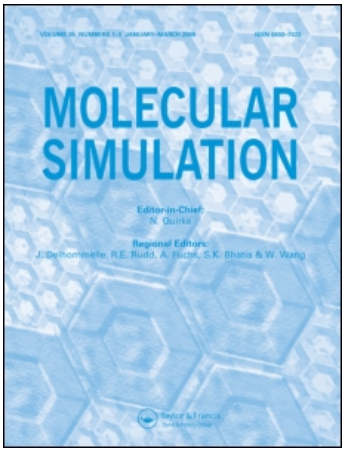

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Molecular Dynamics Studies on Molten Alkali Hydroxides. III. One-particle Dynamics of Ions in Molten LiOH

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MOLECULAR DYNAMICS STUDIES ON MOLTEN ALKALI HYDROXIDES. III. ONE-PARTICLE DYNAMICS OF IONS IN MOLTEN LiOH

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One-particle dynamics of Li^+ and OH^- ions has been investigated by analysing ion trajectories calculated by molecular dynamics simulation of molten LiOH. Direct observation of ionic motions has elucidated that reorientational motion of OH^- ion possesses a strong correlation with the translational motion of the surrounding Li^+ ions. Significantly large forces or torques could not be found just before the large displacement or the reorientation of the ions. The energy fluctuation of the particle was very large and frequent. The potential energy fluctuation, which is a few tens of times larger than the kinetic energy fluctuation, seems to play an important role as the trigger of the large displacement and reorientational motion.

KEY WORDS: Molecular dynamics, molten salt, translation, rotation, fluctuation

1. INTRODUCTION

The structure and dynamics of strongly interacting coulombic liquids have been one of the most attractive topics in liquid chemistry and physics [1]. We have reported theoretical [2–4] and experimental [5–7] investigations for molten alkali hydroxides from the special interest in the physical properties of simple polyatomic OH^- ions [3]. They comprise *ab initio* molecular orbital (MO) calculation [2], molecular dynamics (MD) simulation [3, 4], electromigration [5], Raman scattering [6] and neutron diffraction [7] measurements.

Among various methods for microscopic investigations of liquids, molecular dynamics is one of the most powerful. One of the advantageous points of molecular dynamics simulation, which could not be achieved by usual experiments, is that properties of individual particles and their surroundings can easily be investigated. Molecular dynamics calculations of molten LiOH concerning its averaged static [3] and dynamic [4] properties have already been reported in a series of papers.

With regard to the rotational motion of OH^- ion, the following characteristics were elucidated from a study of MD simulation combined with polarized and depolarized Raman spectroscopy: (i) the rotational autocorrelation function of OH^- ion comprises oscillatory rapid decay at small t, where t represents time, and relatively slow exponential decay at large t, which can be related to very frequent libration and less frequent reorientation of the ion, respectively [4, 6], (ii) the decay rate of the latter shows a good correlation with that of the structural relaxation expressed in terms of the Li–O and O–O distinct parts of van Hove functions [4]. However, the correlation

between the reorientational and structural relaxations have not yet been corroborated.

In the present work, this correlation has been examined by direct observation of perspective pictures for ion trajectories. Time evolution of physical properties of some individual ions such as kinetic and potential energies, force, and torque is discussed. The energy fluctuation of the particles in this system is also studied. It will be compared with that of the H-bonded water by Ohmine's group [8].

2. CALCULATION

Standard molecular dynamics was performed in the NVE ensemble, where number of ions $N = 512$ (256 Li^+ ions + 256 OH^- ions) and density $d = 1.361\,g\,cm^{-3}$ (side length of the basic cell $L = 19.557$ Å). The MO based potential function was revised to satisfactorily reproduce some physical properties experimentally obtained [3]. Step time was 0.25 fs and totally 20,000 steps were generated. The averaged temperature was 767 K. In the present study, the last 4,000 steps were analysed to obtain various one-particle functions. Details of the calculation were presented in the previous paper [3].

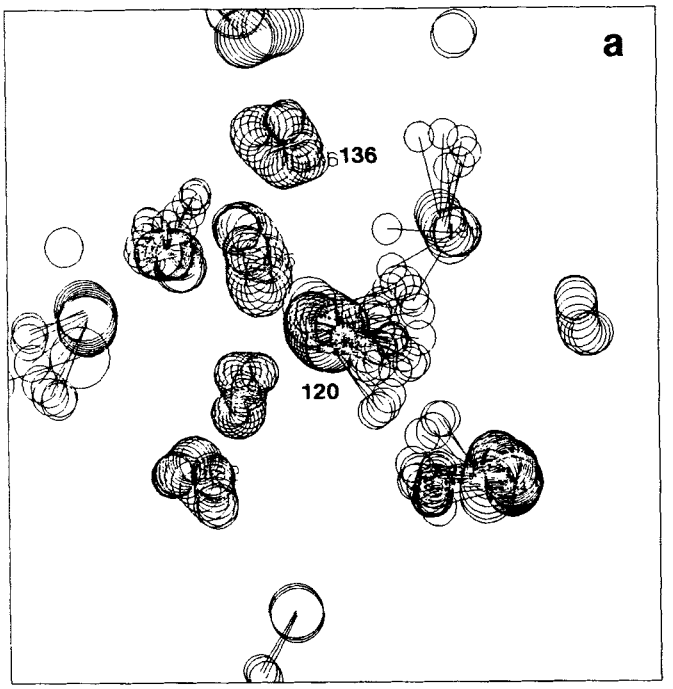

Figure 1 (*See* colour plate I) Perspectives of ionic motion of Li^+ (green) and OH^- (O: white and H: red) ions. An OH^- ion was initially located at the center. The surrounding ions within 3.2 Å from the central OH^- ion were pictured. Trajectories were drawn every 5 fs and the total duration was 0.15 ps. The radii of the ions are reduced for clarity of the pictures. The central ion is (a) No. 120.

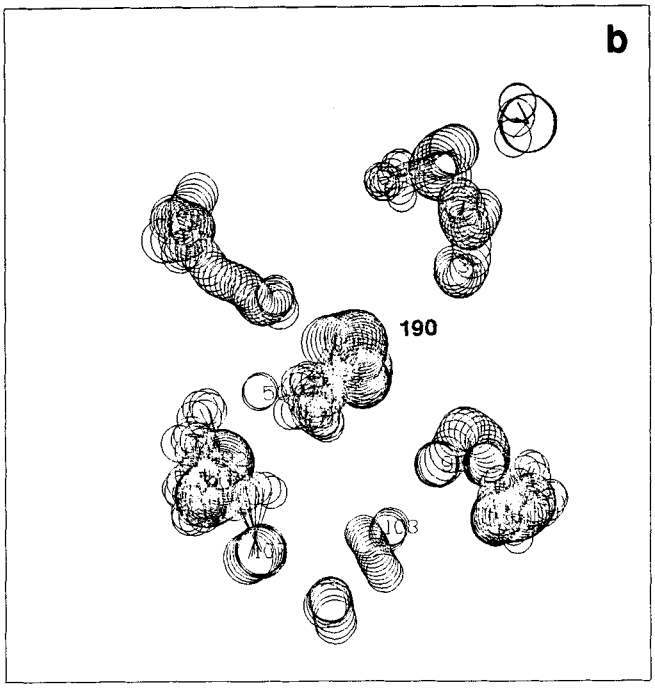

Figure 1 (*Continued*) (*See* colour plate I) (b) The central ion is No. 190.

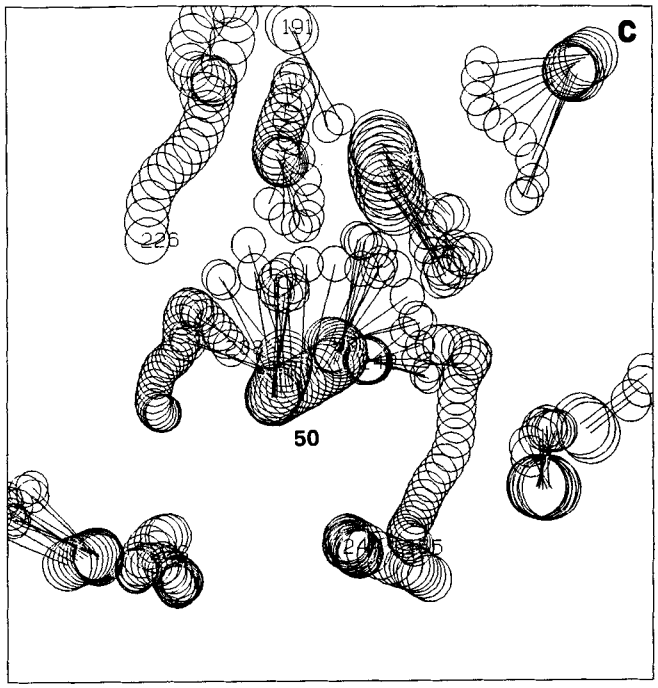

Figure 1 (*Continued*) (*See* colour plate II) (c) The central ion is No. 50.

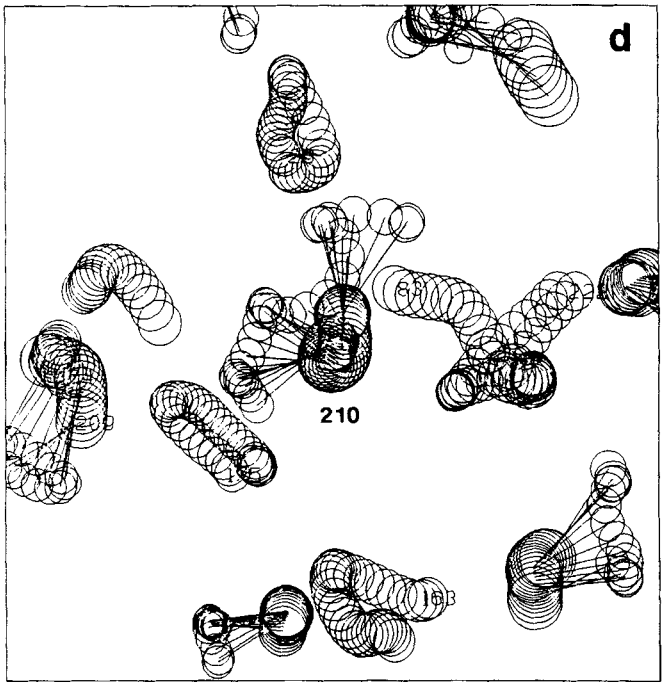

Figure 1 (*Continued*) (*See* colour plate II) (d) The central ion is No. 210.

3. RESULTS AND DISCUSSION

In the previous papers [4, 6], it was elucidated that OH^- ion always librates with the period of 40 ~ 50 fs and sometimes reorientates to a large extent, and that the reorientational relaxation rate at large t is in good agreement with the structural relaxation rate defined by the Li–O and O–O distinct part of van Hove functions. It is thus very interesting to examine motions of the surrounding ions around the librating or reorientating OH^- ion. For this purpose, direct observation of the motions should be very informative. Some perspectives of the trajectories of ions are presented in Figure 1; oxygen atom of an OH^- ion was initially located at the center and the ions within 3.2 Å (the first minimum position of $g_{LiO}(r)$) from the central OH^- ion are included in the pictures. Stroboscopic lamp was flashed at every 5 fs and the total duration of the pictured motion was 0.15 ps (every 20 steps from 16,200th to 16,800th step).

Motions of central OH^- ions No. 120 and 190 in Figures 1(a) and 1(b), respectively, are gentle. They oscillate around a limited area and librate around a slowly reorientating axis. On the other hand, Figures 1(c) and 1(d) show examples for largely translating and reorientating ions. Central OH^- ion No. 50 in Figure 1(c) reorients as well as translates largely. Ion No. 210 in Figure 1(d) reorients but does not translate so much. When the motion of the central OH^- ion is constrained (Figure 1(a) and 1(b)), the surrounding OH^- ions do not translate or rotate, although the Li^+ ions are slightly mobile. The local structure around the central ion is likely to remain nearly unchanged during the libration. It is also clearly shown in Figure 1(a) that four Li^+ ions coordinate just on the O atom side of the central OH^- ion and OH^- ions face

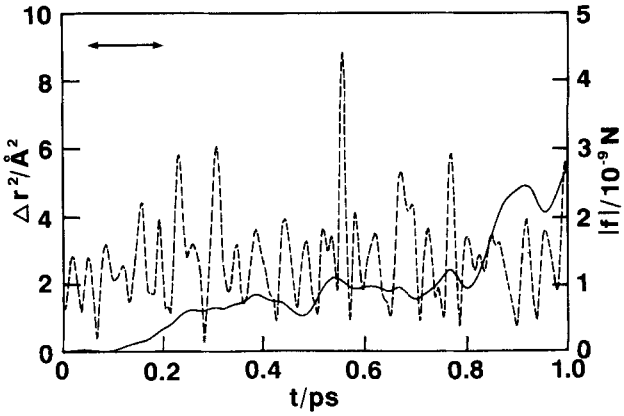

Figure 2 One-particle square displacement $\Delta \mathbf{r}(t)^2$ (solid line) of OH^- ion (No. 210) and force $|\mathbf{f}(t)|$ (broken line) acting on the ion.

each other with their H atoms to form a layered structure in the liquid. This aspect is in good agreement with that of the crystal [3]. This perspective depicts well the structural feature which was elucidated by various structural functions in the previous paper [3]. On the other hand, when the central OH^- ion translates and reorientates, the surrounding Li^+ ions largely translate and the local structure around the OH^- ion is fairly broken as shown in Figure 1(c). Even when only reorientation takes place (Figure 1(d)), the surrounding Li^+ ion moves to a large extent, too. Reorientation and translation of the OH^- ion always cause structural rearrangement of the surrounding Li^+ ions. In other words, the OH^- ion cannot rotate without any breakdown of the coordinating structure of the surrounding Li^+ ions. The correlation between reorientational and structural relaxation is thus clearly revealed.

One-particle square displacement $\Delta \mathbf{r}(t)^2$ and rotational angle $\theta(t)$ formed by the C_∞ symmetry axis at $t = 0$ and $t = t$ are presented in Figures 2 and 3, respectively, for

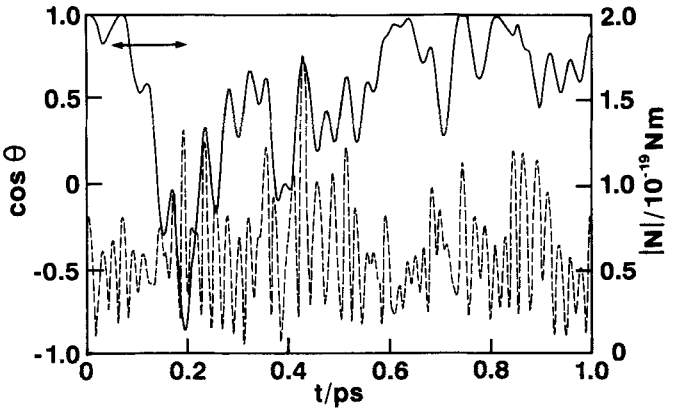

Figure 3 One-particle rotational angle $\theta(t)$ (solid line) of OH^- ion (No. 210) and torque $|\mathbf{N}(t)|$ (broken line) acting on the ion.

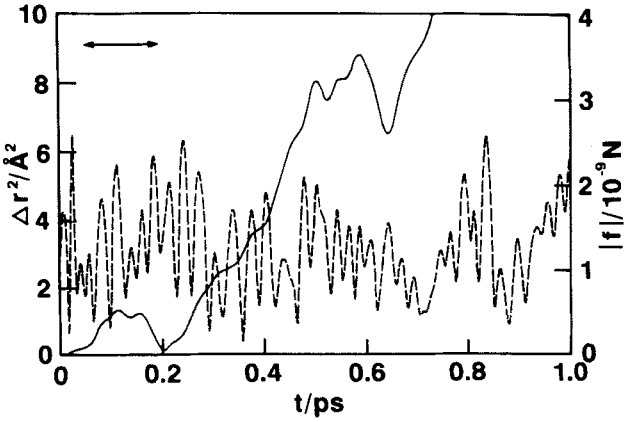

Figure 4 One-particle square displacement $\Delta \mathbf{r}(t)^2$ (solid line) of Li^+ ion (No. 136) and force $|\mathbf{f}(t)|$ (broken line) acting on the ion.

OH^- ion No. 210. The ion is the same with that presented in Figure 1(d) and the duration corresponding to the pictured motion is indicated by the arrow in the figure. The function $\Delta \mathbf{r}(t)^2$ is also given in Figure 4 for Li^+ ion No. 136, which is a member of the surrounding Li^+ ions around OH^- ion No. 120 in Figure 1(a). Both the ions take discrete jumping rather than small step continuous translation, although the jump is not so definite as that in solid electrolytes [9–11]. For example, OH^- ion monitored in Figure 2 is displaced by about 1 Å from $t \approx 0.1$ ps to $t \approx 0.25$ ps after the oscillation around the original position, again oscillates at a new site for as long as 0.6 ps, and restarts further translation at $t \approx 0.8$ ps. The feature is similar to the reorientational motion of OH^- ion. Figure 3 shows that ion No. 210 suddenly reorientates from $t \approx 0.1$ ps to $t \approx 0.3$ ps. Except for this duration, it librates around a slowly reorientating axis.

It is interesting to elucidate the trigger of these sudden and large motions of the ions. Force $|\mathbf{f}(t)|$ and torque $|\mathbf{N}(t)|$ acting on the OH^- ion (No. 210) are plotted in Figure 2 and 3, respectively. In Figure 4, the force is also plotted for Li^+ ion No. 136. The torque is oscillating all the time owing to its libration. The frequency is about twice that of the libration since the absolute value of the torque is plotted in this figure. The force has also oscillatory character. Significantly large force or torque was not observed, however, just before the large displacement or reorientation shown in Figures 2, 3, and 4. These were the case with all the motional events monitored in the simulation. Furthermore, as will be described later, the feature is similar to the case of kinetic energy of the ions. Thus, the large displacement and reorientation of the ions is independent, in appearance, of such properties as the force, torque, and kinetic energy. The field itself may change so that the ion is free to move. This will be discussed below in more detail in relation to the energy fluctuation.

One-particle kinetic energies E_K and potential energy E_P are presented in Figures 5 and 6 for the OH^- ion No. 210 and the Li^+ ion No. 136, respectively, for the same duration. Translational and rotational energies were calculated by

$$E_T = \tfrac{1}{3} \cdot \tfrac{1}{2} m|\mathbf{v}(t)^2| \quad (1)$$

$$E_R = \tfrac{1}{2} \cdot \tfrac{1}{2} I|\boldsymbol{\omega}(t)^2| \quad (2)$$

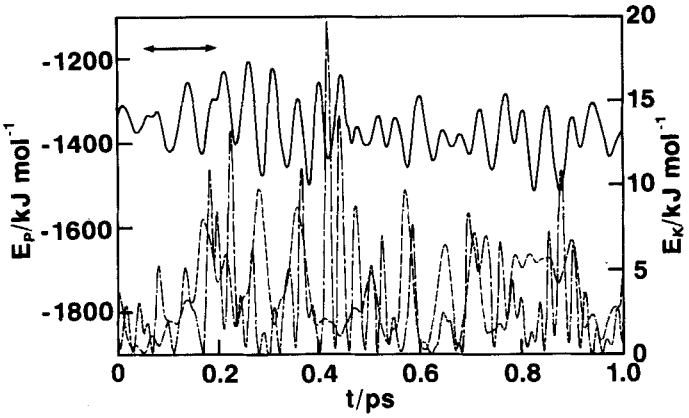

Figure 5 Kinetic and potential (solid line) energy fluctuations of OH^- ion (No. 210). Translational (broken line) and rotational (dash-dotted line) energies are reduced to those of one degree of freedom.

respectively, so that they correspond to kinetic energy of one degree of freedom; m, I, $\mathbf{v}(t)$, and $\omega(t)$ are the mass, moment of inertia, velocity, and angular velocity, respectively. Potential energy E_P of particle i is calculated according to

$$E_P = \sum_j V_{ij}, \tag{3}$$

where V_{ij} is interionic potential function between particle i and j. The energy value defined by Equation (3) is just twice the ordinary potential energy. Total energy ($E_P + E_T + E_R$) was almost the same as E_P, because E_P was much larger than those of E_T or E_R, as will be described below. For this reason, the total energy is not presented here.

Interionic potential energy fluctuation might be coupled with intraionic vibration of OH^- ion in real system. On the present stage of simulation technique, however, such quantum dynamics cannot be easily handled in addition to much complexity and/or ambiguity of the intraionic potential function in condensed phase [2]. Internal

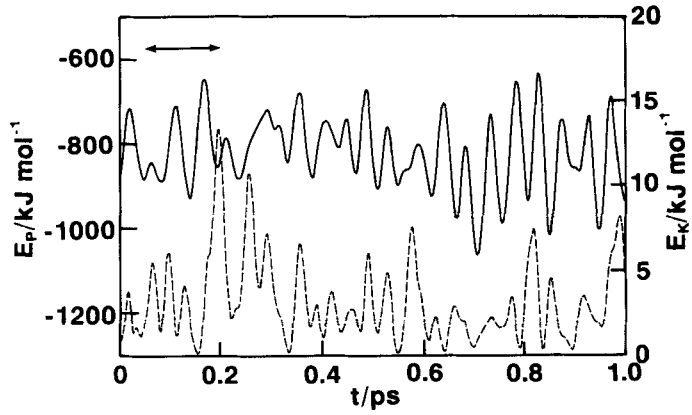

Figure 6 Kinetic (broken line) and potential (solid line) energy fluctuations of Li^+ ion (No. 136). Translational energy is reduced to that for one degree of freedom.

degree of freedom was not included in the present calculation because of much difficulty stated above. The energy fluctuations discussed below thus neglect the coupling with the intraionic vibration.

Kinetic energy fluctuation is large relative to the averaged kinetic energy (ca. 3.2 kJ mol^{-1}). It often takes values which are several times greater than the averaged value. Amplitude of the fluctuation is in the order, OH^- (rotation) > Li^+ > OH^- (translation). This may be caused by the difference in the inertial constant among them. Frequency of the fluctuation of rotational kinetic energy (Figure 5) is about twice that of the libration (Figure 3), because the frequency of kinetic energy corresponds to that of $\omega(t)^2$.

Potential energy fluctuation of OH^- ion is very large. The standard deviation was 61 kJ mol^{-1}. This is, for example, seventeen times greater than that for water [8]. Furthermore, the period is as small as $40 \sim 50$ fs ($700 \sim 800$ cm^{-1}), which implies that the potential energy fluctuation mainly originates from the libration of OH^- ions. In this period, the ions cover a wide range of potential energy which is nearly equal to the full width of the ensemble averaged energy distribution. This indicates that, in this ionic melt, there are no distinguishable energy states which have been found for hydrogen bonding in water [8, 12]. The potential energy fluctuation of an Li^+ ion is as large as that of an OH^- ion. The frequency of the fluctuation of Li^+ ion, which is $700 \sim 800$ cm^{-1}, is nearly equal to that of OH^- ion. It is worth noting here that the frequencies of these potential and kinetic energy fluctuations in this system are roughly similar to those of water [8], although the temperature of the former is about 2.5 times higher than that of the latter. On the other hand, the frequency of the translational oscillation of Li^+ ion is $150 \sim 200$ cm^{-1} [4]. This suggests that the energy fluctuation of an Li^+ ion may correspond to the potential field fluctuation due to the libration of the surrounding OH^- ions and not originate from its own motion alone.

This large fluctuation of the potential energy or the potential field may be responsible for the large and sudden displacement and reorientation of the ions. As described above, any direct trigger could not be observed in properties of the moving ions such as force, torque, and kinetic energy. This can be understood by recognizing that the kinetic energy is only a few percent of the potential energy fluctuations. The ion can largely translate or reorientate only when the potential wall instantaneously decreases so that it can be easily overcome with their small kinetic energy [10]. This condition can be fulfilled statistically in the fluctuation of the field, which is caused even by small structural change of the coordination sphere. In this aspect, the large displacement and reorientation belong to collective properties of the liquid.

As seen from Figures 5 and 6, the change in the amplitude is found in the potential energy fluctuation. The period is $0.2 \sim 0.3$ ps, which corresponds to wave number difference of $100 \sim 150$ cm^{-1}. However, there are not two isolated peaks near the above stated range of $700 \sim 800$ cm^{-1} in the spectra of the autocorrelation functions so far investigated [4]. Thus, it is more reasonable to consider that the environment of the ions itself changes on this time scale than to attribute it to a superposition of two different waves. In this case, time evolution of electric field caused by the relative motion of the neighboring ions is crucial.

4. CONCLUSION

Interesting ion dynamics have been elucidated by direct observation of motions and

the relevant properties of the individual ions. While OH^- ion reorientates, the surrounding ions show large motions and the structural rearrangement takes place. Significantly large forces or torques were not found, however, just before such events as large displacements and reorientations of the ions. The potential energy fluctuation is very large and very frequent. The one-particle potential energy covers in $40 \sim 50$ fs a very wide range which is equivalent to the whole width of the ensemble-averaged energy distribution. This potential energy or potential field fluctuation is much larger than the kinetic energy fluctuation. It plays thus an important role as the trigger of large displacement and reorientation of the ions.

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