

FAR INFRARED SPECTRUM OF WATER BY MOLECULAR DYNAMICS METHOD

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ABSTRACT

The far infrared (pure rotational) spectra of water is calculated by simulating the motion of molecules with molecular dynamics method. Giving the conditions of vapor, liquid and cluster, the characteristic patterns of molecular motion under these states are observed in the simulations. The absorption cross section is calculated from the variation of the dipole moment of the system, which is obtained from the simulated configuration of molecules. From the resultant far infrared spectra for the given conditions, effects of free rotation and inter-molecular motion on the spectrum are discussed.

INTRODUCTION

Since the molecule of water has a permanent electric dipole moment, far infrared spectra of water have strong peaks attributed to the thermal motion of molecules, such as rotation or inter-molecular vibration. It means that the efficiency of radiation energy transfer through a medium including water molecules can be significantly affected by the frequency range of the thermal radiation. It is thus important to have accurate knowledge on far infrared spectra of water in various states, from the view point of thermal engineering. However, these properties are not sufficiently understood, because the motion of water molecules is not simple. Firstly, since the structure of the water molecule is classified as the asymmetric top, quantum mechanics for its rotational spectrum is not simple, even when there are no interactions among molecules. Secondly, there are some characteristic properties of water molecules, such as the hydrogen bondings, which make the inter-molecular motion in the condensed phase very complicated. Finally, the patterns of molecular motion are strongly affected by the density and temperature of the system, and the correspondence of these patterns to particular features observed in the far infrared

spectrum is still not clear. There have been a lot of works on the inter-molecular motion of water, including computer simulation studies. For the water molecule, several inter-molecular potential functions for the molecular dynamics (MD) simulations have been proposed. Recently, some works proved that MD can be an effective method to calculate far infrared (pure rotational) spectra of water molecules. For instance, Guillot[1] calculated the far infrared spectrum of liquid water using the SPC potential, and studied the relation between the inter-molecular motion and the shape of the spectrum to some details. The purpose of our study is to investigate the thermal radiation properties of water in various states, applying MD simulations to calculate the molecular motion. In this paper, we calculate the far infrared spectra of water using the ST2 potential function[2]. In order to obtain the basic information on the relation between the patterns of molecular motion and the features of the far infrared spectra in various states with different types of molecular interaction, simulations are performed with the conditions of vapor and liquid phases, and what we call "clusters" made up with a few hundred condensed molecules. Though it would not be appropriate to use the ST2 potential for the vapor, we consider that the general characteristics of molecular motion under each condition are reasonably simulated.

FORMULATION OF THE SPECTRUM

The absorption spectrum of gas or liquid medium is represented as the absorption cross section per one molecule, $\alpha(\omega)$, which is a property defined in the Beer's equation:

$$I = I_0 \exp(-\alpha N x), \quad (1)$$

where I is the intensity of light with angular frequency ω (I_0 is the initial intensity), N is the number density of the molecules, and x is a path length. According to the quantum mechanical considerations of the energy absorbed by a dipole

per unit time, $\alpha(\omega)$ is given as following[3,4],

$$\alpha(\omega) = \frac{\pi\omega\{1 - \exp(-\hbar\omega/kT)\}}{3\epsilon_0\hbar n c} \cdot I(\omega), \quad (2)$$

where

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) dt \langle \mu(0) \cdot \mu(t) \rangle_0. \quad (3)$$

Noting that the equilibrium average $\langle \mu(0) \cdot \mu(t) \rangle_0$ can be replaced by the auto-correlation of $\mu(t)$ in the equilibrium state, $I(\omega)$ is derived to be the power spectrum of $\mu(t)$. In the current technique, the dipole moment variation is obtained from the results of the classical MD simulation. Since the properties calculated by MD correspond to the classical limits of the quantum properties, one should consider the classical expression of $\alpha(\omega)$ and $I(\omega)$, which are equivalent to the limit of $(\hbar\omega/kT) \rightarrow 0$ [4],

$$\alpha^C(\omega) = \lim_{\hbar \rightarrow 0} \alpha(\omega) = \frac{\pi\omega^2}{3\epsilon_0 k T n c} \cdot I^C(\omega), \quad (4)$$

where the superscript C denotes the classical limit. $I^C(\omega)$ is obtained as the power spectrum of the dipole moment derived from MD simulation. The absorption cross section is then calculated from Eq.(4). For the sake of simplicity, the refractive index n is considered to be constantly 1.

DESCRIPTION OF THE CALCULATIONS

The MD simulations are performed using 216 molecules with ST2 potential[2] in a cubic region with the boundaries of the periodic boundary condition. The inter-molecular potential is truncated at a distance of $L/2$, where L is the unit length of the periodic boundary. The translational and rotational motions of molecules are computed with a time step of 1 femto second for 50,000 steps. The dipole moment of the system is calculated simply as the vector sum of the permanent dipole moment of each molecule in the region and stored every 5 steps. Effects of induced dipole are not considered here. Simulations are carried out for 4 cases summarized in Table 1. For cases 1 and 2, the density of the system is achieved by adjusting the size of calculation region. In the case of liquid, the initial configuration is the ice lattice, and each molecule is given the initial velocity determined from the temperature of the system, with random direction. The type of our MD simulations is basically NVE

Table 1 Conditions used in the simulations.

	State	Density, kg/m ³	Temperature, K
case 1	gas	1.0	270
case 2	liquid	1.0×10^3	270
case 3	cluster	—	270
case 4	cluster	—	320

ensemble, but the potential truncation length for the case of liquid is not sufficiently large (9.3 Å), so that the accumulation of numerical errors on total energy of the system can not be neglected. This error could be avoided by considering the long range interactions with the Ewald method, but it would be time-consuming and its physical meaning is still questionable. So we simply modify the kinetic energy of the system periodically and avoid the drift of the total energy. This operation is required only for the case of liquid (case 2). For the vapor phase, a density larger than in the saturation point is used, because under the saturation density, the opportunity of the inter-molecular collisions is too small to apply the MD method. As described in the next section, the inter-molecular potential energy under the density of case 1 is sufficiently small. The initial condition for the case 1 is created from the positions and velocities of molecules in the liquid phase in the equilibrium state, by expanding each component of the coordinates of molecular positions. Cases 3 and 4 are cluster conditions with different temperatures from each other. In order to create these states, a cubic ice crystal made up with 216 molecules placed at the center of a large calculation region is used as the initial condition. The length of the edge of the calculation region (the unit length of the periodic boundary) is 5 times longer than that of the ice crystal. The initial configuration of the crystal is same as that of the liquid case. As starting the calculation, the lattice structure of the crystal begins to melt and forms a cluster like a tiny drop, which remains one body through the simulation. At the beginning of each calculation, about 5000 steps are required to complete the potential relaxation and achieve the equilibrium state.

RESULTS AND DISCUSSION

Gas and Liquid

Figures 1 (a) and (b) show the calculation regions at a particular instant of case 1 (gas) and case 2 (liquid), respectively. The averaged potential energy per one molecule is

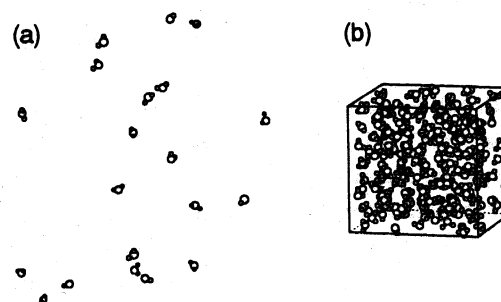


Fig. 1 Instantaneous molecular configurations for (a) case 1 (gas) and (b) case 2 (liquid). Frame illustrated in (b) represents the boundary of the calculation region. Both pictures are the same scale.

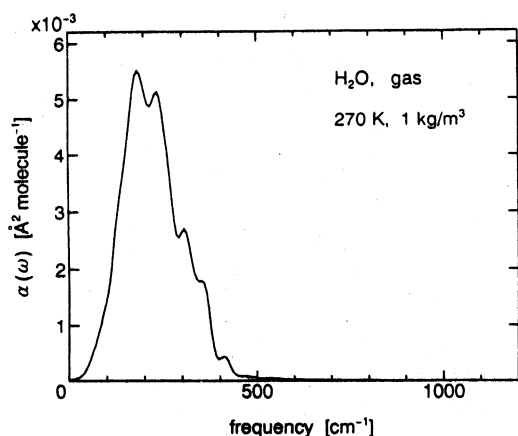


Fig. 2 Far infrared spectrum for gas phase of water (case 1).

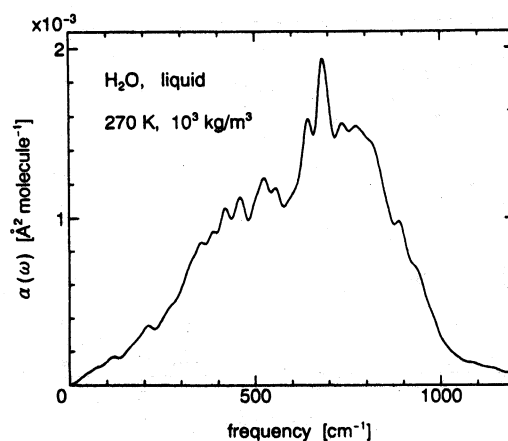


Fig. 4 Far infrared spectrum for liquid phase of water (case 2).

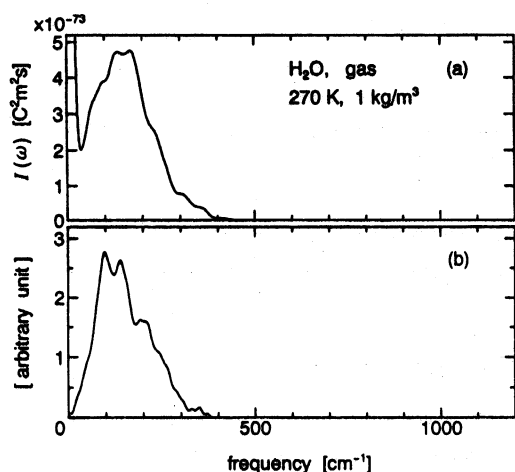


Fig. 3 (a) Power spectrum of dipole moment of the system $I(\omega)$ and (b) angular velocity distribution for case 1 (gas).

-0.002 eV for case 1 and -0.28 eV for case 2, which means that interaction between molecules is negligible in the gas phase. From this fact, the rotational spectrum of gas phase is expected to be determined by the angular velocity distribution of water molecules which are rotating without any interaction. Fig. 2 is the rotational spectrum of gas phase water (case 1). There is a single peak centered at about 200 cm^{-1} . Fig. 3 shows (a) the power spectrum of dipole moment $I(\omega)$ and (b) the angular velocity distribution for this case. The center of the angular velocity distribution is around 150 cm^{-1} , which is close to the center of $I(\omega)$. In the case of gas, it is thus concluded that the shape of rotational spectrum is simply the reflection of the angular velocity distribution. Fig. 4 is the rotational spectrum of liquid phase (case 2). It is noticed that the far infrared spectrum of liquid water has a broad band centered at about 685 cm^{-1} which is related to the libration (oscillation of the molecular axis) of

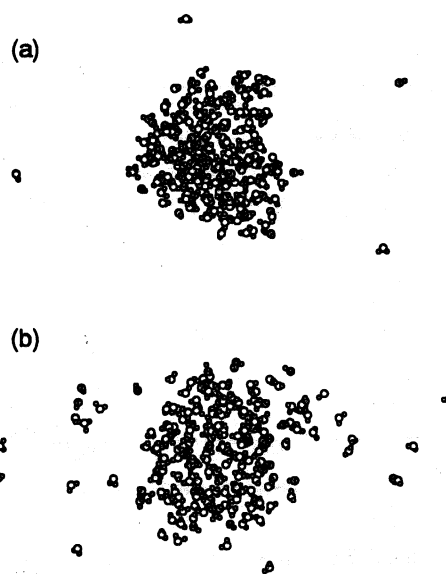


Fig. 5 Instantaneous molecular configurations for (a) case 3 (cluster, 270 K) and (b) case 4 (cluster, 320 K).

the molecules, and an intermediate band around 200 cm^{-1} by the inter-molecular vibration of stretching mode of the $\text{O}-\text{H}\cdots\text{O}$ structure. Our result for liquid phase shows obviously one peak around 750 cm^{-1} and a shoulder around 500 cm^{-1} . Although the centers are shifted to higher frequency region, we consider that these are peaks associated to the inter-molecular motions described above, slightly shifted because of inaccuracy of the inter-molecular potential, since these motions are sensitive to the potential parameters.

Clusters

Figures 5 (a) and (b) shows the instantaneous configuration of molecules of the cluster created in the case 3 (270 K) and case 4 (320 K), respectively. For both cases, the cal-

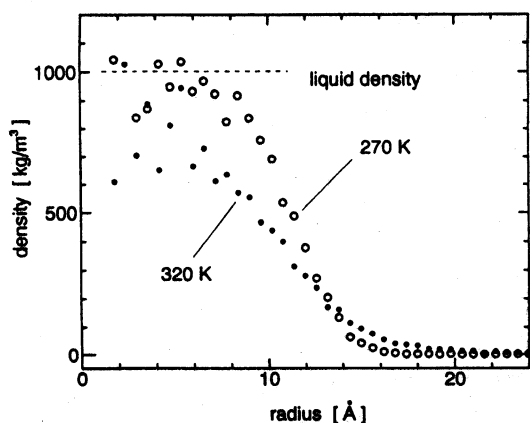


Fig. 6 Averaged density profiles created in the cluster conditions. Values near the center of clusters tend to scatter because of lack of the sample.

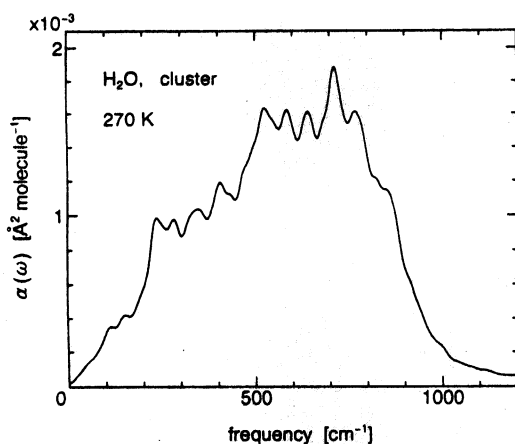


Fig. 7 Far infrared spectrum for the cluster at 270 K (case 3).

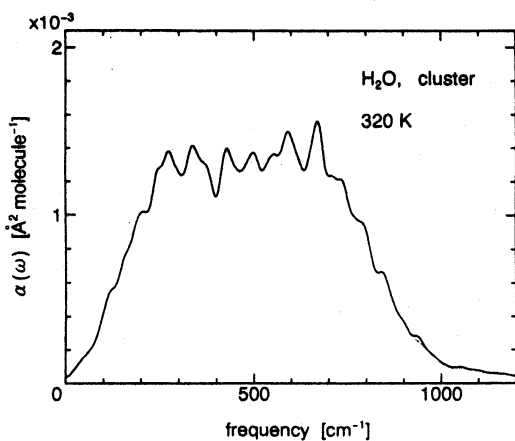


Fig. 8 Far infrared spectrum for the cluster at 320 K (case 4).

culated systems consist of the high-density region and surrounding region containing the evaporated molecules. Fig. 6 shows the density profiles for these two cases, which represent averaged density in the spherical shell centered at the center of mass of the cluster. In the lower temperature case, the density is close to that of liquid in a radius range up to 8 Å, which implies that the far infrared spectrum would include the significant contribution from the liquid part of the system. Fig. 7 is the far infrared spectrum for case 3. The overall feature of the spectrum is similar to that of liquid (Fig. 4) although the peaks are broadened to the lower frequency region. This fact means that the basic patterns of molecular motion are close to that in the liquid phase, but because the restriction on the motion is weaker than in the liquid, the frequency of each motion tends to be lower. In the case of higher temperature (case 4), the density profile shows that the region with liquid density is much smaller than in case 3 and the interface region is broadened. The far infrared spectrum for case 4 is shown in Fig. 8. Reflecting the trend of the density profile, the liberation peak is reduced and merged with the peak around 300 cm⁻¹. We consider that this peak around 300 cm⁻¹ includes the contribution from the inter-molecular vibration of relatively loose bond between molecules in the interface region as well as free rotation of molecules in the vapor region.

NOMENCLATURE

- I : intensity of light,
or power spectrum of dipole moment, C²m²s
- T : temperature, K
- c : speed of light, m/s
- \hbar : Planck's constant, J·s
- k : Boltzmann's constant, J/K
- n : refractive index
- α : absorption cross section per molecule, m²
- ϵ_0 : permittivity, F/m
- μ : electric dipole moment, C·m
- ω : angular frequency of light, rad/s

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