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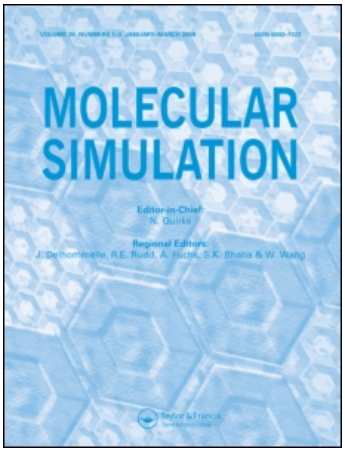

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REARRANGEMENT OF THE HYDROGEN-BONDED NETWORK OF THE CLATHRATE HYDRATES ENCAGING POLAR GUEST

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Rearrangement process of the hydrogen-bonded network of clathrate hydrate of the polar guest ethylamine is examined by the molecular dynamics simulation. The hydrogen-bonded network rearrangements with reorientation of water or migration of water are observed in the 10 ns trajectories and analyzed in term of a representative connectivity pattern of a time zone longer than a time scale of vibrational motion of molecules. The most frequent rearrangement is the reorientation of single water molecule rotating 180° around its twofold axis in the network unlike Bjerrum's picture of molecular rotation in ice. Migration of water in the host lattice rarely occurs and very long time (several hundred pico second) is required to complete the rearrangement process since cooperative reorientation of many neighboring water is necessarily accompanied. The correlation of reorientational motion of water appears to decay not with the Debye type but rather with a power-law behavior.

KEY WORDS: Clathrate hydrates, polar guest, rearrangement, hydrogen-bonded network.

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1 INTRODUCTION

Clathrate hydrates are one of the crystalline solids in which water form a hydrogen-bonded network system. A main difference from ice is that they have a second component called guest. The guest molecules are encapsulated in the cages of the host network and do not participate in the hydrogen-bonded network of the host lattice [1,2]. Study on clathrate hydrates has a quite long history–Davidson pointed out it dates back at least to 1810 [1]–but is still intensively being done. Both scientific interests and industrial needs urge the investigation on properties of clathrate hydrates. Anomalous properties of clathrate hydrates, such as different phase behavior from ice, the low thermal conductivity and its reverse temperature-dependence to that of standard crystalline solids, are still open questions. Mechanism of the forming process has not been clearly answered.

Kinetic properties of the water molecules in clathrate hydrates have been studied by experiments of the dielectric relaxation and the NMR spectra. In either case of ice or clathrate hydrates, the water molecules form a fully hydrogen-bonded network which makes reorientation of a water molecule impossible without the cooperation of neighboring water molecules. The reorientation mechanism of water

molecules in ice was proposed by Bjerrum [3] and this account is also accepted for clathrate hydrates. The picture drawn by Bjerrum is that rotational motion of water molecules is caused by diffusion of the orientational defects, called Bjerrum faults, in the hydrogen-bonded network. Let us imagine how reorientational motions of water molecules occur in a perfect crystalline ice. This condition is never realized in any experiment. Molecular simulation may not be helpful because the reorientation must be highly cooperative and it is an extremely rare event. Even if there exist some Bjerrum defects, the reorientation hardly happens during simulation time now available (an order of nano second) and a very low density of the defects requires a large system size. However, unlike in ice and gas hydrates of apolar guest, it was found that the water molecules in a polar guest-encaging clathrate hydrate show reorientation and, with much less chance, translational jump motion in our previous study [5]. That is to say, the hydrogen-bonded network undergoes some rearrangements in a time scale of the molecular simulation. The polar guest molecule we choose is ethylamine that is known to form a structure I hydrate [1]. The amino group causes some attractive interaction between amine and water molecules although it is not as strong as that of alcohols which form too strong hydrogen bonds with water and inhibit hydrate formation. Owing to this moderately strong attractive interaction between amine and host water, cleavage of hydrogen bonds among water molecules may be induced with higher probability than that in non-polar guest clathrates or in ice, and consequently rearrangement of the hydrogen-bonded network frequently occurs. This picture agrees with the experimental observation that dielectric properties of amine hydrates are quite different from those of ices and non-polar guest hydrates [1]. Thus, we will consider, using molecular dynamics simulation, how the host network of the amine clathrate hydrate is rearranged. Outline of the present study is as follows: firstly, a rough picture for the dynamical properties of the host network encaging the polar guest is given and rearrangements with migration of water are found by comparing the quenched structures; secondly, detailed analyses on rearrangements followed only by reorientation of water are made using a part of the total trajectory; thirdly, rearrangements with migration of water molecules are briefly considered; and finally, a peculiar property of rearrangement process is shown in terms of correlation functions of the events that water molecules change their hydrogen-bonding partners.

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2 METHOD

2.1 System

We adopt ethylamine clathrate hydrate as a polar guest-encaging clathrate. Ethylamine is known to form a clathrate hydrate of structure I, one of the two major lattice types of hydrates. The cubic basic lattice with a lattice constant 12.03 Å contains 46 water molecules and 6 large and 2 small cages. The initial host structure has a proton-disordered form, which is generated according to the ice rule, with a condition of zero net dipole moment for each unit lattice. The polar guest molecules are placed in all the larger cages. All calculations are performed with the periodic

boundary conditions, in which the basic cell is identical to the unit lattice of structure I hydrates. In order to examine the size effects of unit cell, we also perform a simulation for a system in which the basic cell contains the 8 unit lattices.

2.2 *Potential Model*

All the intermolecular interactions are described by a sum of Lennard-Jones and Coulomb pair potential function:

$$\phi = \sum_{i,j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{Z_i Z_j e^2}{r_{ij}}, \tag{1}$$

where i and j denote interaction sites, and the sum is taken over all the site-site pairs. For the water-water interaction, the TIP4P model [4] is adopted. The ethylamine model is the same as that we used in ref. 5 and has a degree of freedom of intramolecular rotation. The Lennard-Jones parameters between unlike sites are determined by the Lorentz-Berthelot rule. The original intermolecular potential functions are tapered by multiplying a switching function in order to avoid a discontinuity at the potential cutoff distance. The functional form of the switching function is given elsewhere [6]. The cutoff distance is equal to 8.655 Å which is half the lattice constant of a structure II hydrate.

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2.3 *Molecular Dynamics Simulation*

Molecular dynamics simulations of microcanonical ensemble are carried out in order to analyze the rearrangements of the hydrogen-bonded network of ethylamine clathrate hydrates. The equations of motion are solved numerically by the predictor-corrector method [7] with a time step of 0.4×10^{-15}s. The SHAKE algorithm [7] is used in treating the torsional motion of ethylamine guest molecules. Initial configurations are chosen of the potential energy local minimum structures that are obtained from an ideal host lattice encaging the guest molecules in all the larger cavities. The detailed method to obtain the local minimum structures is given in ref. 5. Long-time trajectories are required to obtain better statistics of the rearrangements. We calculated two trajectories of 10 ns after 100,000 time steps or more for equilibration: one is that following the 3 ns trajectory previously calculated in examining the kinetic stability of the ethylamine hydrates [5], and the other is that newly obtained from a different initial configuration. Temperatures are adjusted around 273 K. Both the trajectories shows the rearrangements of the host networks. Our analyses are made for the newly calculated trajectory.

3 CHARACTERISTICS IN FLUCTUATION OF THE POTENTIAL ENERGIES

First of all, we consider some time-dependent properties on the whole system. It is necessary to generate very long-time trajectory for the purpose mentioned above, because the potential energies of the water-water interaction and guest-water interaction show very long-time scale fluctuations. This means that the local structure of

the hydrate changes with very long period. In Figure 1, we plot the total potential energy of water-water interactions over 10 ns, which is coarse-grained by averaging over 50 ps in order to remove the shorter-time-scale fluctuations. The Figure shows the potential energy fluctuates with the time scale longer than 50 ps and that large fluctuations leading to higher energy states occurs, on average, about once a nano second. The calculated system has only 52 molecules in the basic cubic box and any local structural change in the fully hydrogen-bonded network system must be followed by a transition with a very high energy barrier compared to that in liquid water which is a partially-disconnected hydrogen-bonded system. Thus any structural change in this system is directly reflected on the potential energies of the whole system. Therefore, it is suggested from the fluctuation of the potential energy that the host structure changes with relatively long period by way of an energetically-unstable state, occasionally through very unstable one in which the host potential energies in the periods (an order of hundred pico second) are very high: more than 1 kJ/mol higher than the mean value. The corresponding potential energy at the local minimum is also plotted in Figure 1. All the values in local minimum structure are shifted in the figure upward by 5 kJ/mol as easily compared with the coarse-grained potential energy. The magnitude of the fluctuation is very large: difference between the maximum and minimum values is 3 kJ/mol. It shows that the host lattice structure encaging the polar guest loiters around energetically-unstable states other than fully hydrogen-bonded states.

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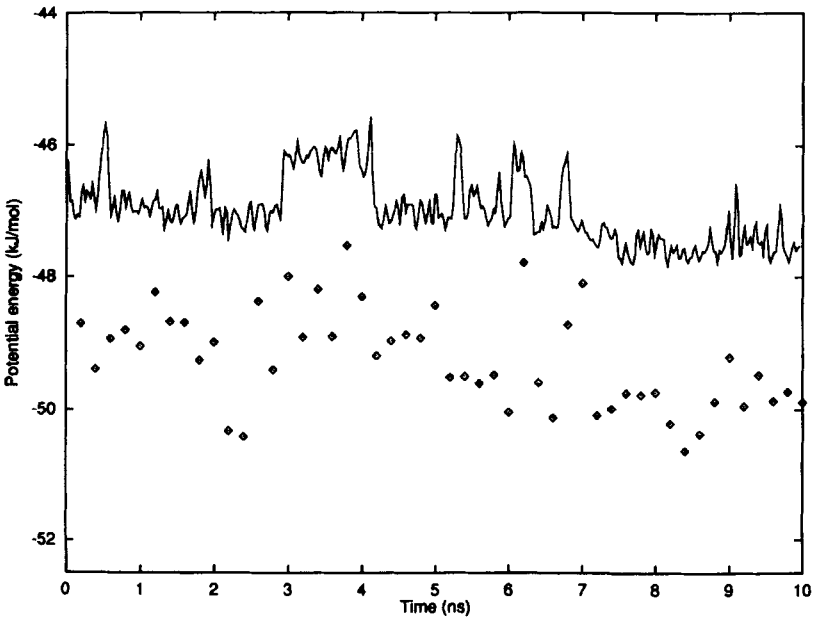

Figure 1 Long-time-scale fluctuations of the potential energies of the host lattice of the ethylamine clathrate hydrates (solid line) and those of the quenched structures (points). The 'host lattice' potential energies are a sum of water-water interactions divided by the number of water. The potential energies of the MD trajectory are coarse-grained over 50 ps in order to remove shorter-time-scale fluctuations. The potential energy of the quenched structure is shifted up by 5 kJ/mol.

In the polar-guest encaging clathrate hydrates, shift from stable to unstable states of the host lattice is accompanied by an increase in the guest-host attractive interaction as showin in Figure 2. Both in short-time scale (Figure 2(a)) and long-time scale (Figure 2(b)), the host potential energy peaks correspond to the guest-host potential wells.

4 REARRANGEMENTS OF THE HYDROGEN-BONDED NETWORK

The term, 'rearrangement of a hydrogen-bonded network', refers to change of the network connectivity. Any change of the connectivity is accompanied by changes of the hydrogen-bonding partners of a proton of water. It is suggested by diffusion coefficient measurements that the primary diffusing species in ices is not an ion, but an intact water molecule [9]. Therefore, our model and treatment can be justified even though rearrangement caused by any proton transfer is not included in our study. In the case of a fully hydrogen-bonded system, there exist two possible ways of rearrangement: (1) the connectivity changes with reorientational motion of water molecules but each water molecule stays in the original lattice site, and (2) some of water molecules move to different lattice sites by translational-jump motions. Note that the second case always accompanies reorientation of water.

We examine whether or not rearrangement of the second type accompanied by diffusional jumps of water molecules occurs during the total simulated time, 10 ns. This is simply done by examining one to one correspondence between lattice sites and water for all the local energy minimum structures separated by 200 ps. Three rearrangements followed by migration of water molecules are found. Two of them are simple exchange of two water molecules at two adjacent lattice sites, which is expressed as single transposition of labeled number of two water molecules. The other is complicated exchange and six water molecule are involved.

The first two rearrangements are completed within 200 ps, but the other takes long time, about 1 ns until the lattice structure recovers. These rearrangements are identified by the peaks of the host lattice potential energy in Figure 1: the peaks at 0.3 ns and 6.1 ns, and the peaks from 3 to 4 ns. Other distinct peaks show that the host network becomes energetically-unstable by some water molecules leaving their lattice sites but finally they return to the original sites.

In the present study, we divide the trajectory into ten blocks of 1 ns and analyze three of them: (1) 0–1 ns, (2) 6–7 ns, and (3) 9–10 ns. Rearrangement with migration of water molecules is involved in the first two; rearrangement is followed only by reorientation of water molecules in the last.

4.1 Rearrangements with Reorientation of Water

In order to find rearrangements of the hydrogen-bonded network only with reorientation of water, firstly, the connectivity of a proton disordered structure must be completely specified. One of the ways is to specify the hydrogen-bonding partner of each proton. Note that the partner of the proton is not necessary oxygen atom of water but may be nitrogen atom of the guest ethylamine. This is done by the

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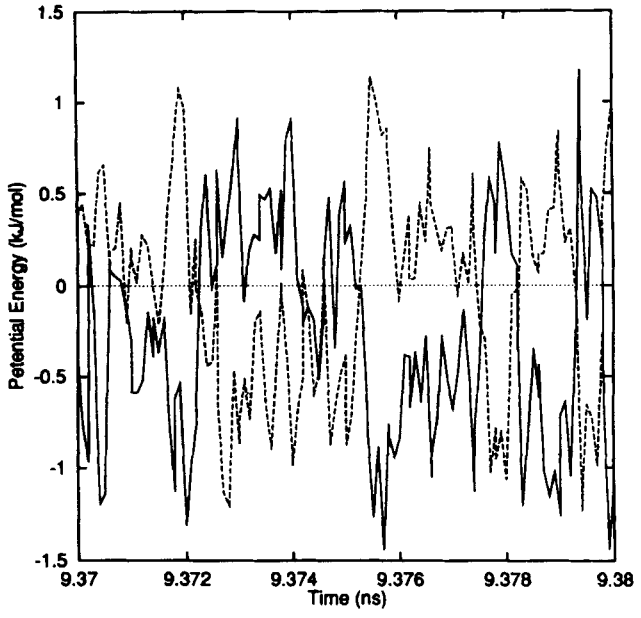

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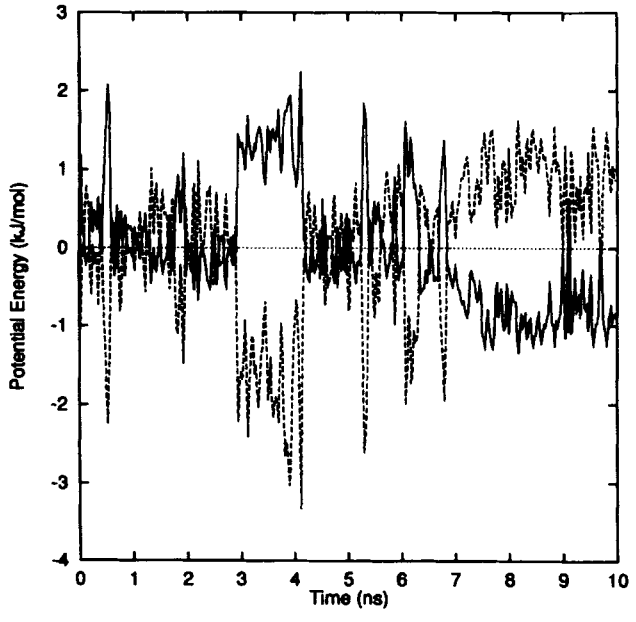

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Figure 2 Comparison of the host lattice potential energy, a sum of water-water interactions (solid line) and the guest-host potential energy, a sum of ethylamine-water interactions (dashed line) in different time scales: (a) short-time scale (10 ps) and (b) long-time scale (10 ns). The potential energies are plotted as the difference from the mean value divided by the standard deviation.

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following procedure: first we regard a pair of molecules as a hydrogen-bonded pair if the pair potential energy u_{ij} is lower than a threshold value u_{HB}, second any bifurcated hydrogen bond is eliminated by choosing a pair whose distance is the shortest among possible pairs of hydrogen and oxygen atoms. Connectivity of the host network does not change in the time scale of vibrational motions of water molecules around their lattice sites while thermal fluctuation in this time scale often induces partial disconnection of the hydrogen-bonded network. In order to discriminate rearrangement phenomena from defects in the network structure frequently induced by thermal fluctuation, we define a representative network connectivity as a pattern of connectivity which appears most frequently in a certain period. The period is set to 1 ps (2500 steps), and an atomic pair that forms a hydrogen bond with a highest probability is chosen as a representative pair in the period. The threshold value, u_{HB}, is -10 kJ/mol.

The analyses on the rearrangement followed only by reorientation of water are done for the last time region (9–10 ns). Figure 3 shows two examples of how protons of a water molecule change their hydrogen-bonding partners. The initial partners are labelled by W1, W2 and new partners by W3, W4,.. or G1, G2, where W and G refer to that the partner is a water molecule or a guest. A typical example of rearrangement is seen in Figure 3(a). The first three rearrangements are that two protons of a single water molecule exchange their hydrogen-bonding partners. That is, the water rotates 180° around the bisector of the HOH angle. This way of reorientation is only one which is possible to be accomplished without cooperative reorientation of neighboring water molecules. The proton also changes its partner to other water molecules (W3 and W4) but life time of the new hydrogen bond is very short and the proton recovers the hydrogen bond with one of the initial partners. Formation of hydrogen bonds between water and guest is displayed in Figure 3(b). However, the bonds are temporary ones and the hydrogen bond with the initial partner is recovered.

The hydrogen-bonded network of the polar-guest encaging hydrate is not always fully connected, but has some defects temporarily. To evaluate the degree of network connectivity, we define the defect number of the hydrogen-bonded network:

$$N_d(t_n) = \sum_i |n_i^{HB}(t_n) - 2|, \tag{2}$$

where n_i^{HB} denotes the number of protons of water hydrogen-bonded with the oxygen atom of i-th water molecule. The defect number over 1 ns is plotted in Figure 4. Accumulation of the time in which the hydrogen-bonded network of the unit lattice has at least one defect is 37.1%. Table 1 shows the distribution of the defect number. This indicates that four or less defects per unit lattice are mostly generated in the host network. The network structure with more defects is rarely observed but it appears in consecutive pattern.

Dynamics of the hydrogen-bonded network is examined by evaluating connectivity changes. Figure 5 shows the number of protons having a different partner from that at preceding point of time. There exist three characteristic peaks, which are separated by about 200 ps, other than many small peaks. In the host network,

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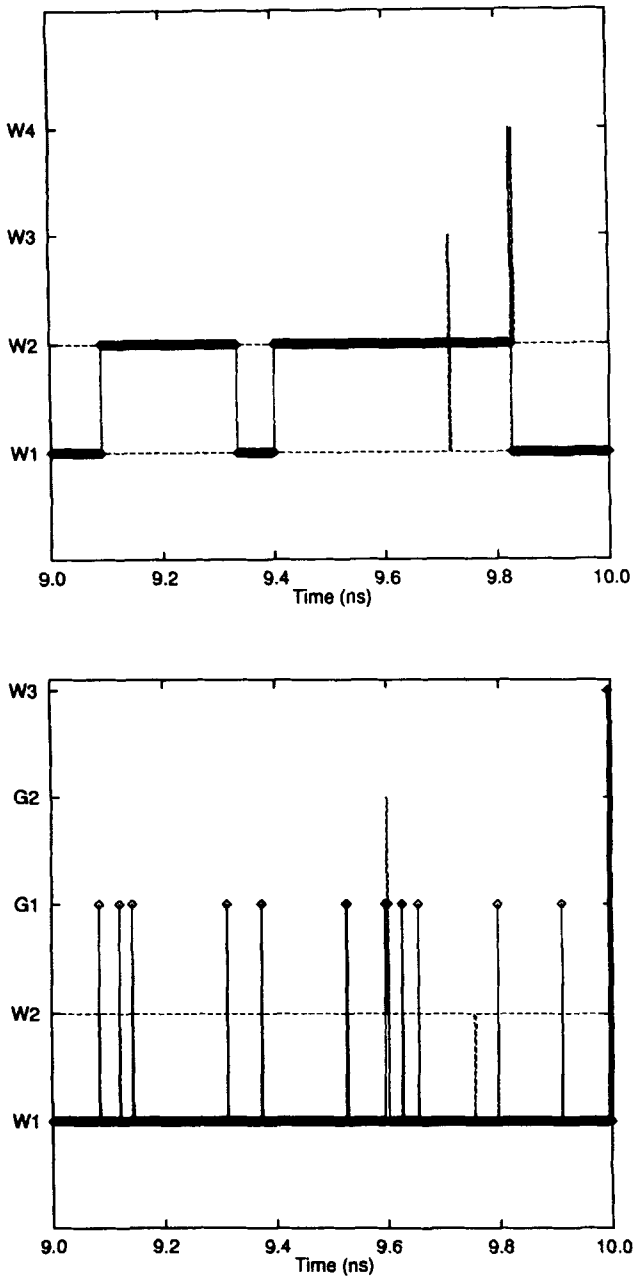

Figure 3 Time evolution of hydrogen-bonding partners of two protons of a water molecule over the time region (9–10 ns). Two typical examples are illustrated: (a) shows rearrangements that the two protons of a water molecule exchange the initial partners, and (b) displays that one of the protons temporarily forms a hydrogen bonds with guest molecules. The initial partners are labelled by W1, W2 and new ones by W3, W4,.. or G1, G2, where W and G refer to molecular species of the partner, water or guest. Definition of the hydrogen-bonding partner is described in the text.

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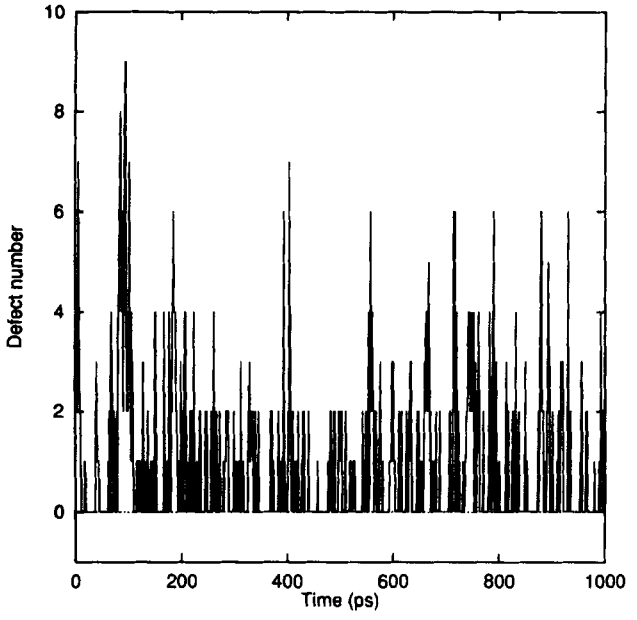

Figure 4 Defect number of the hydrogen-bonded network in the unit lattice over the time region (9–10 ns) in which the network rearranges only with reorientation of water.

Table 1 Distribution of the defect number in the hydrogen-bonded network for the time region in which rearrangements of the network are followed only by reorientation of water. The defect number is evaluated every 1 ps in the period of 1 ns by the definition in the text.

Defect number	0	1	2	3	4	5	6	7	8	9	10
%	62.9	11.0	14.7	4.0	5.0	0.4	1.1	0.5	0.2	0.2	0

about ten to twenty water molecules change their hydrogen-bonding partner simultaneously although it rarely occurs. Further more, it is found that the defect number at that time is not large, only one or two. That is, many water molecules change their partner in relatively short time (1 or 2 ps) under the condition that the hydrogen-bonded network has small number of defects.

A following picture is drawn from our analyses in the time region. The host network of the polar guest hydrates is often partially-disconnected and some of water molecules changes their hydrogen-bonding partners unsteadily during the period, but the ways of rearrangement finally realized are not complicated. Rearrangement is followed mostly by reorientation of single water molecule (single reorientation) and rarely by combination of the single reorientation. Note that there is no change in the proton disordered structure. This mechanism of reorientation of water molecules is different from that proposed by Bjerrum in which reorientation of a single water is impossible without cooperative reorientation of other water molecules.

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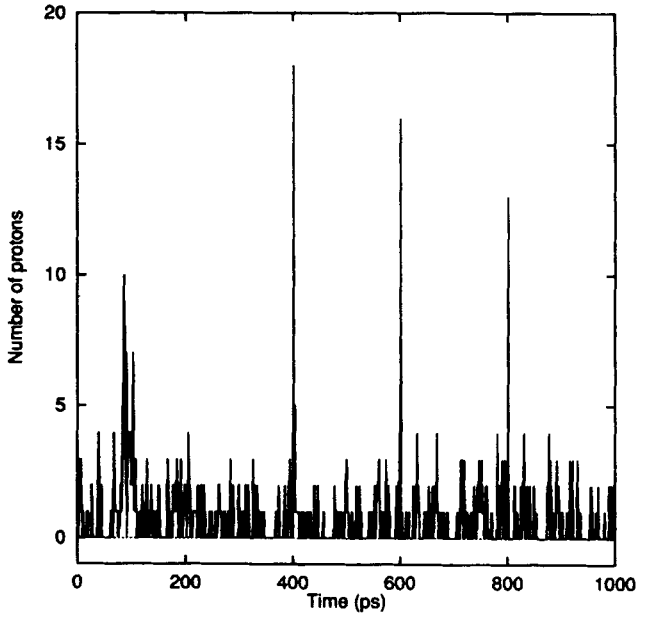

Figure 5 Number of protons that change their hydrogen-bonding partners in the unit lattice. The time region is the same as Figure 4.

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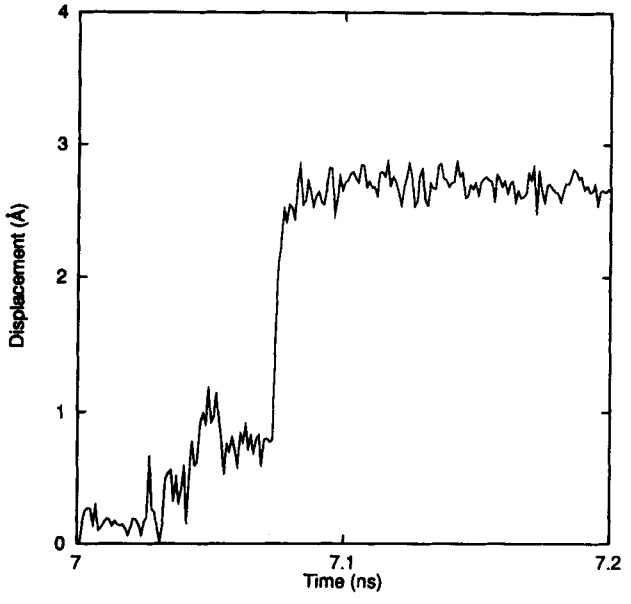
4.2 Rearrangement with Migration of Water

Three rearrangements followed by migration of water are found during 10 ns. Two of them, in which simple exchange of two water molecules occurs, are briefly analyzed.

Figure 6(a) and (b) show displacements of two exchanged water molecules from their initially-occupying lattice sites. Two water molecules migrate 3 Å and exchange their position in 5 ps. To examine cooperative motions of other water molecules, displacements of the nearest neighbor water molecules are plotted in Figure (c) and (d). The displacements due to cooperative motions are at most 2 Å. Displacements of the other four nearest neighbors are not as large as those which is chosen in Figure 6(c) and (d). Two displacements which exhibit the strongest correlations with the exchange of the two water molecules are found in Figure 6(e) and (f). Two water molecules which cooperate most strongly with the exchanged water are those located at next nearest lattice sites. That is, the water molecules and the exchanged ones are not directly hydrogen-bonded but share an intermediate water by bridging.

Very long time is required until the fully hydrogen-bonded network is restored from a partially-disconnected structure when the rearrangement with migration of water molecules occurs. Both in the case of the two rearrangements, the required time is about 70 ps while exchange of their position is completed in a few pico seconds. This is because exchange of two adjacent water molecules requires large scale rearrangement followed by reorientation of other water molecules. We examine how many water molecules shows reorientation after the rearrangements with



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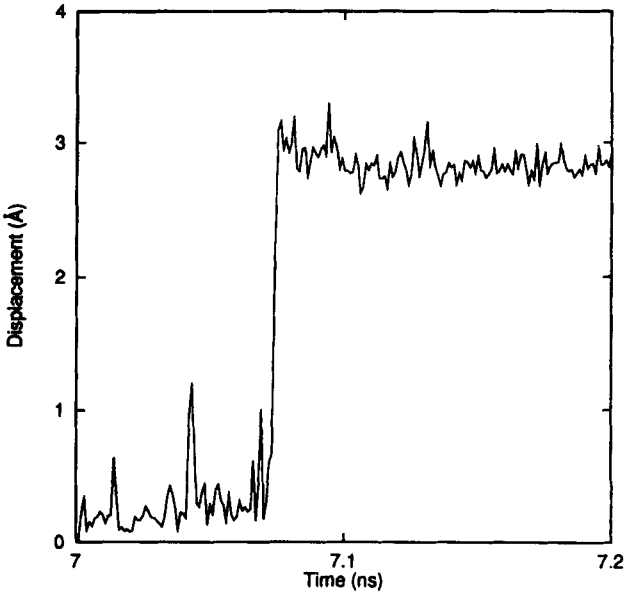

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Figure 6

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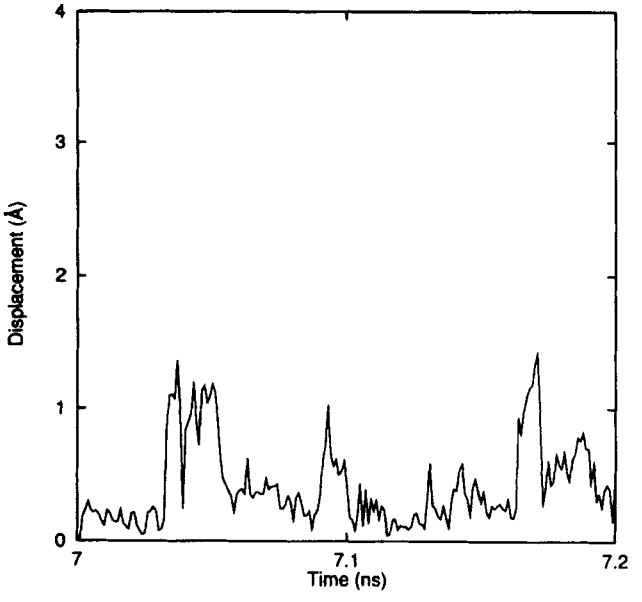

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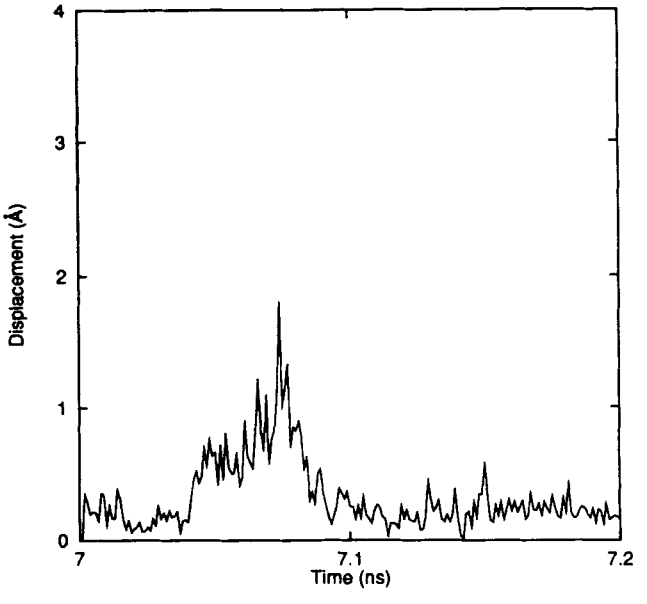

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Figure 6

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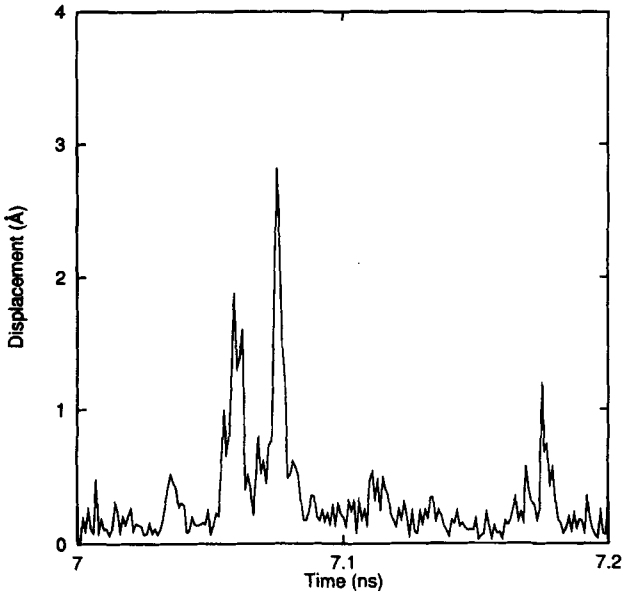

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Figure 6 Displacements of the water molecules from their initial positions: (a)(b) the two exchanged water molecules, (c)(d) the two nearest-neighbor water molecules, and (e)(f) the water molecules which show correlated motion most strongly with the exchanged water.

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migration of water. It is ten and fifteen water molecules that make reorientational motion in the two different rearrangements with migration of water. The ways of reorientation are very complicated in contrast to that in the rearrangement followed only by reorientation of water. These results indicate that rearrangement with migration of water in the polar guest clathrate hydrates is necessarily accompanied by reorientation of many water molecules.

4.3 Correlation Function of the Reorientational Motion of Water

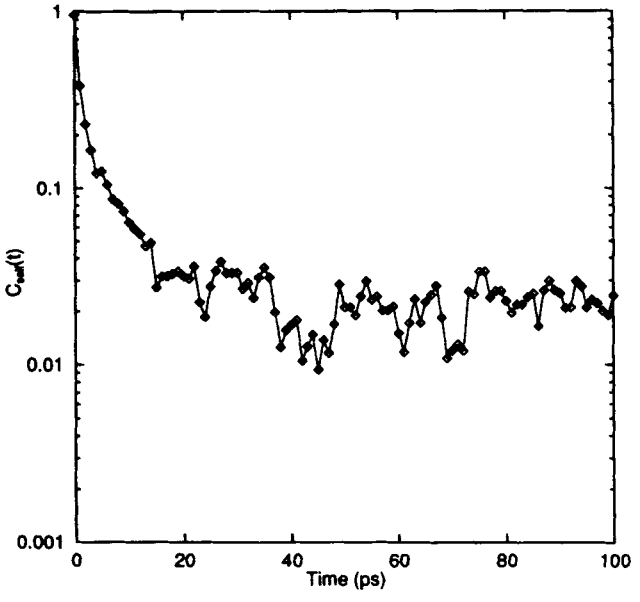
We examine correlation between the events that a water molecule changes the hydrogen-bonding partner. Since the events are accompanied by reorientation of the water molecule, the correlation function is closely related to that of dielectric relaxation process. The autocorrelation functions are defined by,

$$C_{\text{self}}(t_m) = \left\langle \sum_i A_i(t_n + t_m) A_i(t_n) \right\rangle \tag{3}$$

where

$$A_i(t_n) = \begin{cases} 1 & \text{if } j_i(t_n) \neq j_i(t_{n-1}) \\ 0 & \text{if } j_i(t_n) = j_i(t_{n-1}) \end{cases} \tag{4}$$

and $j_i(t_n)$ denotes number labeled on the hydrogen-bonding partner of i-th proton, at $t = t_n$. The correlation function in the time region (3) is plotted by semi-log and log-log scale in Figure 7(a) and (b). These indicate the correlation do not decay exponentially but rather with power of time. The correlation functions calculated



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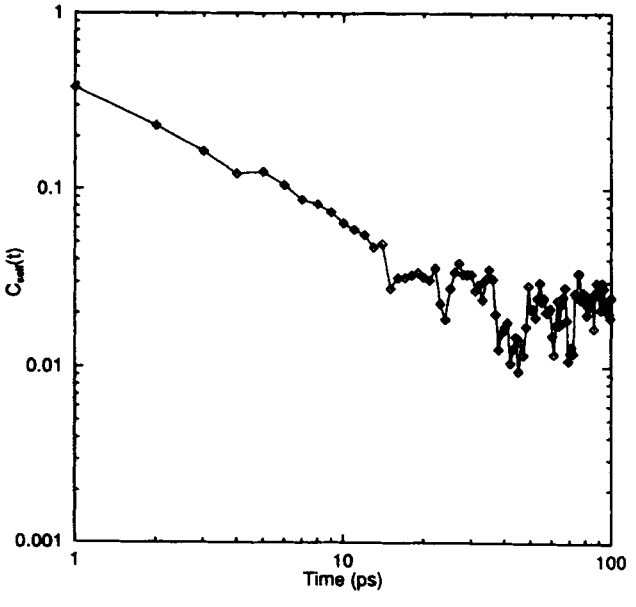

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Figure 7 Correlation function of reorientational motion of water, plotted in semi-log scale (a) and log-log scale (b). Definition of the correlation function is described in the text.

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for other two time regions also show the same decay pattern. The power-law behavior of the correlation function, which is known to be a characteristic of anomalous relaxation process, suggests a different mechanism of rearrangement of the host network encaging amine from that of ice or apolar hydrates. The detailed mechanism of the rearrangement process of the amine hydrate will be studied in future work.

5 SUMMARY

Rearrangement of the hydrogen-bonded network of clathrate hydrate of the polar guest ethylamine has been studied by the molecular dynamics simulation. The rearrangement with no migration of water is mostly accompanied by reorientation of single water molecule although other neighboring water molecules change their hydrogen-bonding partner unsteadily until the rearrangement is completed. Many water molecules rarely exhibit reorientational motion in the host network and in most case each reorientation is an event which is possible to happen independently unlike the mechanism in ice proposed by Bjerrum. Migration of water molecules occurs with much less chance than reorientation. Very long time is required to complete rearrangement with migration of water because cooperative reorientation of many water molecules is accompanied. Correlation between events that water changes the hydrogen-bonding partner does not decay exponentially but rather with power-law behavior as seen in anomalous relaxation process. This peculiar property will be studied in future work.

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