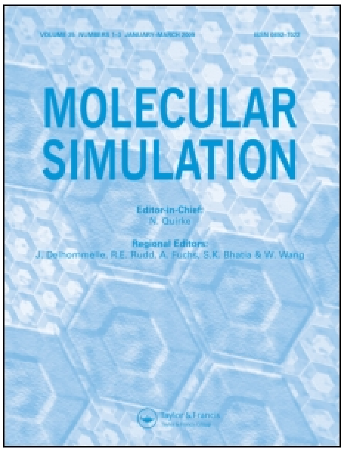

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An Interatomic Potential Model for H_2O: Applications to Water and Ice Polymorphs

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AN INTERATOMIC POTENTIAL MODEL FOR H_2O: APPLICATIONS TO WATER AND ICE POLYMORPHS

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A new interatomic potential model for H_2O which consists of 2-body central (O-H, O-O and H-H) and 3-body teams and does not contain artificial constraints on the motions of oxygen and hydrogen atoms is proposed. The interatomic potential function parameters were determined empirically so as to reproduce the fundamental and essential features of water and ice Ih using molecular dynamics (MD) methods.

We carried out the MD simulations of water, and find the Ice Ih, Ice II and Ice IX using this potential model, in structures and physical properties are in agreement with the experimental results except for the compressibilities of both water and ice Ih. We expect that, by refining this model, we can apply this model to problems involving the reaction of water molecules with other components.

KEY WORDS: Molecular dynamics, water, ice polymorphs, interatomic potential model, 3-body interaction.

INTRODUCTION

A variety of rigid molecular models have been proposed for molecular simulations of water [1-5]. Recently, some models which allow intramolecular motions were developed [6-8]. Because all of them define inter- and intramolecular potentials separately, it is not easy to extend those models to more complex systems such as electrolyte aqueous solutions.

One approach to this problem is to make use of a model which treats H_2O systems as an assemblage of hydrogen and oxygen atoms and describe the inter- and intramolecular interactions by a single interatomic potential function. This type of water model has been proposed by Stillinger and Rahman (SR-model) [9]. However, since the SR-model has only two body interatomic interactions, this potential model has some artificial features in order to maintain the structure of a water molecule and hydrogen bonds.

We propose, in this study, a new interatomic potential model for water and ice polymorphs in which the motions of H and O atoms have total freedom, and confirm its usefulness by means of molecular dynamics simulations of water and ice polymorphs.

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INTERATOMIC POTENTIAL MODEL

The interatomic potential functions consist of two body and three body terms. The two body terms are described as follows for any atom pairs:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left[\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right] - \frac{c_i c_j}{r_{ij}^6}$$
$$+ f_0 D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^*) - 2\exp\{-\beta_{ij}(r_{ij} - r_{ij}^*)\}\}, \qquad (1)$$

where r_{ij} is a interatomic distance and f_0 ($= 6.9511 \times 10^{-11}$ N) is a constant for unit adaptations between these terms. The first and second terms are the Coulomb and short range repulsions, respectively. The third term, the van der Waals interaction, is applied only to the interactions between oxygen atoms, and the forth term, the Morse function, is applied only to the interactions between oxygen and hydrogen atoms. The parameters, z_i, a_i, b_i and c_i are of atom species, and D_{ij}, β_{ij} and r_{ij}^* are of O-H pairs.

The three body part is applied only for H-O-H groups:

$$U_{\mathrm{HOH}}(\theta_{\mathrm{HOH}}) = -f_k\{\cos[2(\theta_{\mathrm{HOH}} - \theta_0)] - 1\} \times (k_1 \cdot k_2)^{1/2}, \qquad (2)$$

where θ_{HOH} is the angle of H-O-H, and f_k and θ_0 are the parameters. The variables, k_1, k_2, define the effective range of the three body potential:

$$k_i = \frac{1}{\exp[g_r(r_{\mathrm{OH}(i)} - r_m)] + 1}, \qquad (3)$$

where g_r, r_m, are parameters. The values of k_1 and k_2 are about unity at the intramolecular O-H distance and approach zero rapidly around the hydrogen bond distance. The three body forces, in this model, act along the directions perpendicular to the O-H bond in the plane involving the H-O-H atoms (Figure 1), and the magnitude is given as follows:

$$F_{\mathrm{H}(i)} = -2\frac{f_k}{r_{\mathrm{OH}}(i)}\sin[2(\theta_{\mathrm{HOH}} - \theta_0)] \times (k_1 \cdot k_2)^{1/2}, \qquad (4)$$

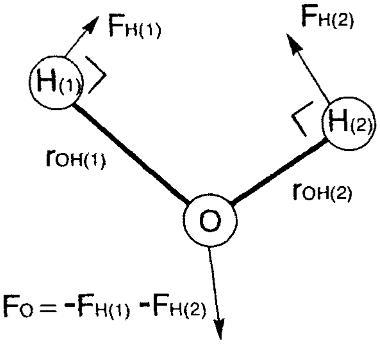

Figure 1 The application of the three body forces of this potential model, in an H-O-H group.

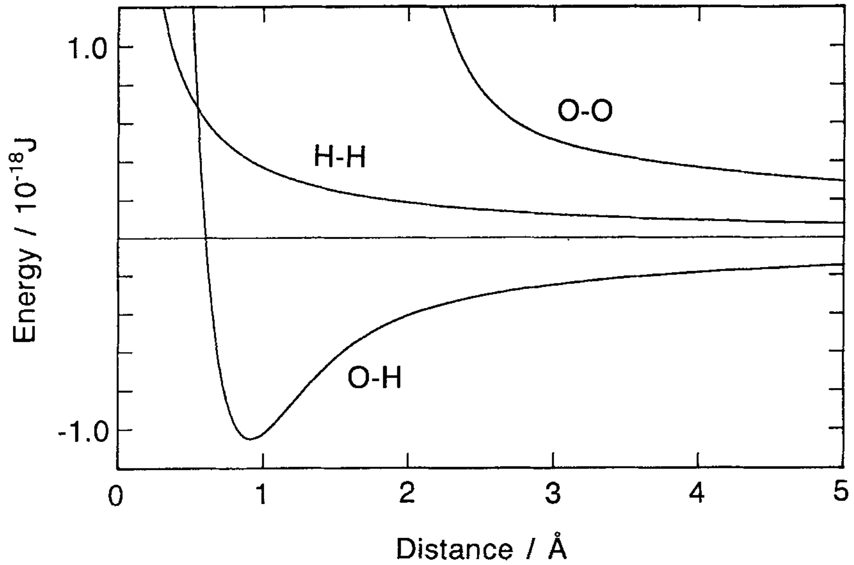

Figure 2 The two body potential curves of the present model as functions of interatomic distances.

These two and three body potential parameters are determined empirically so as to reproduce the H_2O molecular structures, interatomic structural features and the density of water and ice Ih, where the ionic charges assumed to be 40% of the formal charges. The values of the parameters are shown in Table 1, and the two body potential functions with interatomic distances are illustrated in Figure 2.

The potential functions of this model is compared with the energy surface of *ab initio* molecular orbital (MO) calculations with the configuration interaction (CI) [10]. Figure 3 shows the potential energy of an H_2O molecule as the function of

Table 1 Parameters of interatomic potential models.

Two body term	*O*	*H*
z	−0.80	0.40
a/Å	1.841	0.036
b/Å	0.124	0.058
$c/kJ^{1/2}\cdot Å^3\cdot mol^{-1/2}$	57.28755	0.00
	O-H	
D/Å	75.0	
β/Å^{-1}	2.74	
r^*/Å	0.82	
Three body term	O-H-O	
$f_k/10^{-11}$ J	1.1	
θ_0/degree	99.5	
r_m/Å	1.40	
g_r/Å^{-1}	7.0	

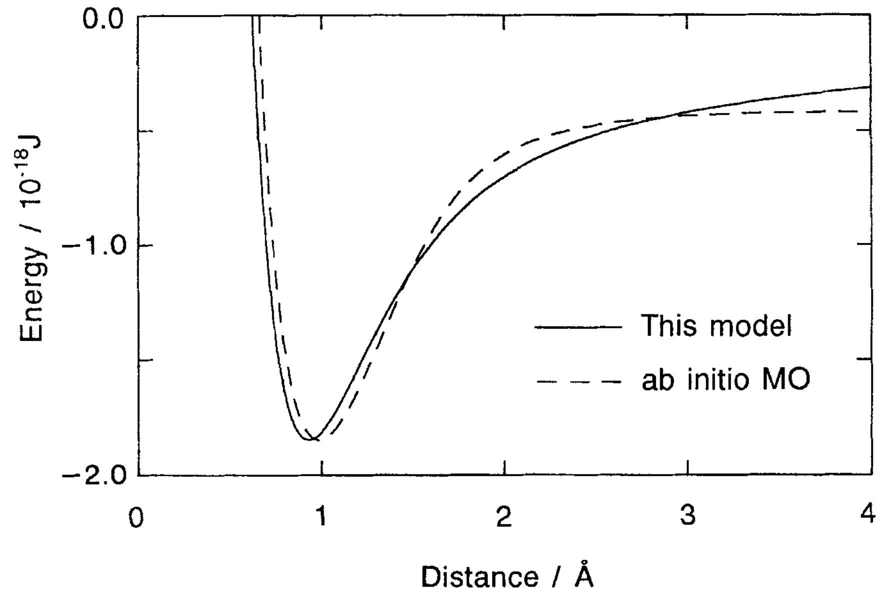

Figure 3 Comparison of energy surfaces of a H_2O group for O-H distances. The energy surface of the present model is drawn by the solid line and that of *ab initio* MO calculation with first order CI [10] is drawn by the broken line. The reference energy is taken as the energy of infinitely separated atoms of the MD model. The *ab initio* curve is drawn to have the same minimum energy level in the plot with the MD model.

the O-H distance obtained by this model and the *ab initio* energy surface. The CI calculations tend to neutralize the atomic charges on O and H with increasing O-H distance, while, on the other hand, our potential model has fixed atomic charges, hence these curves do not agree for large O-H distances. They have similar shape near the energy minima which have great influence on structure and the physical properties of an H_2O molecule.

MOLECULAR DYNAMICS SIMULATION METHODS

Molecular dynamics simulations were carried out using the Verlet algorithm for atomic motions, and the Ewald method for the summations of the Coulombic energies and forces. The basic cell was a rectangular parallelepiped that had three dimensional periodic boundary conditions. The MD systems consisted of 600 atoms (200 oxygen atoms and 400 hydrogen atoms), 900 atoms or 1800 atoms in a basic cell for water, 1080 atoms for ice Ih, 1296 atoms for ice II and 972 atoms for ice IX. The hexagonal unit cell of ice Ih and ice II were converted to rectangular parallelepiped cells, respectively. The integration of equations of motions was carried out at each 4.0×10^{-16} sec, and after equilibration, each run to obtain the time averaged properties was 12500 time steps long (equals to 5.0×10^{-12} sec) for water and 10000 time steps long (equals to 4.0×10^{-12} sec) for ices. All the MD calculations were carried out under the conditions of constant temperature and

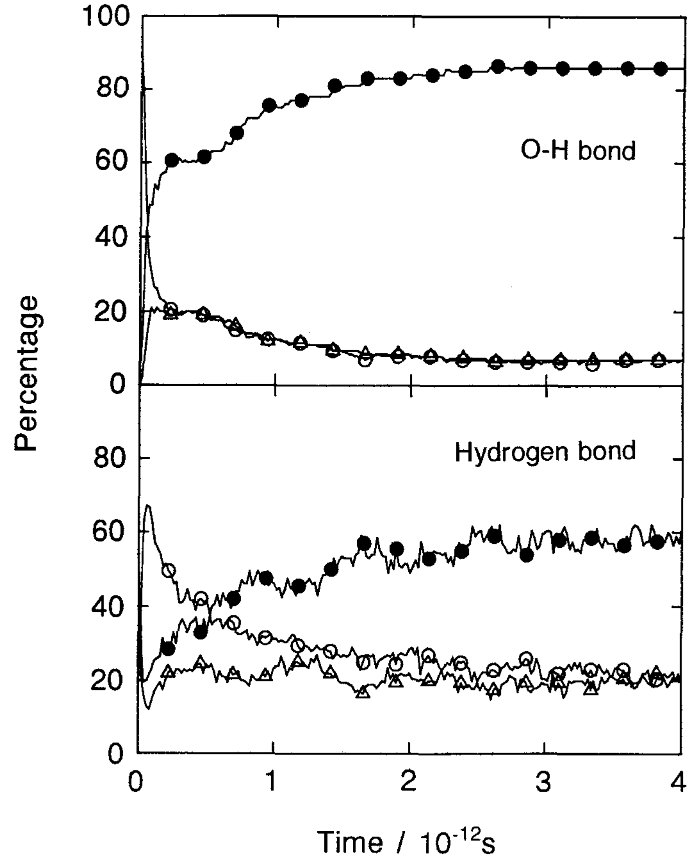

Figure 4 Developments of water structure in terms of O-H bonds ($r_{OH} < 1.2$ A) (upper) and of hydrogen bonds (1.2 A $< r_{OH} < 2.5$ A) (lower) in a MD calculation started from a random configuration where 200 oxygen and 400 hydrogen atoms were put into an MD basic cell using random numbers. Solid circles indicate the percentage of oxygen atoms having two intramolecular O-H bonds (upper) or two hydrogen bonds (lower). Triangles and open circles are of the the percentage of oxygen atoms with those bonds to hydrogen atoms of more or less than two, respectively.

pressure, which were made by the scaling of particle velocities and basic cell edges [11].

The starting configurations of atoms were random for water, and the crystal structures by the x-ray or neutron diffraction experiments for ice polymorphs [12–14].

Initial relaxation to water structures from random configuration of 600 atoms under constant temperature at 300 K and constant pressure at 1 atm. are shown for the initial 10000 steps (4.0×10^{-12}sec) in Figure 4. The ratio of oxygen atoms which have two intramolecular O-H bonds (i.e. a water molecule) to total oxygen atoms increased to more than 0.9 in this time steps. On the contrary, the formation of the network structures by hydrogen bonds increased more slowly but steadily.

RESULTS AND DISCUSSION

Reproducibility of Ice Polymorphs

The results of ice polymorphs, Ih, II and IX, are shown in Table 2. Ice Ih is the phase of atmospheric pressure and ice II and ice IX are the high pressure phases. The cell parameters, densities and interatomic distances and angles are good agreement with those of the experiments. This model can reproduce the difference of density between ice Ih and water ($1.011 \times 10^3\,\mathrm{kg \cdot m^{-3}}$) at 273 K. The structures and densities of ice II and ice IX are also well reproduced by means of MD simulations with the present interatomic potential model.

The density of ice Ih at 0.2 GPa and 273 K was calculated to be $0.929 \times 10^3\,\mathrm{kg \cdot m^{-3}}$, and is smaller than the experimental one, $0.940 \times 10^3\,\mathrm{kg \cdot m^{-3}}$ which is evaluated from the elastic compliances [16]. This disagreement may be due to the small hardness parameters b_i of oxygen atoms.

Table 2 Structures and some properties of MD simulations of ice polymorphs comparing with experimental data.

(a) Ice Ih (273 K, 1 atm.)		*MD*	*Experimental*
Cell parameters/Å	a	4.484	4.5227[a]
	b	7.904	7.8335[a]
	c	7.351	7.3671[a]
Density/10^3 kg·m^{-3}		0.9186	0.9169[a]
O-H bond length/Å		0.973	1.00-1.01[b]
Hydrogen bond length/Å		1.76	1.74-1.75[b]
H-O-H angle/degree		107.1	109.5-109.6[b]
M.s.d./Å^2	O	0.083	—
	H	0.085	—

(b) Ice II (213 K, 0.3 GPa)		*MD*	*Experimental*[c]
Cell parameters/Å	a	12.98	12.98
	b	22.47	22.49
	c	6.194	6.253
Density/10^3 kg·m^{-3}		1.192	1.180
O-H bond length/Å		0.969	0.937-1.014
Hydrogen bond length/Å		1.79	1.808-1.864
H-O-H angle/degree		105.6	103.2-107.6
M.s.d./Å^2	O	0.051	—
	H	0.061	—

(c) Ice IX (110 K, 0.3 GPa)		*MD*	*Experimental*[d]
Cell parameters/Å	a	6.634	6.73
	b	6.649	6.73
	c	6.856	6.83
Density/10^3 kg·m^{-3}		1.187	1.16
O-H bond length/Å		0.972	0.972-0.979
Hydrogen bond length/Å		1.76	1.789-1.821
H-O-H angle/degree		107.5	104.7-106.0
M.s.d./Å^2	O	0.031	—
	H	0.036	—

[a] [15], [b] The values at 223 K [12], [c] [13], [d] [14]

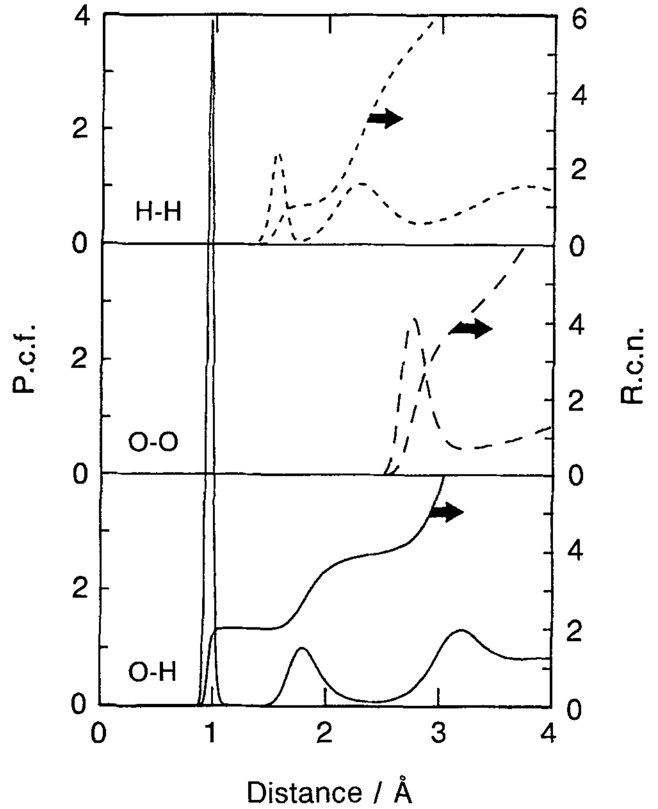

Figure 5 The pair correlation functions (p.c.f.) and the running coordination numbers of the O-H (solid line), O-O (long broken line) and H-H (short broken line) pairs in water at 300 K and 1 atm.

Structures of Water

Figure 5 shows the pair correlation functions (p.c.f.) and running coordination numbers (r.c.n.) in the water of 1800 atoms at 300 K and atmospheric pressure. The p.c.f. of O-H pair has peaks at distances of 0.96 and 1.79 Å. The first peak is the intramolecular O-H bonding distance, and the second one is the hydrogen bonding distance. The first peak at 1.55 Å of the H-H p.c.f. is of the intramolecular H-H distance, and the O-O p.c.f. have a peak at 2.75 Å which is the distance between the oxygen atoms of neighboring water molecules. The mean interatomic distances and angles, and the densities are shown in Table 3. There are no significant differences between the results of the large and small systems, and these results reproduce the experimental data well.

The x-ray interference function of water derived by MD calculations of 1800 atoms is compared with the experimental one [18] in Figure 6. The MD results are in agreement with experimental data on the whole, but the details are different. This difference suggests that the mean O-O distance in the MD simulation is somewhat shorter than that derived by the diffraction studies.

Table 3 Comparison of the geometry and density of water of MD simulations and experiments at 300 K and 1 atm.

	MD		*Experimental*
	900 atoms	*1800 atoms*	
Distances/ Å			
intramolecular O-H	0.961	0.965	0.966[a]
intramolecular H-H	1.55	1.55	1.510[a]
hydrogen bond	1.79	1.79	–
neighboring O-O	2.75	2.75	2.82[b]
Angles/degree			
H-O-H	107.1	107.2	(102.8)[c]
O-H-O	166.5	166.5	–
Density/10^3 kg·m^{-3}	1.000	1.004	0.997

[a] [17], [b] [18], [c] Calculated from O-H bond length and intramolecular H-H distance.

The compressibility of water shows the same tendency as well as the case of ice Ih. The MD result, 1.090 × 10^3 kg·m^{-3} at 0.5 GPa, is smaller than the experimental density, 1.15 × 10^3 kg·m^{-3} [19], and the model water is less compressive in comparison with real water.

Dynamical Properties of Water

Self diffusion coefficients can be obtained from mean square displacement (m.s.d.) of atoms in MD calculations of the 1800 atoms system and the Einstein relation. The self-diffusion coefficients of oxygen, 1.46 × 10^{-9} m^2·sec^{-1}, and hydrogen, 1.60 × 10^{-9} m^2·sec^{-1}, at 300 K is compared with the experimental one of 2.23 × 10^{-9} m^2·sec^{-1} for water molecule at 298.2 K [20]. The MD results are somewhat small in comparison with the experimental one.

Figure 7 shows the power spectrum obtained by the Fourier transforms of the velocity autocorrelation functions of oxygen and hydrogen atoms separately.

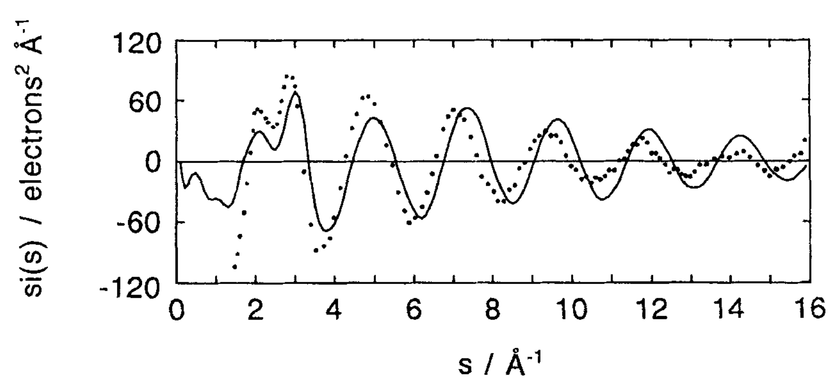

Figure 6 Comparison of the x-ray interference functions between the MD calculations and the experiments. The present simulation result at 300 K and 1 atm. is denoted by the solid line and the experimental result at 298 K [18] is denoted by the dots.

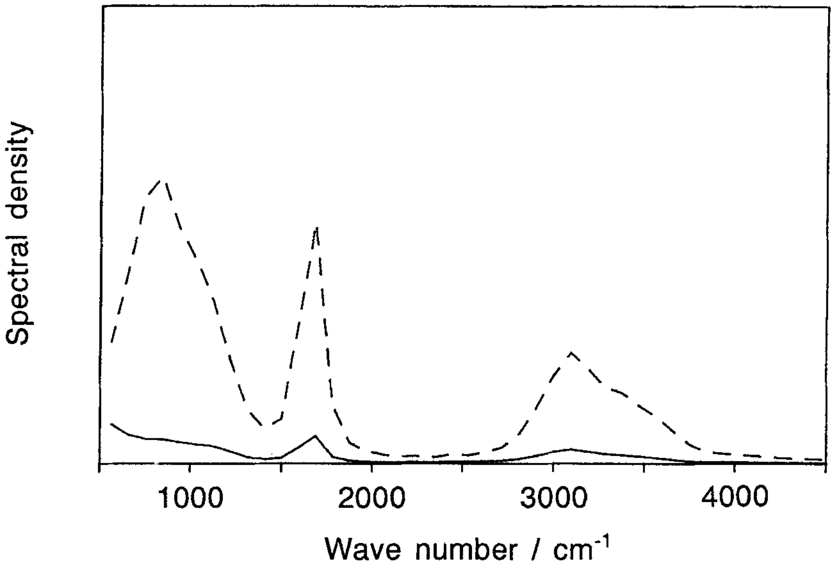

Figure 7 The spectral densities of oxygen (solid line) and hydrogen (broken line) atoms obtained by the Fourier transforms of the velocity autocorrelation functions of component atoms.

Because the water molecules produced by this model are not rigid molecules, the vibrations of the intramolecular motions are also included. The peak at 1700 cm^{-1} shows the intramolecular bending (H-O-H) motions and the broad peaks at 3000-3500 cm^{-1} are assigned to the O-H bond stretching motions. These peaks are agreement with the experimental infra-red and Raman spectra [21].

CONCLUSIONS

We presented a new interatomic potential model which consists of the two and three body interactions. The parameters were determined empirically so as to reproduce the structures and densities of water and ice Ih. This model allows the free movement of oxygen and hydrogen atoms, and can reproduce essential intra- and intermolecular structures of H_2O systems. The compressibilities of water and ice Ih obtained from the MD simulations are small, so it is necessary to improve the parameters which will be softer than the present model. The improved model is expected to be applied to the molecular simulations of multicomponent aqueous systems such as aqueous solutions with electrolytes, aqueous solutions under high temperature and high pressure.

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