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Dielectric properties of SPC/E and TIP4P under the static electric field and microwave field

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HIGHLIGHTS

- The static electric field has effect on the tetrahedral structure of water.
- The interaction between microwave and water is dependent on the hydrogen bonding.
- The 3×10^7 V/m is a threshold intensity for the dielectric constant and polarizability.

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ABSTRACT

Nonequilibrium molecular dynamics simulations of the SPC/E and TIP4P models have been performed both in the absence and presence of the static electric field ($0–3\times10^9$ V/m) and the microwave field (2.45 G, $0–3\times10^9$ V/m). The radial distribution function, dielectric constant, polarizability, dielectric relaxation time, hydrogen bonding and diffusion coefficient were investigated. Significant alteration in the static electric field has effect on the tetrahedral structure of water; the interaction between microwave and water depends on the hydrogen bonding. The 3×10^7 V/m is threshold intensity, as the intensity of the static electric field increases the decline of the dielectric constant becomes more pronounced, and the polarizability obviously increased with the increase of microwave field. And the life of hydrogen bonding is oscillatory under the high static electric field strength.

1. Introduction

Water exists as a kind of widely used solvents in the earth, the properties of water play an irreplaceable role in biology, chemistry, physics and other fields [1–3]. There have been many experimental methods and theoretical studies on the water, including the far-infrared [4], X-ray absorption spectroscopy [5], the NMR Spectroscopy [1], the dielectric relaxation spectroscopy (DRS) [6], IR spectroscopy [7] and molecular dynamics (MD) simulations [8–10]. Comparing to these methods, the MD simulations could better trace the details of motion path, show relatively accurate estimation of water properties [11], it also exposes the structure and some changes at the microscopic level [12] and shows molecular motions on the picoseconds time scale [13]. What calls for special attention is correctly selecting the water models, because they are not only meaningful for the MD simulations but also important for the accurate calculation of the potential parameters [14]. Besides, the dielectric constant represents a very good test for the accuracy of an inter-molecular potential [6], there are many researches which are about the dielectric constant of water models, including SPC [12], TIP5P [15], TIP4P/2005 [14], SPC/E [16], SPC/E and SWM4-DP [9], TIP4P/2005, TIP4P/2005f and TTM3F [17], TIP4P$_{FQ}$ [3,18,19] and SPC$_{FW}$ etc. [3].

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In recent years, microwave has been widely applied on the organic chemistry [20,21], biology [22], physio-chemical researches [23–28], industrial and agricultural production [29]. So, studying the dielectric properties of water models with the microwave field becomes more meaningful work for microwave energy application. Although Niall J. English [27] has carried out an investigation about the influence that the microwave field caused on a rigid/polarizable and a flexible/nonpolarizable potential model, at present, less survey has involved the comparison between the water models with the high strength field yet. Therefore, in this paper, the intention was extended to track the influence on the dielectric properties of SPC/E and TIP4P, including the radial distribution function, dielectric constant, polarizability, dielectric relaxation time, hydrogen bonding and diffusion coefficient, which were caused by the different intensities of the static electric field and the microwave field.

2. Computational method

2.1. Interaction potentials and simulation details

The simulations were performed using a modified version of the GROMACS 4.5.5 [30] simulation package and GROMOS [31] force fields. The simulations involved 512 SPC/E and TIP4P were respectively placed in a cubic simulation periodic box and two concentrations, static electric field and microwave field. Water molecules were added to the system from a relaxed liquid configuration at 298 K and 1 bar.

Prior to system relaxation MD, energy minimization was carried out with a composite protocol of steepest descent, conjugate gradient, and truncated Newton steps, using termination gradients of 5000, 1000, and 100 kJ/mol nm, respectively. MD is coupled to a modified Nose'-Hoover thermostat [32] system. The Particle Mesh-Ewald method [33,34] was used to compute long-range electrostatics to within a relative tolerance of 1×10^{-6}. A cut-off distance of 12.5 Å was applied to real-space Ewald interactions. The same value was used for Van der Waals interactions. The LINCS algorithm [35] was applied to constrain bond lengths to hydrogen atoms. A leap-frog algorithm [36] was used with a time step of 1 fs.

2.2. Incorporation of static electric field and microwave field

To investigate the influence of the external static electric field and the microwave field on the SPC/E and the TIP4P, a series of intensities of the static electric fields and the microwave fields was applied to the water models with frequency 2.45 GHz. The microwave field was represented by a homogeneous time-alternating electric field of the form:

$$E_{ext}(t) = E_0 \cos(\omega t)\, x_0, \qquad B = 0. \tag{1}$$

Prior to production simulations a 1 ns NVT relaxation run and a 1 ns NPT relaxation run were performed. Then equilibrium MD simulations were performed in the NPT ensemble and the first 3 ns were considered as further relaxation, keeping the rest 7 ns simulation time as production run. Then a series of NNPT simulations was carried out for 10 ns at 298 K in fields of frequency 2.45 GHz with RMS intensities of 0, 3×10^5 V/m, 3×10^6 V/m, 3×10^7 V/m, 3×10^8 V/m and 3×10^9 V/m, using the relaxed system as a starting configuration. Simulation details refer to Ref. [37].

The dielectric constants were calculated based on the fluctuation in total dipole moment $M = \sum_i \mu i$ by:

$$\varepsilon_s = 1 + \frac{4\pi}{3Vk_BT\varepsilon_0}\left(\langle M^2\rangle - \langle M\rangle^2\right) \tag{2}$$

where ε_0 is the vacuum permittivity, V is the volume, K_B is Boltzmann's constant and T is the temperature.

The Debye relaxation time constant can be calculated from non-equilibrium MD simulations when an external field is applied [38]. The dipole moment along the field's direction $\langle M\rangle$ can be related to the Debye relaxation time by Eq. (3) [38]:

$$\tau = \tau_s \frac{[\varepsilon_0 + 2 + C_{\mathrm{rf}}(\varepsilon_0 - 1)]}{3}. \tag{3}$$

The parameter C_{rf} can be calculated by Eq. (4) [38]:

$$C_{\mathrm{rf}} = \frac{(2\varepsilon_0 - 2\varepsilon_{RF})(1 + kR_c) - \varepsilon_{RF}(kR_c)^2}{(\varepsilon_0 + 2\varepsilon_{RF})(1 + kR_c) + \varepsilon_{RF}(kR_c)^2} \tag{4}$$

where k is the Debye screening length, R_c is the cut-off radius, and τ is the Debye relaxation time.

The relaxation time τ_s can be obtained from the average dipole moment upon applying an external field at time $t_0[\langle M(t)\rangle_{t0}]$, and the dipole moment at steady state $[\langle M(t=\infty)\rangle_t]$, by Eq. (5) [38]:

$$\langle M(t)\rangle_{t0} = \langle M(t=\infty)\rangle_t \left[1 - \exp\left(-\frac{t - t_0}{t_s}\right)\right]. \tag{5}$$

The molecular polarizabilities were calculated by:

$$\varepsilon_s - 1 = 4\pi \frac{p}{\varepsilon_0 E} \tag{6}$$

where p is the molecular polarizability and E is the intensity of the external field.