

The hydration structure of 18-crown-6/ K^+ complex as studied by Monte Carlo simulation using ab initio fitted potential

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Abstract

The intermolecular potential between a 18-crown-6/ K^+ complex and a water molecule is derived from 1200 energy points obtained from quantum chemical calculations using the 6-31G** basis set. The ab initio fitted potential was then applied to study the structural properties of the complex in an aqueous solution using the Monte Carlo simulation method. The radial distribution function (RDF) centered at K^+ to the oxygen atom of water shows a sharp first peak at 2.88 Å. The corresponding coordination number, integrated up to the first minimum at 3.76 Å, is 2 water molecules. The results indicate clearly that the 18-crown-6/ K^+ complex was solvated by the two nearest neighbors, one above and other below the ligand's plane. Evaluation was focused on the precise position and orientation of the two water molecules. It was found that the oxygen atoms of the two nearest neighbors bind to the K^+ while their hydrogen atoms rotate freely around the vector perpendicular to the ligand's molecular plane. © 2005 Elsevier Inc. All rights reserved.

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1. Introduction

The 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) molecule possesses a special capability to form a complex with the alkali metal ions, especially with K^+ , and has been proposed as a transporter for the ions between two solvent phases [1–3]. Solvation of the crown molecule is a central issue in this field because it can reveal the transport mechanism which may lead to design of more efficient agents. In addition, ligand's solvation leads also to a clearer understanding of the macrocyclic effect, of the extra stability of the complexes between the metal ions and macrocyclic ligand in comparison to those of their open-chain analogues. It was found that the D_{3d} conformation of 18-crown-6 is the most favorable in aqueous solution [4–6]. Experimental studies [7,8] suggest that such conformation is also preserved when the 18-crown-6/ K^+ complex is formed in aqueous solution. In terms of solvation,

previous simulations [4,5,9–26] of both complexed and uncomplexed 18-crown-6 lead to a broad range of coordination numbers. For example, the hydration number of the uncomplexed 18-crown-6 is still under debate, ranging as widely as 1–11.

It is well known that the quality and reliability of the simulation results rest on the use of the intermolecular potential employed, which in the previous studies [4,5,9–26] were based on molecular mechanics (MM) parameterization. This potential energy surface is usually generalized to be applicable for a wide range of molecular systems, leading to a lack of some specific details. Ab initio derived interaction potential would be more appropriate, especially for the present case, where the hydrogen bonding and ion–molecule interactions can be quantum mechanically parameterized to higher precision. Recently, we have applied such an intermolecular potential to the MC simulation of the aqueous 18-crown-6 [27]. That study revealed a rather complex picture of the hydration structure of this molecule which may explain the controversial nature of the results previously obtained.

To provide an answer to the above question, the intermolecular potential between the 18-crown-6/ K^+ complex and a water molecule is derived from quantum chemical

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calculations. A MC simulation is, then, performed using the newly developed ab initio fitted potential to investigate the hydration structure of the 18-crown-6/ K^+ complex.

2. Details of the calculations

2.1. 18-Crown-6/ K^+ –water potential function

The intermolecular potential between the 18-crown-6/ K^+ complex and a water molecule has been derived from quantum chemical calculations. To represent their interactions at all configurations and distances, numerous coordinates of the water molecule around the 18-crown-6/ K^+ complex were generated. The D_{3d} conformation of the 18-crown-6/ K^+ complex taken from Ref. [18] (see Fig. 1a), in which K^+ is located at the center of mass of the 18-crown-6 molecule, was proposed to be the most stable and dominant conformation in the aqueous solution [10,22]. This conformation is used and kept constant throughout this study. Due to its symmetry, the water molecule was positioned within only 1/12 of the entire space surrounding the 18-crown-6 molecule. This volume is described by $0^\circ \leq \theta \leq 180^\circ$, $0^\circ \leq \phi \leq 30^\circ$ and $1 \text{ \AA} \leq r \leq 20 \text{ \AA}$

(see Fig. 1a). Ab initio self-consistent field (SCF) calculations were then performed, with and without correction for the basis set superposition error (BSSE) [29], using the following default basis sets of the Gaussian 98 program [30]: 6-31G** and 6-311G**. The 6-31G** basis set was finally selected (detailed discussion is given in Section 3.1). The 1200 calculated energy points were then fitted to an analytical function of the form,

$$\Delta E(L, W) = \sum_{i=1}^{43} \sum_{j=1}^3 \frac{A_{ij}^{ab}}{r_{ij}^6} + \frac{B_{ij}^{ab}}{r_{ij}^{12}} + \frac{C_{ij}^{ab}}{r_{ij}^4} + \left[\frac{q_i q_j}{r_{ij}} \right] \quad (1)$$

where 3 and 43 are the numbers of atoms in the water (W) and the 18-crown-6 (L) molecule, respectively. A_{ij} , B_{ij} and C_{ij} are the fitting parameters, and r_{ij} is the distance between an atom j of the water and an atom i of 18-crown-6. q_i and q_j are the atomic net charges of atoms i and j (in atomic units, a.u.), determined from the population analysis [31] of the isolated molecules. The superscripts 'a' and 'b' on the fitting parameters have been used to classify atoms of equal atomic number which have different chemical environment, e.g., H and H' (see in Fig. 1). These details are usually omitted in general molecular mechanics force fields. The fitting procedure starts with 800 energy points. The resulting analytical potential function having the best fit for this set of data was tested using additional 400 randomly chosen points, outside the first set. The test points were then included into the fit, and fitting procedure was repeated until the consistency of the fitting parameters was reached.

2.2. Monte Carlo simulation

Monte Carlo simulation was carried out in a periodic cubic box of length 25.0 Å containing 500 water molecules and one 18-crown-6/ K^+ complex at a temperature of 298 K and under atmospheric pressure. The ionic crown complex was fixed at the center of the cube, whereas the solvent molecules were allowed to move freely throughout the simulation. The starting configuration of water molecules was randomly generated. A spherical cutoff of the site–site interaction potentials was set to be half of the box length. Simulation was then performed using the Metropolis Monte Carlo scheme. With above conditions, the reject:acceptance ratio for the simulated system of approximately 40:60 was yielded. The well-known MCY [32] potential model was employed to describe the water–water interactions. After equilibrium was reached, 80×10^6 configurations were generated and 1 out of every 2000 configurations was stored for subsequent analyses.

3. Results and discussions

3.1. 18-Crown-6/ K^+ –water potential function

Using the functional form shown in Eq. (1), the fitting parameters were optimized. The results are summarized in Table 1. The ΔE obtained from the SCF calculations and that obtained from the pair potential are compared in Fig. 1b. The changes in the 18-crown-6/ K^+ –water interaction energies as a

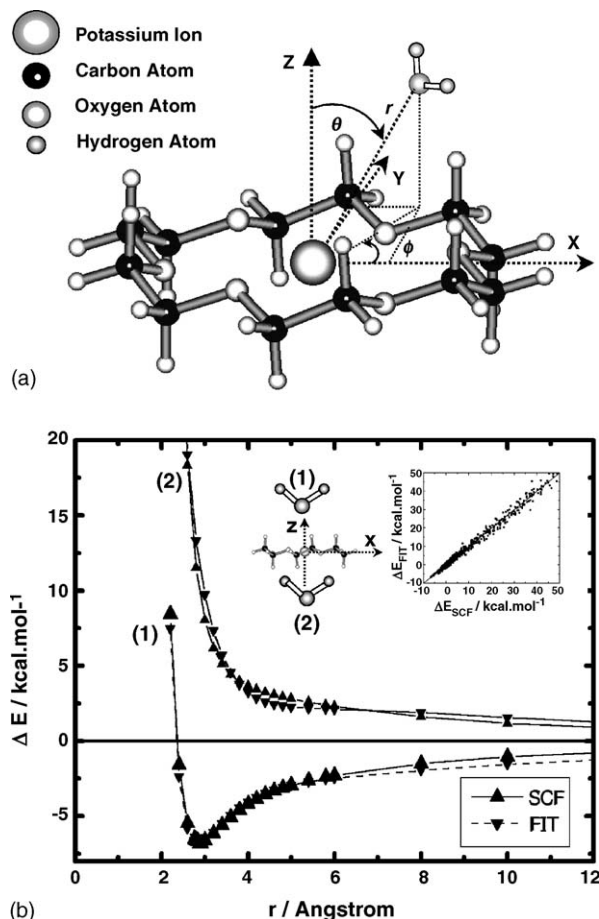


Fig. 1. (a) Definition of water orientation around the 18-crown-6/ K^+ complex in the coordinate system and (b) comparison of the binding energies between the 18-crown-6/ K^+ and water obtained from the SCF calculations (ΔE_{SCF}) and from the potential function (ΔE_{FIT}) in the two configurations which were inserted in the figure. All ΔE_{SCF} and ΔE_{FIT} data points are also compared in the inset.

Table 1

Final optimization parameters for the i th atoms of 18-crown-6/ K^+ complex interacting with the j th atoms of water (water, $q_o = -0.67316$ and $q_H = 0.33658$; 18-crown-6, $q_C = 0.09885$, $q_o = -0.69456$, $q_{HC} = 0.13390$, $q_{HC'} = 0.13159$ and $q_{K^+} = 0.79$ in atomic units)

| $i-j$ | A ($\text{\AA}^6 \text{ kcal mol}^{-1}$) | B ($\text{\AA}^{12} \text{ kcal mol}^{-1}$) | C ($\text{\AA}^4 \text{ kcal mol}^{-1}$) |
|----------|--|---|--|
| C–O | -2.64692181×10^3 | 3.04007356×10^5 | 3.89346992×10^2 |
| O–O | 5.89592185×10^3 | 4.35626672×10^3 | -1.54833414×10^3 |
| H'–O | -2.78857429×10^3 | 4.39946719×10^4 | 8.25440186×10^2 |
| H–O | 6.49438050×10^2 | $0.26094626 \times 10^{-5}$ | -9.15451976×10^1 |
| K^+ –O | 5.53205429×10^3 | 4.60822765×10^4 | -6.65730267×10^2 |
| C–H | -4.27426455×10^2 | 1.97895502×10^3 | 2.23456475×10^2 |
| O–H | -3.72569583×10^2 | 2.69956575×10^2 | 3.08582004×10^2 |
| H'–H | 1.41999664×10^3 | $0.18732948 \times 10^{-4}$ | -5.05510422×10^2 |
| H–H | 2.95911722×10^1 | $0.17756564 \times 10^{-7}$ | -2.01313354×10^1 |
| K^+ –H | -8.75308856×10^2 | 1.23192038×10^4 | 2.07992665×10^2 |

function of separation for the two configurations as obtained from the SCF calculation and from the fit are in good agreement (Fig. 1b). The energy minimum in the configuration (1) obtained from the ab initio calculation using the 6-31G** basis set is $-9.18 \text{ kcal mol}^{-1}$. The corresponding K^+ –O distance is 2.83 \AA , where O denotes the oxygen atom of water molecule. This conclusion was, again, confirmed by the plot shown in the inset of this figure, where all 1200 ab initio and fitted energies are compared. It is also shown in the inset that the best fit was found in negative region between $-5.0 \text{ kcal mol}^{-1}$ and $-9.2 \text{ kcal mol}^{-1}$. However, discrepancy was observed in the region above 20 kcal mol^{-1} in which such configurations are known to take place rarely in the solution.

In comparison, the energy minimum for the bare K^+ –water interaction as obtained from ab initio calculation by Tongraar et al. [33] gives $-18.6 \text{ kcal mol}^{-1}$ at a K^+ –O distance of 2.68 \AA . The reduction in the K^+ –water interaction caused by the 18-crown-6 is due to a charge compensation. One can see that by embedding K^+ into the 18-crown-6 and then computing the 18-crown-6/ K^+ interaction with water, many-body interactions will automatically be included. This is more advantageous than the summing up of the interactions between each pair separately, i.e., K^+ – H_2O , K^+ –18-crown-6, 18-crown-6– H_2O , etc., as usually done by most simulations using molecular mechanics force fields which neglect the many-body effects. Tongraar et al. [33] also reported that the many-body interactions in the $K^+(H_2O)_8$ complex can be as large as 32% of the pair interactions. For the aqueous 18-crown-6/ K^+ , K^+ would be coordinated by eight or more donor atoms (six oxygens from the 18-crown-6 and others from the water molecules). For this large contribution of many-body interactions cannot be avoided.

3.2. Solvation shell and coordination number of 18-crown-6/ K^+

The distribution and probability of finding water molecules around the 18-crown-6/ K^+ can be extracted from the simulation in terms of radial distribution function (RDF) and its integration. The RDF centered at K^+ , O and C atoms of ligand to oxygen (Ow) and hydrogen (Hw) atoms of water are calculated and plotted in Fig. 2. The K^+ –O RDF (Fig. 4a) shows a sharp first peak at 2.88 \AA which is larger than the force-field

based results obtained by Thompson et al. [14] (2.8 \AA) and by Kim [22] (2.7 \AA) (see Table 2). The coordination number, integrated up to the K^+ –O first minimum at 3.76 \AA , gives two oxygen atoms. The corresponding peak in the K^+ –H RDF appears at 3.88 \AA with four hydrogen atoms. These results clearly indicate that the 18-crown-6/ K^+ complex is solvated by the two nearest neighbors, one above and the other below the ligand's plane. This result is in good agreement with the simulation results obtained by Dang and Kollman [16] and Kim

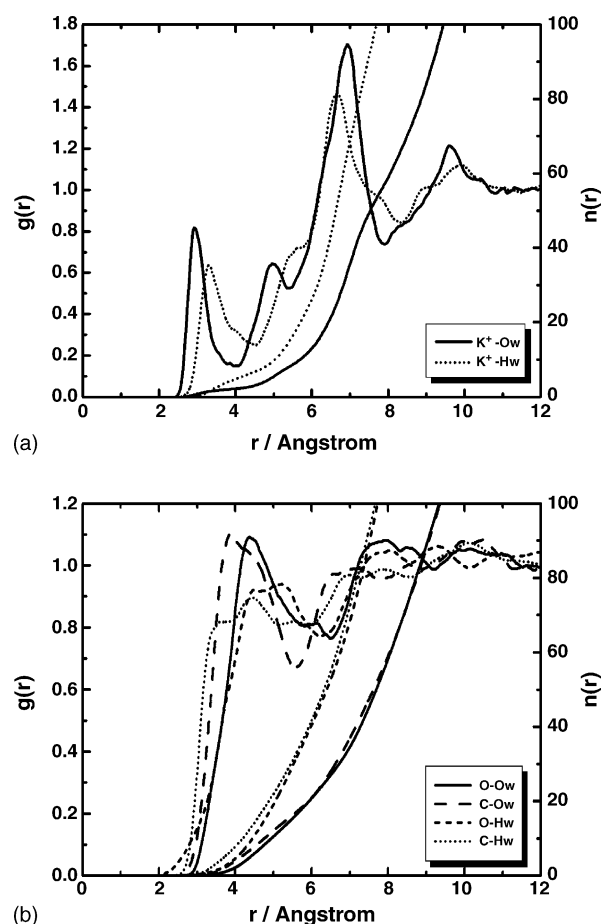


Fig. 2. Radial distribution functions, $g(r)$, and corresponding running integration numbers, $n(r)$, from: (a) K^+ located at the center of mass and (b) O and C atoms of the 18-crown-6 to the oxygen (Ow) and hydrogen (Hw) atoms of water molecules.

Table 2
Comparison of solvation parameters for 18-crown-6 and its complexes with K⁺ in different solvents

| System | r_{max} (Å) | r_{min} (Å) | CN | T (K) | Solute/solvent | Method | Reference |
|---|----------------------|----------------------|-----|---------|----------------|--------------------------|------------------------|
| 18c6/H ₂ O (MCY) | 2.0 | 3.3 | 2 | 298 | 1/500 | MC (ab initio potential) | Kongsuk et al. [27] |
| 18c6/H ₂ O (SPC/e) | 1.75 | 3.0 | 2 | 300 | 1/498 | MD (semi-QM/MM) | Thompson [19] |
| 18c6/H ₂ O (SPC) | 1.6 | 3.0 | 2 | 301 | 1/254 | MD (Force Field Model) | Kowall and Geiger [15] |
| 18c6/K ⁺ /H ₂ O (MCY) | 2.88 | 3.76 | 2 | 298 | 1/500 | MC (ab initio potential) | This work |
| 18c6/K ⁺ /H ₂ O (SPC/e) | 2.8 | 3.5 | 2 | 300 | 1/498 | MD (semi-QM/MM) | Thompson et al. [14] |
| 18c6/K ⁺ /H ₂ O (TIP3P) | 2.7 | 3.5 | 2.2 | 298 | 1/250 | MC (Force Field Model) | Kim [22] |
| 18c6/K ⁺ /CH ₃ OH | 2.7 | 3.5 | 2.0 | 298 | 1/250 | MC (Force Field Model) | Kim [22] |
| 18c6/K ⁺ /THF | 2.7 | 4.0 | 2.0 | 298 | 1/250 | MC (Force Field Model) | Kim [22] |
| K ⁺ /H ₂ O | 2.81 | 3.72 | 8.3 | 298 | 1/199 | MD (ab initio QMMM) | Tongraar et al. [33] |
| K ⁺ /H ₂ O (SPC/e) | 2.80 | 3.65 | 7.2 | | 1/215 | MD (Force Field Model) | Lee and Rasaiah [35] |
| KCl/H ₂ O | 2.8 | | 6 | | 2.0 M | X-rays | Palinkas et al. [36] |

[22]. The appearance of the first peak in the K⁺–O RDF at a distance of 0.50 Å shorter than that of the K⁺–H RDF means that the hydrogen atoms of each nearest neighbor almost point away from the K⁺. The precise orientations of the two water molecules are investigated and discussed in detail in Section 3.3. The next solvation shell of the 18-crown-6/K⁺ complex can be seen as the broad shoulder ranging from 3.5 Å to 5.8 Å

and the sharp peak centered at 6.9 Å of the K⁺–O RDF. These two peaks accumulate 19 and 65 water molecules, respectively. Their positions and orientations are therefore too complicated to be taken into consideration.

The first peaks of the O–Ow and the C–Ow RDFs (Fig. 4b) appear at 4.38 Å and 3.86 Å. The corresponding coordination numbers, integrated up to the first minima at 5.82 Å and

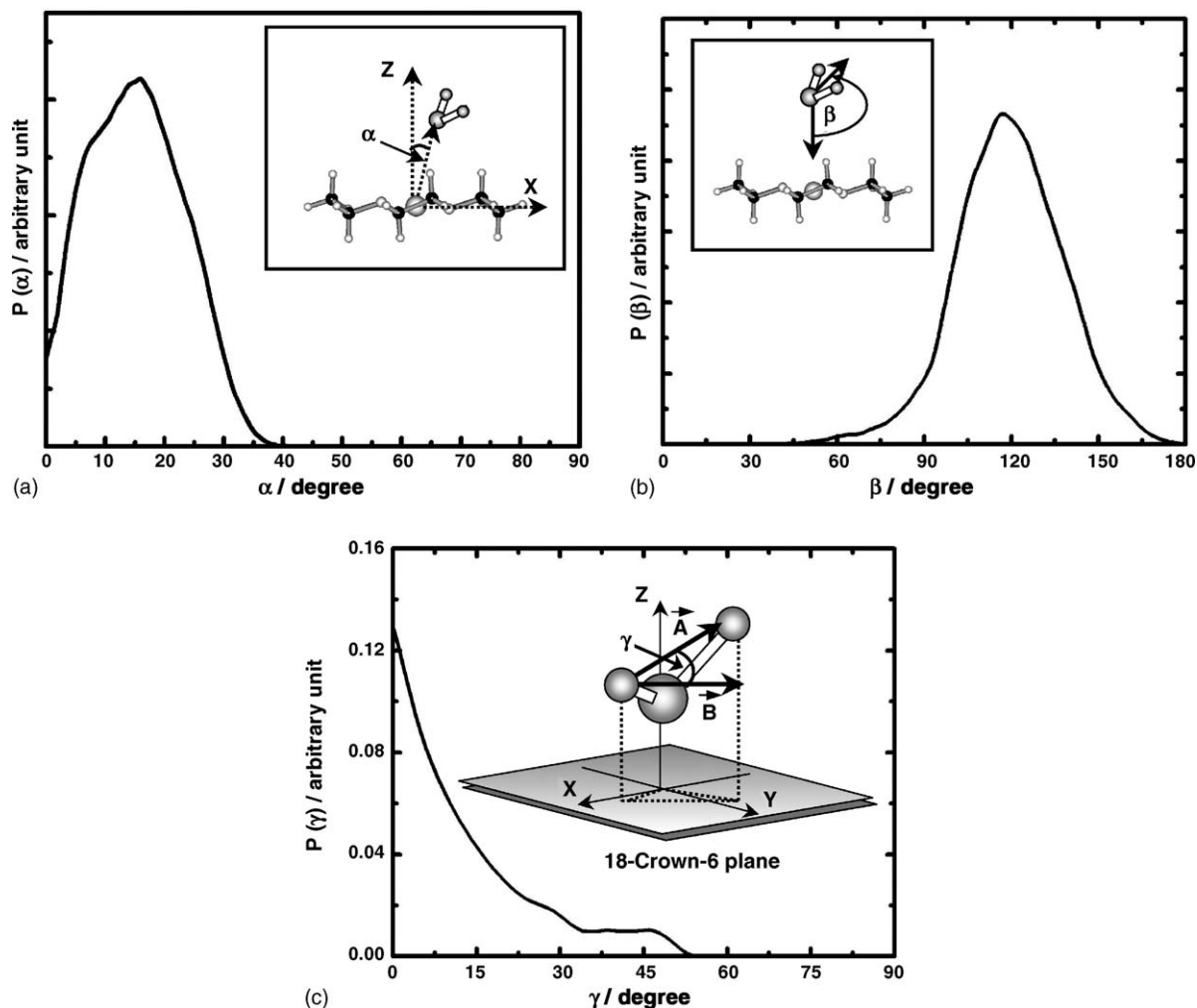


Fig. 3. Distribution of the angle: (a) α , (b) β and (c) γ (each is defined in the respective inset; see text for more details) for the two nearest neighbor water molecules of the 18-crown-6/K⁺ complex lying above and below the ligand's plane.

5.58 Å, are 18.8 and 16.2 water molecules, respectively. The broad distribution and the appearance of the peak shoulder of the first peak in the two RDFs as well as the corresponding ones to the Hw indicate the complexity and overlapping of these RDFs where the water molecules contribute to several of the RDFs. Not much information, on the specific binding as well as water on the orientation, can be exacted from these RDFs.

3.3. Orientation of the two nearest neighbors of 18-crown-6/ K^+

To investigate the precise orientation of the two nearest neighbor of the 18-crown-6/ K^+ , the probability distribution of angles α , β and γ are calculated and plotted in Fig. 3a–c, respectively. These angles are illustrated in the inset in each figure. α is the angle between the vector pointing from K^+ to the oxygen atoms of water and the vector pointing along z -axis. The plot shows a remarkably sharp peak at $\alpha = 15^\circ$, suggesting clearly that the oxygen atoms of the two nearest water molecules lie very close to z -axis one above and the other below the ligand's plane.

The plot of β , defined as the angle between the vector pointing from the oxygen atom of the nearest water to K^+ and the vector pointing opposite to the dipole vector of water, shows a broad distribution ranging from 60° to 170° with a clear maximum at 120° (Fig. 3b). The results suggest that the neighbor water molecules prefer to tilt their dipole off the K^+ –O direction, probably to allow their hydrogens to form H-bond with the oxygen atom of the crown molecule. Feller [34] has performed ab initio calculations on the $M^+18\text{-crown-6}(\text{H}_2\text{O})_n$ complexes, where $M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+$ and Rb^+ . It was reported that for small size metals such as Li^+, Na^+ and K^+ , the two nearest neighbor water molecules are likely to orient one of their hydrogen to the crown's oxygen.

To investigate the alignment of the two hydrogen atoms of the nearest water molecules in more details, we defined γ as the angle between the two vectors shown in the inset of Fig. 3c. The \vec{A} vector points from H1 to H2, while the \vec{B} vector is the projection of \vec{A} on to the 18-crown-6 plane. H1 denotes the hydrogen atom which lies closer to the xy -plane than the other one, H2. This plot shows a broad distribution ranging from 0° to 50° with a clear maximum at 0° (Fig. 3c). The broad distribution indicates highly flexible alignment of the two hydrogen atoms of the nearest water molecules. However, a clear feature of this plot is the highest probability taken place at $\gamma = 0^\circ$, indicating that preferential alignment of the two hydrogen atoms of the nearest water molecules is to arrange the vector linking them to be parallel to the ligand's plane.

3.4. Dynamics and equilibrium of the two nearest neighbors of 18-crown-6/ K^+

To confirm the findings shown in Fig. 3a–c, coordinates of oxygen and hydrogen atoms of the two nearest neighbors are projected onto the xy -plane, and plotted in Fig. 4a and b, respectively. The base of the plot denotes the ligand's molecular plane. The density represents the probability of finding the

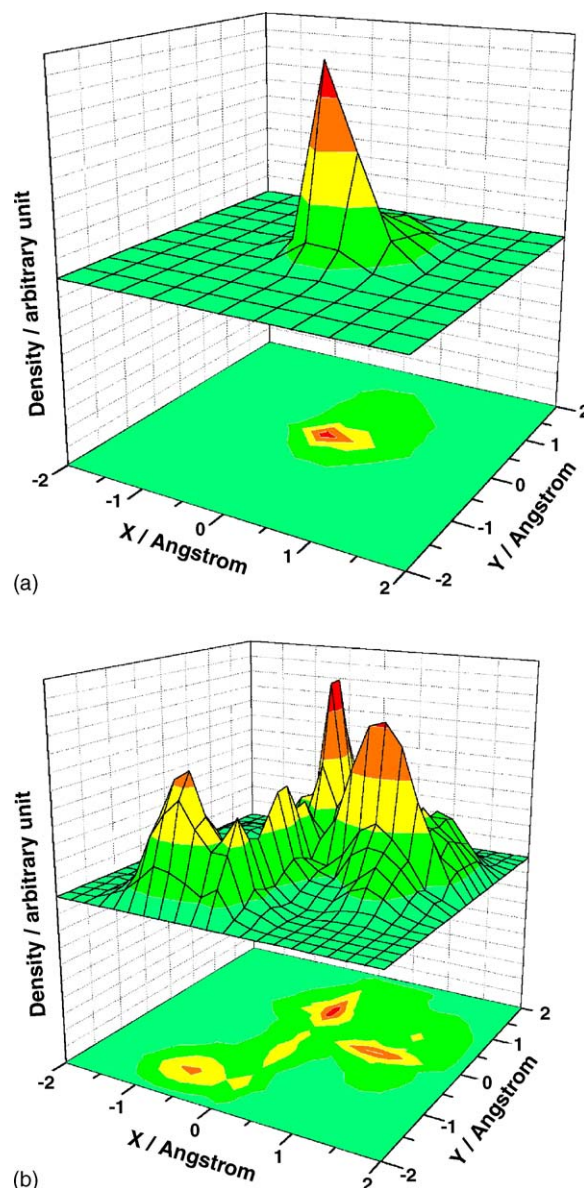


Fig. 4. Distribution of the coordinates of the two O atoms of the two nearest neighbor water molecules which are projected onto xy -plane (a) and similar distribution for the four H atoms of the two nearest neighbor water molecules (b).

oxygen or hydrogen atoms of water above (or below) the molecular plane.

The distribution plot of the oxygen coordinates for two nearest water molecules shows a pronounced peak around the origin of the Cartesian coordinate system. This is consistent with the distribution plot of angle α in which the maximum takes place at 15° . The same plot for hydrogen atoms shows almost non-zero probability around the origin. However, the three broad peaks above the three oxygen atoms of the ligand (the 18-crown-6 has a D_{3d} symmetry in which the three oxygen atoms, O_1, O_3 and O_5 , are above and the other three atoms, O_2, O_4 and O_6 , are below its molecular plane) are also exhibited.

The conclusion that can be drawn from Fig. 4a and b is that the hydration structure of the 18-crown-6/ K^+ complex has two water neighbor in which: (i) their oxygen atoms bind to and are

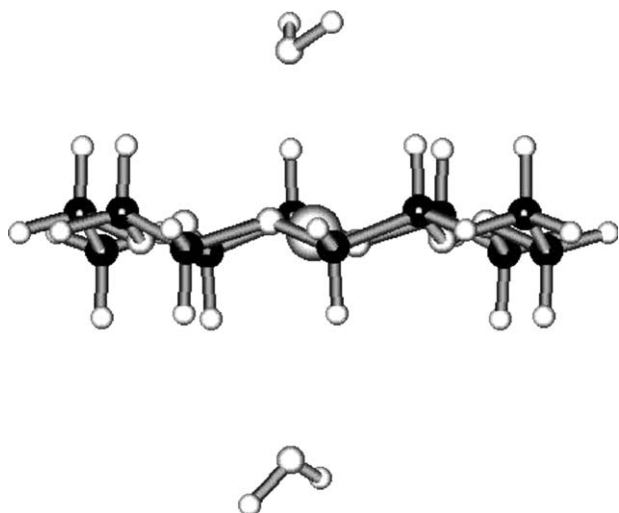


Fig. 5. A snapshot of the two nearest neighbors of 18-crown-6/ K^+ complex which was taken from the MC simulation.

above (or below) the K^+ and (ii) their hydrogen atoms can rotate freely around the z -axis and spend more time when they are close to the three oxygen atoms of the 18-crown-6. A snapshot for the first hydration shell is seen in Fig. 5.

4. Conclusion

The hydration structure of the aqueous 18-crown-6/ K^+ complex has been investigated by Monte Carlo simulation. An ab initio potential between the complex and water was employed so that the macrocyclic effect which screens the interaction between K^+ and water will be appropriately represented. Although the coordination numbers (two waters) for the complex and non-complex 18-crown-6 are the same, the hydration structures in these two cases are significantly different. Presence of the K^+ in the 18-crown-6 causes the two hydration waters' oxygen to be separated at a greater distance away from the center of the crown molecule (from 2.0 Å to 2.88 Å). It will also cause the dipole vector orientation to rotate from an outward to an inward direction towards the crown's center (about 90° change). The hydrated waters' oxygen is quite rigid, whereas its hydrogen atoms are free to rotate around the z -axis.

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