First principle study on the structure of $\text{H}^+(\text{H}_2\text{O})_6$

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Abstract. The structure of $\text{H}^+(\text{H}_2\text{O})_6$ is investigated by examining selected low-lying minima with several first principle methods to benchmark the performance of these methods employed in the previous theoretical studies. Interestingly, we found that DFT methods with a moderate basis set follow the trends of MP2 with a large basis set very closely. In addition to the conventional zero point energy estimated with harmonic oscillator approximation, the contribution of vibrational anharmonicity is also investigated via first principle calculations. We found the anharmonicity contribution to the zero point energy varies between 2.7 to 5.0 mhartree and with that two kinds of tree structures (simple and branched tree) are found to be the most stable forms with nearly the same energy. The effects of Ar-attachment on the relative stability of these two tree structures are also examined and we found that the Ar-attached branched tree is more stable than the Ar-attached simple tree by about 1.4 mhartree. We shall also discuss the relevance of our findings with the recent experimental spectra on both bare and Ar-attached species.

1. Introduction

The structure of protonated water clusters have been the subject of recent experimental studies\(^1\)-\(^6\). In this work, we have chosen to investigate the structure of $\text{H}^+(\text{H}_2\text{O})_6$ by examining the low-lying minima with first principle methods for several reasons. It is well known that $\text{H}^+(\text{H}_2\text{O})_6$ is the smallest protonated water cluster that can carry a fully solvated Zundel type hydronium and very recently Headrick et al. have shown conclusive evidences on its existence in Ar-attached protonated water clusters\(^7\). Previous IR spectra, however, always indicate that bare $\text{H}^+(\text{H}_2\text{O})_6$ is a mixture of two topological isomers even at temperature as low as 77K. This raises concerns regarding the role of the attached Ar atom on the relative stability of different structural isomers – which will be addressed in this article.

Discrepancy also exists among previous theoretical studies carried out with different potential models. With the ASP model\(^8\), Hodges and Wales suggested a multiple-ring isomer (024 – see Fig.1) as the global minimum\(^9\). Based on the MS-EVB model\(^10\), Christie and Jordan found that a branched tree structure (402) is more stable\(^11\). Kuo and Klein\(^12\) identified a single-ring structure (222) as the most stable form of $\text{H}^+(\text{H}_2\text{O})_6$ in the OSS2 model\(^13\). We should point out that these studies were carried out using different empirical models and zero point energy (ZPE) was not included.

Jiang et al. examined seven isomers with B3LYP/6-31+G* and concluded that the 402 structure is the most stable form after including ZPE corrected under harmonic oscillator approximation\(^14\). Their conclusion is supported by the high-level \textit{ab initio} calculations by Mella et al.\(^14\). Nevertheless, Mella et al. found that a simple tree structure (321) is less than 1 mhartree less stable than 402. Based on
OSS2 empirical model, they also suggested that the vibrational anharmonicity has the potential to alter the energetic ordering. In this work, we shall engage different first principle methods to benchmark the performance of the previously used methods. Also, we shall examine the contribution of vibrational anharmonicity using a combination of *ab initio* methods and a vibrational perturbation theory (VPT2) as implemented in the *GAUSSIAN03* Code.

![FIGURE 1. Selected structural isomers of H⁺(H₂O)ₖ. All the structural isomers are labelled with a three-digit integer – with the first integer representing the number of water molecules with single H-bond, the second integer the number of molecules connected with two H-bonds, and so on. In the last two structures, additional tags are added to distinguish their different ring size.](image)

### 2. *Ab initio* Calculations on the selected structural isomers

Apart from the structural isomers examined in the previous theoretical studied; we add two more isomers with 4-member and 5-member rings because in a Monte Carlo study with OSS2 model, the ring structures are found to be energetically favoured. The geometry of these selected isomers is re-optimized by several first principle methods (described below) and unless explicitly stated, all calculations were performed using *GAUSSIAN03* Code.

#### 2.1. Electronic Energy (EE) and zero-point energy with harmonic oscillator approximation (ZPE/HO):

For H⁺(H₂O)ₖ, MP2 method with aug-cc-pvDZ (denote as MaDZ) is the highest level *ab initio* methods with the largest basis set applicable for such system size. In addition, it has been shown that MaDZ allows an accurate characterization of smaller clusters. Thus, we use MP2/aug-cc-pvDZ as the reference to benchmark the performance of the DFT methods previously employed, that is B3LYP/6-31+G* (denote as B6) and B3LYP/aug-cc-pvDZ (denote as BaDZ). To make a more complete comparison, MP2 method with 6-31+G* basis set (denote as M6) is also included.

For a given first principle method, all isomers first undergo geometry optimization to get the electronic energy (EE) on the Born-Oppenheimer surface. Analytic Hessian analysis is then applied to obtain the normal mode frequencies (ωᵢ), with that ZPE under harmonic oscillator approximation (denote as ZPE/HO) can be estimated via $ZPE = \sum \hbar \omega_i/2$ (sum over all vibration modes).

As the absolute value of EE from different first principle methods can not be compared directly, on the left panel of Fig.2, we present the relative stability (with the zero of EE scale being the averaged energy of all the isomers listed in Fig.1) – which indicates a clear tendency that the three ring-structures have lower EE than the two tree structures. On the other hand, the ZPE/HO, shown in the middle panel of Fig.2, counteracts this trend. As a result the difference in approximated total energies (that is EE+ZPE/HO as shown in the right panel in Fig.2) is rather small and the energy gap, separating the most stable isomer (402) from the others, is only 0.7 mhartree (with MaDZ). We should also note that it is evident from the comparisons shown in all three panels of Fig.2 that B6 method gives the most consistent results with MaDZ among all the first principle we tested.

#### 2.2. Anharmonicity:

Beyond the conventional harmonic oscillator approximation, ZPE can be calculated more accurately by vibrational perturbation theory (VPT2). For H⁺(H₂O)ₖ, a VPT2 calculation, as implemented by Barone *et al.* and incorporated in Gaussian 03 code, requires 103 frequency calculations, making the combination of VPT2 and the best *ab initio* method we used (MaDZ) computationally prohibitive. In light of the good agreement between B6 and MaDZ in EE and ZPE/HO (as discussed above), we are
confident to use B6 as an effective and efficient method to examine the vibrational anharmonicity in ZPE ($\Delta$ZPE $\equiv$ ZPE/HO – ZPE/VPT2).

The amounts of $\Delta$ZPE (in mhartree) for all the structural isomers are 2.73 (141-4r), 2.90 (222), 3.79 (402), 4.21 (141-5r), and 5.03 (321) respectively. After including vibrational anharmonicity in ZPE (that is total energy = EE + VPT2), 402 and 321 are predicted to be more stable than the ring structures by about 1 mhartree. Furthermore, the energy difference between them is only 0.1 mhartree. Apparently when dealing with isomers this close in energy, the calculated energy ordering can not be taken as definitive; hence we conclude that 402 and 321 are in fact iso-energetic.

FIGURE 2. First principle calculations results: MaDZ (purple diamond), B6 (pink square), M6 (blue cross), BaDZ (yellow triangle). Designations along the x-axis refer to the structures in fig. 1. See the text for discussions.

3. The role of Ar-attachment on the relative stability between 321 and 402

In contrast to the spectra obtained on the bare H’(H2O)$_6$ which contain vibrational signatures of both 402 and 321 isomers, Headrick et al. obtained a clean spectrum from its Ar-attached counterpart showing the exclusive dominance of the 402 structure. In the following we should investigate effects of the Ar-attachment on the relative stability between the 321 and 402 isomers.

For both structures, we tried to attach the Ar atom to different parts of the cluster, and the location of the Ar atom only has a minor effect (the largest energy difference is less than 0.25 mhartree). Nevertheless, for the following comparison (see table 1), we chose the most favorable Ar-attached form for both isomers. It is evident from table 1 that the difference in EE (between 402 and 321) is not sensitive to the presence of the Ar atom, and the difference in ZPE/HO only decreases by 0.5 mhartree in the Ar-attached species. The major effect of the Ar-attachment is on the $\Delta$ZPE which is found to favor the 402 structure. As a result, the Ar-attached 402 structure is about 1.4 mhartree more stable than the Ar-attached 321 isomer.

|       | W6+ EE(B6) | EE(MaDZ) | ZPE/HO (MaDZ) | ZPE/HO (B6) | ZPE/VPT2 (B6) | $\Delta$ZPE (B6) | EE(MaDZ) + ZPE/HO(MaDZ) | EE(MaDZ) + ZPE/VPT2(B6) |
|-------|-------------|----------|----------------|-------------|---------------|----------------|--------------------------|--------------------------|
| 402   | -458.98187  | -457.99998 | 0.15514        | 0.15424     | 0.15045       | 3.79          | -457.84484               | -457.84953               |
| 321   | -458.98284  | -458.00084 | 0.15713        | 0.15624     | 0.15121       | 5.03          | -457.84370               | -457.84963               |
| 402-321 | 0.81       | 0.85      | -1.99          | -2.00       | -0.76         | -1.13         | -0.86                    | -1.43                    |
| 402+Ar | -986.50224  | -984.95823 | 0.15586        | 0.15476     | 0.14838       | 6.38          | -984.80239               | -984.80985               |
| 321+Ar | -986.50306  | -984.95889 | 0.15737        | 0.15644     | 0.15046       | 5.97          | -984.80152               | -984.80843               |
| 402-321 | 0.81       | 0.66      | -1.52          | -1.68       | -2.08         | -0.86         | -1.43                    |                          |

TABLE 1. Comparison on the EE and ZPE of the bare and Ar-attached 402 and 321 isomers. Units are in hartree, except that the relative quantities (in **bold italic**) are in mhartree.
4. Discussions and Concluding remarks

In this work, we have tested the performance of various DFT methods on predicting the relative EE and ZPE/HO. Interestingly, in both aspects B3LYP with a modest basis set (6-31+G*) give more consistent results with MP2/aug-cc-pvDZ than B3LYP/aug-cc-pvDZ.

Without considering the vibrational anharmonicity, our ab initio calculations predict that the branched tree structure (402) is the most stable form with an energy gap of 0.7 mhartree that separates the 402 from other conformations. This picture, however, is not consistent with the experimental spectra on bare H’(H2O)$_6$ – which indicate that H’(H2O)$_6$ contains a mixture of both 402 and 321 even at temperature as low as 77K. We found this disagreement between the experimental data and ab initio calculations is due to the ignorance of vibrational anharmonicity in the latter.

We employed the vibrational perturbation theory method to gauge the contribution of the anharmonicity and found its amount ranges from 2.7 to 5.0 mhartree based on the isomers we have examined. After including the anharmonicity, we found that the two tree structures (402 and 321) are iso-energetic and both of them are energetically more stable than the other ring-structures. This refined energy ordering can account for the observed IR spectra on bare H’(H2O)$_6$. In other words, even for a qualitative description, it is important to include the anharmonicity in ZPE especially when dealing with isomers with small energy difference.

The effects of the Ar-attachment are also examined, and we found the Ar-attached 402 is about 1.4 mhartree more stable than the Ar-attached 321. Our calculation results are in line with the recent experimental work of Headrick et al. on Ar-attached H’(H2O)$_6$ where they found the exclusive dominance of the 402 isomer in cold cluster. This finding reminds us the possibility that the energy ordering of the H-bonded isomers can be altered by the Ar-attachment – a commonly used technique to cool down hot ionic clusters.

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