

Hydration Structure of Ra (II) and Fr(I): A Quantum Chemical Study

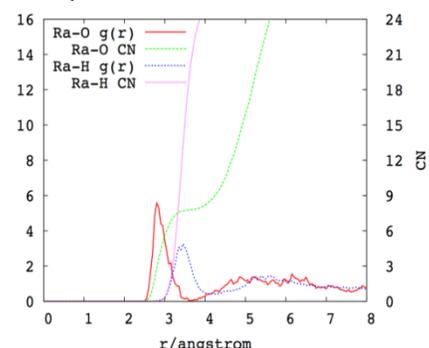
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Radium (Ra) and francium (Fr) are the heaviest alkaline earth/alkali metal in the periodic table. Even they were found over 90 years ago [1], the hydration chemistries of them have not been well known due to the danger associated with the experimental handling as well as the chemical instabilities. In this work, we have studied the hydration structure of Ra^{2+} and Fr^+ using quantum chemical calculations. To investigate hydration structure of Ra^{2+} and Fr^+ , we constructed two hydration models. In the first model, static solvation model, we mainly focused on structures of the first solvation shell using $[\text{M}(\text{H}_2\text{O})_n]^{2+/+}$ ($\text{M} = \text{Ra}, \text{Fr}; n=1-9$) aqua complex models. The effects from second or further solvation shells were taken into account through the conductor-like polarizable continuum (C-PCM) method. Geometry optimizations of the aqua complexes at the *ab initio* HF, MP2 and B3LYP levels of theory were performed. We calculated the solvation free energies to investigate the thermodynamic stabilities of the aqua complexes. In the second model, dynamic model, we focused on fluctuation of the aqua ligands using recently developed FMO-MD simulation [3], where FMO, fragment molecular orbital, is an *ab initio* molecular orbital method for large-scale systems. To simulate thermal fluctuation of the hydrated Ra^{2+} and Fr^+ , we applied water droplet model confined within a sphere (radius = 9.0). The coordinates of the central metal ions were kept fixed during the molecular dynamics simulation. The time step for FMO-MD was 1.0 fs, and the simulation temperature was kept to be 300 K using the Nosé–Hoover chains method. A 1 ps equilibration and a subsequent 2 ps production MD run were performed. Then, radial distribution functions (RDFs) of water molecules were statistically analyzed. In both models mentioned above, we applied MCPdzp basis sets for metal ions [2]. For O and H, 6-31G** and 6-31G were used in the static and dynamic solvation models, respectively. Increasing the number of water molecules (n), we could observe monotonic elongation of the M-O bond length and a corresponding monotonic decrement of the M-H₂O binding energy (per an M-O bond). The solvation free energies in $[\text{Ra}(\text{H}_2\text{O})_n]^{2+}$ and $[\text{Fr}(\text{H}_2\text{O})_n]^+$ ($n=7-9$) were predicted to be *ca.* -267 and -34 kcal/mol, respectively. They showed almost constant values, we could conclude that the hydration numbers of Ra^{2+} and Fr^+ are in the range of 7-9. Radial distribution functions (RDFs) around hydrated Ra^{2+} are shown in Fig. 1. The RDF peaks of Ra-H predicted by our FMO-MD simulations are 2.85 Å, 3.45 Å, respectively. The first peak of the RDF showed a width of 1.0 Å. This means that the structure of hydrated Ra^{2+} is consistent with the one obtained in static model simulations presented on the e-presentation.

Figure 1: Ra–O (red line) and Ra–H (blue line) RDF and their running integration numbers.



References

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