Bull. Chem. Soc. Jpn. Vol. 79, No. 3, 397–405 (2006)

Theoretical Studies on the Li$^+$ Ion Hydration System by the Molecular Dynamics Simulations with Ab Initio IMiC MO Method

Shoji Morita and Shogo Sakai*

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193

Received July 1, 2005; E-mail: sakai@apchem.gifu-u.ac.jp

Molecular dynamics simulations for a lithium cation surrounded with 100 water molecules as a solvent were carried out by using an ab initio integrated multicenter molecular orbitals method (IMiC MO) with HF/6-31G(d,p) level. For the temperature of both 293 and 323 K, the first hydration shell of the lithium cation is preferred to form a tetrahedral structure including four water molecules, and is well separated from the outer hydration shell. The mechanisms for the variation of the coordination number and the exchange of solvent molecules between the first and the second hydration shells were also studied.

The aqueous hydration of metal cations plays an important role in biology and medicine that are related to the ion channel of cell membranes. Especially, the structural properties of the first hydration shell of the lithium cation have been studied by many theoretical and experimental chemists. However, even the coordination number of the first hydration shell of the lithium cation has not yet been clarified.

Neilson and co-workers[1] made neutron diffraction measurements on 1.0–14.0 molal aqueous LiCl solutions. They reported that the coordination number of the first hydration shell of the lithium cation is 6.5 at 1.0 mol kg^{-1} and it lowers to a value of 3.2 with increasing the LiCl concentration. However, the concentration dependence[2] of the hydration number of lithium cation is not established quantitatively. Randai and co-workers[3] reported that an octahedral arrangement with six water molecules in the first hydration shell of the lithium cation was predicted by X-ray measurements, but other X-ray measurements on similar aqueous solutions carried out by Yamaguchi and co-workers[4] indicated the coordination number of 4 for the lithium cation. Michaelian and Moskovits[5] measured Ramam spectra of LiCl solutions of several concentrations and predicted a tetrahedral structure with four water molecules in the first hydration shell of the lithium cation.

On the other hand, Glendening and Feller[6] calculated theoretically the electronic structures for small clusters including a lithium cation and six water molecules by the ab initio MO method, and reported that the structure with a coordination number of 4 has lower energy than that with a coordination number of 6. Bischof and co-workers[7] performed ab initio quantum mechanical molecular dynamics simulations for one lithium cation with 6 to 12 water molecules, and reported that all initial structures converge to a structure with a coordination number of 4 in the first hydration shell. Tongraar and co-workers[8] also studied the structure properties of the first hydration shell of a lithium cation system including 199 water molecules by molecular dynamics simulations with the quantum mechanics/molecular mechanics (QM/MM) method (Hartree–Fock/LANL2DZ method for the Li atom). For the molecular dynamics simulation, a tetrahedral structure with four water molecules was found in the first hydration shell. The above theoretical studies were performed only for small water clusters or conducted by the QM/MM method including empirical parameters. The use of QM/MM methods for trajectory calculations presents important problems from a theoretical viewpoint in that the accuracy of QM/MM methods does not hold during molecular movement. To determine finally the coordination number of the first hydration shell of metal cations, molecular dynamics calculations with the full QM level are important.

Recently, we have proposed a new method,[9] the integrated multicenter molecular orbital method (IMiC MO), for molecular dynamics (MD) calculations in solvent cluster systems with the full QM level. The IMiC MO method was developed as a method to perform geometry optimization and MD simulation for a large solvent cluster system with the full ab initio MO level, and treates all parts in the system with equivalent accuracy.

In this study, we first tested the accuracy of the IMiC MO method for a Li$^+$ small hydration system (including 15 water molecules), and performed ab initio molecular orbital MD calculations for the system of a lithium cation including 100 water molecules as the solvent by the IMiC MO method. From the analysis of the computational results of the MD simulations, the average hydration number of four is found in the first hydration shell of the lithium cation. The exchange process of the water molecules between the first and the second hydration shells was also studied.

Theoretical Method

For calculations of molecular dynamics, the force of each atom in the object system was determined by the IMiC MO method. The IMiC MO method is a new technique for calculating the force of each atom in a system, including molecules such as solvents, and is described in our previous paper.[9] In brief, the method is described as follows: This method divides the entire system into units of molecules, and calculates the force of each atom in the unit. To reduce the number of orbitals to allow the system to be resolved by a single quantum mechanics (QM) method, the system is divided into three regions:

Published on the web March 8, 2006; DOI 10.1246/bcsj.79.397

the molecule for which the force is calculated (target molecule), the region of molecules surrounding the target molecule (adjacent molecular region), and all other molecules (environment molecular region). The target molecule and molecules belonging to the adjacent molecular region are treated by QM, and molecules belonging to the environment molecular region are included in the electrostatic field calculation as a point-charge approximation. The force of each atom in the system is evaluated by repeating this process for all molecules.

In this study, the covalent bond radii of each atom, which are needed in the step of dividing the entire system into the units of molecules, are chosen from the natural bond lengths of the molecular mechanics called universal force field (UFF).[10] The evaluation of each point charge, which is centered on each atom, was performed by Mulliken population analysis.[11]

The system treated by MD simulation is one lithium cation and 100 water molecules as the solvent. The equation of motion was solved by the velocity-Verlet algorithm[12] for each time step of 0.48 fs under the conditions of the temperature of 293 and 323 K. For the simulations under the condition of constant temperature, Woodcock's velocity scaling method[13] was used. The MD simulations started from different initial configurations, and velocities were performed 10 times for each temperature. The total time for each MD simulation was 1.48 ps, and the geometrical parameters used for analysis of the simulation results were obtained for periods of 1.0 ps, 0.48 ps after the starting of MD simulation. The initial conformation in the systems for MD simulations were generated by Monte Carlo calculations with the MM force fields, in which the positions of each water molecule was moved around the lithium atom constrained at the center of system. Namely, one million steps of the Monte Carlo simulations were performed, and the stabilization of the potential energy was confirmed at each temperature. All QM calculations to evaluate the force and point charge were performed at HF/6-31G(d,p)[14–16] level with the Gaussian98 program.[17]

Results and Discussion

To evaluate the accuracy of the IMiC MO method for the system including a Li cation and water molecules, the geometry parameters of the Li cation plus 15 water molecules were obtained by the IMiC MO method at HF/6-31G(d,p) and by the full ab initio MO method at HF/6-31G(d,p). The correlation between the interatomic distances obtained by both methods is shown in Fig. 1. From the figure, it can be seen that the geometry parameters obtained by the IMiC MO method exhibit excellent correspondence with those by the full ab initio MO method.

Conformation and Distribution of Water Molecules. The distribution probability of coordination numbers and the average lifetimes for the first hydration shell of lithium cation systems including 100 water molecules at the temperatures of 293 and 323 K are listed in Table 1. The radius of the first hydration shell in this study was defined as under 3.0 Å for the distance between Li and O atoms from the results of the radial distribution function $g_{\text{Li–O}}(r)$, as discussed later. From the table, the distribution probability of the hydration number 4 dominates over 90% during the MD simulation, and decreased by about 2% with increasing the temperature. The distribution probability of the hydration number 3 and 5 were only 3.3 and 1.1% at 293 K and 0 and 6.7% at 323 K, respectively. A more interesting point of the difference between both temperatures is that the probability of the hydration number 3 disappears at 323 K, whereas the probability of the hydration number 5 increases with increasing the temperature. The hydration number 6 had below 0.4% for the distribution probability, and could be found only for a very short period just after the starting of monitoring in the MD simulation at the temperature of 293 K.

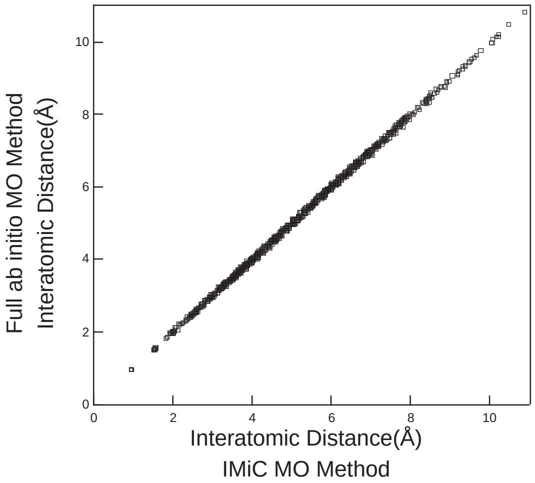


Fig. 1. Interatomic distances of $Li^+(H_2O)_{15}$ obtained by the IMiC MO method against those by the full ab initio MO method.

Table 1. Distributions of Coordination Number and Average Lifetimes

	Distribution of coordination number/%	
Coordination number	293 K	323 K
3	3.3	0.0
4	95.2	93.3
5	1.1	6.7
6	0.4	0.0
Average	4.0	4.1
	Average lifetimes/fs	
3	167.1	—
5	46.4	60.9

The angular distribution of O–Li–O in the first hydration shell is depicted in Fig. 2. The solid and dotted lines in the figure indicate the angular distribution at the temperatures of 293 and 323 K, respectively. One peak around 110 degrees can be found in the figures at both temperatures. The maximum point of the angular distribution of O–Li–O is 109.0 and 108.7 degrees at 293 and 323 K, respectively, and are listed in Table 2. The maximum points of the angular distribution of O–Li–O at both temperatures correspond extremely well with the O–Li–O angle of a $Li^+(H_2O)_4$ cluster with tetrahedral structure. The distribution of the O–Li–O angle at 323 K becomes a little broader than that at 293 K because of the increasing kinetic energy of the water molecules. From the above

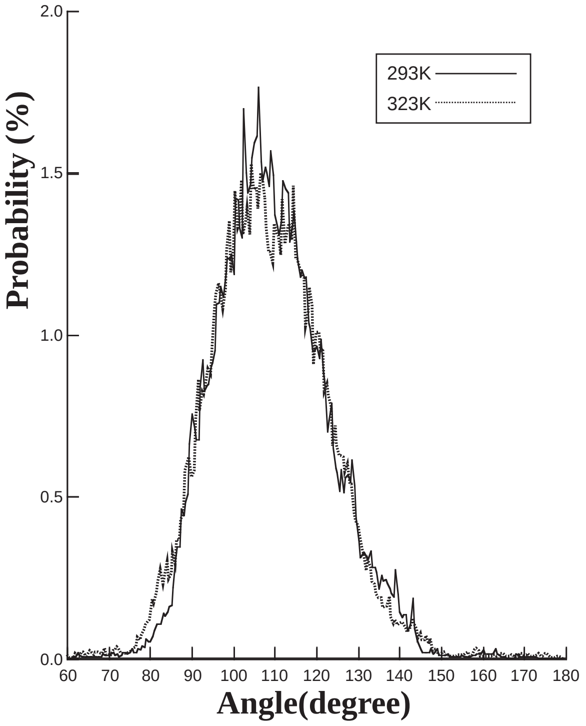


Fig. 2. ∠O–Li–O angular distribution in the first hydration shell at the temperature of 293 and 323 K.

Table 2. Structural Properties of the First Hydration Shell at the Temperatures of 293 and 323 K and the Optimized Tetrahedral Structure of $Li^+(H_2O)_4$ with S_4 Symmetry

	293 K	323 K	$Li^+(H_2O)_4$
Li–O/Å	1.95	1.98	1.968
Li–H/Å	2.56	2.54	2.623 2.655
O–H/Å	0.95	0.95	0.945
∠H–O–H/degree	106.8	106.5	107.3
Tilt angle/degree	19	34	6
∠O–Li–O/degree	109.0	108.7	109.5
Li–Plane$_{\text{(average)}}$/Å	0.650	0.650	0.656
Li–Plane$_{\text{(nearest)}}$/Å	0.427	0.429	—
Li–Plane$_{\text{(intermediate)}}$/Å	0.271	0.267	—
$n_{\text{Li–O}}$	4.0	4.1	—

results, the most probable coordination number is 4 at both temperatures, and the structure of the first hydration shell is the tetrahedral structure.

The radial distribution functions $g_{\text{Li–O}}(r)$ and $g_{\text{Li–H}}(r)$ at the temperatures of 293 and 323 K are shown in Fig. 3. The radial distribution functions are normalized by the average densities of each particle in the sphere, of which the radius from the lithium atom is 8.0 Å. The distances (Li–O and Li–H) of the maximum of $g_{\text{Li–O}}(r)$ and $g_{\text{Li–H}}(r)$ are also listed in Table 2. The Li–O distance of the maximum of $g_{\text{Li–O}}(r)$ at 293 K is 1.95 Å, which has good agreement with the 1.96 Å for experimental observation by neutron diffraction measurement in a LiCl solution,[1] whereas the distance is shorter than the 2.2 Å derived by X-ray diffraction measurement in a LiI solution.[4] The average structures of water molecules in the first hydration shell are not changed much for the difference of temperature from the values of O–H bond length and H–O–H bond angle in Table 2. In comparison with the geometry of water molecules in the first hydration shell and that in the optimized $Li^+(H_2O)_4$ cluster with $\boldsymbol{S}_4$ symmetry, a drastic structural difference is not found. The $g_{\text{Li–O}}(r)$ distributions between 2.6 and 3.0 Å for both temperatures are almost zero. Namely, the first hydration shells of the lithium cation are clearly separated from the outer hydration shells. The running coordination numbers ($n_{\text{Li–O}}$) are obtained at the temperatures of 293 and 323 K (Table 1). The values of $n_{\text{Li–O}}$ are 4.0 and 4.1 at 293 and 323 K, respectively. From the running coordination number, the most probable hydration number of the Li cation is also 4 at both temperatures.

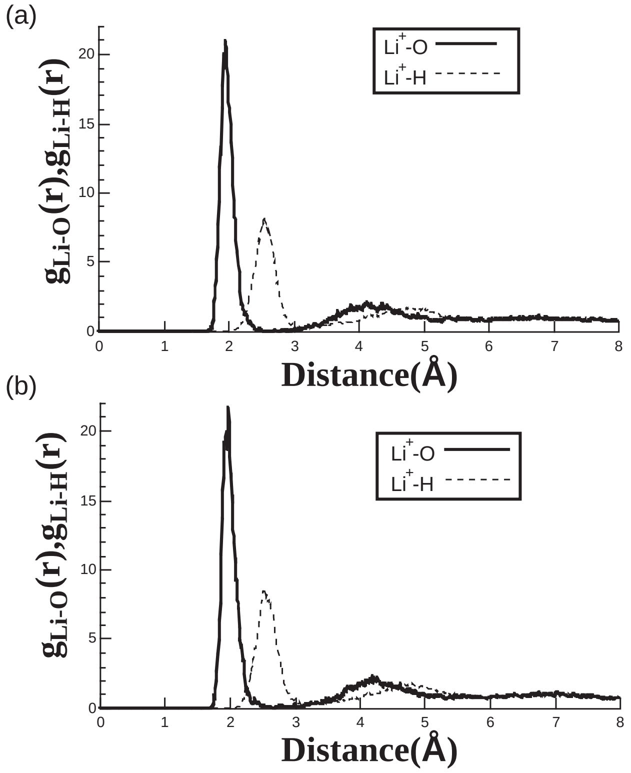


Fig. 3. Li–O and Li–H radial distribution functions at the temperatures of 293 (a) and 323 K (b).

The maximum of $g_{\text{Li–H}}(r)$ and the average structure of water molecules in the first hydration shell are important information for the determination of the orientation of water molecules. Although the distance of the maximum of $g_{\text{Li–O}}(r)$ at 323 K is 1.98 Å, which is longer by 0.03 Å than that at 293 K, the distance of the maximum of $g_{\text{Li–H}}(r)$ at 323 K is shorter by 0.02 Å than that at 293 K. It is indicated that the orientation of water molecules in the first hydration shell changes with the variation of temperature. Thus, the angle of orientation, which is defined as "Tilt angle," between the dipole vector of the water molecules and the lithium–oxygen position vector were evaluated at temperatures of 293 and 323 K. The angular distributions of the tilt angle of water molecules in the first hydration shell at both temperatures are plotted in Fig. 4. The angle of the maximum distributions at each temperature is listed as "Tilt angle" in Table 2. The angle at 323 K is larger by 15.5 degrees than that at 293 K. This shows that the flopping mode of the vibration between Li and water molecules is enhanced

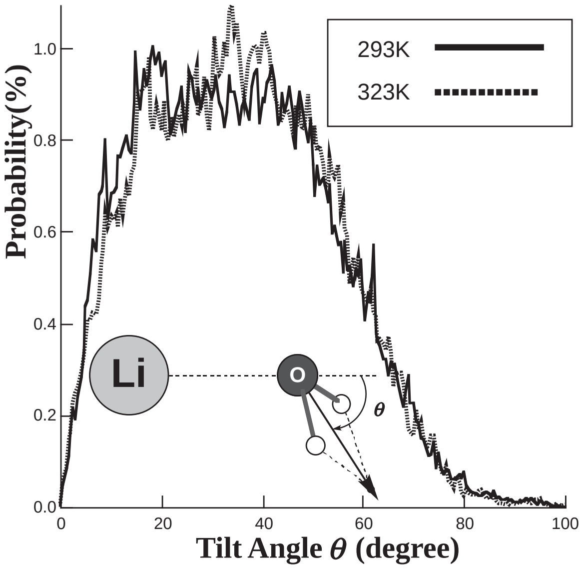


Fig. 4. Probability distribution of tilt angle of water molecules in the first hydration shell at the temperatures of 293 and 323 K.

by increasing the temperature. In fact, the frequency number of the flopping mode for a $Li^+(H_2O)_4$ cluster is only 275 cm^{-1} at the HF/6-31G(d,p) level.

Variation of Coordination Number and Exchange Mechanism. In this section, we classify the mechanisms for the variation of the coordination number or the exchange of solvent molecules between the first and the second hydration shells. During the MD simulations, the decrease from 4 to 3 in the coordination number of the first hydration shell occurred two times at 293 K and zero times at 323 K. In contrast, the increase from 4 to 5 in the coordination number occurred two times at 293 K and seven times at 323 K. From the structural variation along the MD simulations, it is found that the exchange of solvent molecules between the first shell and the second one occurs through two-types of mechanisms.

Two mechanisms (dissociation and addition), for the decrease and increase processes of the coordination number observed from the results of the MD simulations, are shown in Scheme 1. One mechanism is the dissociation process of one water molecule from the first hydration shell, as shown in the left side of Scheme 1. This mechanism includes the motion of the lithium atom toward the center of the trigonal plane composed of the remaining three water molecules in the first hydration shell upon the dissociation of one water molecule. Namely, after the dissociation of one water molecule from the tetrahedral coordination, it leads to trigonal plane coordination through the trigonal pyramidal coordination. On the other hand, the addition mechanism is the insertion process of an external water molecule to the first hydration shell of the coordination number 4 from outer shell. In this mechanism, the first hydration shell leads to the bi-pyramidal structure. Both mechanisms lead to variation of the coordination number or the exchange mechanisms of solvent molecules between hydration shells.

To compare the simulation system treated here and small cluster systems for the dissociation and addition mechanisms, the stationary points geometries of small clusters for processes (1) and (2) were calculated at the HF/6-31G(d,p) level.

Dissociation process:

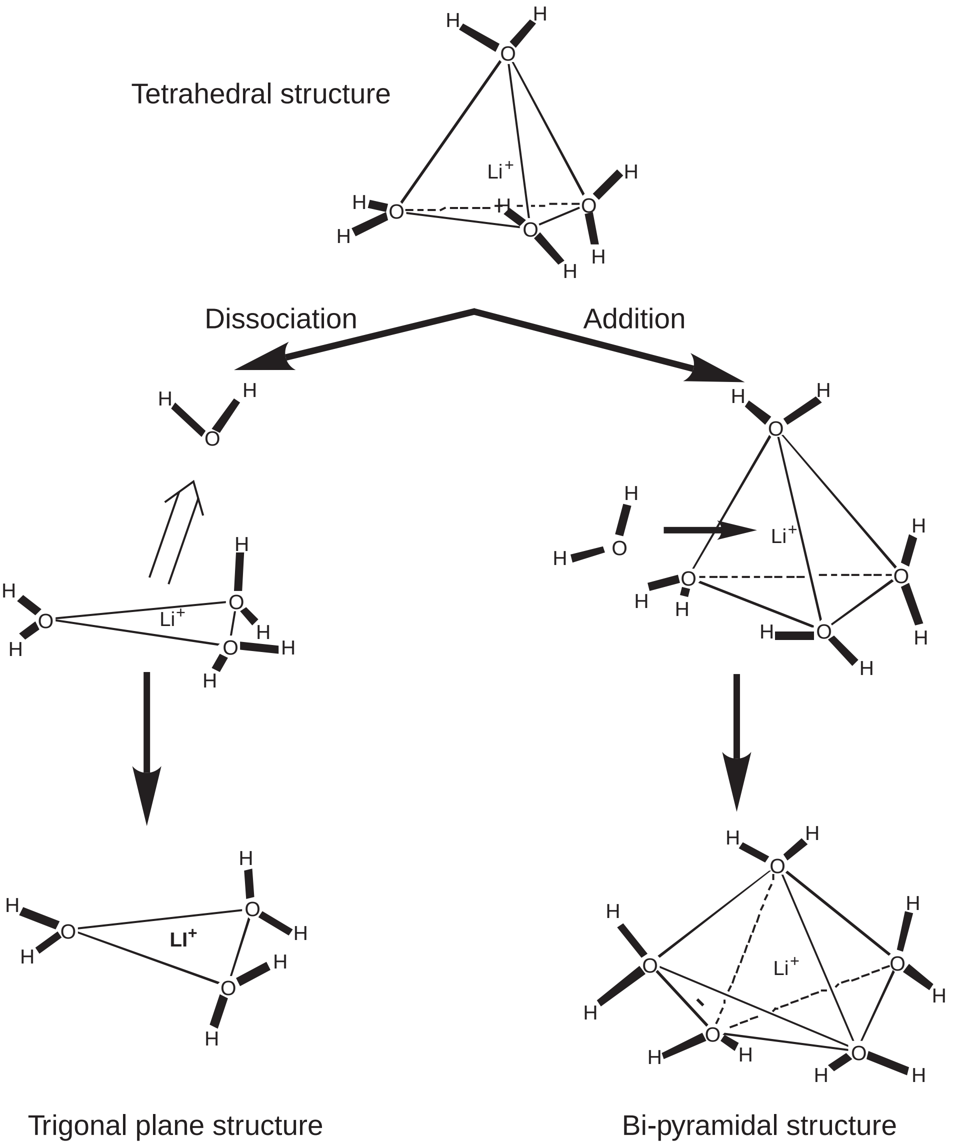
$$Li^+(H_2O)_4 \rightarrow Li^+(H_2O)_3{:}(H_2O). \tag{1}$$

Addition Process:

$$Li^+(H_2O)_4{:}(H_2O) \rightarrow Li^+(H_2O)_5. \tag{2}$$

The stationary point geometries of the small cluster systems for the dissociation and addition processes are illustrated in Figs. 5 and 6, respectively. Although the models of the small cluster do not include the influence of outer shells, the structures of the models are similar to those shown in MD calculations. The total and relative energies for the stationary points geometries are listed in Table 3. The energies for the stationary points geometries with the HF-optimized structures were also calculated at the CCSD(T)/6-311++G(d,p) level. For the addition process (2), two reaction paths were obtained. One is the approaching of a water molecule on one surface of the tetrahedral structure of $Li^+(H_2O)_4$ through the transition state (TS1). Another is the approaching of an external water molecule along one surface of OLiO of $Li^+(H_2O)_4$ through the transition state (TS2). The energy barrier of the reaction through TS2 for the variation of the coordination number from 4 to 5 is 6.82 kcal mol^{-1} above $Li^+(H_2O)_{4+1}$, and 0.7 kcal mol^{-1} higher than that of TS1 at the HF/6-31G(d,p) level. At the CCSD(T)/6-311++G(d,p) level, the difference of the energy barrier between TS1 and TS2 increases to 1.4 kcal mol^{-1}. Moreover, the variation of coordination number or the exchange of solvent molecules through the transition state (TS2) was not observed in the results by the MD simulation. However, the structural change through TS2 may be obtained on the MD simulation under the condition of higher temperature and/or external pressure. Although the energy barrier heights for both processes of dissociation and addition are about 5 to 6 kcal mol^{-1} above $Li^+(H_2O)_4$ and/or $Li^+(H_2O)_{4+1}$, the energy barriers from $Li^+(H_2O)_{3+1}$ and $Li^+(H_2O)_5$ are less than about one kcal mol^{-1}. Especially, the energy barrier of TS1 is less than about 0.3 kcal mol^{-1} above $Li^+(H_2O)_5$. On the cluster model, the tetrahedral structure is more stable in energy than the trigonal plane and bi-pyramidal models. This corresponds to the average lifetime of coordination numbers 3 and 5 in the MD simulations as listed in Table 1. The average lifetime (167.1 fs) of coordination number 3 is longer than that (46.4 fs) of coordination number 5 at 293 K. The average lifetime of coordination number 5 increases at 323 K. Thus, the probability of the formation of coordination number 5 may increase with increasing temperature. Accordingly, the structure of coordination number 3 or 5 during the two processes has a short average lifetime and easily returns to the tetrahedral structures.

The structures of $Li^+(H_2O)_{3+1}$ and $Li^+(H_2O)_5$ clusters have a similar character for the orientation. Namely, the lithium atom locates near the trigonal plane consisting of three oxygen atoms of water molecules. For example, the structure of a $Li^+(H_2O)_{3+1}$ cluster is trigonal planar in the first hydration shell. For $Li^+(H_2O)_5$, the lithium atom locates near the center of the bi-pyramidal structure, which is the center of one trigonal plane constructed from three water molecules. Thus, the trigonal planar structure in the first hydration shell probably



Scheme 1.

is an important condition for the variation of the coordination number or solvent exchange process. To examine whether the trigonal plane as mentioned above is observed during the MD simulation, we define here the distance between the lithium atom and the plane consisting of three oxygen atoms of water molecules in the first hydration shell. It is decided by the following procedures. First, the nearest four oxygen atoms of water molecules from the lithium atom are chosen. Then, the distances between the lithium atom and the four planes, which can be defined from any three oxygen atoms of four water molecules, are evaluated. The nearest distance (Li–Plane) between lithium and the plane can be defined for each plane. The Li–Plane$_{\text{(average)}}$ listed in Table 2 is the average value of the four nearest distances at each temperature. The Li–Plane$_{\text{(nearest)}}$ is the average value of the shortest distances in the four nearest distances, and Li–Plane$_{\text{(intermediate)}}$ is the average value of the shortest distances, which does not include the distances during the period of coordination number 4. The Li–Plane$_{\text{(average)}}$ values at both temperatures indicate the same distance of 0.650 Å, and are close to the distance (0.656 Å) of the Li–Plane for an optimized $Li^+(H_2O)_4$ cluster structure. Consequently, the lithium atom locates around the center of the tetrahedral structure of the first hydration shell. On the other hand, Li–Plane$_{\text{(intermediate)}}$ is distinctly shorter than Li–Plane$_{\text{(nearest)}}$ and Li–Plane$_{\text{(average)}}$. It means the lithium atom locates close to one of the trigonal planes for the exchange of solvent molecules or the variation of the hydration number during the MD simulation.

The distances (Li–O) between the lithium and the oxygen atom of a water molecule and the Li–Plane$_{\text{(nearest)}}$ along the time developments are shown in Figs. 7–10, and these correspond to the processes of the solvent exchange and the variation of the coordination number. Figure 7 shows one simulation result for the variation of the coordination number through the addition type process. In this case, one external water moves into the region of the first hydration shell defined by 3 Å from the second (outer) hydration shell (Fig. 7a), and the distance between the lithium atom and the nearest plane ap-

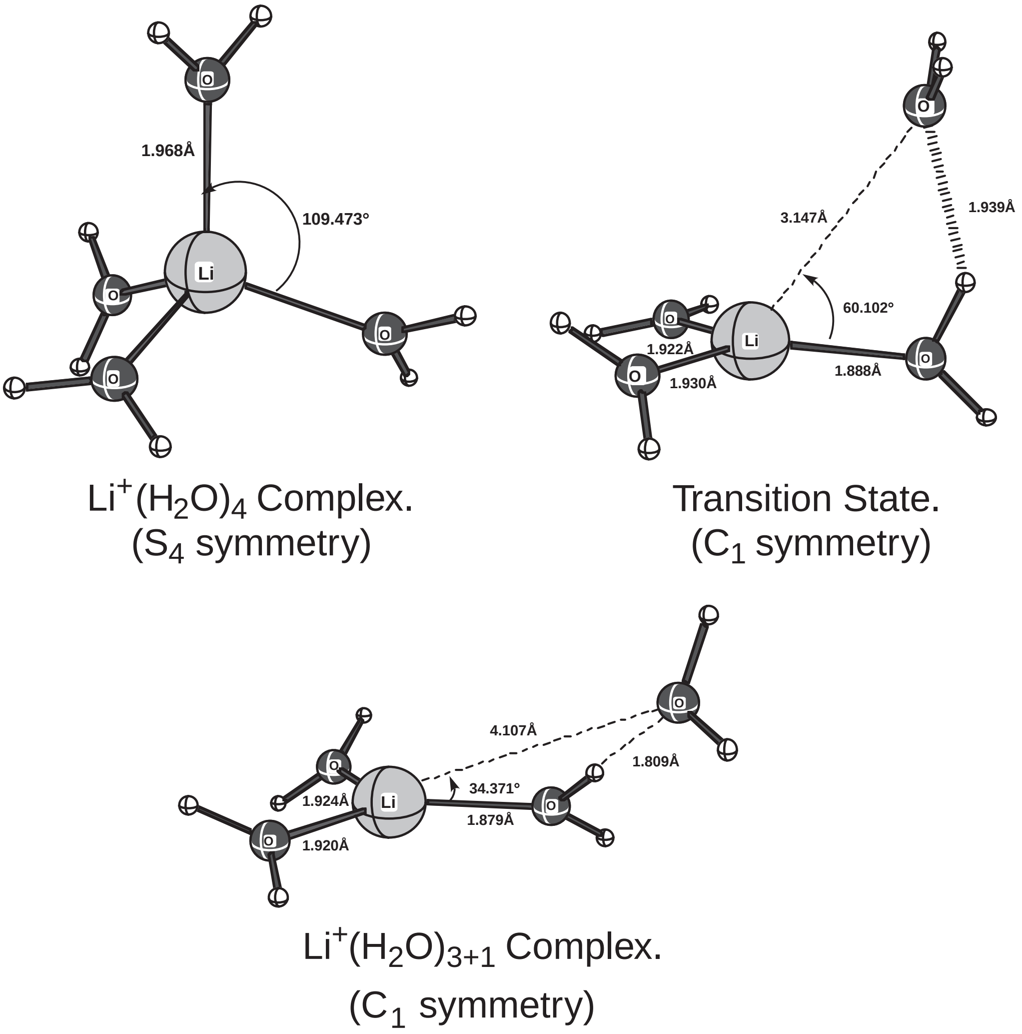
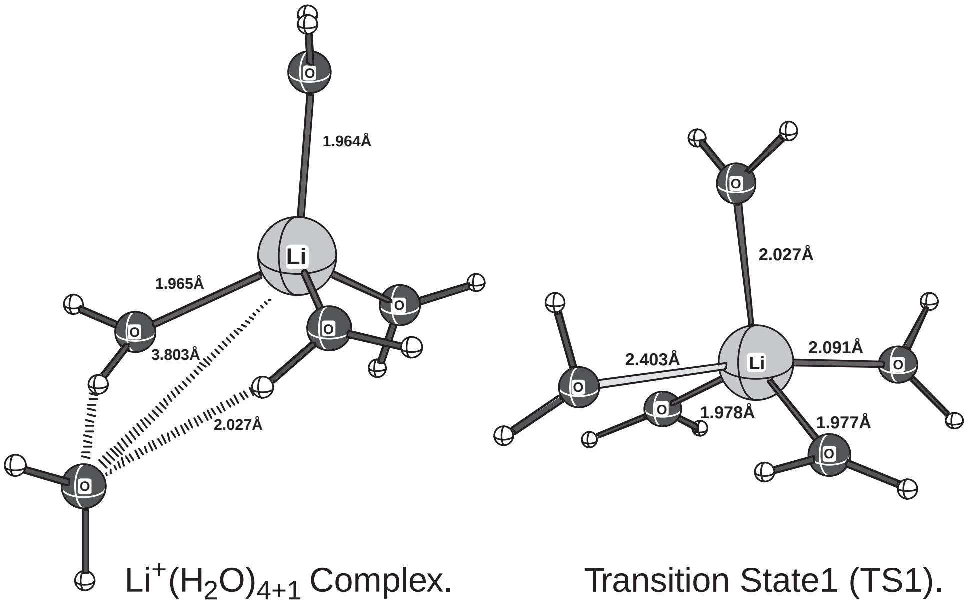


Fig. 5. The stationary points geometry of dissociation process for $Li^+(H_2O)_4$ clusters.

proaches 0.19 Å (Fig. 7b). In all simulations of the variation of coordination number through the addition type process, it is confirmed that the distances between the lithium atom and the nearest plane become shorter than 0.3 Å during the period of 50 fs before or after the changing of the coordination number. Figure 8 shows one simulation result for the variation of the coordination number through the dissociation process. In this case, similarly, the lithium atom approaches the nearest plane 0.21 Å away upon the dissociation of one water molecule from the first hydration shell. One simulation result of the solvent exchange through the addition process is also plotted in Fig. 9. In this type, the lithium atom approaches the center of the bi-pyramidal structure through the transition-state structure of TS1. At the crossing point of two Li–O distance lines for the exchange molecules, the Li–O distance is 2.25 Å, only 0.07 Å longer than the longest Li–O bond distance of the five coordinated complex, the $Li^+(H_2O)_5$ cluster as illustrated in Fig. 6. Figure 10 shows one simulation result for solvent exchange through the dissociation type process. For the dissociation of one water molecule from the first hydration shell, the first hydration shell forms the trigonal plane structure (corresponding to $Li^+(H_2O)_{3+1}$ in Fig. 5). The variation of the first hydration shell from trigonal planar to pyramidal structure relates closely to the approaching of one water molecule to the first hydration shell from the outer shell.

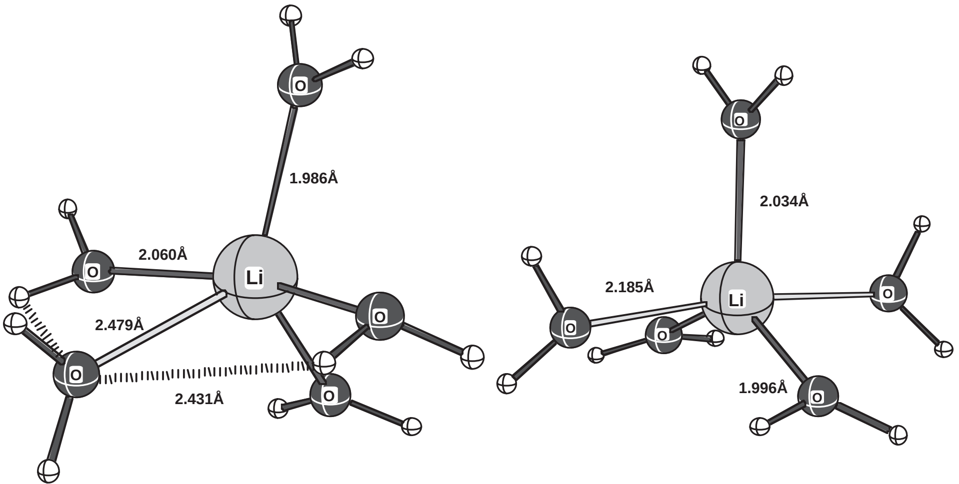
Conclusion

The structure of the first hydration shell of the lithium cation in a solvent and the coordination number were studied by using ab initio MD simulation on the basis of the IMiC MO method at the HF/6-31G(d,p) level. The hydration system treated here is one lithium cation and 100 water molecules as the solvent. The ab initio MD simulations were performed ten times for each different initial geometry at the two temperatures of 293 and 323 K. The most probable structure of the first hydration shell derived from the MD simulation was the tetrahedral structure including four water molecules. Moreover, the first hydration shell was clearly separated from the outer shells. Although the Li–O bond length derived from radial distribution at the temperature of 293 K is in fair agreement with that by the neutron diffraction method, the coordination number obtained by the MD simulations differs from that suggested by the neutron diffraction method. From our results at the IMiC MO (full QM) level, it is concluded that the hydration number 4 of the first shell for the lithium cation is more reliable.



$Li^+(H_2O)_{4+1}$ Complex. (C_2 symmetry)

Transition State1 (TS1). (C_1 symmetry)



Transition State2 (TS2). (C_2 symmetry)

$Li^+(H_2O)_5$ Complex. (C_2 symmetry)

Fig. 6. The stationary points geometry (in Å) of the addition process for $Li^+(H_2O)_5$ clusters.

Table 3. Total and Relative Energies of Stationary Points Geometry for $Li^+(H_2O)_4$ and $Li^+(H_2O)_5$ Clusters

	Total Energy/Hartree		Relative Energy/kcal mol^{-1}	
	HF/6-31G(d,p)	CCSD(T)/ 6-311++G(d,p)	HF/6-31G(d,p)	CCSD(T)/ 6-311++G(d,p)
Dissociation process				
$Li(H_2O)_4$	−311.52406	−312.55746	0.00	0.00
TS	−311.51430	−312.54801	6.12	5.93
$Li(H_2O)_{3+1}$	−311.51567	−312.54980	5.27	4.81
Addition process				
$Li(H_2O)_{4+1}$	−387.57241	−388.86861	0.00	0.00
TS1	−387.56278	−388.86130	6.04	4.59
TS2	−387.56154	−388.85903	6.82	6.01
$Li(H_2O)_5$	−387.56293	−388.86180	5.95	4.27

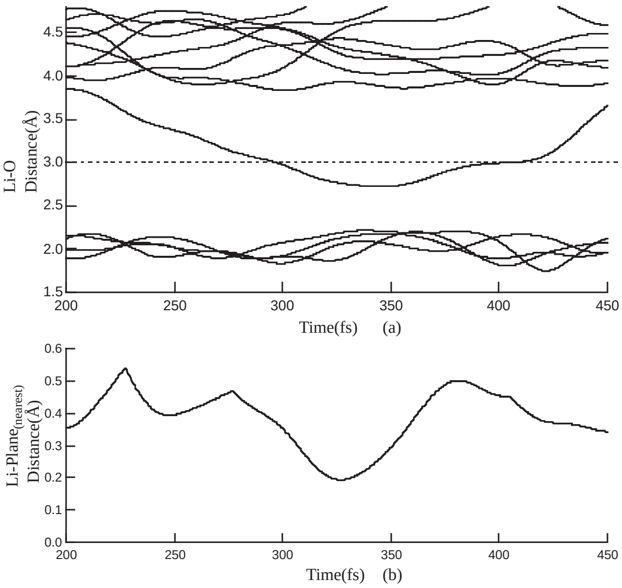


Fig. 7. Li–O distance and Li–Plane$_{\text{(nearest)}}$ along the time development for the variation of coordination number in the addition process.

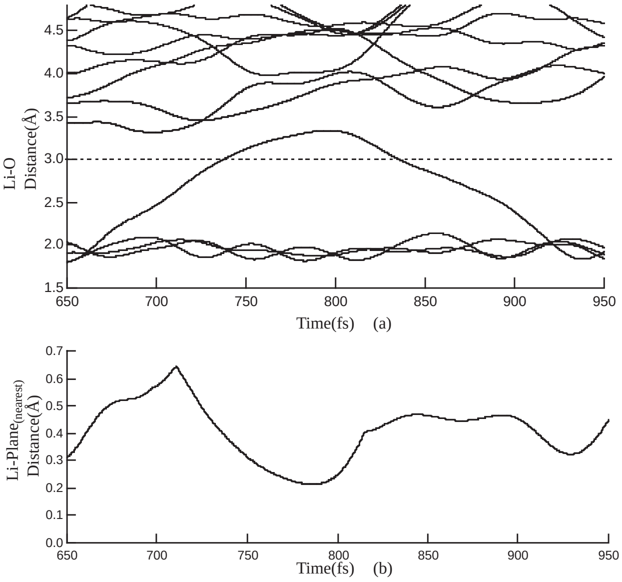


Fig. 8. Li–O distance and Li–Plane$_{\text{(nearest)}}$ along the time development for the variation of coordination number in the dissociation process.

Two mechanisms for the variation of the coordination number in the first hydration shell and/or the solvent exchange between the first and outer shells were classified by ab initio MD calculations. The stationary point geometries of the cluster models for the mechanisms were also evaluated. The energy barrier for the increase of the coordination number from four to five is slightly lower than that of the decrease from four to three. For the solvent exchange mechanism of the cluster models, the lithium atom approaches one surface of the triangle planes constructed from three oxygen atoms. Similar motion of the lithium atom can be found in the MD system treated here.

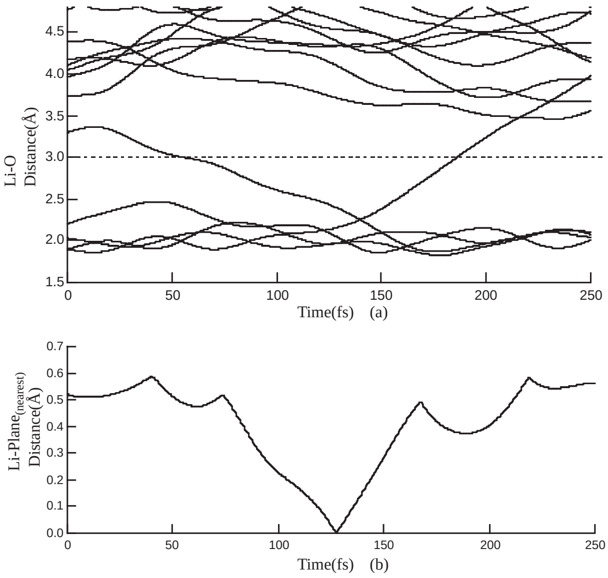


Fig. 9. Li–O distance and Li–Plane$_{\text{(nearest)}}$ along the time development for the exchange of solvent in addition process.

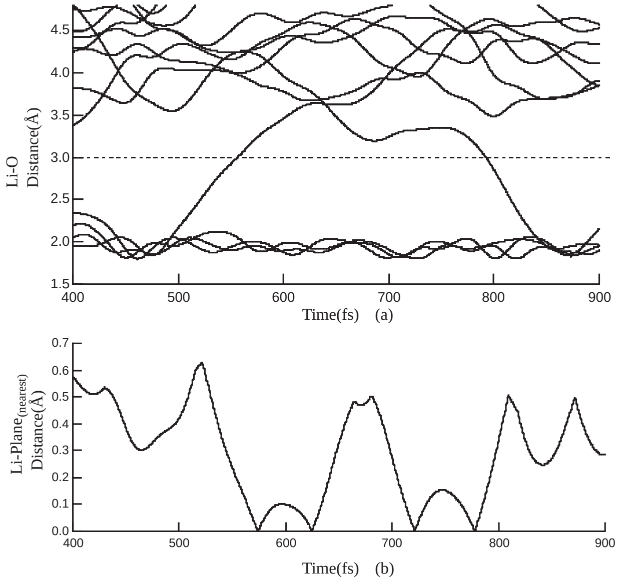


Fig. 10. Li–O distance and Li–Plane$_{\text{(nearest)}}$ along the time development for the exchange of solvent in dissociation process.

The present research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Computing time was made available by the Computer Center of the Institute for Molecular Science and by Osaka Sangyo University utilizing its SGI Power Challenge computer.

References

1 I. Howell, G. W. Neilson, *J. Phys.: Condens. Matter* **1996**, *8*, 4455.

2 H. Ohtaki, T. Randai, *Chem. Rev.* **1993**, *93*, 1157.

3 T. Randai, G. Palinkas, G. I. Szasz, K. Heinzinger, *Z. Naturforsch.* **1981**, *36a*, 1076.

4 Y. Tamura, T. Yamaguchi, I. Okada, H. Othaki, *Z. Naturforsch., A: Phys. Sci.* **1987**, *42*, 367.

5 K. H. Michaelian, M. Moskovits, *Nature* **1978**, *273*, 135.

6 E. D. Glendening, D. Feller, *J. Phys. Chem.* **1995**, *99*, 3060.

7 G. Bischof, A. Silbernagl, K. Hermansson, M. Probst, *Int. J. Quantum Chem.* **1997**, *65*, 803.

8 A. Tongraar, K. R. Liedl, B. M. Rode, *Chem. Phys. Lett.* **1998**, *286*, 56.

9 S. Morita, S. Sakai, *J. Comput. Chem.* **2001**, *22*, 1107.

10 A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, III, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024.

11 R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833.

12 R. W. Hockney, *Methods Comput. Phys.* **1970**, *9*, 136.

13 L. V. Woodcock, *J. Chem. Phys. Lett.* **1971**, *10*, 257.

14 P. C. Haviharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

15 M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163.

16 From the test calculations of $Li^+(H_2O)$ by HF method with basis sets of 6-31G, 6-31G(d,p), 6-311+G(d,p), 6-31++G(d,p), 6-311++G(d,p), the Li–O distance obtained by the HF/6-31(d,p) is the most near to that by MP2/6-311++(d,p) level. Therefore, we used the HF/6-31G(d,p) method for the evaluation of the force and point charge of each atom.

17 K. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cislowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Comperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 98*, Gaussian, Inc., Pittsburgh, PA, **1998**.