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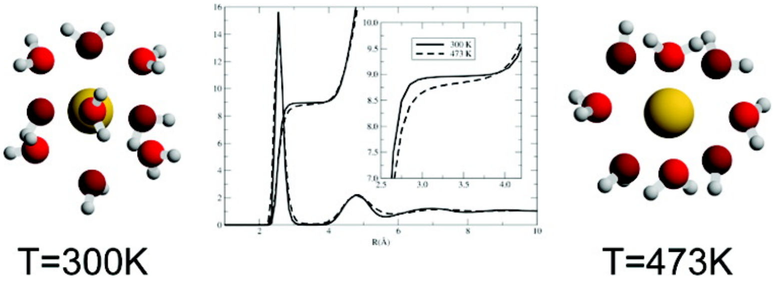

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A Quantum Chemical and Molecular Dynamics Study of the Coordination of Cm(III) in Water

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The study of the behavior of actinide ions in aqueous solution plays a fundamental role in the quest for a better understanding of actinide waste storage problems and separation processes. Considerable progress has been made both experimentally and computationally in recent years, with special attention given to the uranyl ion,[1,2] as well as trivalent lanthanide and actinide ions. Systematic studies of the aqueous trivalent lanthanide ion first coordination sphere show the number of water molecules changes from nine to eight between Pm(III) and Dy(III) at 25 °C. Similar behavior is found for the trivalent actinide ions with the transitional region occurring between Am(III) and Es(III).[3,4] Cm(III)[5] is in the middle of the actinide series and provides a bridge between the early actinides and the less common later actinides.

Several studies have been performed on this species. Lindqvist-Reis et al.[6] have used time-resolved laser fluorescence spectroscopy to study the hydration of Cm(III) from 20 to 200 °C. They found a strong temperature dependence for several of the spectroscopic quantities associated with the $^6D'_{7/2}-^8S'_{7/2}$ luminescent spectra. The emission band shifts to lower energy with increasing temperature, which is attributed to an equilibrium among hydrated Cm(III) ions with different numbers of water molecules in the first coordination sphere, namely $[Cm(H_2O)_9]^{3+}$ and $[Cm(H_2O)_8]^{3+}$. More recently they have also studied[7] the ground-state and excited-state crystal field splitting of 8-fold-coordinate Cm(III) in $[Y(H_2O)_8Cl_3$.15-crown-5] crystals using laser spectroscopy, at temperatures between 20 and 293 K. Skanthakumar et al.[8] and Lindqvist-Reis et al.[9] have analyzed single-crystal X-ray diffraction data from $[Cm(H_2O)_9](CF_3SO_3)_3$ to understand the hydration of Cm(III) in solution. According to their studies, the Cm species in the crystal is surrounded by nine coordinating waters with a tricapped-trigonal-prismatic geometry, with six short Cm−O distances at 2.453(1) Å and three longer Cm−O distances at 2.545(1) Å. Skanthakumar et al.[8] also reported high-energy X-ray scattering data for Cm(III) in perchloric acid solution. Two peaks were assigned to the oxygen atoms of H_2O, the first peak at 2.48(1) Å was from the first coordination shell (8.8(3) oxygen atoms), and the second peak from the second water coordination shell at 4.65(10) Å (13(4) oxygen atoms). Their EXAFS measurements for Cm(III) in perchloric acid suggested that the nine coordinate structure, found in the triflate crystal, persists in solution but with an expanded splitting of the first coordination shell by ∼ 0.07 Å. Yang and Bursten[10] have studied the first and second hydration shells of Cm(III) using quantum chemical and molecular dynamics methods and they have shown that the inclusion of a complete second hydration shell has a significant effect on the primary coordination sphere. To understand the structural and chemical behavior of Cm(III) (and actinyls in general) in solution from a computational perspective, it is necessary to go beyond a quantum chemical model and combine it with molecular dynamics simulations. We recently studied[1,11] the coordination of uranyl in water with such an approach, showing that five water molecules coordinate around uranyl in the first shell, with a U−O(water) bond distance of 2.40 Å, in agreement with experiment. A second coordination shell was predicted to be at a distance of 4.7 Å from the central uranyl. This study was the first truly ab initio determination of the solvation of an actinyl system.

With the same approach we have now studied Cm(III) in aqueous solution. The method is described in detail in the Supporting Information. The basic idea is to determine the wave function for the two moieties Cm(III) (fragment A) and water (fragment B) at the multiconfigurational level of theory followed by perturbation theory (CASSCF/CASPT2). From the wave functions of A and B one obtains a set of charges, dipoles, quadrupoles, and polarizabilities for all the atoms, from which electrostatic (E_{ele}), induction (E_{ind}), and dispersion (E_{disp}) energies are calculated. E_{ele} is obtained through a distributed multipole expansion. With the non-empirical, NEMO approach[12] to intermolecular forces, the potential between Cm(III) and water was generated by fitting a repulsive and a charge-transfer energy term to the difference between the total interaction energy computed at the CASPT2 level and the three previously defined energies. A subsequent molecular dynamic (MD) simulation was then performed, in which the Cm(III) ion was placed in a water droplet. As a first test, three droplets of different size, with the radius of 10, 15, and 20 Å, respectively, were simulated.

The radial distribution function (RDF) and the coordination number (CN) for the three different droplets were compared. The results indicate that the solvation environment is similar in the three cases, up to a radius of about 7−8 Å from the central Cm(III). At a larger radius, the water concentration reduces considerably in the two simulations with smaller droplets (10, 15 Å). It was thus decided to focus only on the results of the simulations performed using the largest droplet (20 Å), corresponding to 1120 water molecules at the temperatures of 300 and 473 K, respectively. These temperatures are similar to the two temperatures used by Lindqvist-Reis et al.[6] in their experiment.

The RDF and the CN of water molecules around Cm(III) are reported in Figure 1 for the two temperatures. The most interesting feature is that in going from $T = 300$ K to $T = 473$ K the average number of water molecules coordinating the curium ion varies from close to nine to a smaller number thus shifting the relative weights of configurations of nine and eight coordination. At both temperatures the RDF for the first peak occurs at a Cm−O distance of 2.55 Å, which is longer than the one obtained by Yang and Bursten[10] at 298 K, 2.48 Å or that found from EXAFS of Cm(III) solution 2.470(6)[6] or 2.477(5) Å.[7] The second peak occurs at a distance of 4.9 Å, while the one obtained by Yang and Bursten, occurs at 4.7 Å. Their calculations also suggest that the nine water molecules organize themselves into a trigonal bipyramidal configuration of six shorter and three longer bonds. (6 + 3 coordination). However, when they include more shells of water molecules, the 6 + 3 coordination is not valid any longer. The difference between

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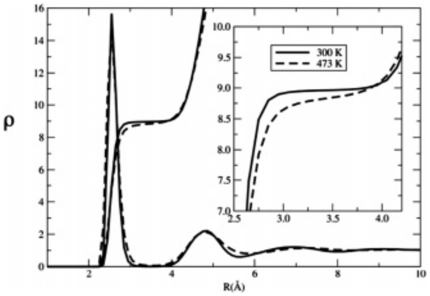

Figure 1. The radial distribution function.

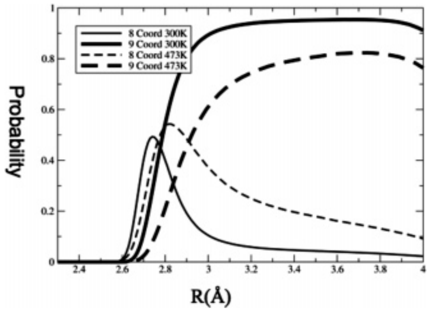

Figure 2. Probability for CN = 9,8 at T = 473 and 300 K.

Yang's results and ours is most likely due to the fact that we use a dynamical description of the water molecules.

The number of water molecules captured in the first solvation shell ($R \leq 3.4$ Å), as judged by the RDF, can reflect a weighted average of different possible CNs. In Figure 2 the probability of different CNs is plotted as a function of the radial distance. At T = 300 K the two most probable CNs are 9 and 8. At R = 3.4 Å, CN = 9 has a probability of 95% and CN = 8 has a probability of 5%. At T = 473 K the probability of CN = 9 drops down to 80%, while the probability of CN = 8 increases to 20%. The experimental value for CN = 9 in ref 6 is ~90% at the lower temperature and ~60% at the higher temperature.

The two probabilities for CN = 9 and CN = 8 depend on the choice of the cutoff defining the first solvation shell. If such a cutoff were to be moved at R = 3.0 Å, the probability of CN = 9 would still be 90% at T = 300 K, and it would decrease to 60% at T = 473 K. Given the arbitrariness with which the cutoff can be defined, the agreement between experiment and our simulation can be considered satisfactory.

The second solvation shell is associated with the second peak in the RDF, namely it occurs at R between 3.4 and 5.6 Å for the 9-coordinated ion. Yang and Bursten[10] performed simulations of the second solvation shell for the 9-coordinated ion using the hydrated ion concept. According to our simulation, the CNs of 15, 16, and 17 water molecules have a probability of 22%, 26%, and 21%, respectively, during the simulation, in the defined range. With the definition of the second solvation shell given above, we even found configurations containing 10 and 23 water molecules. The probability of different CNs in the second shell around the ion is well represented by a Gaussian curve. This reveals the fact that the second hydration shell is not stable enough to be defined in terms of the CN and the number of water molecules in the second coordination shell is thus not uniquely defined. The most probable value for CN is 16. This number is in reasonable agreement with the value obtained from high-energy X-ray scattering for the second shell of Cm(III) solution, 13(4) oxygen atoms at a distance of 4.65(10) Å.[6]

Snapshots of the water molecules surrounding Cm(III) in the first solvation shell at T = 300 K and T = 473 K are reported in Figures 3 and 4, respectively. These are the structures that were considered statistically meaningful. The viewing angles have been chosen to emphasize the similarity of the two structures with a square antiprism and/or a tricapped trigonal prism. By visual inspection it is not obvious which of the two geometrical forms the structures resemble better, indicating that the system is dynamical and a unique selection of the coordination symmetry is not possible.

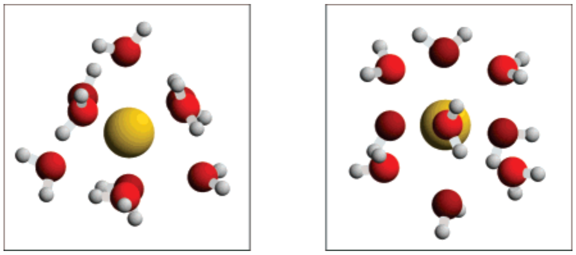

Figure 3. Two snapshots of the coordination of water around Cm(III) at T = 300 K. Nine water molecules preferentially coordinate Cm(III).

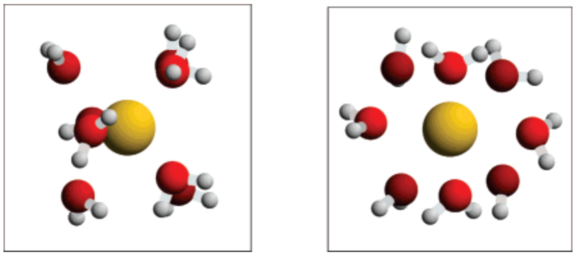

Figure 4. Two snapshots of the coordination of water around Cm(III) at T = 473 K. Eight water molecules preferentially coordinate Cm(III).

Molecular dynamics simulations of Cm(III) in water were performed at two different temperatures, namely T = 300 K and T = 473 K. Fully ab initio intermolecular potentials were employed. This study showed that at the lower temperature, T = 300 K, nine water molecules coordinate preferentially to the Cm(III) ion in the first coordination sphere, while at the higher temperature, T = 473 K, the coordination number is lower, indicating a shift toward eight coordination. The number of water molecules in the second coordination sphere is not uniquely defined, but the most probable number is 16.

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Supporting Information Available: Details of the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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