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SPECIAL TOPIC — Water at molecular level

Discontinuous transition between Zundel and Eigen for $H_5O_2^+$*

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The hydrated-proton structure is critical for understanding the proton transport in water. However, whether the hydrated proton adopts Zundel or Eigen structure in solution has been highly debated in the past several decades. Current experimental techniques cannot directly visualize the dynamic structures *in situ*, while the available theoretical results on the infrared (IR) spectrum derived from current configurational models cannot fully reproduce the experimental results and thus are unable to provide their precise structures. In this work, using $H_5O_2^+$ as a model, we performed first-principles calculations to demonstrate that both the structural feature and the IR frequency of proton stretching, characteristics to discern the Zundel or Eigen structures, evolve discontinuously with the change of the O–O distance. A simple formula was introduced to discriminate the Zundel, Zundel-like, and Eigen-like structures. This work arouses new perspectives to understand the proton hydration in water.

Keywords: Eigen, Zundel, infrared absorption, *ab initio* calculations

PACS: 31.15.A−, 33.20.Ea, 33.15.Bh, 33.20.Tp **DOI:** 10.1088/1674-1056/ab973d

1. Introduction

Water and hydrated protons are ubiquitous in various environments, e.g., biological bodies and industrial reactions.[1–16] Studies on water are still hot even now.[17–20] However, identifying the configuration of hydrated proton in aqueous solutions remains one of the mysterious scientific and technical problems because of the high fluidity of solution.[21] Similarly, although it is well recognized to own anomalously high mobility, how the proton transfers in solutions or at the interface is also not clear because people now still do not have capable equipment to capture its detailed process.[22–27]

During the past several decades, extensive attention was paid to water clusters, which were treated as the simplified models of liquid water. A number of studies have identified Eigen (H_3O^+) and Zundel ($H_5O_2^+$) as the two most possible configurations for the hydrated proton.[4,28–30] Structurally, Eigen represents those with relatively short O–H^+ distance to make the proton individually owned by one O atom, while Zundel usually indicates that the proton is more likely being shared by the two adjacent O atoms as given in Fig. 1.[31] Vibrational spectrum on the proton stretching mode has been recognized as the most effective tool to discriminate the molecular structure of Eigen and Zundel experimentally.[32] Both experimental and theoretical works suggest that the proton stretching frequency of Eigen ranges from 2000 cm^{-1} to 2800 cm^{-1} and the one of Zundel is around 1000 cm^{-1}.[4,33,34]

However, identification of the IR spectrum is more difficult in aqueous solution.[35] Through the 2D infrared spectroscopy, several works are able to identify the mysterious species in pure water and in acidic solutions.[2,29] In the IR spectrums of these works, the feature absorption peaks at 1760 cm^{-1} and 3200 cm^{-1} were assigned to the HOH bend and water OH stretch of a Zundel arrangement according to the computed spectrum of $H^+(H_2O)_6$, which is regarded as the smallest gas-phase cluster that can mimic the solvated Zundel. Although there is a low IR continuum band of $\sim$ 2000–2800 cm^{-1}, the absence of the peak absorption in this range makes the researchers draw the conclusion that the vibrational spectrum of the acid solution system matches that of the Zundel-like motif.[29] But this work did not totally exclude the possibility of the presence of Eigen-like configuration.[29] However, how to discern the Zundel-like and Eigen-like configurations, and how to interpret the IR spectroscopy for solution studies is still an open question and yet to be answered.

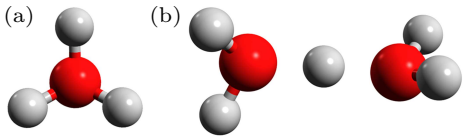


Fig. 1. The structures of (a) Eigen and (b) Zundel. Red: O atom; grey: H atom.

Theoretically, early studies by Parrinello *et al.* have claimed that configurations during proton transfer cannot be assigned as ideal Zundel form or ideal Eigen form.[24] This is also the case for more recent studies which is responsible for the difficulties in interpreting the experimental continuum IR

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spectrum.[2,27,29] There also have been extensive studies on the correlation between the vibrational frequency and the corresponding geometrical parameters following the well-accepted Badger's rule.[33,36,37] Xantheas *et al.* found the linear correlation between the O–H length and its intramolecular bridge OH frequencies in several cyclic water clusters $(H_2O)_n$, $n = 1$–6 through careful *ab initio* studies.[36,37] They also gave the same correlation between the proton stretch band and the O–H^+ length for several protonated $(H_2O)_n$ clusters, $n = 1$, 3, 4, 5, 10, and 21.[32] Later, Bowman *et al.* examined dependence between the proton stretch and its harmonic frequencies and obtained the same conclusion as in Xantheas's work.[33] However, these works only focused on the relationship between the frequency and a few chosen static structures in protonated water clusters, which are significantly different as those in aqueous solution. It is known the O–O and O–H^+ distances are the key to determine the Eigen, Zundel, Eigen-like, or Zundel-like configuration. The O–O distance has a broad distribution, e.g., 2.52–2.88 Å in $H^+(H_2O)_{21}$ water cluster and $\sim$ 2.47–3.39 Å in aqueous solution,[38,39] which may cause the different O–H^+ distance to affect the configuration of the protonated water structures. However, it remains unclear how the structures will evolve upon altering the O–O distance successively.

In this work, using $H_5O_2^+$ as the model system, we employed the first-principles calculations to show that the variation of the O–H^+ bond is discontinuous with the continuous variation of the O–O distance, which induces the discontinuous evolution of the IR spectra. This work calls upon the revisit of the IR spectra and the hydrated proton configuration in aqueous solution, and may provide a new perspective to understand the proton transfer in solution.

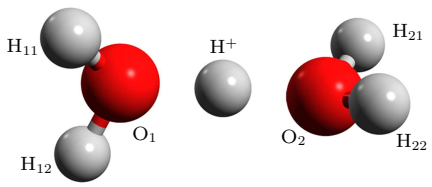
2. Computational section

The calculations were carried out by using CCSD(T), DFT, and MP2. Functionals including PBE, PBE0, B2PLYP-D, B3LYP, wB97xd were used in the DFT calculations. Grimme's DFT-D3 correction was considered if available. As geometrical parameters for comparison, the reference structure was optimized using CCSD(T)/cc-pVTZ. Then, DFT and MP2 calculations with basis sets of 6–311++G(3df,2p), aug-cc-pVDZ, and def2-TZVP were used for comparison. Very tight threshold (maximum force: 2×10^{-6} Hartree/Bohr, RMS force: 1×10^{-6} Hartree/Bohr, maximum displacement: 6×10^{-6} Å, RMS displacement: 6×10^{-6} Å) combining untrafine integration grids were implemented in the geometry relaxations. The DFT and the MP2 calculations were done using Gaussian09-D01 package.[40] The resolution-of-the-identity based explicitly-correlated couple-cluster calculations with perturbative triples correction (CCSD(T)-F12/RI) were done using the Orca software package.[41] The vibrational scaling factors for different methods and basis sets were obtained from the website of National Institute of Standards and Technology, U.S. Department of Commerce.[42]

3. Results and discussion

3.1. Overview of the structures and IR spectrum of H_3O^+ and $H_5O_2^+$

The optimized geometry of $H_5O_2^+$ using CCSD(T)-F12/cc-pVTZ is given in Fig. 2. The O–O distance is 2.387 Å with the proton rightly localizing in the middle of the two O atoms. The angle of O–H^+–O (173.84°) shows a deviation from the linear configuration. To show the interactions between the proton and the O atoms, the results of natural population analysis (NPA) and Wiberg bond order analysis are also given in Fig. 2. The NPA charges of the two O atoms and the proton are $-0.91e$ and $0.61e$, respectively. The averaged bond order of (O_1/O_2)–H^+ is 0.32. We note that the charges of the O atom and the H atom in H_2O are $-0.92e$ and $0.46e$, respectively. The comparison of the charge distribution between H_2O and $H_5O_2^+$ suggests that the positive charge of $H_5O_2^+$ delocalizes over the whole cluster which agrees well



				NPA charges	
				O_1/O_2	$-0.91e$
				$H_{11}/H_{12}/H_{21}/H_{22}$	$0.55e$
				proton H^+	$0.61e$
O_1-H^+	1.195 Å	O_1-H_{11}/H_{12}	0.965 Å	Wiberg bond order	
O_2-H^+	1.195 Å	O_2-H_{21}/H_{22}	0.965 Å	$(O_1/O_2)-(H_{11}/H_{12}/H_{21}/H_{22})$	0.70
O_1-O_2	2.387 Å	$O_1-H^+-O_2$	173.84°	$(O_1/O_2)-H^+$	0.32

Fig. 2. Optimized $H_5O_2^+$ with several selected parameters calculated through CCSD(T)-F12/cc-pVTZ.

with previous studies.[29,43] We also note that the bond order of (O_1/O_2)–(H_{11}/H_{12}/H_{21}/H_{22}), i.e., the normal O–H bond of H_2O, is 0.70. These results show that the (O_1/O_2)–H^+ interaction combines the electrostatic interaction as well as the weak covalent interaction, which is also consistent with previous works.[35]

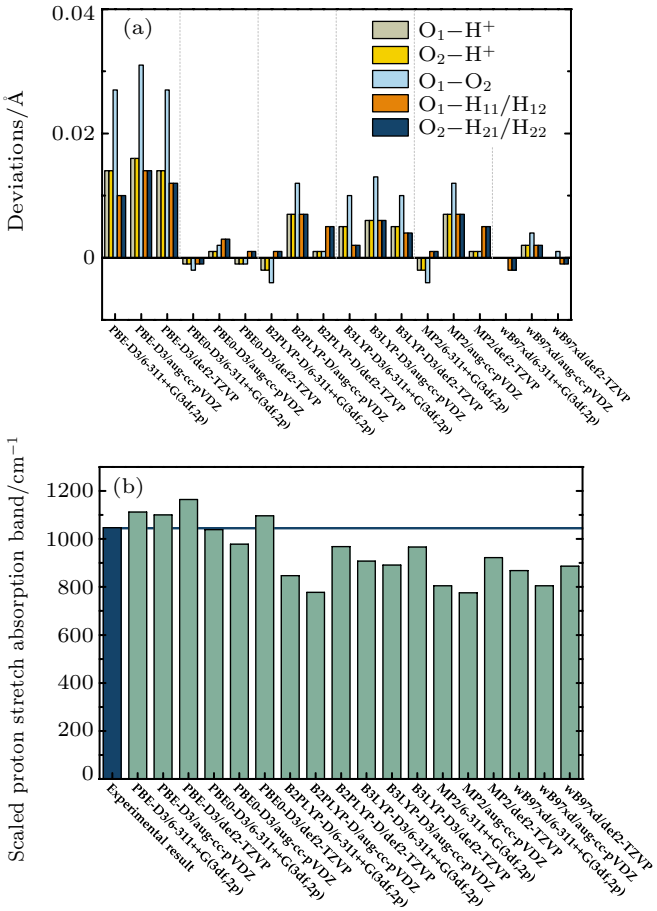


Fig. 3. (a) Deviations of key bond lengths between those of different methods and those of CCSD(T)-F12/cc-pVTZ. (b) Proton stretch absorption band from experimental results and results of different methods.

In comparison, DFT and MP2 with several basis sets including 6–311++G(3df,2p), aug-cc-pVDZ, and def2-TZVP were examined. The structure of $H_5O_2^+$ calculated using CCSD(T)-F12/cc-pVTZ was taken as the reference and the deviations are shown in Fig. 3(a) which shows PBE0-D3/def2-TZVP and wB97xd-D3/def2-TZVP give the closest results to the result of CCSD(T)-F12/cc-pVTZ. Further examination on the absorption band of the proton stretch shows that the result of PBE0-D3/def2-TZVP (1097 cm^{-1}) is closest to the experiment (1047 cm^{-1}), as shown in Fig. 3(b).[44,45] Considering the PBE0-D3/def2-TZVP can give desired geometry and proton absorption band simultaneously, it will be adopted in the following part unless otherwise specified.

3.2. Potential energy surface of various O–O and O–H$^+$ distances

In bulk water or in water cluster, the bond lengths of O–O can be affected by the local chemical environments. For example, the O–O distance of $H_5O_2^+$ is 2.387 Å, the O–O distance in the magic H^+–$(H_2O)_{21}$ ranges from 2.52 Å to 2.88 Å upon optimization at the theory level of PBE0-D3/def2-TZVP. Previous first-principles molecular dynamics simulations also revealed that the O–O distance in the first layer of water can rise up to 3.39 Å or longer for different temperatures.[38,39] Obviously, the wide range of O–O distance could affect the location of the proton significantly. Figure 4 gives the potential energy surface (PES) over O–O distance and the shorter O–H$^+$ distance. This PES was obtained through altering these two variables while freezing the other degrees of freedom of the optimized $H_5O_2^+$. In Fig. 4(a), the PES is not symmetric and the lowest energy can be found with the structure of $H_5O_2^+$. With the increase of the O–O distance from 2.3 Å to 3.6 Å, the potential energy surface gradually exhibits double-well feature. It can also be seen that an energy barrier needs to be overcome for certain O–O distances if the proton transfers from one well to the other for the double-well part. The height of the double-well deepens if the O–O distance continues to be enlarged to 3.6 Å. The different energy scenarios should be responsible for the phenomenon that there exists the alternation of rapid succession period as well as quiescence period during proton transfer.[21] To reflect the possible effects of the surrounding water molecules, PES with polarizable continuum model (PCM) using water as solvent was built as given in Fig. 4(b). The results reflect that the main character is not affected much in calculations with PCM, which indicates that

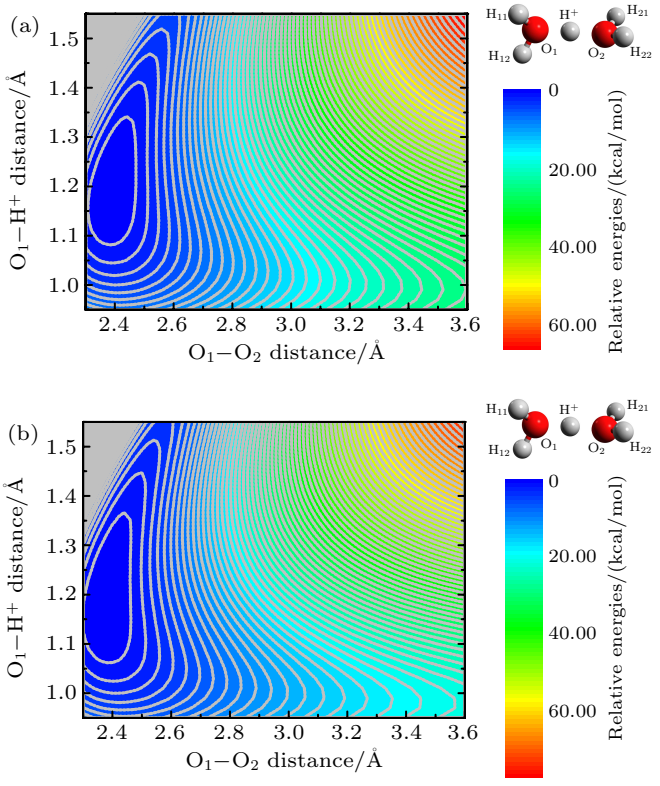


Fig. 4. PES calculated through varying the O_1–O_2 and O_1–H^+ distances of the optimized $H_5O_2^+$ in (a) gas-phase and (b) water. Theory level: PBE0-D3/def2-TZVP.

the conclusion of this work may also stand in bulk water. It has to be stated that this work only represents a prior endeavor that uncovers the possible model of the structure of the hydrated proton. Detailed explorations on various possible structures of hydrated-proton are part of our future work.

3.3. Structural and normal-mode analysis for structures with different O–O distances

To further understand how the O–H^+ distance and the proton stretch absorption band change along with the variations of the O–O bond, the structural and normal-mode analysis was carried out on the re-optimized structures with various fixed O–O distances. The vibrational frequencies of the proton stretch are positive in all the calculations. The results are shown in Fig. 5.

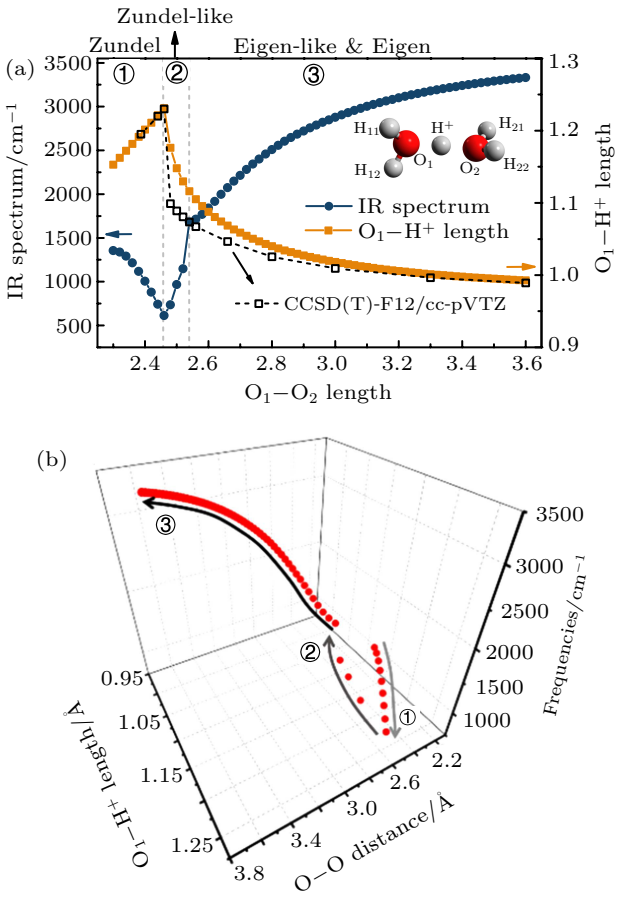


Fig. 5. (a) Absorption band of the proton stretch of optimized $H_5O_2^+$ and the O_1–H^+ distance at various O_1–O_2 distances. (b) A 3D plot of the process of the change of O–O distance, O_1-H^+ distance, as well as the change of the corresponding proton stretch band. Theory level: PBE0-D3/def2-TZVP. Note: 0.96 on the denominator of the equation is the O–H^+ length in H_3O^+ (optimized through CCSD(T)/cc-pVTZ).

Figure 5(a) shows that the variation of the O–H^+ distance is discontinuous when continuously increasing the O_1–O_2 length. As the O_1–O_2 length increases from 2.30 Å to 2.46 Å, the corresponding proton stretch absorption band decreases from 1358 cm^{-1} to 615 cm^{-1}. The turning point of 2.46 Å was further confirmed by CCSD(T)-F12/cc-pVTZ calculations. This part corresponds to the single well part of the PES. As the O–O distance increases from 2.46 Å to 2.54 Å, the O_1–H^+ length drops suddenly (from 1.23 Å to 1.12 Å) to cause fast increase of the proton stretch band (from 615 cm^{-1} to 1684 cm^{-1}). Next, when the O_1–O_2 distance continues to increase, H^+ continues to approach O_1 with a slower rate until $H_5O_2^+$ is split into H_3O^+ and H_2O. In this region, the corresponding absorption band increases slowly from 1684 cm^{-1} to 3331 cm^{-1}. The whole process of Fig. 5(a) can be better presented if using a 3-D like trajectory as depicted in Fig. 5(b). It is clear that the O_1–H^+ distance and the proton stretching absorption band discontinuously evolve as continuously enlarging the O_1–O_2 distance from 2.3 Å to 3.6 Å.

Previous studies have extensively used $d_{O_1-H^+} - d_{O_2-H^+}$ as one of the variables to get the two-dimensional probability distribution during the proton transfer in the multistate empirical valence bond simulation, AIMD, or PIMD.[22,24,27] However, its value can only be used to assign the structure if the structure is an ideal Zundel cation or ideal Eigen cation. Actually, the different proton stretch band and O–H^+ length represent the different properties of Zundel, Zundel-like, Eigen-like, and Eigen structures. For Zundel, the proton always locates in the middle of the two O atoms. When the proton begins to be away from the center of the two O atoms, the structure becomes more Zundel-like. Then the structure turns to Eigen-like if the proton continues to approach one of the O atoms. Finally, Eigen is formed. The structural characteristics of Zundel and Eigen are well recognized, however, it is ambiguity to discern the Zundel-like and Eigen-like structures until now. Here, we propose a simple formula to discriminate Zundel, Zundel-like, and Eigen-like structures as follows:

$$\rho = \frac{d_{O_1-H^+} - 0.96}{0.5 d_{O_1-O_2} - 0.96}.$$

In this formula, 0.96 Å corresponds to the O–H^+ length of the Eigen structure. Calculation shows that $\rho = 0.50$ corresponds to the structure with the O–O distance of 2.54 Å which also signifies an obvious change of the gradient of the proton stretch absorption band over the O–O distance. What is more, the proton precisely locates at the mid-point between the centers of O_1–O_2 (Zundel configuration) and O_1–H of 0.96 Å (Eigen configuration) when ρ equals to 0.50. When this value is smaller than 0.50, the proton is closer to the O atom and the structure can be classified as Eigen-like, and vice versa. If the proton continues to approach one of the O atoms, H_3O^+ (Eigen) can be formed finally.

Previous results have shown that the proton stretching band for Eigen locates between 2000 cm^{-1} and 2800 cm^{-1},[33] which is consistent with our study. Here we show that the structures with the absorption lower than 2000 cm^{-1} or higher than 2800 cm^{-1} are the Eigen-like structures, which correspond to the O–O distance of 2.54–2.66 Å (1684.3–1998 cm^{-1}) or longer than 2.96 Å (2820 cm^{-1}), respectively.

As the O–O distance of bulk water ($\sim$ 2.47–3.39 Å) covers the discontinuous region, which may indicate the coexistence of the Zundel-like and Eigen-like structures.

4. Conclusion and perspectives

To summarize, we performed the first-principles study to show that the O–H^+ distance and the proton stretching absorption band are discontinuous with continuously altering the O–O distance of $H_5O_2^+$. When the O–O distance is smaller than 2.46 Å, the Zundel configuration is preferred with the proton locating in the middle of the two O atoms. The adsorption band ranges from 1358 cm^{-1} to 615 cm^{-1}. The structure switches to the Zundel-like structures as the O–O distance increases from 2.46 Å to 2.54 Å. The O–H^+ distance decreases from 1.23 Å to 1.12 Å and the vibrational frequency increases to 1684 cm^{-1}. With the further increasing of the O–O distance (larger than 2.54 Å), the cluster structure turns to Eigen-like structure. The proton stretch absorption band increases from 1684 cm^{-1} to 3331 cm^{-1}, and H_3O^+ and H_2O are formed finally. The discontinuous evolution of the proton stretching absorption band indicates the inherent differences among the Zundel, Zundel-like, and Eigen-like structures. To discriminate Zundel-like and Eigen-like structures, a simple formula is introduced to evaluate the relative position of the O–H^+ length. Considering the Eigen structure can give absorption out of 2000–2800 cm^{-1}, the previous categorization of the Zundel or Eigen structures through the identification of the proton stretch band may be biased. This work calls upon the revisit on this issue through focusing on both the IR spectra and the hydrated proton configuration in aqueous solution.

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