# Structural Fluctuation of a Protonated Water Cluster

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**Abstract.** *In the present study we adopt a dissociable and polarizable potential model to simulate how a protonated water cluster $H^+(H_2O)_8$ structure changes over different levels of temperature. Potential energy plays a major role in defining the configuration of the molecular cluster. For the lowest temperature we examined, 20 K, generated structures by the simulation are dominated by a flowerlike structure, in line with the structure of the known minimum energy configuration for the $H^+(H_2O)_8$ cluster. As temperature increases, the structure changes to more open ones, complemented with single ring characteristic. In higher temperature the ring decreases in size, indicating tendency to be more open as temperature rises. At the highest examined temperature, 260 K, treelike structures instead dominate the cluster. Each kind of structure corresponds to a certain range of potential energy. Higher temperature contributes to higher potential energy, thus confirming that higher potential energy corresponds to more open structures, or longer range of molecular configuration.*

**Keywords:** Protonated water cluster, structural fluctuation, molecular dynamics method

## 1 Introduction

The nature of proton transfer in hydrogen bonds can be found in many disciplines. Such as in biology, where the proton pump mechanism in cellular membrane occurred; the proton pump mechanism involves the occurrence of proton transfer. Further understanding of the process of proton transfer and structure of protonated water would also constitute in the understanding of molecular components found in interstellar cloud. Interstellar cloud also consists of molecular components, being formed by many ice-layered grains.

Extreme space condition and cosmic ray impact are ones of the condition affecting these molecular components. Not only does it absorb light, interstellar cloud also reflect light. The accretion of molecular components as potential formation of refractory clusters in interstellar cloud has intrigued many astronomers. Explanations include cosmic ray sputtering of the components, creating $H_3^+$ and $H_3O^+$ in the ice layer, creating for instance $H_3O^+(H_2O)$ among others[1].

Detection of the above mentioned interstellar component previously eluded astronomers. But further understanding of the components of interstellar cloud and how they are created put detection of such cloud at an advantage. Predicting the components constructing these interstellar cloud and then investigating its spectroscopy, helped the detection. Rate of creation and destruction of those components, and their spectroscopy which replicated in laboratory, further help understand the formation and density of interstellar cloud.

## 2 Method

One of the potential models that specifically designed for describing $H^+(H_2O)_N$ (protonated water cluster) is the OSS model[2]. The OSS model is presented in three different versions, each with

increasing complexity of calculating water potential. Overall the OSS model uses parameterization of energy surface as its main characteristic, but certain details differ between OSS1, OSS2, and OSS3 models.

Using the OSS3 model as the basis for our potential model, we adopted the velocity verlet as our integration method. The algorithm of velocity verlet calculate the velocity and position of each particle involved at the same time. It is considered to be less memory consuming, because it does not necessarily keep the velocity for each time step.

Another method also used in our simulation is the Nosé-Hoover chain. Our simulations demand a steady value of temperature during the time step, thus a scheme to keep the temperature relatively constant is needed. The Nosé-Hoover thermostat enables the temperature of the system to be kept around an average.

All that is left is to describe the initial structure needed to start the simulation. The Cambridge Cluster database[3] provides a water cluster section under their website, including a link to protonated water cluster database. The optimized minimum for the $H_{17}O_8^+$ for the simulation in this research was taken from that database.

We intended to simulate $H_{17}O_8^+$ starting from temperature 20K. The temperature will be increased by adding another 20K to the system for every ten million steps reached. Thus, after the 20K, the next simulation temperature would be 40K, then 60K, and so on until 260K, totaling a number of 13 simulations. The final configuration of the previous temperature calculation was used for the initial of the next temperature simulation.

For each end of ten millions steps, some values regarding the system were extracted, such as its Hamiltonian, kinetic energy, potential energy, etc. These would be useful for analyzing the final results later. An xyz file was also created for each temperature, to observe the structural fluctuation that occurred during the simulation.

## 3 Results and Discussion

The result shows that the dominant structure for the lowest temperature is a closed one. Similar to its minimum energy structure, this closed structure dominating the lower temperature continue until 120K. Minor variation occurred in the structure, such as orientation, but the general dominant structure is still a closed one. Higher than 120K, we found that the dominant structure changes to a more open one, almost linear. The dominant linear structure in the 140K-180K is characterized with a single ring. In the 200K-240K, the dominant structure is similar to that of the 140K-180K, also characterized with a single ring, but smaller in size. The highest temperature does not have a particular dominant structure. Rather, almost all structures present in the 260K are of the linear type, with varying branches along the structure. Figure 1 summarizes the structural fluctuation of our simulation.

Figure 2 is the closed structure similar to the minimum energy structure that is dominant in the temperature 20K-120K. With short potential energy distribution, the structure of these temperatures do not vary quite much. Several slight variation seldom occurred, especially approaching the upper limit temperature. Structures occurred include several rare linear ones, with long branches.

The dominance of the closed structure is broken starting from the 140K temperature. Here, up to 180K, the dominance is ruled by a longer type of structure, characterized with a single ring, shown in Figure 3. The ring consists of five atoms, with variations including orientation and small bending of bonds. As observed, this kind of structure also appeared in the first region (20K-120K), but not in dominance and almost only as transitional structures. The closed structure

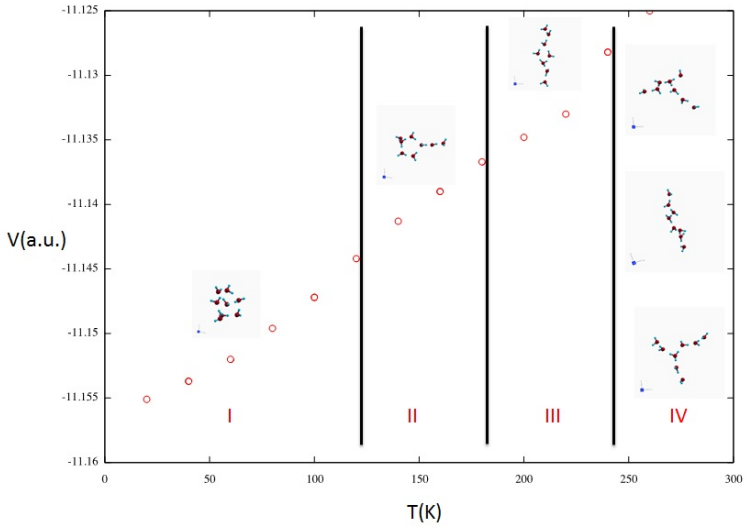


Figure 1: Averaged potential energy of the cluster as a function of temperature. The dominant structure can be divided into four different regions.

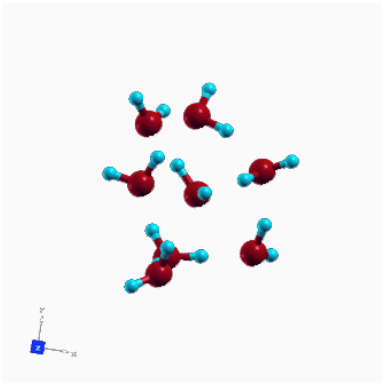

Figure 2: A closed structure similar to that of the minimum energy structure.

in the second region (140K-180K) is almost non-existence, as the rising temperature corresponds to higher potential energy, making the atomic distance longer.

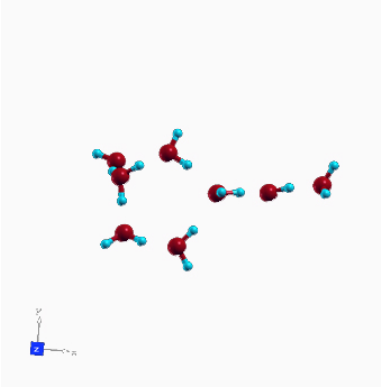

Figure 3: A more open structure characterized with a single ring.

The dominant structure of the third region (200K-240K) is similar to that of the second region. The difference is in the size of the ring, as seen in Figure 4. As mentioned before, a single ring characterized the dominant structure of temperature above 120K, but in the case of the third region, the ring size decreases into consisting of four atoms. The additional one atom from the previous ring size of the second region contributes to a longer structure. Beside the single ring structure, various linear structures almost dominate this region.

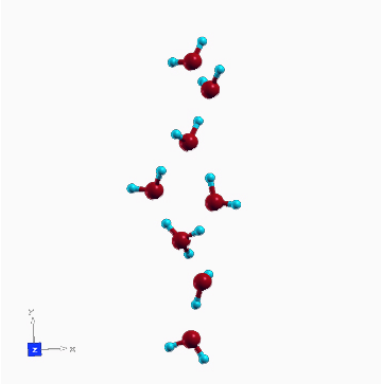

Figure 4: The characteristic ring becomes smaller in size.

In 260K, the structure of $H_{17}O_8^+$ are mostly linear (Figure 5 and Figure 6). Almost all structures in this region (260K) are in the form of tree-like structure, sometimes characterized with branch with various locations and lengths. A few of these structures are characterized with a single ring, as leftovers of previous regions' dominant structures.

In theory, higher potential energy would correspond to a broader range of atomic distance **r**. With broader range of atomic distance, the configuration of the structure would be also longer, owing to the longer atomic distance. An illustration of the correspondence between potential energy and atomic distance **r** is shown in Figure 7.

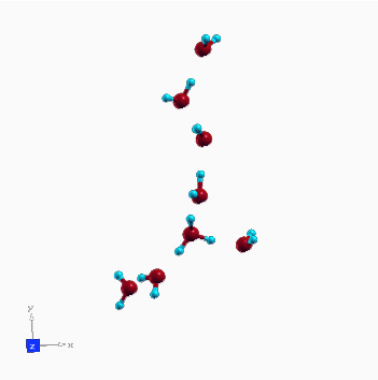

Figure 5: An example of tree-like structures in 260K.

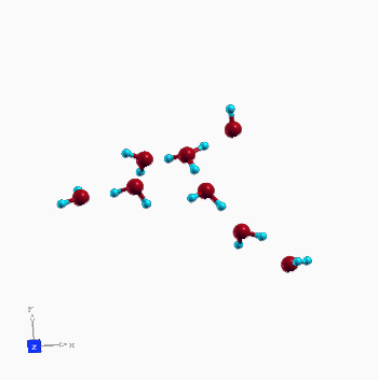

Figure 6: An example of tree-like structures in 260K.

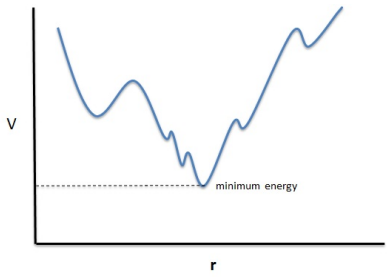


Figure 7: Higher potential energy corresponds to broader configurations.

Table 1: Range of Potential Energy of Dominant Structures

| Region | Temperature | Potential Energy (au) |
|---|---|---|
| I | 20K-120K | -11.15548 to -11.14537 |
| II | 140K-180K | -11.14281 to -11.13866 |
| III | 200K-240K | -11.13855 to -11.13035 |
| IV | 260K | -11.12965 to -11.12262 |

As confirmed by theory, rising temperature contribute to more open structures. Open structure means that the structure formation is longer, sometimes called tree-like with occasional branch between each end of the bonds. As oppose to more open structures, lower temperature means closed structures, structures with short atomic distance, meaning that the bonds are bent, forming a cube-like structure to meet the lower atomic distance requirement.

## 4 Conclusion

The structure of $H_{17}O_8^+$ fluctuates more with rising temperature. The lower temperatures correspond to a more closed one, similar to that of the minimum potential energy. As the temperature rises, the entropy of the system also rises, contributing to a higher potential energy. The higher potential energy itself corresponds to a broader range of atomic distance, hence the more open structure (longer, tree-like structure).

Upon further analysis, we can observe the potential energy range for each dominating structure. As it is just a rough estimation, the uncertainty of these values would certainly need a better analysis. The following table summarized the potential energy range for each dominating structure found in $H_{17}O_8^+$ for temperature 20K up to 260K.

Thus, structure of a protonated water corresponds to the dominant structure in a certain temperature. Higher temperature would present a more open dominant structure, compared to the minimum energy compact structure.

## References

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