

Dynamism of structure and properties of water molecule

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ABSTRACT

The water molecule with diverse properties is the most studied molecule of natural system. Various models have been designed to describe the molecular dynamics of water molecule and its chemistry. The observational outcomes that helps in understanding molecular structure and thermodynamics of water molecules is reviewed. Further, the differences in H-O-H length and angle for all the three phases of water viz., ice, liquid and vapor and role of vibrational state of the water molecule are also discussed. The study concludes that the use of computer simulations which is an integration of equations or algorithms and system model, have emerged technically more viable and proves best in understanding the molecular mystery and dynamic characteristics of water molecule.

Keywords: - water molecule structure, water properties, computer simulations

1. INTRODUCTION

Water the most abundant and studied compound on the earth [1] and an important molecule of biological and engineered systems [2] existing in three phases-solid, liquid and vapor, has always being a central theme of research for understanding its microscopic structure and properties. Water has unique physical and chemical properties and high solvent capacity due to intra-molecular transitions and presence of free hydroxyl group [3]. It is an electrically polar molecule with a bent structure having asymmetric distribution of the charge, highly cohesive showing interaction with one another, and have high surface tension due to hydrogen bond. The liquid water contains three types of clusters viz, trimmers, tetramers, hexamers under standard temperature and atmosphere pressure ranging 0°C–100°C. Only one hydroxyl group take part in hydrogen bonding. The second hydroxyl group when proton get linked causes electron density redistribution and disturbance in first hydroxyl group of hydrogen bond [3]. The hydrogen bonds number per molecule is temperature dependence and this along with tetrahedrality describes structural functions mainly the anomalous nature of dielectric permittivity and density of the water molecule [4].

2. MOLECULAR CHARACTERISTICS

Water molecules consists of two light atoms (H) and a relatively heavy atom of oxygen and approximately 16-fold difference in mass allows its ease of rotation and constant relative movements of the hydrogen nuclei even at absolute zero temperature. It has molecular diameter of about 2.75 Å. The water molecule vibrates in a number of ways [5]. For gaseous phase the O-H length is 0.95718 Å and H-O-H angle 104.474° [6]. However, the actual values depends on vibrational state of the water molecule with even values of 180° that are exhibited during high order bend vibrations when bending is more than or equal to 7 and length less than 900 nm for H-O-H angle [5]. In the gas state, the vibration [7] depends on symmetric stretch (ν_1), bending (ν_2) and asymmetric stretch (ν_3) of the covalent bonds with absorption intensity [8]. The diffraction studies shows variation in the O-H length in liquid water, however ab initio study suggests the O-H length 0.991 Å and H-O-H angle 105.5° [9], or even 106.3°±4.9° [10]. The changes in length and angle are attributed to polarization shifts, in different H-bonded environments and local solutes and ions. In general for a perfect tetrahedral arrangement the mean O-H length is 0.097 nm and bond-lone pair, lone pair-lone pair and bond-bond angles is 109.47° [5]. In solid phase (Ice) the H-O-H angle is 108.4°±0.2° [10] and some studies reported H-O-H angle 106.6°±1.5° and O-H length to be 0.985 Å [11].

3. STRUCTURE AND THERMODYNAMICS

The thermodynamic properties of water molecules can be better understood by inhomogeneous fluid solvation theory by analyzing statistical mechanics which revealed that the total free energy of bulk water is mainly due to hydration sites. A biomolecule with a negative and positive charge disquiet the free energy to a distance nearly 6.0 Å [12]. The structure of water molecule is inhomogeneous with three-dimensional network containing hydrogen-bonded molecules whose average lifetime is nearly a few picoseconds and it changes neighbors continuously [13]. The inhomogeneity structure of water molecules using molecular dynamic method reveals that an independent unit cell contains 3456 molecules and they should be categorized into two classes the one showing higher and the other smaller critical value of the volume of the Voronoi polyhedron formed around oxygen atom, potential energy of the molecule (E_{pot}) and tetrahedrality index (T). The structure inhomogeneity also shows that it is surrounded by dissimilar molecules half of all molecules are donors and other half acceptors for two H bonds and the molecule with a_2d_2 type of coordination, are assigned to one class and all other molecules belongs to another class [14].

The molecular dynamics and replica exchange molecular dynamics simulation used to study the structure and thermodynamics of the water molecules in a hydrophobic solutes order–disorder transition of a nanometer length-scale as the tetrahedral order of water molecules in hydration shell is independent of the polymer size in extended state of the polymer due to a sub-nanometer cross-sectional length-scale, allowing water molecules to form hydrogen bonds with the polymer chain. The collapsed states of polymer chains is responsible for disorder in the surface water molecules. Thus the topology of the polymer decides tetrahedral order and local number density of the hydration layer. The local density fluctuations and hydrophobic collapse of the polymer shows direct coupling while the local density fluctuation of the solvent is independent of solute length-scale [15].

4. WATER MODELS

The success of water models truly depends on the prediction of physical properties of liquid water no matter whether it is hypothetical (computer water model). The models have orienting electrostatic effects and Lennard-Jones sites that either or either not coincide with charged sites. The Lennard-Jones interaction depends on the size of the molecules and it repulses at short distances making sure that structure do not collapse due to the impact of electrostatic interactions. Starting from simple rigid followed by 2-site, then 3-site rigid and flexible SPC model shows superiority over each other for some specific characteristics. In this series Bernal and Fowler's 4-site water model developed in 1933 with negatively charged dummy atom clarifies electrostatic distribution of water molecule. In sixties the advent of molecular simulations brought acceleration in the theoretical studies of water and its force field. The Ben-Naim and Stillinger (BNS) followed by ST2 are 5-site model proposed in 1971 and 1974, respectively, whereas Nada and van der Eerden's a 6-site model are some other common models. The last three decades witnessed a cohort of model potentials through computer simulations [16]. In order to understand water molecule's behavior in pure liquid and in solution there is a need of quantitative understanding of the water molecule like functioning in a range of environments and experimental conditions [17]. The approaches to experimental information for making predictions are more preferable as it helps to understand a deeper physical insight of the properties of water. The model is generally based on a particular physical parameter like radial distribution function, the density anomaly, or the critical parameters to give perfection with these parameters [5]. Zalizniak [18] proposed one site model which includes the angular averaged dipole-dipole interaction and Lennard-Jones interaction that reproduces important characteristics of water and is computationally more efficient than multi-site atomistic water models.

TIP4P a four site condensed phase water model, introduced in 1983 consisting of one Lennard-Jones center and three fixed point charges including melting and vaporization, condensed phases, pair distribution function, dielectric constant and self-diffusion coefficient proved to be effective in the terms of properties and thermodynamic conditions [19]. At different temperatures an intermolecular potential is produced which contains two-body additive interactions and non-additive contributions obtained from both three-body interactions and polarization. Thus, Polarization is an important nonadditive influence, resulting improved agreement with experiment for dipole moment, dielectric constant and radial distribution function of liquid water [20]. TIP4P/2005 followed by TIP5P, TIP4P model generally describes all properties of the water except the dielectric constant [21]. Coarse-grained model (CGM) referred as "CAVS" (charge is attached to a virtual site) designed by integrating MARTINI and BMW models adapting topology of TIP4P water model, explains certain bulk properties like dielectric constant, density, etc. [22]. The polarizable model, short-range directional hydrogen-bonding interactions model involving a single Drude oscillator site with hydrogen-bond interactions, clarifies vapor–liquid equilibrium properties [23]. The short simulations provide better predictions of analyzing free energy of water molecule thus reducing the computational cost of fluid solvation theory analysis. The thermodynamic properties predicted for hydration sites of hydrogen bonding functioning shows contradiction for different water models [12].

5. COMPUTER SIMULATION AND WATER MODELLING

Computational chemistry using computer simulation, an integration of equations and/or algorithms and running of the system model, has emerged as an efficient tool in studying structure and properties of various molecules of natural system. Computer simulations are significant in understanding the dynamic characteristics of water at a molecular level as it reproduces anomalous properties under various conditions. The degree of tetrahedrality is an important factor in reproducing the pure liquid which has been well studied by TIP5P, TIP4P-Ew, and TIP4P/2005 models however they have different quadrupole moments. Thus the soft-sticky dipole-quadrupole-octupole (SSDQO) potential energy function, which includes a Lennard-Jones interaction easily describe a soft repulsion and “sticky” attractive dispersion, with multipole expansion and also clarifies the electrostatics and hydrogen bonding [24].

The water models TIP3P, TIP4P, and TIP5P shows variations of planar walls that appears as a honeycomb-structure of graphene under ambient conditions, as they interact with water molecules in different ways. In hydrophobic regime the smooth wall shows good abstraction of atomically rough walls, whereas in hydrophilic regime there are contrasting differences in structure and dynamics of all stages of wall roughness. Among these models the TIP5P is least perturbed by the presence of the wall and shows highest degree of tetrahedral ordering [25]. The models TIP3P-Ewald, TIP4P-2005, TIP5P-Ewald, and SWM4-NDP can also be used to calculate the relative angular distributions, the radial distribution functions (RDFs), and the excess entropies, enthalpies, and free energies. TIP5P-Ewald model proves best in calculation of radial distribution functions, TIP4P-2005 and SWM4-NDP models were accurate in calculating entropies, enthalpies, and free energies. Further, the TIP5P-Ewald model suits best for the relative angular distributions calculation and act both as donors and acceptors of tetrahedral hydrogen bond, whereas the SWM4-NDP model act only as acceptors [2].

Through computer simulations it was observed that water molecules in the liquid and gas phase have larger quadrupole moments mainly due to the p -orbital nature which is perpendicular to the molecular plane of the highest molecular orbit and also due to a slight shift of negative charge for hydrogen. The multipole models use correct multipoles and electrostatic potential from the quantum mechanical/molecular mechanical multipoles than that from TIP4P- or TIP5P-type site models. The Monte Carlo simulations suggest that increasing the quadrupole in the point multipole model like soft-sticky dipole-quadrupole-octupole multipole (SSDQO) model shows better radial distribution functions. This model allows large quadrupole by enhancing the value of the existing quadrupole thus computationally faster than 3-site models because of multipole expansion and this also help in better modelling of electrostatic potential arising due to the electron density from the quadrupole moments calculations [26].

6. APPRAISAL OF COMPUTER SIMULATION MODELS

A single-site multipole model of water accounting for the average polarization explains in-plane and out-of-plane electrostatic abilities of a water molecule in the liquid phase are important for computer simulations for resolving problems in sciences [27]. Chemical structure of ionic liquids can be better understood by atomistic simulations that depend on accurate simulation methods, standard techniques used for determining heat and densities and quality of the force field used for computation of transport properties [28]. The simulations like molecular dynamics can be employed in studying the characteristics of soft sticky dipole-quadrupole-octupole water model and explains water-water relation using Lennard-Jones term and sticky potential, which disclose radial distribution functions of pure water [29] and disclosing the role of nonadditive interactions on structure and dielectric properties of water [20]. The SSDQO model is also used to study the impact of multipole moments of water on the aqueous solvation of ions by determining orientation around Na^+ and formation of linear hydrogen bonds to Cl^- [30].

Russo and Tanaka [31] used computer simulations to study microscopic structure of water molecule and identified a locally favor structures of water molecule showing mixed character with extreme degree of translational order in second shell which helps in crystallization and a five-membered rings of H-bonded molecules that is responsible for frustration against crystallization. The charge distribution features make ease to generate liquid state of water molecule for computer simulations but understanding multipole models algorithm for obtaining truncation schemes the use of Lennard-Jones along with this model, discloses durability of non-hydrogen-bond conformation of the simulated liquid [32]. The “optimal” 3-charge, 4-point rigid water model (OPC) is another designed alternative of point charge models in describing the electrostatics of the water molecule as it includes a bulk properties that are significantly more accurate than rigid models at different temperatures along with hydration free energies of small molecules are also very much accurate [33].

In conclusion, a water molecule with a vent structure and tetrahedral arrangement along with self-organized inter-molecular network and its physical, chemical and molecular dynamism are always epicenter of research for all discipline of sciences. In

recent year the application of computer simulations to crack the molecular structure of various natural substances has made possible to resolve the mystery and thus requires more detailed study of this universal solvent.

7. REFERENCES

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