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Molecular Dynamics Simulation Study of Distribution and Dynamics of Aqueous Solution of Uranyl Ions: Effect of Varying Temperature and Concentration

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ABSTRACT: Investigating the characteristics of the actinyl ions has been of great interest due to their direct relevance in the nuclear fuel cycle. All atom molecular dynamics simulations have been employed to study orientational structure and dynamics of aqueous solutions of uranyl ions of varying concentrations. The orientational structure of water around a uranyl ion has been thoroughly investigated by calculating different orientational probability distributions corresponding to different molecular axes of water. The orientational distribution of water molecules in the first coordination shell of a uranyl ion is found to be markedly different from that in bulk water. Analysis of counterion distribution around the uranyl ion reveals the presence of nitrate ions along with water molecules in the first solvation shell. From the comparison of numbers of coordinated water and nitrate ions at various uranyl nitrate concentrations, it is evident that these two species compete for occupying the first solvation shell of the uranyl ion. Orientational dynamics of water molecules about different molecular axes of water in the vicinity of uranyl ions have also been investigated and decreasing orientational mobility of water with increasing uranyl concentration has been found. However, it is observed that the orientational dynamics remains more or less the same whether we consider all the water molecules in the aqueous solution or only the solvation shell water molecules. The effect of temperature on the translational and orientational characteristics of the aqueous uranyl solutions has also been studied in detail.

KEYWORDS: uranyl ion, molecular dynamics simulation, orientational distribution, orientational dynamics, concentration dependence, temperature dependence.

1. INTRODUCTION

With more and more expansion of nuclear power as a source of energy, the importance of radiotoxic actinyl ions is increasing. As use of these ions in nuclear reactions gives rise to the generation of radioactive waste, the attempts are being made first, to minimize the waste by extracting the reusable material from it and then, to safely dispose the radioactive waste. Knowledge of hydration and transport properties of these actinyl ions is essential for designing advanced separation processes for recycling of the radiotoxic material in the waste. Also, the storage of radioactive waste temporarily or the permanent waste disposal involves geological matrices involving the groundwater system. Studying their behavior in aqueous solutions will help in understanding the migration characteristics of these radionuclides in hydrogeological conditions in geological structures. As the experimental investigations involving actinyl ions are quite difficult to execute because of their highly radiotoxic nature, molecular dynamics and other computational investigations have been shown to be a useful alternative for understanding the structural, dynamic and thermodynamic behavior of these ions.¹⁻³⁰

Theoretical studies involving actinyl ions in aqueous and other environments can be classified into two broad categories. In one hand, one can use computationally expensive quantum mechanical calculations and ab-initio molecular dynamics simulations^{14,16,25-27} to understand the characteristics of uranyl ions in water clusters and bulk aqueous solutions. Garcia-Hernandez et al²⁵ and Buhl et al^{26,27} have not only investigated the effect of counter ions on the stability of uranyl(VI) complexes but also predicted the free energy profile of the dynamic solvent exchange between the bulk and the solvation shell. On the other hand, force-field based classical molecular dynamics simulations, which provide a computationally inexpensive but

accurate enough method to understand structure as well as dynamics of these ions in different condensed phase environments, are extensively used now-a-days.^{1-4,6-9,12-13,19-24,29,30} In a classic review, Buhl and Wipff²⁸ have discussed the abilities of ab-initio MD simulations in the framework of Car-Parrinello approach as well as force-field based classical MD simulations to describe various aspects of coordination and solvation shell structures and energetics of different actinyl ions in presence of different counterions. Most of the existing molecular dynamics based investigations have dealt with single uranyl ion in an aqueous solution. Pioneering work of Guilbaud and Wipff¹⁻³ on various aspects of uranyl ion hydration is important to mention in this respect. Apart from developing force field parameters³ for uranyl ions and investigating complexation and hydration behaviors of uranyl ions,¹⁻² Wipff and coworkers⁵⁻¹¹ have extended their work to understand the characteristics of lanthanide ions in different solvation media as well. Very recently, Maginn and coworkers have developed force fields for the different actinyl ions dissolved in water by taking into account the many-body solvation effects.^{4,23} They have further used this force field to investigate detailed solvation structure and dynamics^{23,24} of different actinyl ions. Residence time of water molecules in the solvation shell of these ions²⁴ has also been investigated. Kerisit et al.^{12,13} have also generated a modified force-field of uranyl-water system based on free energy calculations to study in detail the structure, diffusion and free energy of uranyl hydration. The structure and dynamics of the uranyl ion and its different complexes at various solid-liquid and liquid-liquid interfaces have also been studied.¹⁹⁻²²

Most of these studies involving aqueous solution of uranyl ion consider only one actinyl ion in a box of water molecules. Water being a hydrogen-bonded liquid with tetrahedral structure, it is very likely that presence of a large number of ions or neutral solutes will modify the hydrogen-bonded and tetrahedral structure of water and therefore it is expected that the

dynamics of the solution will also be modified with increasing concentration of the ions or solutes. In a recent study, it is shown that a neutral solute like urea does not really break the H-bonding structure of water, but many of the tetrahedral oxygen sites of water get replaced by nitrogen or oxygen site of urea.³¹ Uranyl ion being a doubly positive molecular ion, it has a greater chance of modifying the structure and dynamics of its aqueous solution at high concentrations. In fact, very recently Chopra et al.^{29,30} have studied the effect of varying uranyl ion concentration on the structural and dynamical aspects of the various species present in its aqueous solutions. They have reported³⁰ that although with change in concentration in the range 0.1 to 1.0 M, there is not much variation in the structural arrangement of water molecules around the uranyl ions, but the mobility of different species present in the solution reduces considerably with increasing uranyl concentration. It is observed that although the mobility of the solvation shell water molecule gets reduced significantly, reduction of overall translational mobility of water and that of ions are shown to be due to long-range effect.³⁰

Although many literature reports deal with the structural arrangement of water molecules around the uranyl ions and the translational dynamics of various species in aqueous solutions of uranyl ions, studies on the orientational distribution and dynamics of water molecules in bulk water as well as in aqueous solutions of uranyl ions are rather few. For instance, Clavaguera-Sarrio¹⁵ has carried out modeling of uranyl cation-water system and from the analysis of cation-water and water-water interactions it is shown that water molecules are strongly oriented around the uranyl cation. Frick et al.¹⁷ have employed quantum mechanical charge field molecular dynamics (QMCF-MD) framework for simulating the behavior of uranyl (VI) (UO_2^{2+}) cations in its aqueous solution. They estimated the distribution of the first shell water molecules around the uranyl ion in terms of tilt angle (i.e. the angle between the plane defined by the three atoms of a

water molecule and the straight line that connects uranium and the oxygen atom of the respective water) and the Θ angle (i.e. the angle between the same straight line and the water dipole vector).¹⁷ The tilt and Θ angles show peaks at around 0° and 180° respectively. Later, they extended the same approach to understand the orientational distribution of water molecules around uranyl (V) (UO_2^+) cations.¹⁸ The angular distribution of $\text{O}_\text{U}-\text{U}-\text{O}_\text{U}$ angle showed a peak at around 180° which corresponds to a perfectly linear geometry with a tilt of not more than about 10° . The $\text{O}_\text{W}-\text{U}-\text{O}_\text{W}$ angle showed two main peaks, one at around 90° and the other one close to 180° which corresponds to a square planar configuration. Also, not much literature is available on the effect of concentration variation on the orientational distribution and dynamics of water around uranyl ions. Very recently, Chopra et al.³⁰ have made an attempt to study the orientational dynamics of water in the bulk phase of aqueous solutions of uranyl ions of concentration range varying from 0.1 to 1.0 M. They have observed slight slowing down of angular dynamics of water molecules with increase in concentration of uranyl ions in aqueous solution. As far as we are aware of, the orientational distribution and dynamics of solvation shell water molecules and the effect of concentration of the uranyl ions on these characteristics have not been investigated in detail. Not only that, not enough literature reports available on the effect of temperature on the structure and dynamics of the uranyl solution. Therefore, the present study can be divided into two parts. In the first part, we intend to estimate the orientational distribution of water molecules within the coordination shells of uranyl ion with respect to various angles in comparison to that in bulk water as obtained from the atomistic molecular dynamics (MD) simulations.³² Also, an attempt has been made to investigate the effect of concentration of uranyl ions on the orientational characteristics of solvation shell water. Finally in part two, we have presented the results on the effect of temperature on the structural and dynamical properties of the uranyl solutions at varying concentration of the uranyl nitrate.

2. MODELS AND SIMULATION DETAILS

In the present work, aqueous solutions of uranyl ions of three different concentrations are considered where (i) one uranyl ion (hereinafter we call it system U1), (ii) five uranyl ions (hereinafter we call it system U5) and ten uranyl ions (hereinafter we call it system U10) are solvated in a cubic box of around 500 water molecules with a bulk water density of around 0.98 g cm⁻³. The concentrations of these three solutions correspond to 0.106 M, 0.53 M and 1.06 M for U1, U5 and U10 systems respectively. The back end of the nuclear fuel cycle, especially reprocessing of spent fuel from uranium-based reactors deal with concentrations of this order.^{33,34} The total number of molecules i.e. water plus uranyl nitrate in the systems in all the cases was fixed at 513. The nitrate (negative) ions were introduced in the solution as counter-ions to maintain the electrical neutrality of the system. Molecular dynamics simulations were performed in canonical (NVT) ensemble, in which temperature of the system was maintained at a target value by using extended system approach of Nose.³² Atomistic models were used for uranyl ion with one uranium and two oxygen sites, and for the nitrate ion with one nitrogen and three oxygen sites. TIP3P model for water was used in all the cases. Lennard–Jones and Coulomb (for charged sites) potentials were considered for non-bonded site-site interactions and usual harmonic terms are used for bonds and angles in the intra-molecular potential terms for uranyl and nitrate ions. The potential energy of the system is thus given by the equation³⁰:

$$U = \sum_{bonds} 0.5K_r (r - r_{eq})^2 + \sum_{angles} 0.5K_\theta (\theta - \theta_{eq})^2 + \sum_{i < j} \left[\frac{q_i q_j}{r} + 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} \right] \quad (1)$$

where the symbols have their usual meaning. The third term consisting of Coulomb and Lennard-Jones (LJ) interactions represents the non-bonded interaction. The values of the potential parameter for both inter- and intra-molecular interactions are taken from literature.^{1,4,29,30,35} The LJ parameters for solvated uranyl ion are taken from the work of Rai et al.⁴ whereas for water molecules, those reported by Jorgensen et al.³⁵ for TIP3P are taken. The parameters related to bonded interactions and the LJ parameters for the nitrate ion are taken from the work of Guilbaud et al.¹ The values of different bonded and non-bonded parameters for different species are explicitly given in our earlier study.³⁰ Lorentz–Berthelot mixing rule is used to estimate all cross parameters for the LJ potential.

Most of the simulations were carried out at a target temperature of 298 K. The RATTLE algorithm³² was used to constrain the OH bond lengths and the HH distance of the water molecules during the simulations. The Velocity Verlet algorithm³² was used as a tool for integrating equations of motion with a time step of 1 fs. A cut-off distance of 12.0 Å in real space was used for all non-bonded interactions. In all simulations, periodic boundary conditions and minimum image conventions in all three directions have been employed. The Ewald's method was used for treating electrostatic interactions. After an equilibration period of 1 ns, trajectories were saved at every 0.01 ps during the next 1 ns production run for post analyses. All the results on radial distribution functions and coordination numbers related to nitrate ions (see Figure 5 and Table 1) are obtained from averaging over a 30 ns simulation trajectory. To study the effect of temperature, additional simulations were carried out at temperatures of 240 K, 270 K, 330 K and 360 K.

3. RESULTS AND DISCUSSION

The orientational structure of water molecules around uranyl ions is studied by estimating the distribution of angles formed by U-O_w distance vector with different molecular axes of the water molecule. Here O_w stands for the oxygen atom of water molecule. Our aim is to investigate the angular distributions of solvation shell water molecules around uranyl ions in aqueous uranyl solution and compare these with those obtained for water around a central water molecule in bulk water. Apart from orientational structure, orientational dynamics of water in the vicinity of uranyl ions is also investigated by calculating orientational time correlation functions involving different molecular axes of the water molecules. The orientational dynamics of the water molecules within the first coordination shell of uranyl ions is then compared with those obtained for all the water molecules (hereafter we call these as overall water molecules) in the aqueous solution. Recently, Chopra et al.³⁰ have observed that the translational mobilities of solvation shell water molecules get reduced significantly as compared to those water molecules not residing in the solvation shell. Therefore, it will be interesting to investigate whether similar slowdown is observed in case of angular dynamics of the solvation water molecules. Before looking into the dynamical aspects, we first analyze how the water molecules in the first solvation/coordination shell around uranyl ion are arranged orientationally.

(i) Orientational distribution of water molecules in the vicinity of uranyl ions

We have calculated angular distributions of the water molecules around uranyl ion in its first coordination shell (FCS) and second coordination shell for U1, U5 and U10 systems. The first coordination or solvation shell boundary is defined by the position of first minimum³⁰ (3.0 Å), whereas the lower and upper boundaries of the second coordination or solvation shell are defined

by the first minimum and second minimum (5.5 Å) of the respective $g(r)$.³⁰ We have considered four different angles (Figure 1), namely, angle formed between the line joining uranium atom of the uranyl ion and oxygen atom of the solvation water molecule (i.e. U- O_w distance vector) and (i) water dipole moment vector (θ), (ii) a vector perpendicular to plane of water molecule (ψ), (iii) O-H bond vector (γ) and (iv) U- O_U bond vector (χ), O_U being the oxygen atom of uranyl ion. The distribution of these angles for the water molecules in the first and second coordination shells of uranyl ions for U1 system are shown in Figure 2 (a) and (b) respectively. In Figure 2 (a), the distribution of θ reveals a peak at around 0° with a spread in the distribution of around 22° indicating that the dipole moment vectors of the FCS water molecules are directed along the U- O_w vector as demonstrated earlier by Frick et al.¹⁷ Thus $\theta=0^\circ$ reveals that H atoms of water are away from the U of UO_2 .

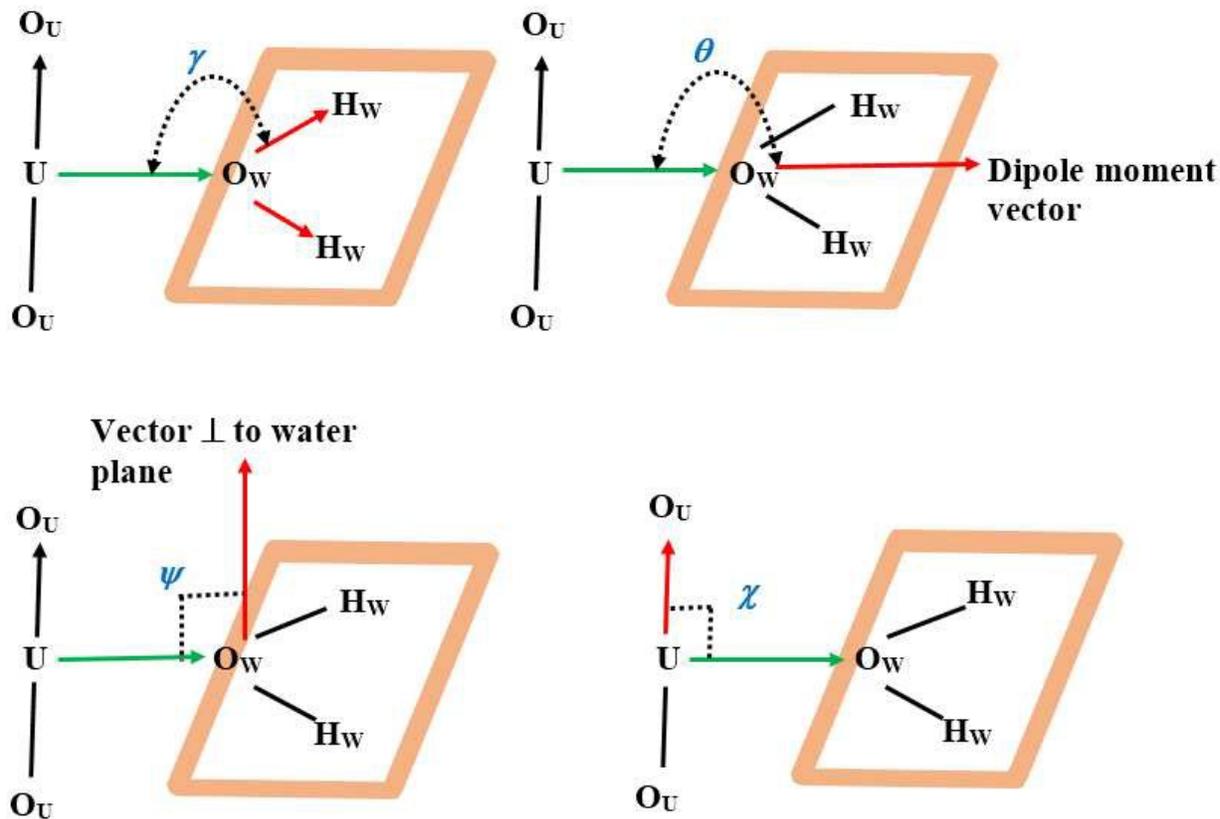


Figure 1. Schematic representation of various angles considered for orientational distribution of the water molecules around uranyl ions in the aqueous uranyl nitrate solution.

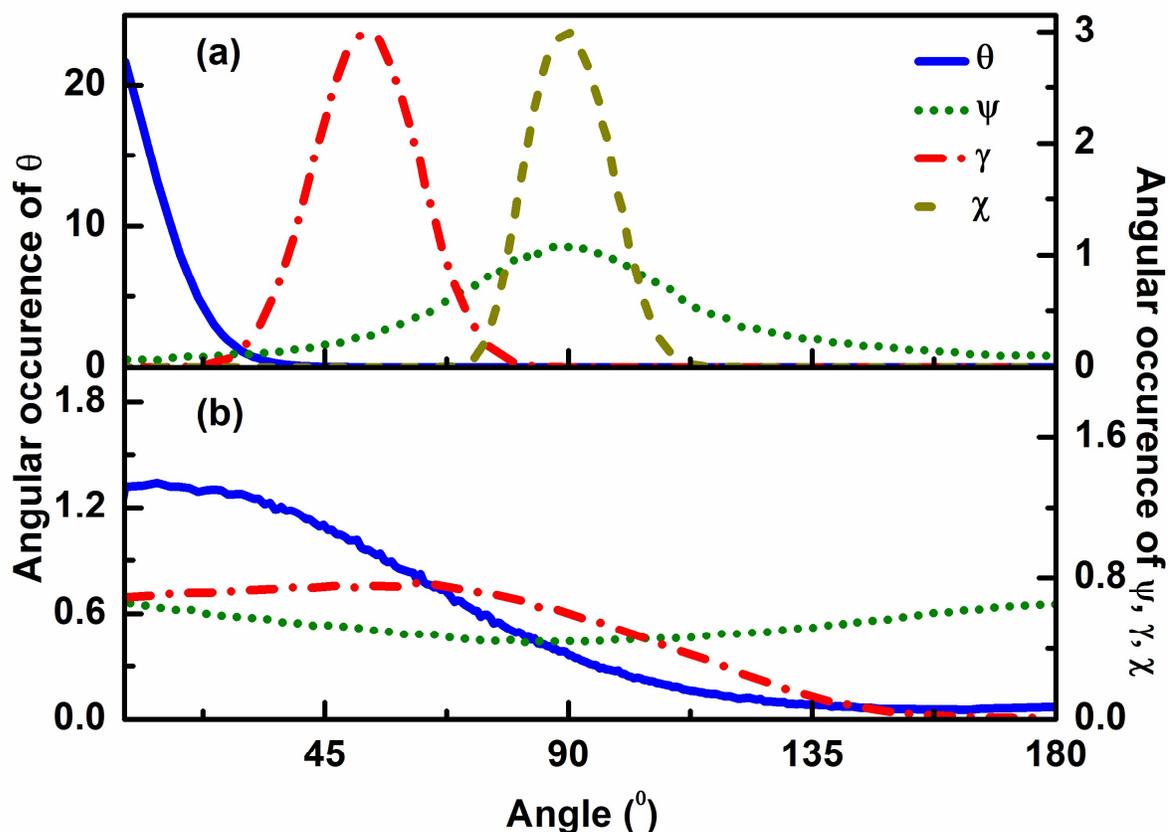


Figure 2. Distributions of various angles made by different orientational vectors of a water molecule in the (a) first and (b) second coordination shells of a uranyl ion in the aqueous uranyl nitrate solution.

As the water dipole moment vector and U-O_w vectors point in the same direction, it is expected that the plane-perpendicular (CR) vector will be perpendicular to U-O_w vector and in fact, the distributions for ψ shows a peak at around 90° . This result is consistent with the tilt angle distribution given by Frick et al.¹⁷ The distribution of γ has a peak at around 52.4° , which is consistent with other orientations (Figure 2a); in particular the dipole orientation of 0° . The peak

corresponding to 90° for angle χ indicates that the U-O_U bond vector preferably remains perpendicular to U-O_W vector. All these orientational distributions suggest that the water molecule stays in a plane perpendicular to O_U-U-O_U line (UO₂ being almost a linear molecule) passing through the uranium atom of UO₂ (see Figure 3). Although not shown here, the angular distribution remains more or less the same with change in concentration of uranyl ions in the solution. The analysis of Figure 2 (b) shows that the water molecules within the second coordination shell of uranium atom do not show such preferred orientations as evident from the comparison of the intensities of different distributions in Figure 2(a) with the corresponding distributions in Figure 2(b).

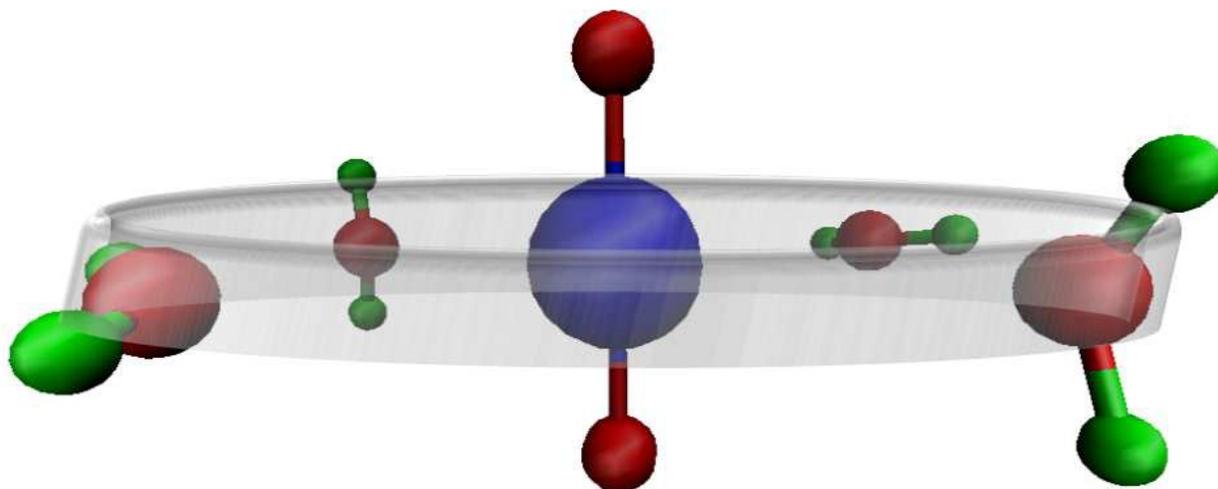


Figure 3. Pictorial representation of water molecules in the first coordination shell of a linear UO₂ molecule.

For comparison, the angular distributions of water molecules around a central water molecule have also been estimated for bulk water i.e. for a water molecule in the solvation shell of another water molecule. Here, the angles are considered between O_W-O_W distance vector and

three molecular orientational vectors of the water molecules as mentioned above within first and second coordination shells. A water molecule around a central water molecule can act as a hydrogen bond acceptor or donor depending on whether it offers its oxygen or hydrogen atom for the formation of hydrogen bond with the central molecule. Depending on this, the OH bond vector can form two angles with the O_W-O_W vector; one at 0° and another at 180° and in fact we found (see Figure 4(a)) these two peaks in the distribution of angle γ . If a neighbor acts as a hydrogen donor, then the OH bond should point towards the central O_W and in that case the dipole moment vector should form an angle with the O_W-O_W vector of around 126° ; whereas for an acceptor, the angle should be around 54° and in fact, two peaks at θ equals to 126° and 54° are observed in this case. As expected, the angle ψ shows a peak at 90° as it is a vector perpendicular to the plane of water molecules and hence to the O_W-O_W vector. As in the case of aqueous solution of uranyl ions, the water molecules in the second coordination shell of a central water molecule in bulk water also do not show much preference to any particular orientation (see Figure 4(b)).

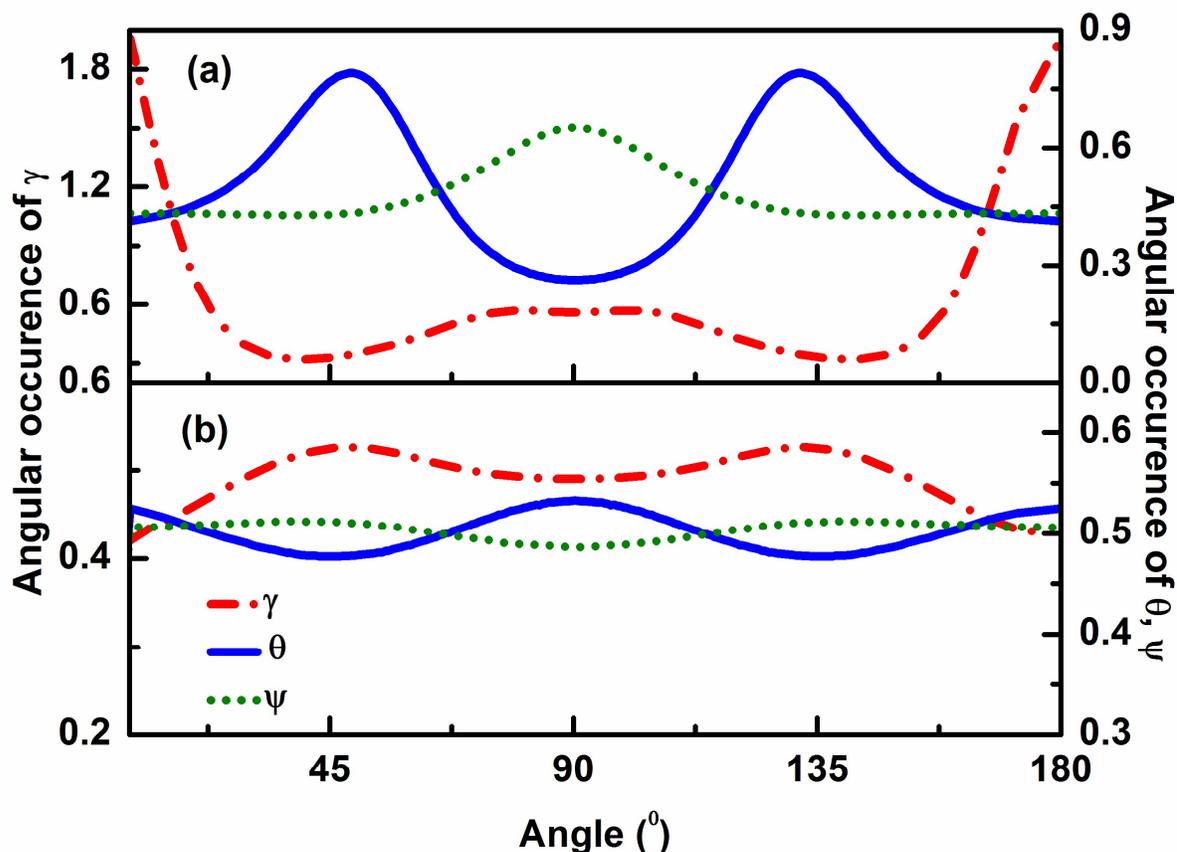


Figure 4. Distributions of angles made by different molecular orientational vectors of a water molecule in the (a) first and (b) the second coordination shells of a central water molecule in bulk water. The angles are defined in the same way as in Figure 1 except that UO_2 ion is replaced by a water molecule.

(ii) Radial distribution of counter ions (nitrate ions) with respect to uranyl ions

As already mentioned, we have studied the distribution of counter ions (nitrate ions) with respect to uranyl ions in U1, U5 and U10 systems by simulating each of the systems for 30 ns. The radial distribution functions of oxygen atoms of water molecules (solid blue line), nitrogen atoms of nitrate ions (dashed red line) and oxygen atoms of nitrate ions (dotted green line) with respect to

uranium and oxygen atoms of the uranyl ion are given for U10 system in Figures 5 a and b respectively. We have shown earlier³⁰ that water oxygen (O_W) comes closer to uranyl oxygen (O_U) as compared to water hydrogen (H_W) due to the compensation of negative charge of uranyl oxygen by the large positive charge (+2.5) of uranium, creating an overall positive environment around uranyl ion. Figure 5 also shows that the oxygen of nitrate ion (O_{NO_3}) occupies positions closer to O_U of uranyl ion as compared to positively charged nitrogen (N_{NO_3}). However, positively charged U gets closer to negatively charged oxygen atoms (O_W or O_{NO_3}) as compared to negatively charged O_U . It is interesting to observe that the location of the first peak of $g(r)$ s of O_{NO_3} and O_W being almost in the same distance from the central uranyl ion, one can conclude that both are in the solvation shell of the uranyl ion. We have also calculated the coordinated numbers (CNs), defined as the number of these atoms in the first solvation shell of uranyl ion, of O_W and O_{NO_3} around the U (first solvation shell radius 3.0 Å) and O_U (first solvation shell radius 4.0 Å) sites of the uranyl ions in U5 and U10 systems (Table 1). For U1 system, the first peak of $g(r)$ for O_{NO_3} around uranyl ion is not observed most of the time during the 30 ns trajectory analyzed here. It can be seen (see Table I) that as the concentration of uranyl ion is increased (U5 to U10), the CN of O_W is reduced whereas that of O_{NO_3} is increased. It is interesting to note that the oxygen atom of water and that of nitrate ion compete with each other to occupy the first coordination shell of the uranyl ion (blue solid and dotted green lines).

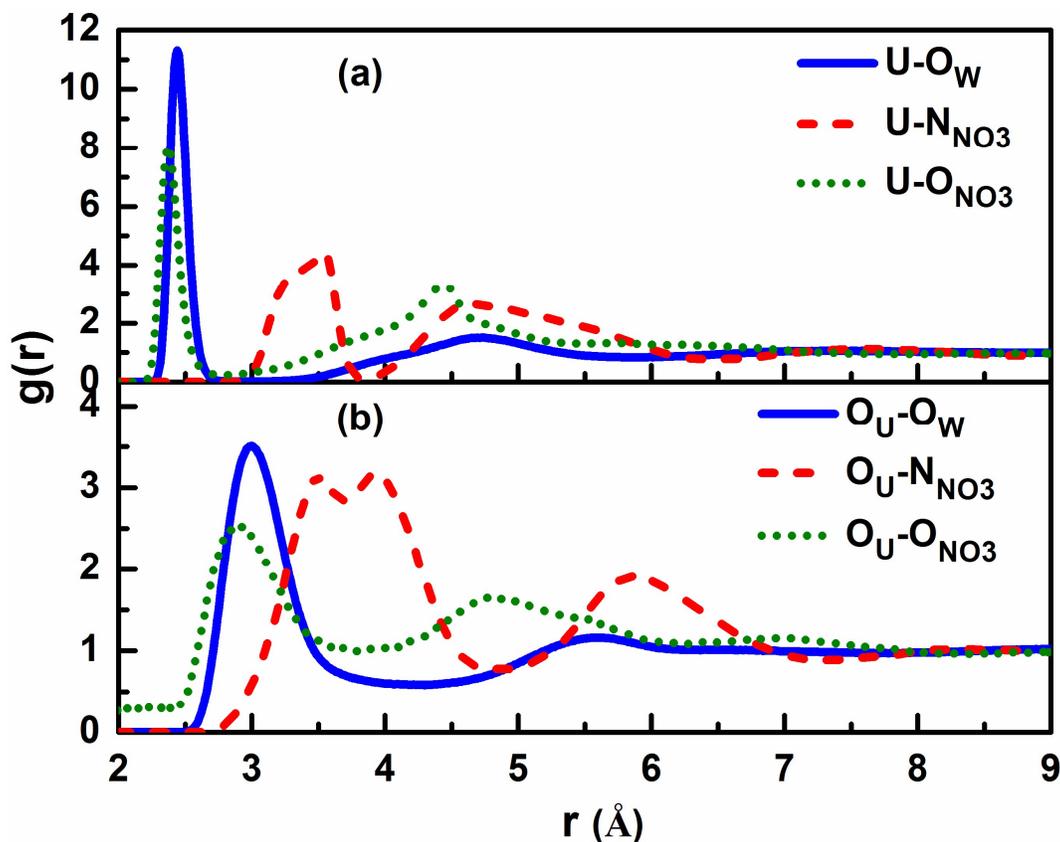


Figure 5. Radial distribution functions of oxygen (O_W) atoms of water molecules, nitrogen (N_{NO_3}) and oxygen (O_{NO_3}) atoms of nitrate ions with respect to (a) uranium (U) and (b) oxygen (O_U) atoms of uranyl ions.

Table 1. Coordination numbers of oxygen atoms of water and nitrate with respect to uranium and oxygen atoms of uranyl ions for different uranyl ion concentrations

System	CN of O_W with respect to		CN of O_{NO_3} with respect to	
	U	O_U	U	O_U
U5	4.70	9.50	0.32	0.84

U10	4.61	9.34	0.43	1.32
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(iii) Orientational dynamics of water molecules in the vicinity of uranyl ions

We analyze orientational dynamics of water molecules in terms of time correlations functions

$\Gamma_l^\alpha(t)$ of the orientational vectors, u_α defined as

$$\Gamma_l^\alpha(t) = \langle P_l(u_\alpha(t) \cdot u_\alpha(0)) \rangle \quad (1)$$

where P_l is the Legendre polynomial of order l . It defines the time evolution and hence the orientational dynamics of the molecular vector u_α . The angular brackets in the above equation represent average over time origins as well as the number of molecules.^{30,36} In present work, three unit vectors (u_α) along three different molecular axes namely (i) dipole moment vector ($u_\alpha = \mu$) (ii) H-H vector ($u_\alpha = \text{HH}$) and (iii) a cross vector ($u_\alpha = \text{CR}$) i.e. a vector perpendicular to plane of water molecule³⁶ have been considered. The first ($l=1$) and second ($l=2$) order autocorrelation functions for the above mentioned three unit vectors as obtained by considering all the water molecules in the system, and water molecules in the first coordination shell are given in Figures 6 and 7 respectively for U1 system. Similar curves are obtained for U5 and U10 systems too. For all the three different orientational correlation functions, a slight slowing down of the rotational motion of water is observed with increase in concentration of uranyl ions, this effect being more prominent for the dipole moment vector.³⁰ Figures 6 and 7 suggest that there is not much difference between the autocorrelation functions calculated by considering all water molecules (red solid lines) and only the coordination shell water molecules (black dashed lines). To confirm this, more simulations i.e. six simulations of 1 ns each were carried out and it was

observed that the variation in the orientational correlation functions as we go from all water molecules to only solvation shell water molecules, is within the statistical uncertainties for different trajectories. For instance, Figure 8 shows the first order dipole moment orientational correlation functions of solvation shell water molecules (black dashed lines) for different trajectories for all the three systems U1, U5 and U10 overlapped by the corresponding orientational correlation function (red solid lines) for overall water molecules. It is clear from the Figure 8 that orientational dynamics of water molecules remains the same whether they are inside or outside the solvation shell of uranyl ions. Thus, although the translational mobilities of solvation shell water molecules are severely reduced as compared to those of all water molecules,³⁰ both the orientational structure and dynamics of solvation water remain the same as compared to the that obtained for all the water molecules in the system.

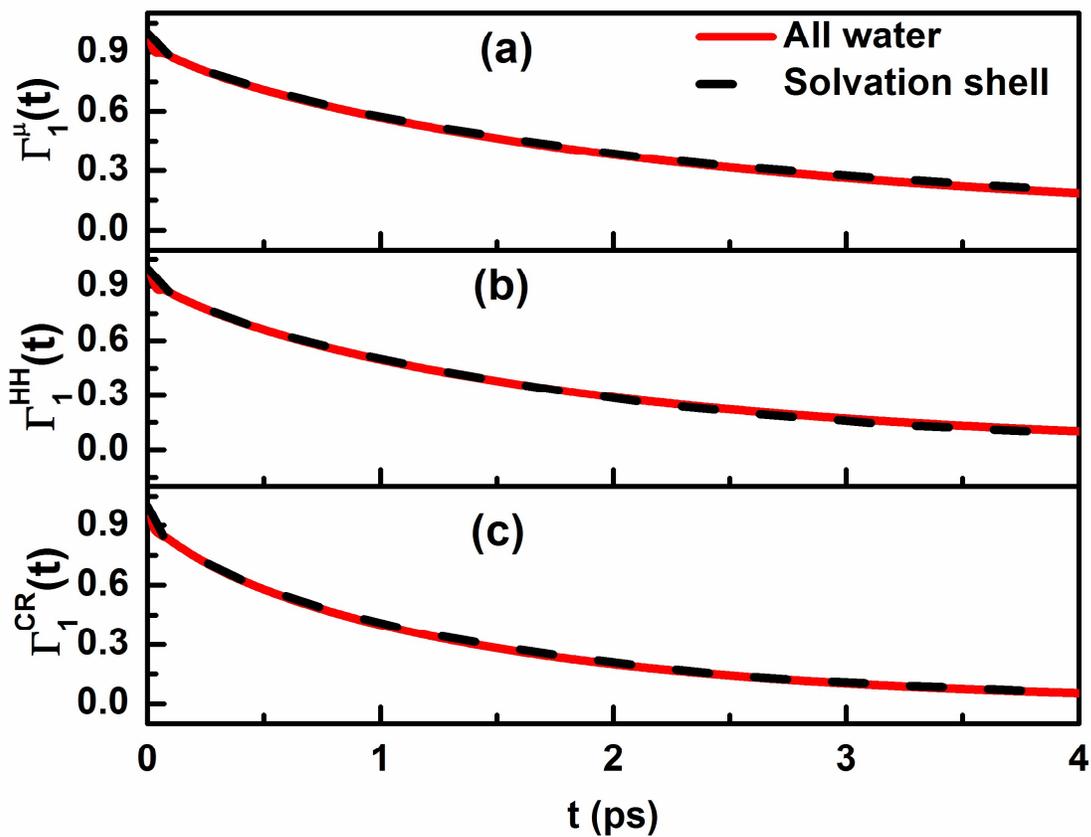


Figure 6. First order orientational correlation functions of solvation shell (black dashed line) and overall water molecules (red solid line) with respect to (a) water dipole moment vector (μ), (b) water H-H vector (HH) and (c) water cross vector (CR) for U1 system.

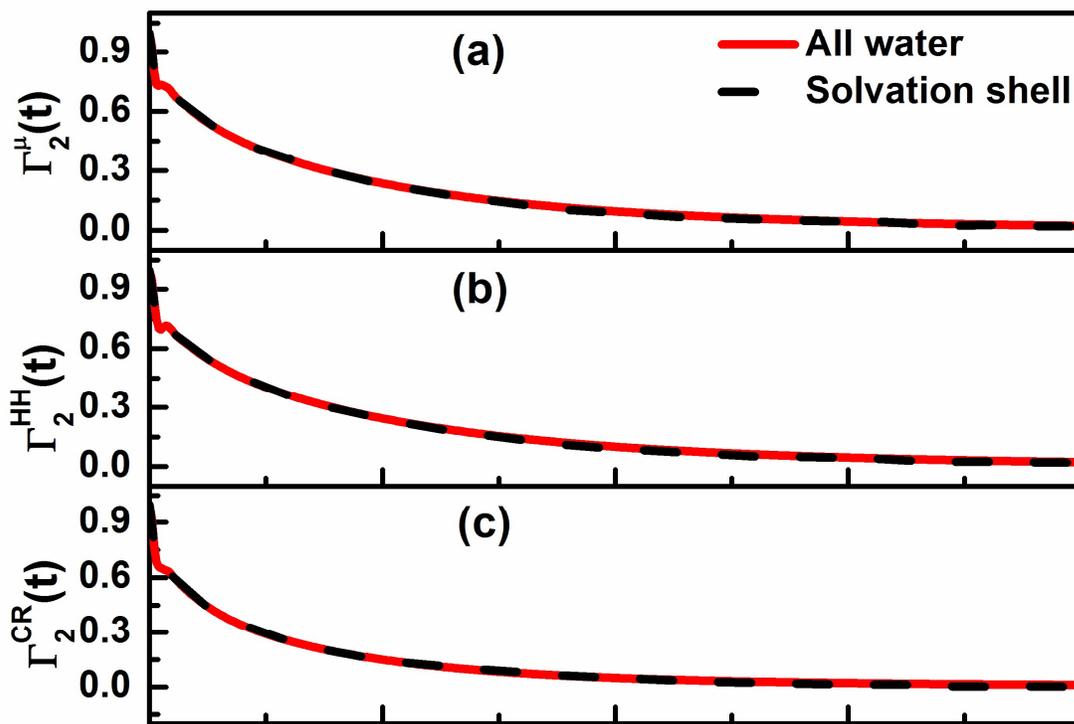


Figure 7. Second order orientational correlation functions of solvation shell (black dashed line) and overall water molecules (red solid line) with respect to (a) water dipole moment vector (μ), (b) water H-H vector (HH) and (c) water cross vector (CR) for U1 system.

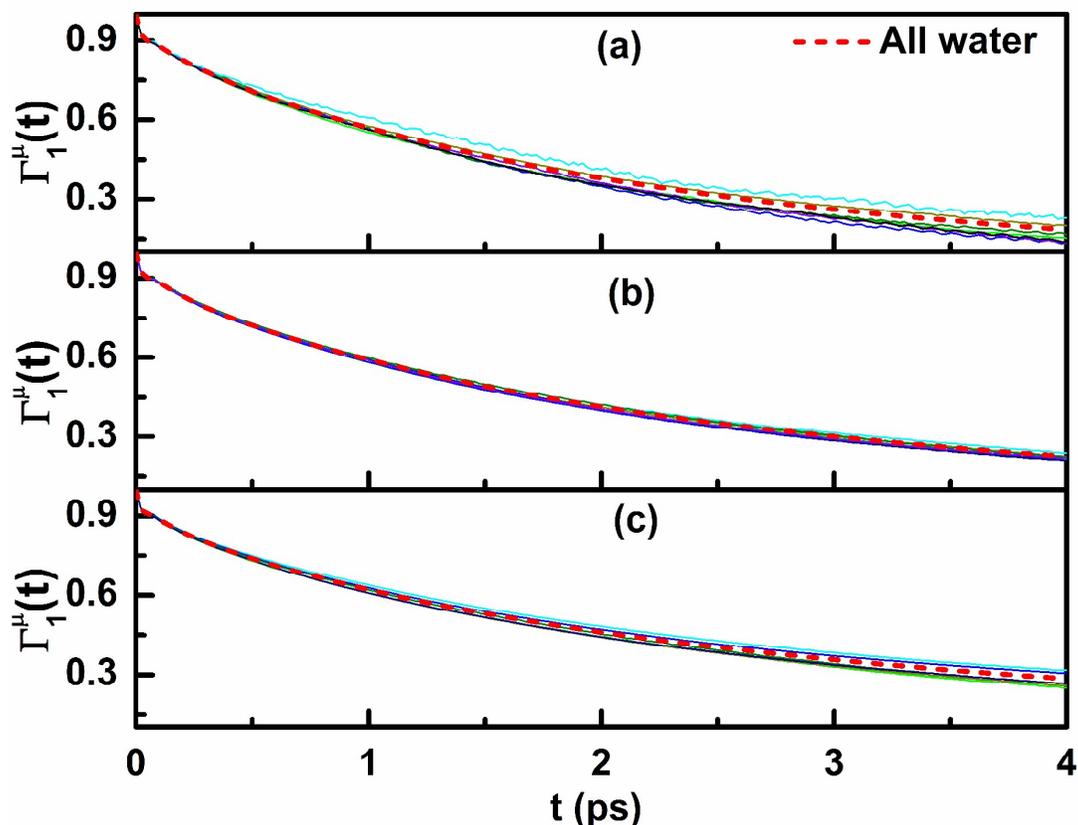


Figure 8. First order orientational correlation functions of solvation shell water molecules with respect to water dipole moment vector (μ) for different trajectories (solid lines). Red color dashed line shows the average first order orientational correlation function of overall water molecules in the solution (a) U1, (b) U5, and (c) U10 systems.

(iv) Effect of temperature on the structural and dynamical characteristics

To study the effect of temperature on the structural, translational and orientational properties of overall water molecules as well as those within the solvation shell around uranyl ions, the U1, U5 and U10 systems are simulated at different temperatures around 298 K i.e. 240 K, 270 K, 330 K and 360 K. As observed in the simulations discussed above, the orientational dynamics remains the same whether the overall water molecules are considered or only the water molecules within the coordination shells around uranyl ions. However, translational dynamics show a considerable difference for overall water molecules and those within the coordination shell of uranyl ions.³⁰

Hence, the effect of temperature on the translational dynamics will be discussed separately for overall water molecules and for those in the vicinity of the uranyl ions. The effect of temperature on diffusivities of water and uranyl ions, radial and orientational distribution, and orientational dynamics of the water molecules are analyzed and the results are presented in the following sub-sections.

(a) Effect of temperature on the radial distribution of water molecules around uranyl ions

The radial distribution functions for the oxygen and hydrogen atoms of the water molecules around the uranium atom of the uranyl ion are plotted at various temperatures (Figure 9). It can be seen that there is slight lowering of the peak as the temperature of the system is increased; however the area under the curve appears to remain the same.

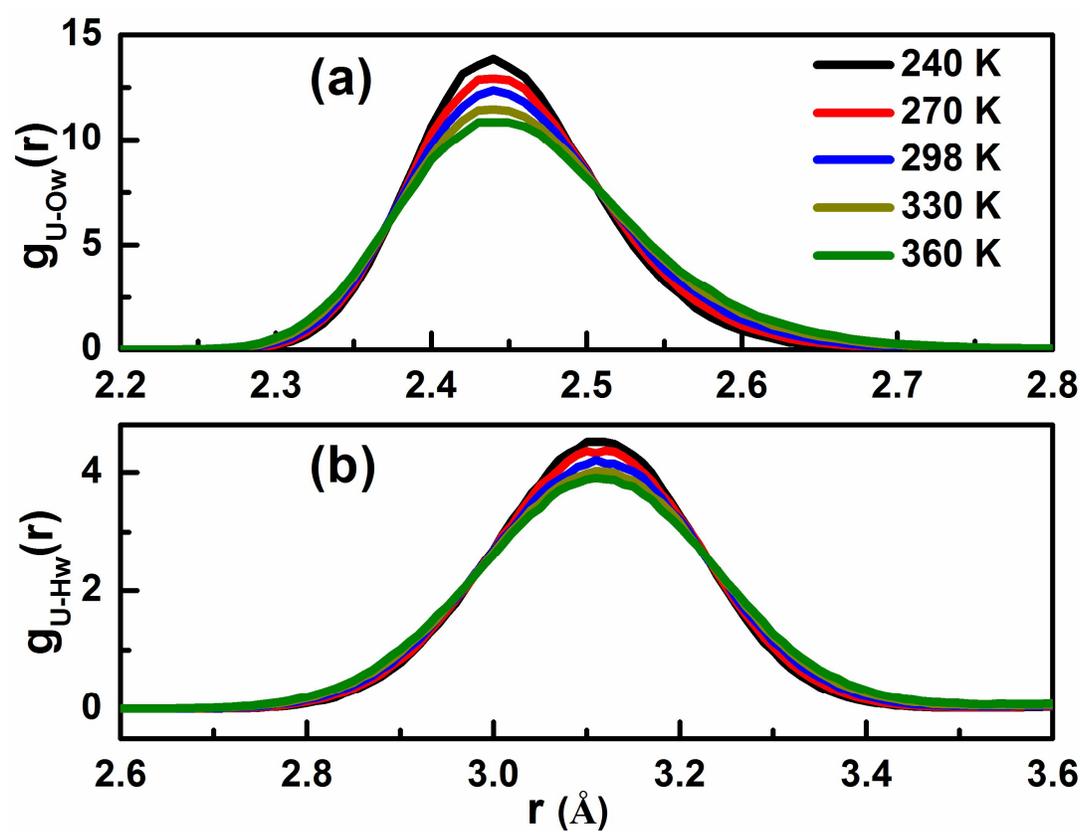


Figure 9. The radial distribution functions of (a) oxygen and (b) hydrogen atoms of water molecules with respect to uranium atom of uranyl ions at different temperatures.

(b) Effect of temperature on the orientational distribution of water molecules in the vicinity of uranyl ions

The distributions of four angles discussed above i.e. θ , ψ , γ and χ between different vectors of water molecules and uranyl ions are estimated at different temperatures and are shown in Figure 10. In Figure 10, only peaks are shown rather than showing the whole range of angles from 0° to 180° for better visual representation. It is observed that there is slight reduction in the peak values with increase in temperature. However the angles, corresponding to which the peaks in the distributions occur remain the same.

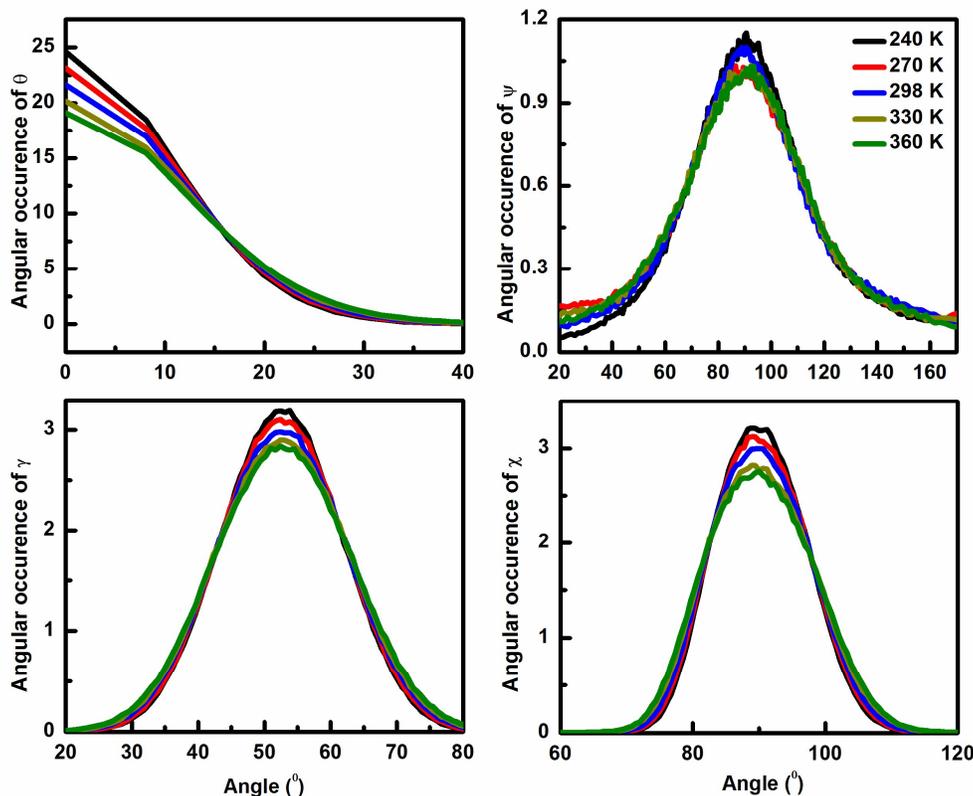


Figure 10. Distributions of angles made by different molecular orientational vectors of a water molecule in the first coordination shell of a uranium atom of the uranyl ion at different temperatures.

(c) Effect of Temperature on the Orientational Dynamics of Water Molecules

The orientational dynamics of water molecules with respect to three vectors (i) dipole moment vector ($u_\alpha = \mu$) (ii) H-H vector ($u_\alpha = \text{HH}$) (iii) a cross vector ($u_\alpha = \text{CR}$) i.e. a vector perpendicular to plane of water molecule are analyzed at different temperatures and results are given in Figure 11. The Figure 11 shows the orientational correlation functions of water molecules at different temperatures for these three vectors in case of U1 system. It can be seen that with increase in temperature, the times of relaxation of these functions reduce i.e. the relaxation becomes faster. In other words, the relaxation times of these functions reduce with reduction in concentration of uranyl ions or with increase in temperature of the systems.

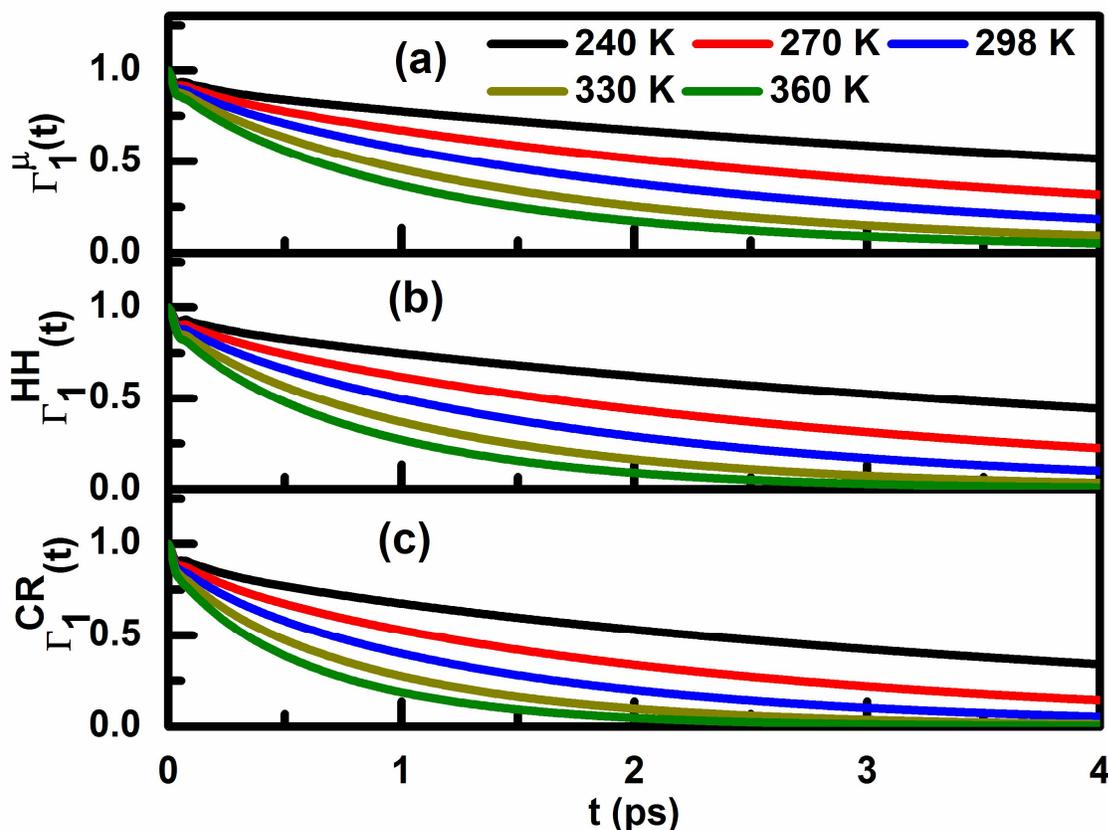


Figure 11. First order orientational correlation functions of water molecules with respect to (a) dipole moment vector (μ), (b) H-H vector (HH) and (c) a vector (CR) perpendicular to the plane of the water molecule for U1 system at different temperatures.

(d) Effect of temperature on the translational dynamics

The mean squared displacements (MSDs) obtained by considering overall water molecules in the solution as well as for water molecules within the coordination shell of uranyl ions and of uranyl ions for U1, U5 and U10 systems are analyzed at different temperatures. Hence, the variation in diffusion coefficients with temperature is studied.

Overall water molecules in the solution

The variation of mean squared displacements (MSDs) of overall water molecules with temperature for the U1, U5 and U10 systems are given in Figure 12. The mean square displacement gives the information about the diffusion processes in the medium as it is a good measure of translational mobility of a fluid. According to the well-known Einstein relation,^{29,30,37,38} the self-diffusion coefficient (D_{PBC} , PBC stands for Periodic Boundary Condition) of the fluid is related to the long time limit of the MSD obtained using periodic boundary condition, viz.

$$D_{PBC} = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle \Delta r^2 \rangle}{\Delta t} = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{\Delta t} \quad (2)$$

where $\mathbf{r}(t)$ is the position vector at time t and d is the dimensions of the system. A linear fitting is carried out for MSD curves obtained from simulation trajectory as a function of time and the slope of the fit gives the diffusion constant. The slopes of the MSD curve becomes higher and higher as the temperature of the system is increased. In other words, diffusivity of water molecules increases with increase in temperature. The diffusion coefficients of overall water molecules at various temperatures are given in Table 2.

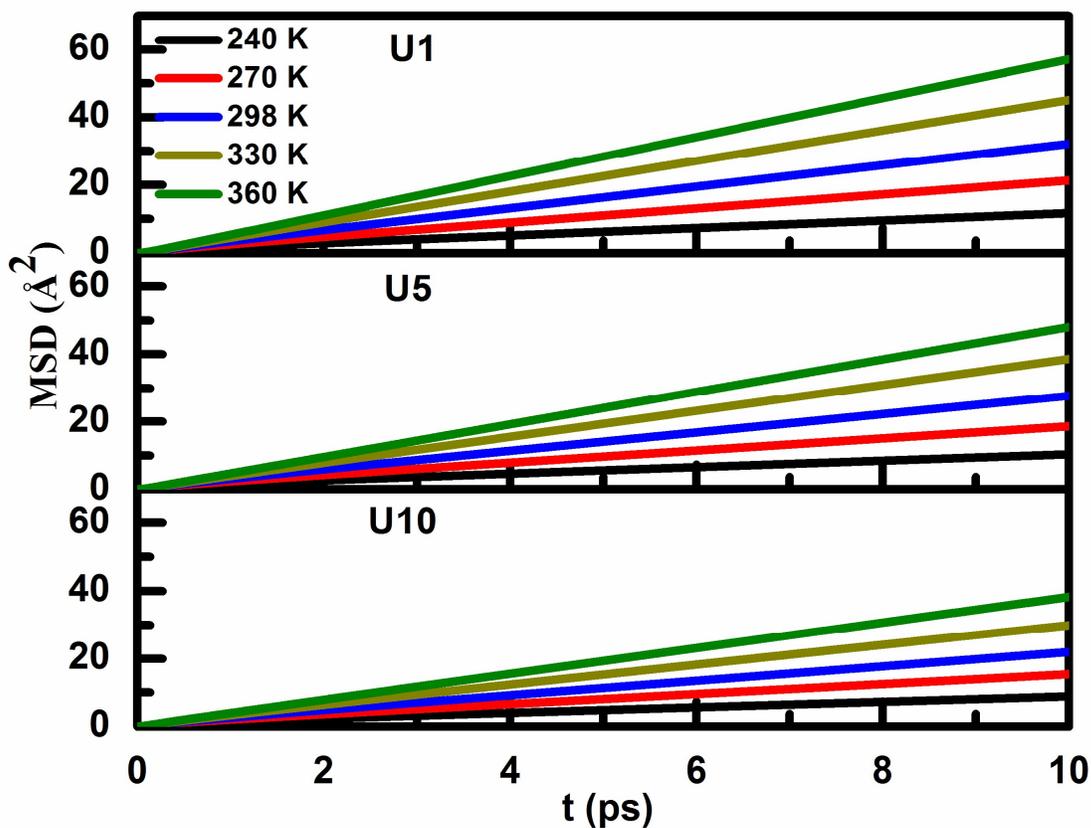


Figure 12. MSD profiles of overall water molecules for U1, U5 and U10 systems at different temperatures.

Table 2. Diffusion coefficient values of overall water molecules at different temperatures for U1, U5 and U10 systems

Diffusion coefficients, D_{PBC} ($\text{cm}^2 \text{s}^{-1}$) of overall water molecules					
	240 K	270 K	298 K	330 K	360 K
U1	1.82	3.43	5.28	7.51	9.60

U5	1.59	2.98	4.50	6.42	8.01
U10	1.36	2.45	3.58	4.88	6.27

Water molecules within the first coordination shell of uranyl ions

The water molecules within the first coordination shell of uranyl ions also show an enhanced diffusivity with increase in temperature from 240 K to 360 K, although the diffusivity values are lower for these as compared to those for the overall water molecules. The MSD curves are shown in Figure 13 for U1, U5 and U10 systems and the diffusivity values are given in Table 3.

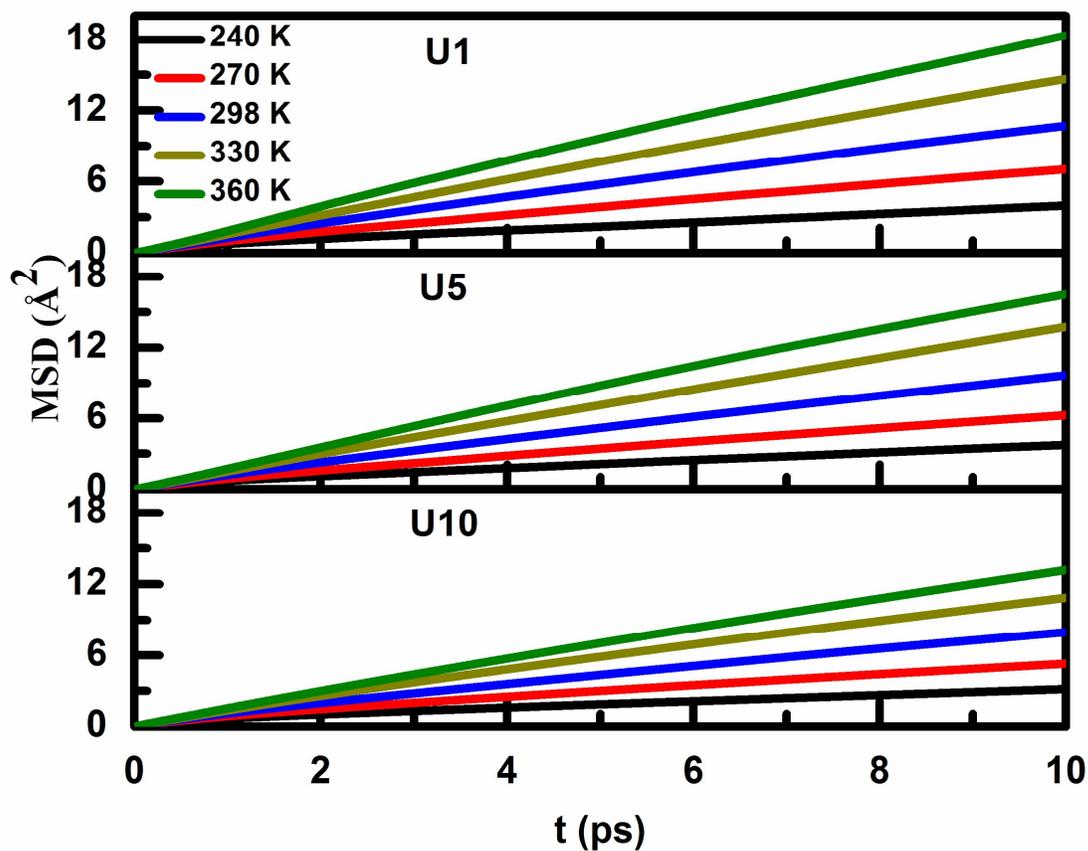


FIGURE 13. MSD profiles of water molecules within the first coordination shell of uranyl ion for (a) U1, (b) U5 and (c) U10 systems at different temperatures.

Table 3. Diffusion coefficient values of water molecules within first coordination shell of uranyl ions at different temperatures for U1, U5 and U10 systems

Diffusion coefficients, D_{PBC} ($\text{cm}^2 \text{s}^{-1}$) of coordination shell water molecules					
	240 K	270 K	298 K	330 K	360 K
U1	0.56	0.93	1.86	2.19	2.94

U5	0.54	0.86	1.35	2.09	2.44
U10	0.43	0.75	1.20	1.61	1.94

Uranyl ions

The diffusivity values of uranyl ions show an increasing trend with the increase in temperature from 240 K to 360 K, although being heavier than water, the diffusivity values are smaller as compared to those for water. The MSD curves for uranyl ions are shown in the Figure 14 for U1, U5 and U10 systems and the diffusivity values are given in Table 4. The values of diffusion coefficients for overall water molecules in U1 system and uranium atom of uranyl ion in U1 system are similar to those given by Tiwari et al. for TIP3P model of water.²⁴

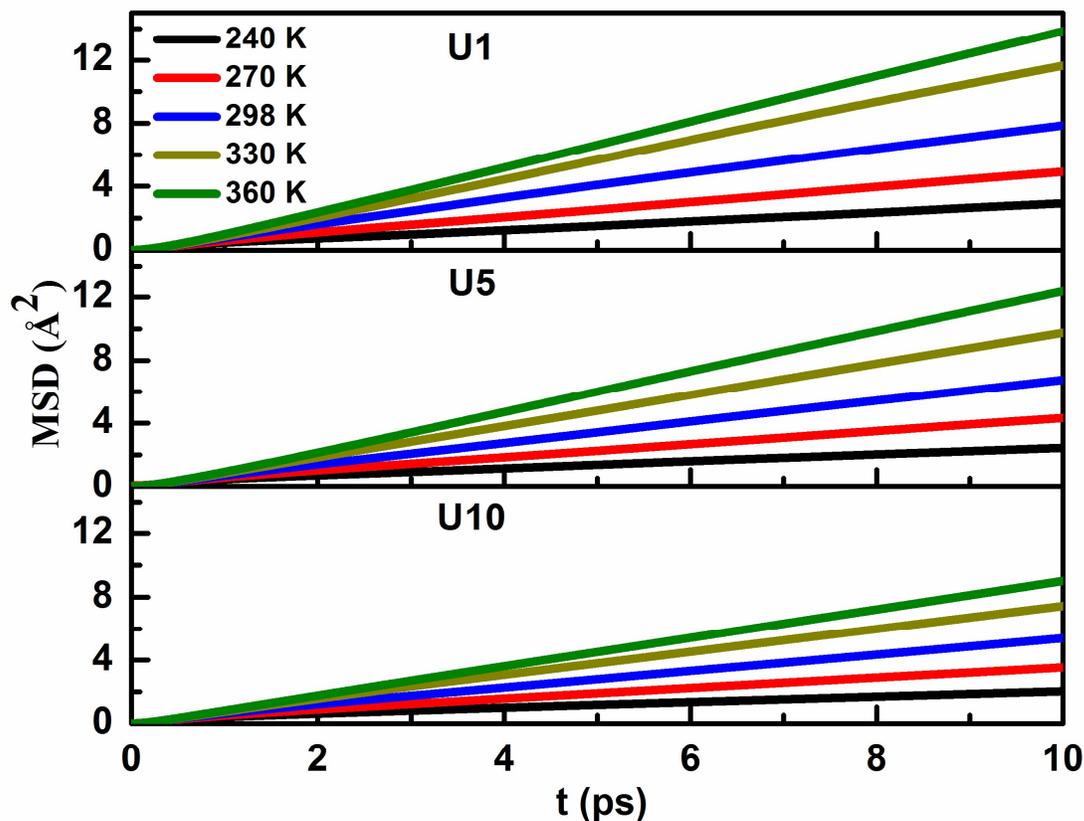


Figure 14. MSD profiles of uranium atom of uranyl ions for (a) U1, (b) U5 and (c) U10 systems at different temperatures.

Table 4. Diffusion coefficient values for uranium atom of uranyl ions at different temperatures for U1, U5 and U10 systems

Diffusion coefficients, D_{PBC} ($\text{cm}^2 \text{s}^{-1}$) for uranium atom of uranyl ion					
	240 K	270 K	298 K	330 K	360 K

U1	0.46	0.76	1.37	1.89	2.43
U5	0.36	0.70	1.09	1.63	2.12
U10	0.29	0.55	0.87	1.19	1.46

It is important to mention that the diffusion coefficients are dependent on the system size.^{13,39}

The correction for system size is applied to the diffusivity (D_{PBC}) values by using the method employed by Yeh et al.³⁹ and Kerisit et al.¹³ The corrected, system size independent diffusivity (D_0) can be obtained from the equation

$$D_o = D_{PBC} + \frac{2.837297 K_B T}{6\pi\eta L}, \quad (3)$$

where η and L are shear viscosity of water and simulation box length respectively. Using the shear viscosity values for TIP3P water⁴⁰ at different temperatures, the diffusion coefficient values are corrected for system size dependence and are given in Table 5. As the shear viscosity values are not available at low temperatures (240 K and 270 K), an exponential function [$A \cdot \exp(-xT)$] is fitted to the shear viscosity data given for temperature range 283 K to 363 K.⁴⁰ From the fitted function, the shear viscosity of water is generated at 240 K and 270 K which is used to estimate the corrected diffusion coefficients (Table 5). The diffusion coefficient value of uranyl ion in U1 system, normalized with respect to that of water³⁰ at 298 K is found to be 0.315. It is observed to be in overall good agreement with the normalized diffusivities obtained experimentally⁴¹⁻⁴³ (except the one given by Awakura et al.⁴⁴) or theoretically^{13,30}. It is to note that the diffusivity value in 0.1 M uranyl solution as given by Awakura et al.⁴⁴ normalised with respect to water

diffusivity¹³ ($2.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) is considerably lower as compared to the same obtained from other experimental and simulation studies. Similar comparison of the normalized (with respect to water) diffusivity with the experimentally obtained values has been reported by Kerisit et al.¹³, Tiwari et al.²⁴ and Chopra et al.³⁰

Table 5. Diffusion coefficient values of water molecules and uranyl ions corrected for system size at different temperatures for U1, U5 and U10 systems

Corrected diffusion coefficients, D_o ($\text{cm}^2 \text{ s}^{-1}$) of overall water molecules					
	240 K	270 K	298 K	330 K	360 K
U1	2.25	4.01	6.07	8.59	10.98
U5	2.02	3.56	5.29	7.50	9.39
U10	1.79	3.03	4.37	5.96	7.65
Corrected diffusion coefficients, D_o ($\text{cm}^2 \text{ s}^{-1}$) of coordination shell water molecules					
U1	0.99	1.51	2.65	3.27	4.32
U5	0.97	1.44	2.26	3.17	3.82
U10	0.86	1.33	1.99	2.69	3.32
Corrected diffusion coefficients, D_o ($\text{cm}^2 \text{ s}^{-1}$) of uranium atom of uranyl ions					
U1	0.89	1.34	2.16	2.97	3.81

U5	0.79	1.28	1.88	2.71	3.50
U10	0.72	1.13	1.66	2.27	2.84

4. CONCLUSIONS

In summary, orientational behavior of aqueous solutions of uranyl ions is studied with respect to the water molecules within first coordination of the uranyl ions. Also the effect of concentration of uranyl ions on the orientational structure and dynamics of water molecules is investigated. The angular distributions of water within the first coordination shell of uranium atoms have demonstrated that dipole moment vectors of water molecules are oriented along U-O_w distance vector and all other orientational vectors show consistent orientations. The angular distribution remains more or less the same with change in concentration of uranyl ions in aqueous solution. As expected, both in case of bulk water as well as aqueous solution of uranyl ions, the water molecules in the second coordination shell do not show much preference to any particular orientation. From the positions of the first peaks of the radial distribution functions of oxygen atom of the water and that of the nitrate ions with respect to uranyl ion it transpires that the oxygen atoms of water and nitrate both are in the first solvation shell of uranyl ions. From the coordinated numbers of water oxygen and oxygen atom of the nitrate ion as a function of uranyl nitrate concentration it is evident that a competition exists between the nitrate ion and the water molecules for occupying the first solvation shell of the uranyl ion. In our earlier work³⁰, we have reported that the orientational correlation functions of overall water molecules with respect to

different molecular axes of water demonstrate decreasing orientational mobility of water with increasing uranyl concentration. In present work, we investigated the orientational correlation functions of water molecules within the solvation shell of uranyl ions. It is observed that the orientational dynamics of the water molecules remains the same whether they are inside or outside the solvation shell of uranyl ions. The effect of temperature is studied on the various structural, translational and orientational features of the systems with varying uranyl ion concentrations. As expected, the effect of increasing temperature enhances the translational and orientational mobilities of water molecules.

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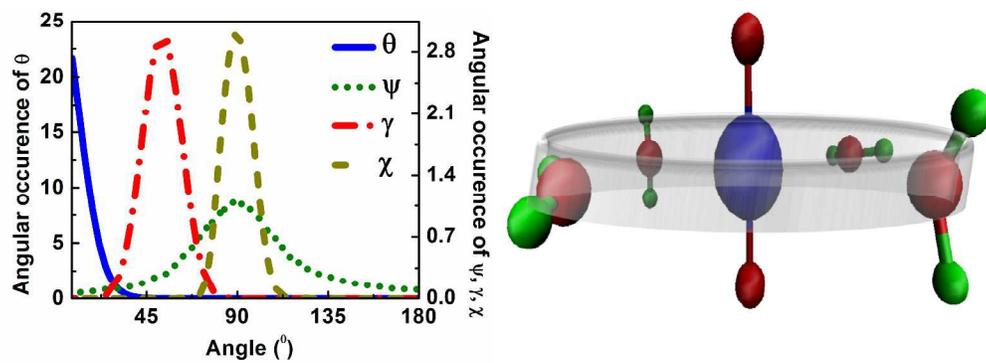
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Orientational distribution and dynamics of aqueous solutions of uranyl ions are studied at different concentrations and temperatures using Molecular Dynamics simulations.



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