**A DFT assessment of the activation barrier for concerted proton transfer in cyclic water clusters (H2O)n where n = 3-8**

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**Abstract**

Currently the proton mobility in water clusters is an area that is relatively unexplored and very important for biochemical and catalytic processes occuring in water. We therefore investigate the barrier for proton transfer in a concerted fashion in water clusters where n = 3-8. Our findings at the B3LYP/aug-cc-pVDZ level of theory indicate that protons can transfer in a low barrier process of 15.5 kJ/mol per H-bond. This is still larger than the average thermal energy at 298K and therefore suggests that proton tunneling is also happening in water. We reveal the dynamic behavior of protons in cyclic water clusters in which concerted proton transfer occurs through an intermediate Zundel cation. We also offer the proton transfer barrier per H-bond in cyclic water clusters as a function of the size of the water cluster. This study helps in the understanding of the dynamic properties of protons in water.

**Keywords:** water clusters, proton transfer, DFT, Zundel, Eigen

**Introduction**

Water, with its seemingly simple molecular structure, exhibits a complex array of behaviors and interactions, particularly when it forms clusters. These clusters, ranging from dimers to larger assemblies, are critical for understanding water’s role as a solvent, its phase behavior, and its participation in chemical and biological processes. Advanced computational techniques, including quantum mechanical calculations and molecular dynamics simulations, have provided insights into the hydrogen bonding patterns, electronic properties, and dynamic behaviors of water clusters, serving as a foundational aspect of modern chemical physics and physical chemistry.[1-5]

Despite these advancements, a significant limitation in existing computational studies is their typical focus on static properties of water clusters without adequately exploring the dynamic aspects such as proton mobility. This gap is particularly notable in the quantification of proton transfer barriers—a key element in many chemical and biological processes that we explore in this study.

Gerber *et al.* underscore the importance of dynamic computational studies by examining atmospherically relevant chemical reactions in water clusters and on surfaces of liquid water and ice. Their research highlights how the dynamics of water clusters can influence chemical reactivity, particularly in understanding the processes that occur in atmospheric chemistry. This work provides a compelling argument for the need to include dynamic considerations in computational models to accurately capture the transient phenomena that drive chemical transformations in aqueous environments.[2]

To address these challenges, our study introduces computational techniques that include detailed bond scanning within water clusters with the structure (H2O)n, where n = 3-8. This approach allows us to systematically vary bond lengths and investigate the corresponding changes in potential energy. By doing so, we can capture a more comprehensive picture of the energy barriers and pathways involved in proton transfer, offering deeper insights into the kinetic mechanisms that govern these processes. Furthermore we can see the effect of the cyclic hydrogen bonded network onto the proton transfer barrier in relatively large water clusters, an area unexplored at the moment. Our method aims to fill a critical void in current research by providing detailed, dynamic measurements that many previous studies have overlooked.

Foundational studies by Xantheas and Dunning have been instrumental in identifying optimal structures and vibrational spectra for cyclic water clusters (H2O)n, n=1–6, yet these primarily focus on the static properties without directly quantifying the dynamics and barriers for proton transfer.[6, 7]

In our computational studies, we have extended this understanding by exploring the H-bonded networks in cyclic water clusters up to n = 8, which has highlighted the complexity of these structures and hinted at the potential mechanisms of proton mobility through these networks.[8] However, while these studies provide deep insights into the energetics and structural preferences of water clusters, they stop short of explicitly calculating the proton transfer barriers, which are crucial for a full understanding of reaction dynamics in aqueous environments.

Further, studies by Heßelmann *et al.* have explored correlation effects and many-body interactions in water clusters. Yet, these studies do not provide direct measurements or calculations of the energy barriers involved in proton transfer, highlighting a gap in linking many-body effects with proton mobility.[9]

Additional work by Rakshit *et al.* on the atlas of putative minima and low-lying energy networks of water clusters for n = 3–25 offers a comprehensive map of the potential energy landscape of these clusters. This atlas is crucial for understanding where proton transfer might be energetically favorable or hindered, yet it does not specifically address the kinetic barriers that protons need to overcome during transfer processes.[10] Moreover, our collaborative experimental and computational studies on hydrogen bonding in ethanol/water mixtures provide insights into the behavior of hydrogen bonds in mixed systems and hint at the complex interplay between different molecular species that could affect proton dynamics.[11] However, these insights into mixed clusters still leave room for detailed studies on purely aqueous systems.

Lastly, the computational studies by Romero-Montalvo and DiLabio have shed light on hydrogen bond interactions in water cluster–organic molecule complexes, further illustrating the intricacies of hydrogen bonding and its potential implications for proton transfer.[12] Although these studies enrich our understanding of cluster dynamics, the direct computation of proton transfer barriers within water clusters remains a critical and unaddressed area. Ignatov and Mosin[13], Masella and Flament[14], and Dang and Chang[15] provide extensive computational studies on hydrogen bond interactions in water clusters and the influence of nonpairwise effects upon their stability and geometry.

This collection of studies collectively underscores the significant opportunity for advancing our knowledge of proton dynamics in water clusters by focusing future research on directly quantifying the proton transfer barriers. At the heart of proton transfer in water are the Zundel (H5O2+) and Eigen (H9O4+) cations. These entities are not mere transient structures but fundamental components that reveal the complexity of proton transfer processes. They embody the balance between structure and dynamics within hydrogen-bonded networks, facilitating a deeper understanding of how protons traverse these networks with remarkable efficiency. The formation and transformation of these cations are crucial for modeling and understanding proton mobility, laying bare the quantum mechanical nature of hydrogen bonds in aqueous environments.[16, 17]

The Grotthuss mechanism, proposed over two centuries ago by von Grotthuss, remains a cornerstone concept in the study of proton dynamics in water. This mechanism describes how protons move through water via a "relay race" along hydrogen bonds, without the need for water molecules themselves to traverse the liquid. Von Grotthuss's original 1806 paper laid the foundational theory for understanding how electrical conductivity occurred in solutions, sparking subsequent explorations into the molecular mechanisms of proton transfer.[18]

Popov *et al.* conducted experiments that visually captured the movement of protons in aqueous solutions, providing direct evidence of the Grotthuss mechanism in action. They used advanced spectroscopic techniques to observe and measure how protons transfer through hydrogen-bonded networks, confirming the theoretical predictions made over two centuries ago and providing new insights into the efficiency and dynamics of the process.[19]

Noam Agmon offered a detailed review of the Grotthuss mechanism, examining the chemical physics behind proton transfer. Agmon's work delves into the molecular structure of water and how the orientation and strength of hydrogen bonds affect proton mobility, providing a theoretical framework that has been critical for subsequent studies aiming to understand and model these phenomena.[20]

Konermann and Kim utilized molecular dynamics simulations to explore proton hopping in electrosprayed water droplets, a novel approach to studying the Grotthuss mechanism in non-equilibrium conditions. Their findings illustrate the role of external electric fields in facilitating proton transfer and shed light on how environmental factors can modify the mechanism's operation in real-world chemical and biological systems.[21]

Hassanali *et al.* explored proton transfer through the "water gossamer," a term they use to describe the delicate and intricate network of water molecules that facilitate proton hopping. Their study integrates molecular dynamics simulations with experimental observations to show how subtle changes in water structure can significantly impact proton mobility.[22]

Our research has significantly advanced the understanding of the electronic properties of water by focusing on cyclic water clusters, particularly those comprising eleven molecules (n=11). Our computational study revealed these clusters to exhibit small bandgaps indicative of conductive states, which opens up novel pathways for understanding proton conductivity.[8] Our previous work investigated hydrogen-bonded networks in cyclic water clusters ranging from n = 3 to 12. This study provided comprehensive insights into the stability and electronic properties of these clusters, showing how their structural characteristics can lead to small bandgaps, suggesting a predisposition for enhanced proton conductivity. The findings underscore the complex interplay between molecular structure and electronic behavior, highlighting how specific configurations can influence conductive properties.[8]

Bao *et al.* expanding on the concept of proton transport mechanisms, Bao *et al.* explored the role of second sphere ligands surrounding the catalytic metal cluster in facilitating water oxidation. Their research illustrates how the structural environment around catalytic sites can significantly impact proton transport processes. This work complements our findings by showing that not only the intrinsic properties of water clusters but also their interactional contexts (such as with second sphere ligands) play a crucial role in modulating proton transport. Their conclusions point to the importance of the surrounding environment in enhancing or hindering proton mobility, which parallels the influence of cluster configuration on conductivity in our studies.[23]

A report on the use of time-dependent DFT (TD-DFT) for calculating free-energy barriers in excited-state proton transfer processes. The case study outlined in their paper shows TD-DFT's capability in accurately capturing the dynamics of proton transfer under non-equilibrium conditions, which parallels our approach to probing similar dynamics in water clusters.[24] By demonstrating TD-DFT's effectiveness, their findings support the extension of DFT methodologies, emphasizing the potential for capturing complex dynamical behavior in proton transfer.

In this investigation we explore the barrier for proton transfer in water clusters (H2O)n where n = 3 -8 using the B3LYP/aug-cc-pVDZ(5d, 7f) method on realtively large water clusters that are cyclic. This is to the best of our knowledge the first attempt to evaluate these activation barriers on large water clusters.

**Computational Method**

All water clusters were fully optimised with the B3LYP/aug-cc-pVDZ(5d, 7f) method.[25, 26] All calculations were done in Gaussian 16.[27] Vibrational analysis confirmed that we had global minima on the potential energy surface and the transition states were confirmed by the existence of one negative (imaginary) vibrational frequency. We have tried many structures for the water clusters with the structure of (H2O)n where n = 3 – 8. We only considered cyclic water clusters that were H-bonded. In order to obtain the barrier for proton transfer we scanned the O-H bond in the H-bonded network in 0.05 Angstroms increments for 15 – 20 steps until the O-H bond was dissociated. Dissociation of the O-H bond resulted in a concerted movement of protons in the cyclic H-bonded network which could be visualised by the images of the bond scan. Both the initial (before) structure and the final structure (after) were confirmed to be local minima on the potential energy surface. The structures of the cyclic water clusters are provided as supporting information. The choice of computational method in this study was a compromise between computational accuracy and computational demand and there have been more advanced methods used on smaller clusters recently.[28] We have calculated the proton transfer barrier rather than the H-atom transfer that would be the occasion where the proton in hydrogen along with the 1s electron are transferred between oxygen atoms in water.

Haunschild *et al.* provides a bibliometric analysis of the historical development of DFT, illuminating how this methodology has evolved to become a fundamental tool in theoretical chemistry. This analysis underscores the robustness and reliability of DFT for studying complex molecular interactions, validating our choice of method for exploring proton transfer barriers.[29] ​​This established the credibility of DFT, forming a solid foundation for the B3LYP calcualtions used here.

Further enhancing our computational strategy, Grimme *et al.* discusses the consistency of structures and interactions determined by DFT using small atomic orbital basis sets. Their study underscores the importance of selecting appropriate basis sets to achieve accurate and consistent results in DFT calculations. This work informs our choice of basis sets, ensuring that our simulations of proton transfer in water clusters are both precise and reliable.[30]

Hill *et al.* emphasizes the importance of choosing the right basis sets for molecular applications. Hill discusses Gaussian basis sets designed for molecular applications, while Laury and colleagues provide scale factors for vibrational frequency calculations using DFT with the polarization-consistent basis sets. These studies collectively offer guidance on selecting and utilizing basis sets that ensure reliable and precise results in our DFT calculations.[31]

**Results and Discussion**

We have examined the proton transfer mechanism in various cyclic water clusters (H2O)n where n = 3-8. For the water trimer (H2O)3 the activation barrier for proton transfer through the formation of a Zundel cation that forms at the transition state is E3 = 47.3 kJ/mol. This corresponds to a barrier per H-bond of 15.8 kJ/mol. This proton transfer can be seen in Fig. 1 and at the maximum of the potential energy curve the O-H bond is 1.424 Å.

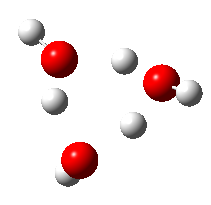
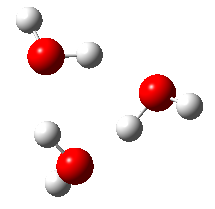
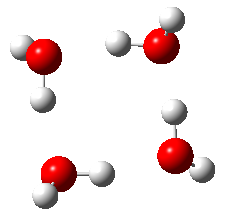
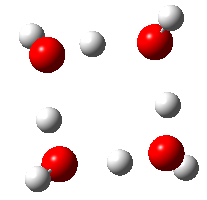


Fig. 1 Proton transfer in water trimer at B3LYP/aug-cc-pVDZ level of theory

For the water tetramer (H2O)4 the proton transfer occurs again through the formation of a Zundel cation which abruptly decomposes leading to a concerted proton transfer in the tetramer. The O-H bond that is scanned is elongated to 1.487 Å before the proton transfer occurs. The activation barrier for the concerted proton transfer is E4 = 110.3 kJ/mol which corresponds to a 27.6 kJ/mol barrier per H-bond. This barrier is larger than the barrier of the trimer which may be attributed to the stability of the Zundel cation that is formed in the transition state. This means that the Zundel cation forming in cyclic water clusters is less stable than the water trimer Zundel cation.



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Fig. 2 Proton transfer in water tetramer at B3LYP/aug-cc-pVDZ level of theory

For the water pentamer (H2O)5 the activation barrier for concerted proton transfer is E5 = 126.0 kJ/mol which corresponds to activation barrier of 25.2 kJ/mol per H-bond. We have scanned the O-H bond for 16 steps in 0.05 Å. increments and obtained the potential energy curve shown in Fig. 3 Here the length of the O-H that leads to the concerted motion of the proton is somewhat longer than the one observed in the trimer and tetramer and is 1.589 Å. Here it appears that the formation of the Zundel cation is more stable than the water tetramer which maybe a result of the bond angles in the water pentamer.

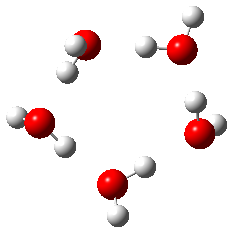
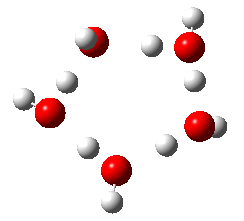


Fig. 3 Proton transfer in water pentamer at B3LYP/aug-cc-pVDZ level of theory

For the cyclic water hexamer (H2O)6 the barrier for concerted proton transfer is E6 = 149.7 kJ/mol which corresponds to an activation barrier of 24.9 kJ/mol per H-bond. Here we scanned the O-H bond in the direction of the H-bond in 20 increments of 0.05 Å. The potential energy curve for this bond scan is shown in Fig. 4. Here the bond length for concerted proton transfer is even longer than that found in the trimer, tetramer and pentamer and is 1.739 Å. The activation energy barrier however remains similar to what was found for the water pentamer. This indicates similar stability of the intermediate Zundel cation that is formed during the concerted motion of the protons.

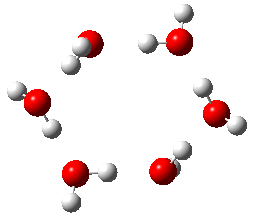
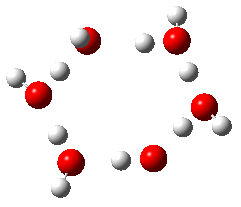


Fig. 4 Proton transfer in water hexamer at B3LYP/aug-cc-pVDZ level of theory

During the proton transfer the cluster from a heptameric cyclic structure changes to a pentameric cyclic structure and a tetrameric cyclic structure. Therefore, an additional H-bond is formed. This results in a decrease of the barrier for cyclic proton transfer. Eventually the cyclic proton transfer just happens in the pentameric ring with an activation barrier of E’5 = 86.6 kJ/mol which corresponds to a activation barrier of 17.3 kJ/mol per H-bond. This is significantly a low barrier process than the one that we observed in the plain cyclic water pentamer and has to do with the lower energy of the Zundel cation transition state in the water heptamer. The potential energy curve for this process can be seen in Fig. 5 and in this process that O-H bond was scanned in 20 steps of 0.05 Å. The cyclic proton transfer occurs when the O-H bond becomes 1.488 Å long.

The formation of the H-bond before the cyclic proton transfer can be seen as a kink in the 1D scan of the total energy shown by the red arrow in Fig. 5.







Fig. 5 Proton transfer in water heptamer at B3LYP/aug-cc-pVDZ level of theory

The largest cluster of water that can have a cyclic structure is the water octamer (H2O)8. The cyclic water octamer during the scanning of the O-H bond forms an intercluster H-bond resulting in two adjacent cyclic pentameric structures shown in Fig. 6. The activation barrier for proton transfer of E5 = 77.7 kJ/mol which is somewhat lower to the activation barrier of 86.6 kJ/mol found for the water heptamer suggesting that the pentameric transition state is stabilised further in the octameric water cluster. This result suggests that the barrier for proton transfer in cyclic pentameric water clusters that are embedded with other water molecules is 15.5 kJ/mol. Here again the O-H at the joined region of the two cyclic water pentamers is scanned in 16 steps of 0.05 Å. Here the elongation of the O-H bond prior to the concerted proton motion is 1.486 Å. This is similar to the bond length of O-H observed in the cyclic water tetramer proton transfer.

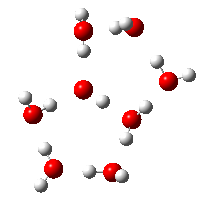
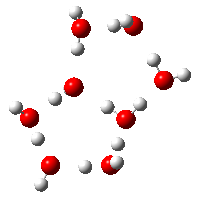


Fig. 6 Proton transfer in water octamer at B3LYP/aug-cc-pVDZ level of theory

The barrier of concerted for proton transfer in cyclic water clusters (H2O)n where n = 3-8 are tabulated in Table 1. We find that the minimum barrier for proton transfer is 15.5 kJ/mol per H-bond and that it becomes smaller as the size of the H-bonded network increases with the exception of the water trimer which has a barrier of 15.8 kJ/mol.

Table 1 Barriers of concerted proton transfer in cyclic water clusters shown in Fig. 1-6 using B3LYP/aug-cc-pVDZ method.

|  |  |  |
| --- | --- | --- |
| **n** | **Water cluster** | **Barrier per H-bond (kJ/mol)** |
| n=3 | (H2O)3 | 15.8 |
| n=4 | (H2O)4 | 27.6 |
| n=5 | (H2O)5 | 25.2 |
| n=6 | (H2O)6 | 24.9 |
| n=7 | (H2O)7 | 17.3 |
| n=8 | (H2O)8 | 15.5 |

We have not investigated the cyclic proton transfer in larger water cluster where n > 8 as these clusters would generally form smaller cyclic clusters when the O-H bond length was elongated. Our technique of scanning the bond length although very reliable as the rest of the structure is allowed to relax freely does not take into account the possibility of proton tunneling. Currently no other study has offered reliable barriers for cyclic proton transfer in water clusters and there is no study where proton tunneling is considered. The inclusion of proton tunneling would affect the barrier for proton transfer but it is currently unknown to what degree. This remains as a topic for future studies of the dynamics of proton transfer in water clusters.

**Conclusions**

By elucidating the conditions under which water clusters exhibit enhanced conductivity, our research opens new theoretical and practical applications, from designing better catalysts to understanding biological signal transduction. The integration of findings from both the structural examination of water clusters and the role of environmental factors in proton transport, as demonstrated in this study, underlines the potential for exploiting these mechanisms in various scientific and technological domains. This collective body of work not only deepens our understanding of the fundamental aspects of proton dynamics in aqueous systems, but also highlights the broad applicability of this knowledge in enhancing industrial and biological processes.

We have studied via DFT the proton transfer barrier in cyclic water clusters (H2O)n where n = 3-8. We find that the minimum barrier for proton transfer is 15.5 kJ/mol per H-bond and that it becomes smaller as the size of the H-bonded network increases. The structure goes through a temporary Zundel cation prior proton transfer. This is a very low barrier but it is still higher than the average thermal motion in water which is 3/2RT = 3.7 kJ/mol. This clearly suggests that protons are tunneling in water which reduces the effective barrier to that of the average thermal energy.

**Conflicts of Interest**

The authors declare no conflicts of interest

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