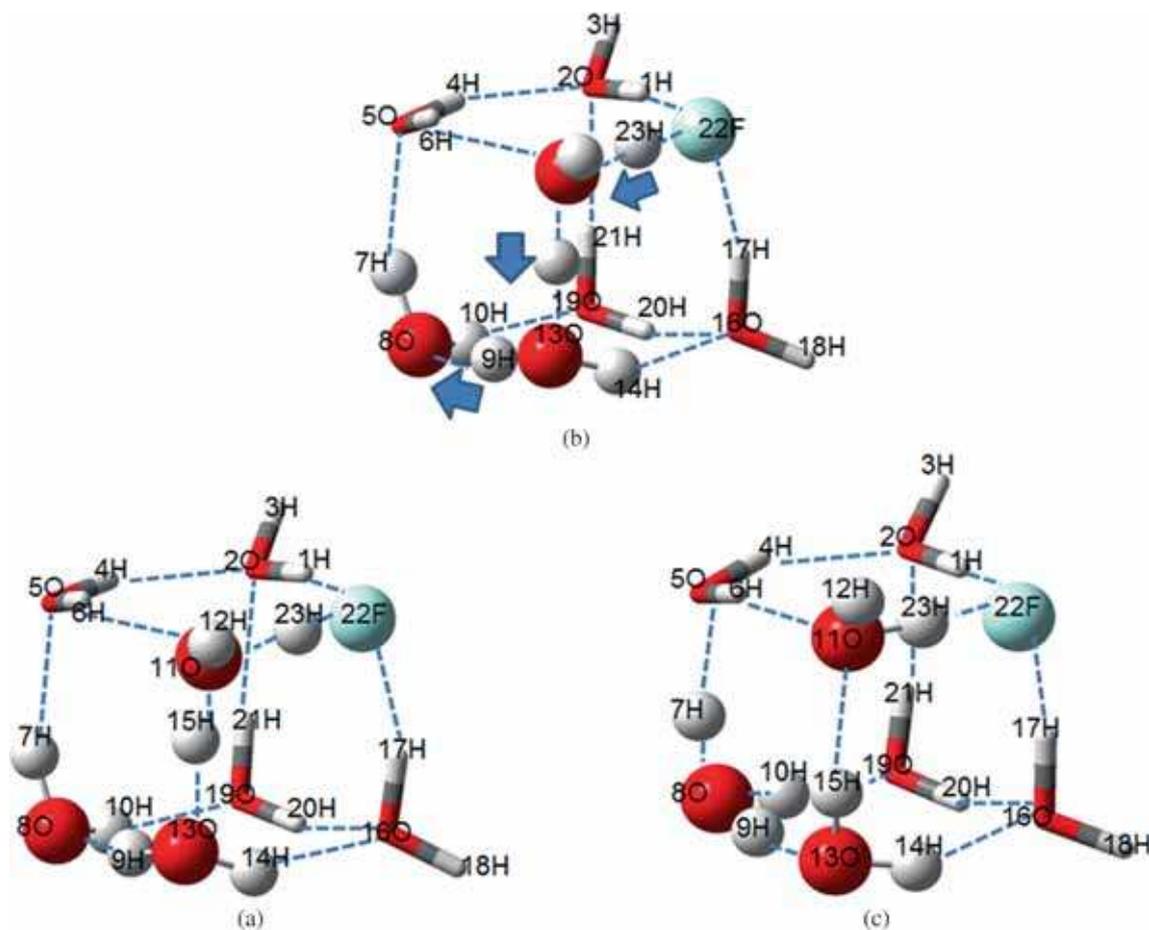


Figure 1. Optimized geometries of, (a) initial, (b) transition and (c) final states of HF-water cluster.

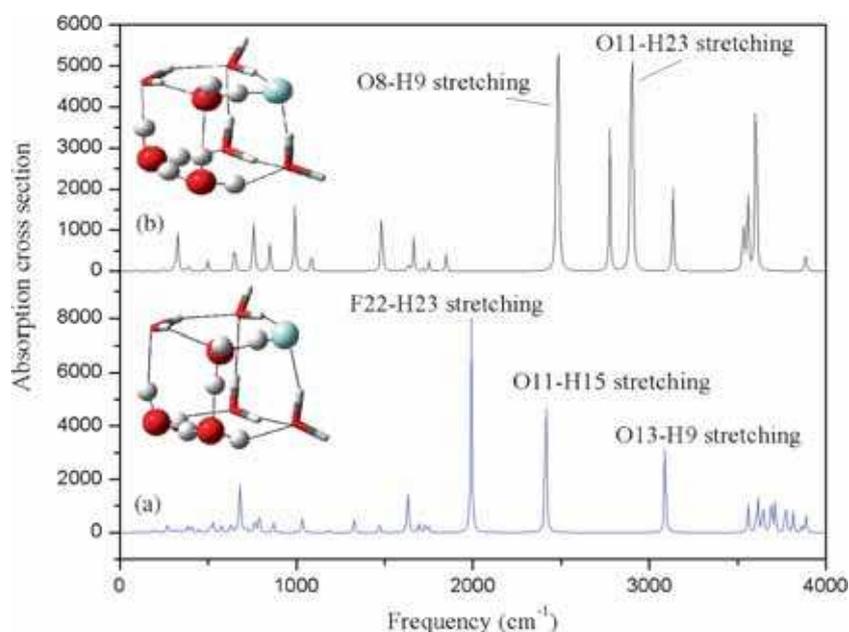


Figure 2. IR spectrum of, (a) reactant and (b) product at B3LYP/6-31+G(d,p) level of theory.

and product were characterized by all real vibrational frequencies while the transition state is characterized by one imaginary vibrational frequency. QST3 approach has been employed in case of restricted geometries,²⁹ which have closed ring type structures. pK_a values were obtained by relation, $pK_a = \frac{\Delta G}{2.303RT}$, where ΔG is change in Gibbs free energy, R is universal gas constant and T is temperature.

Rate constant at different temperatures were obtained by the relation, $K_{RP}(T) = \frac{k_B T}{h c^0} e^{-\frac{E_a}{RT}}$, where E_a is activation energy of the dissociation process, h is the Planck constant, k_B is the Boltzmann constant, c^0 the transmission coefficient value of which is taken as unity and the rest of the symbols have their usual meanings.

3. Results and Discussion

The movement of protons during dissociation process is depicted in figure 1, which shows optimized geometries of the reactant, product and transition state. The optimized geometries are shown in tube and ball-stick models. Those molecules which are involved in dissociation process are represented in ball-stick model. During the dissociation, barrier height of reaction was estimated to be about 0.604 kcal/mol and 0.404 kcal/mol with B3LYP and M06-2X, respectively. Our calculations suggest that final state geometry is stable by 5.88 kcal/mol (B3LYP)/4.33 kcal/mol (M06-2X) compared to the initial geometry. H-F bond length [1.04 Å] in cluster was found to be lengthened as compared to isolated HF molecule [0.92 Å] similar result has been reported by Smith *et al.*¹²

Infrared (IR) spectra of reactant and product are shown in figure 2 to get the insight of proton transfer during dissociation process. Spectra depict change in location of IR peaks due to proton transfer in the cluster. The intensity of stretching vibration provides information about weakening of the covalent bond.¹⁶ More intense IR peaks correspond to greater change in dipole moment during vibration and hence larger separation between poles (atoms). This indicates low force constant bond, thus, larger separation between atoms during vibration approaches closer to dissociating distance. Therefore, intensity of stretching modes can be used to predict the probability of translocation of atoms. In cluster, H-F and O-H stretching modes

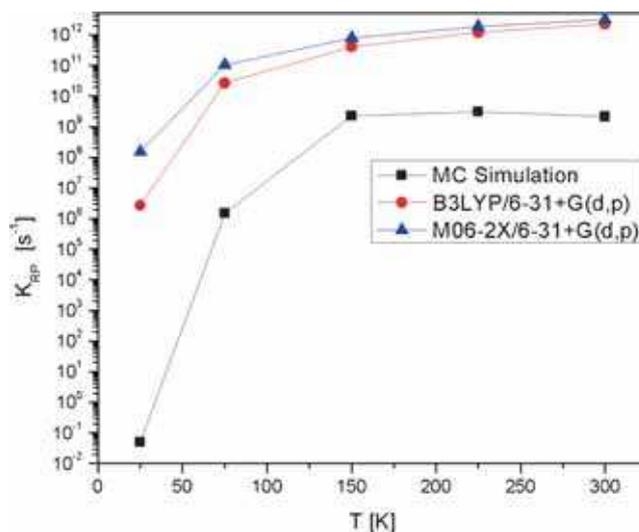


Figure 3. Temperature dependence of reaction equilibrium constant, K_{RP} .

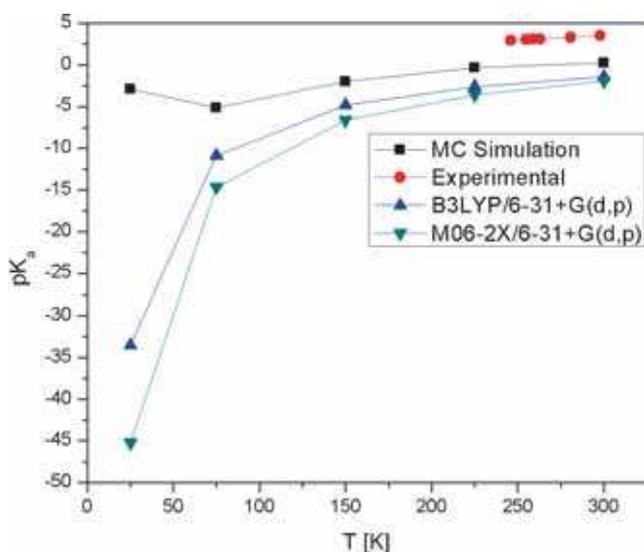


Figure 4. Variation of pK_a with temperature. (Experimental data in bulk water taken from reference³⁰).

lie in range 1992–3889 cm^{-1} for the initial (reactant) geometry. From figure 2, it is clear that peak intensity of stretching vibration follows the order F22-H23 (1992 cm^{-1}) > O11-H15 (2413 cm^{-1}) > O13-H9 (3090 cm^{-1}). Therefore, the dissociation of A-H covalent bond will also follow the same order. Interestingly, only these sites take part in dissociation process. IR spectrum of the final geometry shows all stretching modes in range 2476–3886 cm^{-1} , the most intense stretching vibrational peak at 2476 cm^{-1} corresponding to asymmetric H-O-H stretching vibration of hydronium (H_3O^+) ion. The O-H stretching vibration surrounding to F^- ion and H-O-H asymmetric vibration at oxygen centers O19, O13 and O5, have notable intensities. H_3O^+ ion resides at opposite corners of F^- , fixing the maximum separation of positively charged and negatively charged ions.

In figure 3, we have compared temperature dependency of K_{RP} , computed by DFT method with MC

simulation. It is clear from the figure that both DFT and MC simulation give qualitatively same dependency of K_{RP} on T. We observed a rapid change in K_{RP} in temperature range of 25–150 K but very slow change in temperature range 225–300 K. Due to the exponential factor [$\exp(-E_a/RT)$], as temperature increases, the factor E_a/RT decreases and consequently the value of K_{RP} increases as shown in figure 3. Additionally, Elena *et al.*¹⁹ explained its steeper behaviour in range 25–150 K in terms of increase in hopping frequency and decrease in free energy barrier in this range. DFT calculations gave higher values of K_{RP} compared to that of MC simulation at 25 K. Value of K_{RP} obtained by DFT calculations were found to be ~ 6 orders of magnitude of MC simulation for B3LYP/6-31+G(d,p) and ~ 8 orders of magnitude of MC simulation for M06-2X/6-31+G(d,p) at 25 K, whereas in range of 150–300 K it is higher by ~ 2 orders of magnitude with respect to MC simulation. This difference arises mainly due to use of different exchange correlation functional. The reason behind the large difference in the value of K_{RP} at lower temperature might be due to transmission coefficient c^0 , which has smaller value than unity at lower temperatures.

One of the most interesting features about this process is that HF shows highly negative pK_a value at low temperature (figure 4). This figure shows the plots of pK_a value against temperature obtained by DFT and MC simulation along with experimental results. DFT study shows consistently decreasing pattern of acidity with increase in temperature, whereas in MC simulation acidity increases from 25 to 75 K and then decreases with increase in temperature. At 25 K, MC simulation¹⁹ of water cluster the pK_a value was obtained nearly -2.8 ; while in DFT calculation, it was estimated to be -33.5 by B3LYP and -45.2 by M06-2X. Highly negative values of pK_a indicate that HF is completely dissociated in the cluster. On decreasing the temperature,

Table 1. Variation of different thermo dynamical quantities with temperature (in eV).

Temperature	ΔE	ΔG	ΔH	T ΔS
B3LYP/6-31+G(d,p)				
25	-0.16686	-0.16615	-0.16683	-6.80285E-4
75	-0.17353	-0.16153	-0.17353	-0.012
150	-0.18974	-0.14349	-0.18974	-0.04626
225	-0.20795	-0.11652	-0.20792	-0.0914
300	-0.22651	-0.08321	-0.22651	-0.1433
M06-2X/6-31+G(d,p)				
25	-0.12465	-0.12403	-0.12465	-6.25853E-4
75	-0.12852	-0.12092	-0.12852	-0.0076
150	-0.14103	-0.10890	-0.14103	-0.0321
225	-0.15690	-0.08949	-0.15692	-0.0674
300	-0.17360	-0.06449	-0.17361	-0.1091

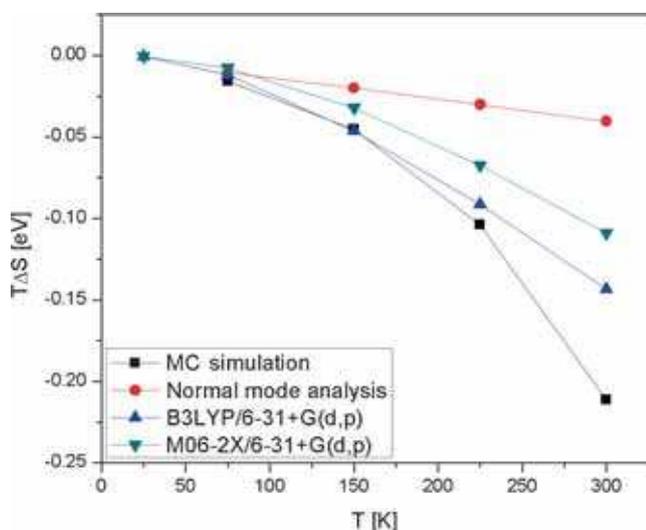


Figure 5. Plot of $T\Delta S$ vs temperature obtained by frequency calculation and normal mode analysis.¹⁹

change in Gibb's free energy becomes more negative (table 1) and pK_a values indicate the acidic strength of dissociated HF in water cluster increases and the system attains more stability. In range of 75–300 K MC simulation shows variation in pK_a value from -5.2 to 0.28 , whereas the values obtained by DFT calculation vary from -10.8 to -1.4 in this range. The experimental pK_a value in bulk water was found to be 2.9 – 3.5 ³⁰ in the range 250–300 K. Including experimental results performed in bulk water, it can be deduced that HF is a weak acid in bulk water. High acidity of HF at low temperature and low acidity in bulk water originate from its entropic change with temperature. The change in entropic contribution can be calculated by $\Delta G = \Delta H - T\Delta S$, where ΔG is change in Gibbs free energy, ΔH is change in Enthalpy and $T\Delta S$ is the entropic contribution ($\Delta S = S_p - S_r$; S_p is the entropy of product and S_r is the entropy of reactant). Comparative variation of $T\Delta S$ in case of MC simulation and DFT calculations is shown in figure 5. The variation of various quantities *viz.* ΔG , ΔH and $T\Delta S$ with temperature is also shown in table 1. Table 1 clearly points out that both the quantities, ΔH and $T\Delta S$ show decreasing pattern with increase in temperature but the variation of $T\Delta S$ is steeper than ΔH . This results in a regular increment in ΔG with temperature, leading to a rise in pK_a value. This clarifies that the variation of pK_a is governed by entropic contribution.

4. Conclusion

A DFT study of HF dissociation in HF(H₂O)₇ cluster at B3LYP/6-31+G(d,p) and M06-2X/6-31+G(d,p) level

of theory has been carried out to compute the rate constant and the pK_a value for H-F dissociation. The results obtained by DFT calculation have been compared with the earlier reported results obtained from MC simulation. DFT calculations are qualitatively consistent with the result of MC simulation but quantitatively different from MC results in range (25–75 K). DFT study also discloses that HF in HF(H₂O)₇ cluster is a stronger acid at low temperatures but becomes a weak acid at higher temperatures. Moreover, it can be inferred by variation of pK_a value with temperature that HF is a very strong acid in water cluster than in bulk water. Rate constant of dissociation strongly depends on temperature. The variation of rate constant is steep in range of $25 \leq T \leq 150$ K and beyond this range (i.e., at $T = 225$ K and 300 K) it is nearly constant.

Supplementary Information

Additional information regarding temperature dependent quantities are given in the supporting information available at www.ias.ac.in/chemsci.

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