Hydration and coordination of K + solvation in water from ab initio molecular-dynamics simulation

Yi Liu, Haigang Lu, Yanbo Wu, Tuoping Hu, and Qiaoling Li

Articles you may be interested in

Ab initio and classical molecular dynamics studies of the structural and dynamical behavior of water near a hydrophobic graphene sheet
J. Chem. Phys. **138**, 204702 (2013); 10.1063/1.4804300

Structure and dynamics of the hydration shells of the Zn 2 + ion from ab initio molecular dynamics and combined ab initio and classical molecular dynamics simulations
J. Chem. Phys. **132**, 194502 (2010); 10.1063/1.3421542

OD vibrations and hydration structure in an Al 3 + (aq) solution from a Car-Parrinello molecular-dynamics simulation
J. Chem. Phys. **124**, 104501 (2006); 10.1063/1.2131062

Ab initio molecular-dynamics simulation of aqueous proton solvation and transport revisited
J. Chem. Phys. **123**, 044505 (2005); 10.1063/1.1961443

Ab initio molecular dynamics study of aqueous solvation of ethanol and ethylene
J. Chem. Phys. **118**, 8831 (2003); 10.1063/1.1567258

Hydration and coordination of K⁺ solvation in water from *ab initio* molecular-dynamics simulation

Yi Liu,[1,2] Haigang Lu,[1,a)] Yanbo Wu,[1] Tuoping Hu,[2] and Qiaoling Li[2]

[1]*Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry,*
Institute of Molecular Science, Shanxi University, Taiyuan, Shanxi 030006, China
[2]*Department of Chemistry, North University of China, Taiyuan, Shanxi 030051, China*

Potassium ion in water plays a very important role in chemistry and biology. In this paper, we investigated the hydration structure and coordination of K⁺ solvation in water at 300 and 450 K using *ab initio* Car–Parrinello molecular dynamics. The K⁺-oxygen radial distribution function indicated that the perturbation of K⁺ on the water structure is strong in the first hydration shells, while it is mild outside of this region in normal liquid. According to our natural geometric criterion for the coordinated oxygen atom, the average coordination number of K⁺ is 6.24 and 6.53 at 300 and 450 K, respectively, which agrees with the experimental value (6.1). This geometric criterion can also be used to define strong, moderate and weak hydrogen bonds in liquid. © *2010 American Institute of Physics*. [doi:10.1063/1.3369624]

I. INTRODUCTION

The solvation of ions is a fundamental problem encountered in a wide range of biological and chemical systems.[1,2] For example, the ion selectivity in biological potassium channels is dependent on the characteristics of the K⁺ solvation shell.[3] Accordingly, a great deal of experimental and theoretical work has been devoted to characterization of K⁺ solvation, such as determination of the ion-water distance, hydration structure, coordination number and dynamical properties of the hydrated ion.[2] However, because the K⁺-oxygen distance is very close to the oxygen-oxygen distance in bulk water, x-ray and neutron diffraction experiments cannot easily separate the structural factors and radial distribution functions (RDFs) of the different species.[4–8] Nevertheless, neutron diffraction experiments with isotope substitution (NDIS) augmented by computer modeling have recently enabled a detailed description of the hydration structure of KCl solution.[8–10]

Car–Parrinello molecular dynamics (CPMD) simulations,[11–17] Monte Carlo simulations[18] and quantum mechanical/molecular mechanical simulations[19,20] have also provided atomistic insight into the structure and dynamics of K⁺ solvation in water under ambient conditions. However, the inherent flexibility of K⁺ solvation shells results in water exchange between the first and second solvation shells occurring at the rate of a few picoseconds or less, so that the first K⁺ solvation shell, and therefore the K⁺-water coordination number, are not well-defined.

Recently, Yoo *et al.*[21] determined the melting temperature (T_m) of ice I_h from constant enthalpy and pressure (*NPH*) Born–Oppenheimer molecular dynamics simulations to be 417 ± 3 K for the Perdew–Burke–Ernzerhof[22,23] and 411 ± 4 K for the Becke–Lee–Yang–Parr (BLYP)[24,25] density functionals. To study the physical, thermodynamic and

structural properties of the ion solvation in water with these two functionals and to compare these properties at ambient conditions, simulations at $T > T_m$ need to be performed.

In this study, we investigated the K⁺ hydration structure at 300 and 450 K. Based on the results of this investigation, we proposed a geometric criterion to determine the K⁺ coordination number naturally. The remainder of the paper is organized as follows. In Sec. II, we describe the computational method including some technical details relevant to the present study. In Sec. III, the hydration structure and ion-water coordination of the K⁺ solvation in water are discussed in detail. Finally, we draw some conclusions based on the overall findings of the study.

II. COMPUTATIONAL METHODS

We performed *ab initio* molecular-dynamics simulations using the Car–Parrinello scheme.[26] Our approach was based on the BLYP functional. Because the BLYP functional produces an overstructured liquid at room temperature and up to 411 K,[21] our CPMD simulations were performed at 450 K and 300 K to ensure that both the normal and supercooled liquids were simulated. Temperature control during the simulations was accomplished using a Nosé–Hoover algorithm[27,28] to keep the systems in the so-called canonical ensemble (*nVT*-ensemble).

The K⁺ hydration systems consist of one ion and 48 water molecules in a periodic cubic box with a size of $L = 11.3061$ Å ($\rho = 1.038$ g/cm³). The core-valence interactions are described by ultrasoft pseudopotentials (USPPs) (Ref. 29) for K, O, and H with an energy cutoff of 25 Ry. A fictitious electron mass of 400 a.u.[30] and a time step of 4.0 a.u. (0.097 fs) were employed to ensure good control of the conserved quantities. After classical equilibration, the CPMD simulations were run 9.7 ps (100 000 steps), with the first 50 000 steps being used for equilibration and the last 50,000 steps being used to collect the statistical data with an interval

a)Electronic mail: luhg@sxu.edu.cn.
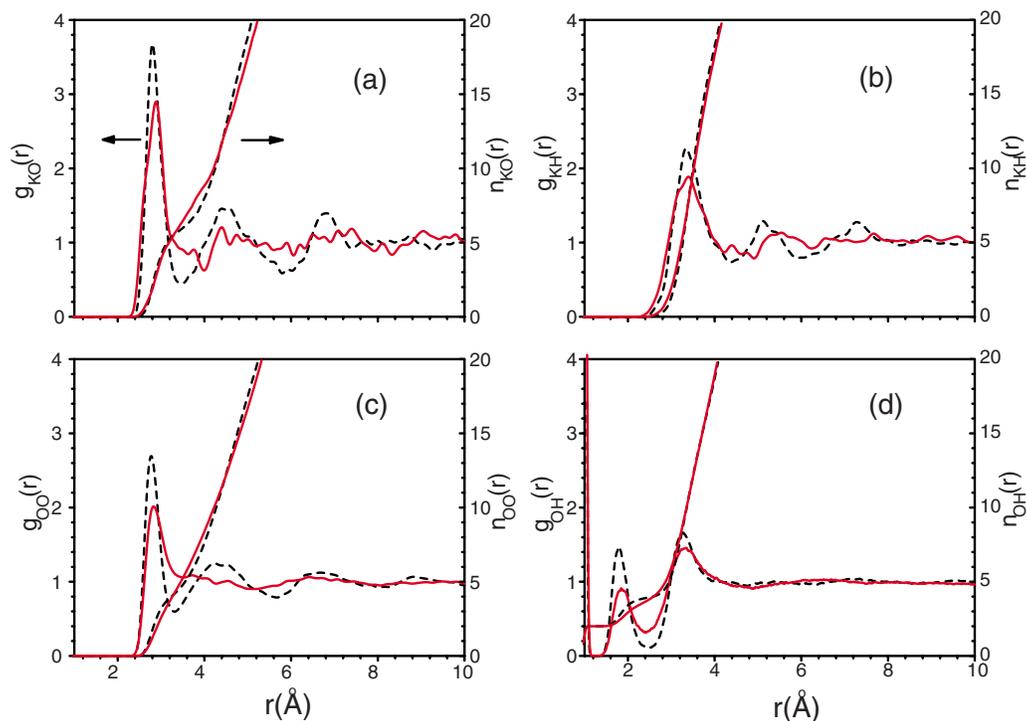
FIG. 1. RDFs (a) $g_{KO}(r)$, (b) $g_{KH}(r)$, (c) $g_{OO}(r)$, and (d) $g_{OH}(r)$ and their corresponding running coordination number $n(r)$ for K$^+$ in liquid water at 300 K (dashed line) and 450 K (solid line), respectively.

of 10 steps. This simulation time is found to be sufficient for convergence of the K$^+$-oxygen distance. Because CPMD does not allow for calculation of the stress tensor with US-PPs, the stress tensors and pressures were calculated using Troullier–Martins norm conserving pseudopotentials[31] and the plane-wave basis set with the energy cutoff of 140 Ry.

III. RESULTS AND DISCUSSION

A. Hydration structure

The simplest quantities that reveal the hydration structure are the RDFs $[g_{KO}(r), g_{KH}(r), g_{OO}(r),$ and $g_{OH}(r)]$ shown in Fig. 1. The corresponding radial integration numbers

$$n(r) = 4\pi\rho_0 \int_0^r g(x)x^2 dx, \qquad (1)$$

are also shown. ρ_0 is the number density of oxygen or hydrogen, respectively. Their average pressures of 50 snapshots are 5.6 and 6.5 kbar at 300 and 450 K, respectively. The first peaks of $g_{KO}(r)$ centered at 2.82 and 2.86 Å at 300 and 450 K, which is in rather good agreement with the results of other *ab initio* molecular dynamics simulations [2.81 Å (Ref. 12) and 2.85 Å (Ref. 13)] and about 0.2 Å longer than the results [2.65 Å (Ref. 10)] recently obtained from neutron diffraction experiments augmented by computer modeling of KCl solutions.

In normal liquid (450 K), the first peaks of $g_{KO}(r)$ and $g_{KH}(r)$ were obviously lower than those in supercooled liquid, which indicates that the simulation performed using the BLYP functional also provides an overstructured K$^+$ solution under ambient conditions (300 K and ρ=1.038 g/cm^3). In

contrast to the pronounced second and third peaks of $g_{KO}(r)$ and $g_{KH}(r)$ obtained in the supercooled liquid, there were only a few fluctuations near 1.0 (the ideal gas value) outside the first peak in the normal liquid, which is in agreement with the results of the neutron diffraction experiments.[9] These findings demonstrate that the perturbation of K$^+$ on the water structure is strong in the first hydration shells, but mild outside of this region in normal liquid, as determined by the neutron diffraction experiments.[8]

B. Coordination number

The coordination number of K$^+$ with water molecules is an important parameter that describes the hydration structure. Due to the large size of K$^+$, its first minimum of the ion-oxygen RDF is much less pronounced than the remaining values of smaller alkali ions (Li$^+$, Na$^+$).[17] Consequently,
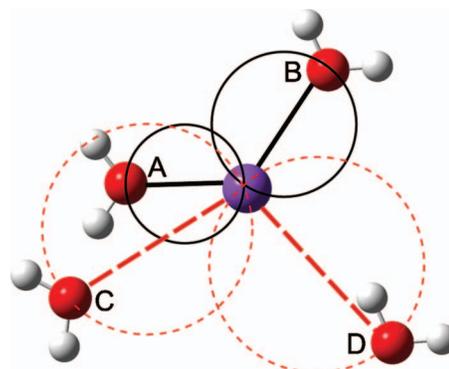
FIG. 2. Illustration of the possible coordinated water oxygen atoms of K$^+$ solvation in water. The purple, red, and white balls are K$^+$, oxygen and hydrogen atoms, respectively.
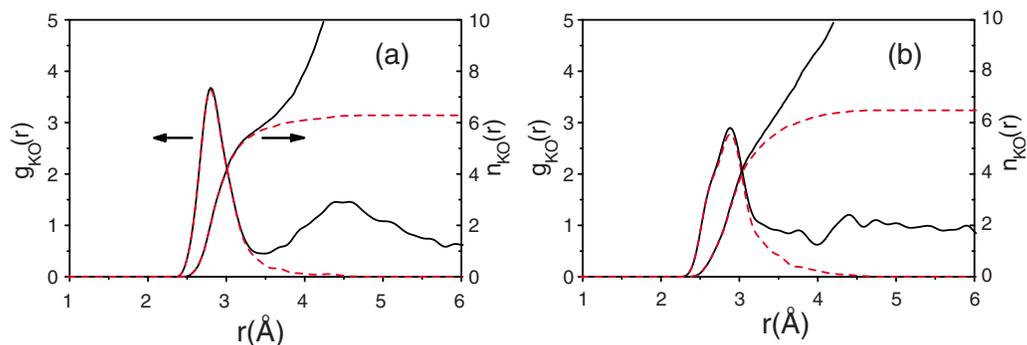
FIG. 3. RDFs $g_{KO}(r)$ (solid line) and those of the coordinated oxygen atoms $g^0_{KO}(r)$ (dashed line) (a) at 300 and (b) 450 K and their corresponding running coordination number $n(r)$ for K+ solvation in water, respectively.

the radial integration number does not show a clear plateau and the coordination number is not sharply defined [Figs. 1(a) and 1(b)]. In particular, it is very difficult to find a reasonable cutoff of K+-oxygen distance in $g_{KO}(r)$ because of the lack of an obvious gap in normal liquid [Fig. 1(a)].

Here, we propose geometric criteria to define the water oxygen atoms coordinated directly with the ions in liquid, such as oxygen atoms A and B shown in Fig. 2, from which we can count the coordination number of the ion. In liquid, the water oxygen atoms in the second solvation shell are shielded by the water molecules in the first shell, such as oxygen atom C shown in Fig. 2. On the other hand, the water oxygen atom in the first shell might be shielded by the hydrogen atoms present between the ion and the oxygen atom, such as water oxygen atom D shown in Fig. 2. In the above two cases, the water oxygen atom should not be regarded as coordinated with the ion. Rather, we define a water oxygen atom coordinated with the ion when there is no other atom in the three-dimensional sphere with a center and diameter that are the middle point and distance of the ion and the oxygen atom. Accordingly, the RDF, $g^0_{KO}(r)$, of the coordinated oxygen atoms can be calculated from the trajectory of simulation, similar to the calculation of $g_{KO}(r)$ by the "AWK" program "pair-coord.awk."[32]

The $g^0_{KO}(r)$ values either completely (300 K) or approximately (450 K) coincide with their corresponding $g_{KO}(r)$ values at the first peak and disappear gradually outside of this region (Fig. 3). These findings demonstrate that the geometric criterion naturally extracts the coordinated oxygen atoms in liquid. The instantaneous coordination numbers, n, for K+ are primarily 6 and 7 at 300 and 450 K
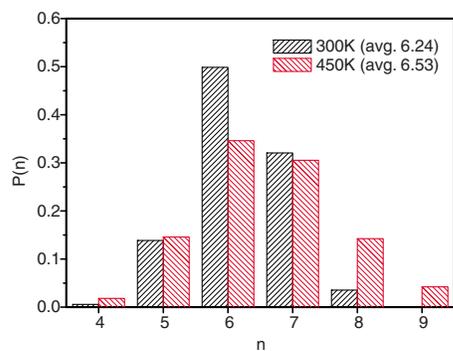
(Fig. 4) and their average coordination numbers are 6.24 and 6.53, which are both consistent with the experimental value (6.1 at a KCl:H$_2$O mole ratio of 1:40 with a geometric cutoff of 3.45 Å)[10] and the comprehensive value (6.0) obtained from experimental and theoretical studies, respectively.[14]

This geometric criterion can also be used to define the O···H hydrogen bonds in liquid. In K+ solution, we can extract the RDF, $g^0_{OH}(r)$, of hydrogen bonds from the trajectory of the simulation. As shown in Fig. 5, the $g^0_{OH}(r)$ values coincide completely with their corresponding $g_{OH}(r)$ values in the first and second shells, decrease gradually in the third shell, and are null outside of the shells. After ruling out the chemical bonded hydrogen atoms, the hydrogen bonds were 4.9−2.0=2.9 and 5.5−2.0=3.5 per oxygen atom at 300 and 450 K, respectively. Because the two water hydrogen atoms formed the same hydrogen bonds as the water oxygen atom in liquid, the total hydrogen bonds are were 2.9×2=5.8 (300 K) and 3.5×2=7.0 (450 K) per water molecule. It is interesting to note that these hydrogen bonds can be divided by the minimum (2.5 Å) between the second and third shells into strong and moderate ($R_{O···H} < 2.5$ Å) and weak (2.5 Å $< R_{O···H} < 4.0$ Å) hydrogen bonds. In K+ solution, the strong and moderate hydrogen bonds were 4.0 and 3.6, while the weak bonds were 1.8 and 3.4 at 300 and 450 K, respectively. Consequently, our geometric criterion can define strong and moderate hydrogen bonds, as well as weak bonds ruled out by other criteria.

IV. CONCLUSION

In summary, we investigated the hydration structure and coordination of K+ solvation in water at 300 and 450 K using *ab initio* Car–Parrinello molecular dynamics. The K+-oxygen RDF indicated that the perturbation of K+ on the water structure is strong in the first hydration shells, while it is mild outside of this region in normal liquid. According to our natural geometric criterion for the coordinated oxygen atom, the average coordination number of K+ is 6.24 and 6.53 at 300 and 450 K, respectively, which agrees with the experimental value (6.1). This geometric criterion can also be used to define strong, moderate and weak hydrogen bonds in liquid.

FIG. 4. Instantaneous coordination number, n, for K+ at 300 and 450 K.
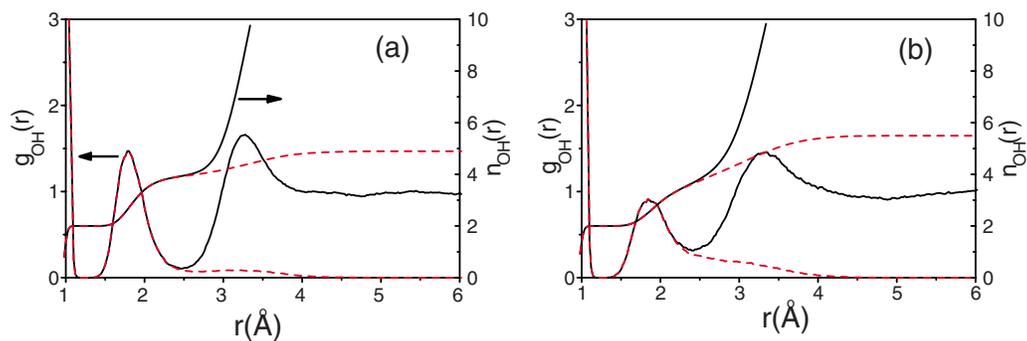
FIG. 5. RDFs $g_{OH}(r)$ (solid line) and those of the bonded hydrogen atoms $g^0_{OH}(r)$ (dashed line) (a) at 300 and (b) 450 K and their corresponding running number $n(r)$ for K^+ solvation in water, respectively.

[1] H. Ohtaki and T. Radnai, Chem. Rev. (Washington, D.C.) **93**, 1157 (1993).
[2] Y. Marcus, Chem. Rev. (Washington, D.C.) **109**, 1346 (2009).
[3] S. Yu. Noskov and B. Roux, Biophys. Chem. **124**, 279 (2006).
[4] R. M. Lawrence and R. F. Kruh, J. Chem. Phys. **47**, 4758 (1967).
[5] N. Ohtomo and K. Arakawa, Bull. Chem. Soc. Jpn. **53**, 1789 (1980).
[6] G. W. Neilson and G. W. Skipper, Chem. Phys. Lett. **114**, 35 (1985).
[7] A. C. Barnes, G. W. Neilson, and J. E. Enderby, J. Mol. Liq. **65–66**, 99 (1995).
[8] A. K. Soper and K. Weckström, Biophys. Chem. **124**, 180 (2006).
[9] R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci, and A. K. Soper, Phys. Chem. Chem. Phys. **9**, 2959 (2007).
[10] R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci, and A. K. Soper, J. Phys. Chem. B **111**, 13570 (2007).
[11] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[12] L. Ramaniah, M. Bernasconi, and M. Parrinello, J. Chem. Phys. **111**, 1587 (1999).
[13] S. B. Rempe, D. Asthagiri, and L. R. Pratt, Phys. Chem. Chem. Phys. **6**, 1966 (2004).
[14] S. Varma and S. B. Rempe, Biophys. Chem. **124**, 192 (2006).
[15] C. Krekeler, B. Hess, and L. Delle Site, J. Chem. Phys. **125**, 054305 (2006).
[16] C. Krekeler and L. Delle Site, J. Phys.: Condens. Matter **19**, 192101 (2007).
[17] T. Ikeda, M. Boero, and K. Terakura, J. Chem. Phys. **126**, 034501 (2007).
[18] M. Carrillo-Tripp, H. Saint-Martin, and I. Ortega-Blake, J. Chem. Phys. **118**, 7062 (2003).
[19] A. Tongraar, K. R. Liedl, and B. M. Rode, J. Phys. Chem. A **102**, 10340 (1998).
[20] S. S. Azam, T. S. Hofer, B. R. Randolf, and B. M. Rode, J. Phys. Chem. A **113**, 1827 (2009).
[21] S. Yoo, X. C. Zeng, and S. S. Xantheas, J. Chem. Phys. **130**, 221102 (2009).
[22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
[24] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[25] C. T. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[26] CPMD code, Version 3.11.1, Copyright IBM Corp. 1990–2006, Copyright MPI für Festkörperforschung Stuttgart, 1997–2001.
[27] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[28] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
[29] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10142 (1993).
[30] I.-F. W. Kuo, C. J. Mundy, M. J. McGrath, J. I. Siepmann, J. VandeVondele, M. Sprik, J. Hutter, B. Chen, M. L. Klein, F. Mohamed, M. Krack, and M. Parrinello, J. Phys. Chem. B **108**, 12990 (2004).
[31] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[32] See http://faculty.sxu.cn/luhg/pair_coord.txt.