



Research paper

Vibrational, energetic-dynamical and dissociation properties of water clusters in static electric fields: Non-equilibrium molecular-dynamics insights

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HIGHLIGHTS

- Water clusters (2, 6, 12 and 20) are simulated under additional forces of varying magnitude of 0.1–25 % of the total force.
- The original cluster breaks immediately within 1 ns and alternate arrangements are taken up even at low fields.
- The librational peaks are most effected with 20 water clusters being most effected, they are suppressed with time.

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ABSTRACT

Water clusters are hydrogen bonded molecular assembly of water molecules. They have been extensively studied using experiments, ab initio calculations and molecular simulations. The molecular arrangement of water in water cluster provide significant insights into behavior of water in bulk, confinement and close to surfaces. Here molecular dynamics simulations of TIP4P/2005 water clusters are performed in weak electric fields. These fields introduce additional forces of varying magnitude 0.1–25% of forces existing in without-field water clusters. Autocorrelation functions of distance, energy and velocities are analysed. Molecular arrangements in water clusters does not disintegrate under additional forces.

1. Introduction

Hydrogen bonding is generally relatively weak, essentially Coulombic interaction between a hydrogen atom bonded covalently to an electronegative atom (such as oxygen) and another electronegative atom. Hydrogen bonds are directional, their strength typically ≈ 1 –10 kcal/mol range. In the condensed phase, hydrogen-bond vibrations, dynamics and stability govern the properties of liquid water, ice and clathrate hydrates [1–4], whilst this holds also for gas-phase clusters of water molecules [5–8]; indeed, these properties have been investigated extensively using both theoretical and experimental techniques [9,10]. For instance, using ab initio molecular dynamics (MD), Kühne and Khallilulin have studied the asymmetry of co-existing weaker and stronger hydrogen bonds in liquid water [11], serving to rationalise SAXS measurements and the controversial two-liquid model of water as an explanation of thermodynamic anomalies [12]. Hydrogen-bond orientational mechanisms have been studied explicitly by MD in terms of a jump mechanism explaining water reorientation via

hydrogen-bond cleavage and molecular reorientation occurring concertedly [13]. A wide range of hydrogen-bonding energetic and vibrational properties has been studied using quantum-chemistry methods, density functional theory (DFT) and empirical-potential methods for a whole suite of water clusters, ranging from dimers to $(\text{H}_2\text{O})_{20}$ [5–8], with the latter $(\text{H}_2\text{O})_{20}$ case not dissimilar to pentagonal dodecahedral 5^{12} cages in clathrate hydrates [4]; indeed, Yoo et al. have studied further $(\text{H}_2\text{O})_{24}$ clusters, and their incorporation into clathrate-hydrate lattices via proton-network optimisation, in view of their similarity to tetrakaidecharal cages [14]. In particular, Ref. [6] discusses with acuity and insight the importance and subtleties of anharmonicity in vibrational properties in determining the relative energies of water clusters.

The influence of electric fields on water and aqueous systems is crucial in underpinning our knowledge of electric-field effects on wider systems, e.g., in biology, and molecular simulation has much to offer in terms of mechanistic understanding [15]. Electric fields have been applied to water cluster, and many of the fascinating physico-chemical

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properties been dissected by molecular simulation. Indeed, due to the inherent difficulty in defining time in optimising structures between states to locate putative transition paths, static fields have been applied to eigenvector-following/basin-hopping optimisation methods by James et al., and applied to the study of change in structure of water clusters (without PBC) based on both increasing field strength and the number of water molecules in each type of cluster, using model potentials [16]. It was found that structures became extended in more intense fields, echoing the findings of dipole stretching in MC of flexible structures [20–23]. Choi et al. carried out aperiodic DFT-based geometry optimisation of a series of water clusters increasing in size in a static electric field, and concluded that clusters open to form a linear chain in the direction of the field, due to dipole alignment [24]; this is broadly in line with the findings of James et al. [16] from transition-path sampling using model potentials. There has been much interest in static-field effects on water clusters, chiefly from a structure-perturbation perspective [20,24–33] using either geometry-optimisation, Monte Carlo, transition-path sampling or MD with force fields [20,25,26,31], DFT [24,27–30,32] and CCSD(T) [33]. The threshold for altering the structure of water clusters is generally higher in static fields than for the bulk liquid, although this depends on the size of the cluster. At lower-intensity fields, less than around 0.3–0.5 V/Å, hydrogen-bond structural reorganisation takes place with physical effects of (partial) dipolar alignment with stretching along the field direction in some cases, whilst above this intensity, chemical characteristics of the atoms and molecules can be altered. Similarly, the physical response of water clusters to static fields has been studied in terms of dipolar alignment, and this polarisation response quantified at various field intensities [20,25–33].

In any event, despite this encouraging progress in the past decade or so of water-cluster research in external electric fields, an open question in the water-cluster literature relates as to the dynamical effect of static electric fields on vibrational properties as well as those of stabilising hydrogen bonds across a wide range of intact clusters, as probed by finite-temperature MD. In addition to a more rigorous establishment of approximate field intensities required to rupture, and rearrange permanently, the underlying stabilising hydrogen-bonding arrangements of a broad gamut of clusters over sub-microsecond timescales is needed. In the latter case, assessing applied-field strengths of those present intrinsically is important, so as to study these trends in field-intensity thresholds and survival times as function of external-to-intrinsic field-intensity ratios. Here we perform molecular dynamics simulations of 2, 6, 12 and 20 water clusters under the influence of low (0.01, 0.1 and 0.25 V/nm) and strong (0.5, 1.0, 1.5 and 2.0 V/nm) electric field. The relaxation behaviour of hydrogen bond distances, energies and velocities are understood and the survival times of hydrogen bonds as a function of electric field strength are obtained and analysed. Improving the overall understanding hydrogen-bonding arrangements in bulk water is of great interest to scientists. Hydrogen bonds, and their abilities to form various structures, result in different anomalous properties of water [34]. The hydrogen-bonding arrangement in the local neighbourhood of a water molecule holds the key towards understanding the behaviour of water. Water clusters are an important set of systems where local hydrogen-bonding arrangements can be investigated easily and understood. Water clusters under the influence of electric fields give us additional insights into understanding hydrogen-bond patterns, and their snapping tendencies. In previous simulations, asymmetry in hydrogen bonding [11], phase change [26] and electro-freezing of bulk water under the influence of electric fields, has been investigated [35]. The application of electric fields to water clusters has resulted in different hydrogen-bonding arrangements, and, as such, serves as a potent reminder of the importance of the entropic agent of field-induced dipole alignment. Indeed, this has been highlighted in the case of subtle differences in phase changes in nanoscale water clusters very recently [36]. In the present study, motivated by this background, we assess the structural changes of hydrogen bonding in water clusters under the influence of electric fields.

Table 1
Potential parameters used in the simulations.

Model	q	σ (nm)	ϵ/k_B (K)
TIP4P/2005	-1.1128	0.3159	93.20

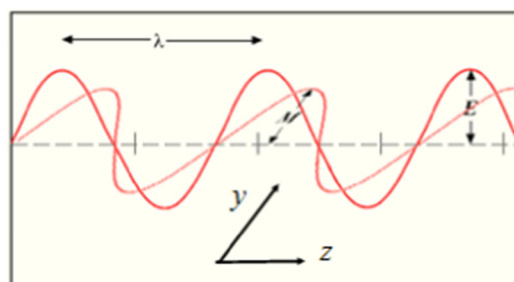


Fig. 1. Schematic model of plane-polarised e/m wave.

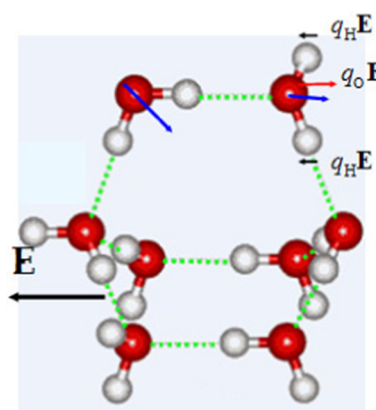


Fig. 2. Electric field/force vectors on a sample water-cluster system. The external electric force vector \mathbf{E} is shown by the heavy black arrow, whilst the electric force vectors exerted on the oxygen and hydrogen atoms are shown by lighter red and black arrows, respectively, with blue dipole vectors shown for comparison. Hydrogen bonds are depicted by dotted green lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Average forces on water Oxygen under zero field.

Cluster size	Force (pN)
2	1005
6	2279
12	2551
20	2449

Table 3
External-field forces on water Oxygen under varying fields.

Electric field intensities (V/nm)	Forces (pN)
0.01	2.01
0.10	18.3
0.25	44.3
0.50	88.4
1.00	177
1.50	266
2.00	354

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