Behavior of water dimer under the influence of external electric fields

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A detailed quantum chemical study has been carried out at the CCSD(T) level of theory to understand the behavior of water dimer under the influence of external electric fields. The energy values obtained at this level of theory follow the same trend as observed with the DFT and MP2 levels of theory. Our calculations show that water dimer gets stabilized with increase in the strength of electric field. A slight increase in the hydrogen bond distance and relatively larger decrease in the hydrogen bond angle is found with the increase in the strength of electric field. The dipole moment and HOMO-LUMO energy gap increase with the increase in the strength of electric field.

Keywords: Water dimer, Electric field, Coupled cluster methods, Dipole moments, HOMO-LUMO energy gap

Water clusters are group of water molecules (ranging from two to a few) that are held together by hydrogen bonds. Unlike atoms and molecules and solids, the properties exhibited by the clusters under the influence of external field are unique in many ways. It is important to study water clusters in order to understand properties of the bulk water, cloud and ice formation, solution chemistry, electrochemical and biochemical processes. To get an insight into water clusters, it is necessary to know its behavior under external influences, in particular, in the presence of electric field. Various methods used for understanding the interaction of water molecules like new laser spectroscopy experiments, combined with the global analysis of potential surfaces and diffusion Monte-Carlo methods are explained in the previous reports.1,2

Several attempts have been made by researchers to understand the effect of external electric field on water, both experimentally3-4 and theoretically.5-23 For ease of understanding, the studies have been segregated into two groups on the basis of the number of water molecules involved. Water clusters (H₂O)ₙ in which n ≤ 20 comprise one group and the ones containing more than 20 water molecules fall in the other. In the literature, we find that molecular dynamics simulations have been carried out in order to explain the bulk water and liquid water which involve more than 20 molecules of water.10-15 On the other hand, quantum chemical calculations16-19 employing very high level of theory have been used to describe the interactions of small size clusters (n < 20) to get accurate numbers for the observables like stabilization energy, dipole moment, etc., which further help in better understanding of the physics involved.

Girardi and Figueiredo5 in their square model water showed that the number of hydrogen bonds per molecule is a monotonic decreasing function of the field magnitude. In 1991, Zhu et al.6 studied the effect of an intense laser field on liquid water using classical molecular dynamics simulations using a water model SPC-FP. They showed that both the liquid structure and intramolecular geometry get distorted by forming a large number of bifurcated hydrogen-bonds. Suresh et al.7 developed a theory based on reaction equilibria and Boltzman distribution for studying hydrogen-bond network of water in external electric field and predicted that at practically attainable field strengths, the electric field cannot disrupt the hydrogen-bond network. However, weakening of the bonds is observed at higher field strengths which cannot be attributed to the effect of electric field alone. Very recently Saitta et al.8 studied liquid water using ab initio molecular dynamics and observed (i) significant modification in the hydrogen-bond length and molecular orientation at low-to-moderate fields, and, (ii) dissociation and ionic current at high fields (above 0.35 V/Å). A number of studies on
bulk water using molecular dynamics is available which focus on structural modification by external electric field.\textsuperscript{9,15} The molecular dynamics simulations, in general, suggest that the structure of water (bulk, liquid and clusters) changes after a particular threshold electric field, which is higher for clusters when compared to that for the bulk or liquid water.

At this juncture, we would emphasize on the literature pertaining only to the clusters containing less than 20 water molecules. Dykstra\textsuperscript{16} using a model potential found that in a weak field, minor distortions in trimer cyclic structure occurs, whereas at very high field (~0.08 a. u.) the trimer ring opens since the field overcomes the intermolecular interaction. A DFT based study by Karahka and Kreuzer\textsuperscript{17} showed that for small external electric fields the water whiskers polarize and align along the field. The alignment of dipole moment with the field is favoured because of the formation of staggered conformation (in this case, helical) which is usually lower in energy. At high fields, charge-transfer and re-hybridization leading to closing of the HOMO-LUMO gap is observed which finally results in fragmentation. Acosta-Gutiérrez \textit{et al.}\textsuperscript{18} carried out molecular dynamics simulation with TIP4P and polarizable Dang-Chang potential to study the global minimum structure, energy, dipole moment of water cluster ($n \leq 20$) in low and moderate electric fields ($E \leq 0.6$ V/Å). They observed two distinct transitions in the electric field: (i) field range of 0.1–0.3 V/Å, in which the hydrogen bond reorganizes, and, (ii) field range of 0.3–0.5 V/Å in which elongation of cluster in direction of electric field occurs with enhanced dipole moments. For large enough fields (0.6–1 V/Å), the larger structures ($n > 10$) converges to helical structures. Choi \textit{et al.}\textsuperscript{19} have investigated small water clusters ($n = 3–5$) in external electric field employing DFT and concluded that with increasing electric field, the clusters open up to form a linear chain along the direction of the field. Their results compare well with those of James \textit{et al.}\textsuperscript{20}, who showed the change of structure of water clusters from compact to more extended structures at higher fields, employing classical rigid-body models of the TIP$n$P ($n = 3–5$) family of effective pair potentials. Similar results are reported for small methanol clusters, in terms of effect of enhanced electric field on structure, although threshold field is slightly higher for cyclic clusters of methanol.\textsuperscript{21} Rai \textit{et al.}\textsuperscript{22,23} have studied water clusters for $n = 6–8$ and $n = 9–20$ using DFT and found that due to applied electric field above a certain threshold value, the three-dimensional structure of clusters opens up and forms linear, branched or net-like structures such that dipolar water monomer align in direction of electric field. Results for octamer are also found to be consistent with those of James \textit{et al.}\textsuperscript{20} In each case, the threshold values depend on size of the cluster. Toledo \textit{et al.}\textsuperscript{24} have investigated the effect of external electric field on water clusters $n = 2–16$ using DFT and noticed a change in the number of hydrogen-bonds, thereby leading to reduction in cluster sizes having stronger inter-cluster hydrogen bonds.

From the available literature, Karahka and Kaeuzer\textsuperscript{17} made some generalizations regarding the field effects on water clusters, as follows: (a) at low fields, only “physical effects” such as polarization of the atoms and molecules occur, and, (b) the high fields are responsible for the alterations in the chemical characteristics of atoms and molecules. In the present work, we explore and analyze systematically the effect of external static electric field on the electronic properties of water dimer in the ground state using CCSD(T) level of theory\textsuperscript{25} which is the “gold standard in quantum chemistry”.

\section*{Methodology}

All calculations were performed using the GAUSSIAN’03 package.\textsuperscript{26} The structure optimization, with and without electric field, for water dimer were carried out under the second order Moller-Plesset perturbation (MP2)\textsuperscript{27} level of theory employing the 6-311+G** basis set. Then the single point calculations for the MP2 theory optimized geometries (with and without electric field) were performed at the CCSD(T) level of theory.

\section*{Results and Discussion}

The optimized geometries and the energy values for the corresponding equilibrium geometries without any external perturbation for the monomer, dimer, trimer and its higher oligomers ($4 \leq n \leq 20$) calculated at a higher levels of theory (MP2 and DFT) can be found elsewhere.\textsuperscript{28–31} Herein we have calculated the energies corresponding to the equilibrium geometries of water dimer. The initial geometry is optimized in the absence of field and this value is reported as the energy at zero field or field-free energy. To study the effect of electric field, the field is applied in the OH–O hydrogen bond direction as shown in Fig. 1 and the structure of the dimer is optimized in the
increasing electric fields up to $100 \times 10^{-4}$ a. u. The maximum field strength considered in this study is approximately equal to 0.5142 V/Å (1 a.u. = 51.4220652 V/Å). MP2 was used to optimize the structures and CCSD(T) was used to obtain the single point energy of the optimized structures. As can be seen in Fig. 2, the energy values calculated at MP2 and the CCSD(T) levels of theory follow the same (decreasing) trend for the different electric fields considered. We observed a small decrease in energy at the CCSD(T) level which shows that the obtained energy is close to the true ground state energy which is expected when a more accurate level of theory is used. It was also observed that the energy of the dimer decreases with increasing electric field (Fig. 3a). This shows that the water dimer attains a more stable structure with the increasing electric field. Earlier researchers also observed similar phenomena in their studies.\textsuperscript{18-20} Acosta-Gutiéuez \textit{et al.}\textsuperscript{18} suggested that this decrease in energy is not a particularly effective diagnostic for structural changes as the electric field intensity changes. Toledo \textit{et al.}\textsuperscript{24} in their study argued that the small cluster becomes stronger with the increase in electric field which confirms the findings of this study. Change in dissociation energy of the dimer with the increasing electric field is plotted in Fig. 3b. We find a steady increase in the dissociation energy up to 0.008 a.u. (0.4114 V/Å) followed by a decrease at higher fields.

The hydrogen bond distance plotted against the electric field shows an overall increase in the hydrogen bond length up to 0.008 a.u. and an appreciable decrease thereafter (Fig. 4). On close scrutiny, we find that there are oscillations in the value of the H-bond distances and the observed increase is not perfectly linear. It is worth mentioning...
here that H–bond length increases over a very small range (1.951–1.963 Å) and at this range such oscillations are expected. Acosta-Gutiéuez et al. 18 attributed this increase to reorganization of hydrogen bonds whereas James et al. 20 concluded that the higher fields favor a more extended structure which can align with the field in a more effective way. Profound decrease in the O–H–O bond angle was observed with increasing electric field. Change in the O–H–O bond angle and the O–H bond distances with the electric field are illustrated with a series of dimer geometries (Fig. 5). It is apparent from Fig. 5 that the second H₂O molecule tries to align itself in order to minimize the energy and maximize the interaction of the dipole with the field. It has been proposed that there exists a second energy channel to minimize the interaction energy. 9 The synergistic action of increase in dipole moment along with the increase in hydrogen bond length and the decrease in the O–H–O hydrogen bond angle leads to decrease in the energy of the system.

Fig. 4 – Variation of OH—O angle and OH bond distance of dimer with increasing electric field. [1, O–H bond distance; 2, OH—O bond angle].

Fig. 5 – Change in the orientation of the water molecule with the electric field showing the increase in the O—H bond distance and the change in orientation angle.

Fig. 6 – Change in the values of dipole moment and the HOMO-LUMO energy gap for the water dimer with the increasing electric field. [1, HOMO-LUMO gap; 2, dipole moment].

The plot of dipole moment and HOMO-LUMO energy gap versus electric field is shown in Fig. 6. We see that the dipole moment of the water dimer increases with the increasing electric field. There is a steep increase in the very low field strength region (up to 0.0045 a.u.) after which the increase appears to be slower. This increase in dipole moment is due to the contributions from the individual polarizability of the water dimers. As the electric field increases, the dimers are more polarized and they try to align in the direction of the field. Similar results related to the orientation of dipole moments of water along the field taking place in such low electric field (0.1 – 0.2 V/Å) has been reported. 17,18 The increase in the HOMO-LUMO energy gap with the increase in the field is evident from Fig. 6. This increase attains a threshold value at 0.008 a. u. after which it starts decreasing. Similar behavior was exhibited by a trimer in a previous study wherein it was found additionally that the energy gap closes at the point of dissociation. We may also expect such behavior for the dimers in very high field strengths.

The above discussion shows that the field strength of 0.008 a.u. corresponds to some physical phenomena which are yet unclear. With the help of available literature we may assume it might that the rearrangement of hydrogen bond takes place prior to the threshold field strength. Increase in the field strength beyond this point may lead to dissociation of the dimer, which requires further detailed investigations.
Conclusions
A detailed quantum mechanical study at the CCSD(T) level of theory has been carried out to understand the influence of electric field on water dimer. Our calculations show that electric field has negligible effect on hydrogen bond distance but has a large effect of hydrogen bond angle. It has also been found that dipole moment and HOMO-LUMO energy gap increase with increase in the strength of electric field. It is also important to note that the results obtained in our study agree qualitatively with previous DFT and MP2 studies, while however, the energy computed by CCSD(T) method are quite different from the above mentioned methods.

References