Communication: Hydration structure and polarization of heavy alkali ions: A first principles molecular dynamics study of Rb^+ and Cs^+

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Communication: Hydration structure and polarization of heavy alkali ions: A first principles molecular dynamics study of Rb⁺ and Cs⁺

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Hydration structure and polarization of Rb⁺ and Cs⁺ in liquid water at ambient conditions were studied by first principles molecular dynamics. Our systematic analysis of the relevant electronic structures, based on maximally localized Wannier functions, revealed that the dipole moment of H₂O molecules in the first solvation shell of the ions slightly increases with increasing the atomic number. We also found that the polarization of heavy alkali ions, particularly Cs⁺, tends to stabilize a peculiar asymmetric hydration structure with relevant consequences in the extraction of the harmful ¹³⁷Cs resulting from nuclear wastes. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742151>]

Understanding the Hofmeister series, which is a classification of ions according to their ability to structurize water (or their affinity to bind to proteins and nucleic acids), is a long standing research target in many areas at the crossroad among physics, chemistry, and biology. Nonetheless, the mechanism leading to enhancement or weakening of the hydrogen bond (H-bond) network has not been entirely elucidated. Experimentally, the hydration of metal ions has been investigated using elaborate techniques which have provided fundamental pieces of information, such as ion-water distance, hydration structure, and dynamics of hydrated ions, as shown in renowned monographs^{1–4} and review articles.^{5,6}

Besides the evident physico-chemical importance, selectivity of alkali ions is a crucial issue also in biology and environmental sciences. Specifically, understanding adsorption and desorption processes of highly soluble radionuclides, such as ¹³⁷Cs, in clays has become one of the urgent requests in order to develop efficient extractors of radionuclides from contaminated clay minerals, as the recent accident occurred to the Fukushima dai-ichi nuclear plant in Japan has proven.^{7,8} For most clays, the observed Hofmeister series is Cs⁺ > K⁺ > Na⁺ > Li⁺, indicating that the affinity of the ions increases with the (non-hydrated) ionic radius.⁹ However, this observation cannot be fully rationalized by simply considering the crude electrostatic interaction, which would actually favor smaller unhydrated ions. Therefore it is clear that a yet unidentified quantum mechanical interaction comes into play, along with electrostatics, enhancing the affinity of heavy alkali ions to clay minerals.

In our previous works,^{10–12} hydration of Li⁺, Na⁺, and K⁺ was investigated by first principles molecular dynamics (FPMD), providing detailed insight not only into the interplay between solutes and solvents, but also into the strict relationships among molecular orientation, H-bond formation polar-

ization of hydration waters, and infrared spectra. The scope of this work is, on one hand, to examine whether the observed trends still hold for heavier alkali ions, and, on the other hand, to inspect the hydration behavior specific to heavy alkali ions, along with its related electronic properties, which are likely to be responsible for the mentioned selectivity of heavy alkali ions.

We performed Car-Parrinello¹³ FPMD simulations¹⁴ of alkali ions in liquid water at ordinary density (1.0 g/cm³) and temperature ($T = 300$ K), within the density functional theory¹⁵ (DFT) approach, including the generalized gradient approximation (GGA) to exchange and correlation after Hamprecht-Cohen-Tozer-Handy¹⁶ (HCTH), previously benchmarked for our target.^{10,17–19} The valence-core interaction was described by a von Barth-Car pseudopotential²⁰ for H, a norm-conserving Troullier-Martins pseudopotential²¹ for O, and a Goedecker-Teter-Hutter type pseudopotential^{22,23} for Rb and Cs, in which semicore states were included as valence states. Valence orbitals were expanded in a plane wave (PW) basis set with an energy cutoff of 80 Ry. The Brillouin zone was sampled at the Γ point only. The equations of motion were integrated with a time step of 4 a.u. (0.0968 fs) and a fictitious electron mass of 400 a.u. ensuring reliable static and dynamical properties^{24,25} and a good adiabaticity of the Car-Parrinello trajectories.²⁶ Our approach was validated by examining the ion-oxygen distances d and related hydration energies ΔE for M⁺H₂O complexes (M = Rb and Cs). Our estimated d and ΔE of 2.830 (3.013) Å and 14.7 (13.2) kcal/mol for Rb⁺H₂O (Cs⁺H₂O), respectively, agree well with the corresponding estimate of 2.763 (2.962) Å and 16.3 (13.5) kcal/mol made with a standard quantum chemistry method at the MP2 level of theory.^{27,28}

Our Rb⁺ and Cs⁺ aqueous solution systems are similar to the ones used in our former studies.^{10,17} Specifically, we used a cubic simulation cell of side $L = 12.417$ Å in which the metal cation was solvated by 63 H₂O molecules and periodic

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boundary conditions were applied. The excess charge of the systems was compensated by a uniform background charge²⁹ instead of adding counterions explicitly. After equilibrating the system for ~ 2 ps at 300 K, the trajectories were collected for at least 40 ps. All the simulations were done in a (NVT) canonical ensemble using a Nosé-Hoover thermostat^{30,31} to control the temperature. Additionally, the trajectories for solvated Li^+ , Na^+ , and K^+ , reported in Ref. 10 were re-analyzed whenever needed to support the discussion.

Figure 1 shows our computed radial distribution functions (RDFs) $g_{\text{MO}}(r)$ and $g_{\text{MH}}(r)$ for $M = \text{Rb}$ and Cs in ambient liquid water along with those for lighter alkali ions¹⁰ for comparison. The position of the first peak of $g_{\text{MO}}(r)$ and $g_{\text{MH}}(r)$ shifts steadily to the right and its height decreases with increasing alkali-ions atomic number, in remarkable agreement with reported experiments.^{33,34} Simultaneously, the second peak of $g_{\text{CSO}}(r)$ almost disappears, in agreement with known experimental results,³² whereas the corresponding peak for Rb^+ remains visible, indicating that the interaction between Cs^+ and H_2O molecules is likely to be exceptionally short-ranged.

The location of the first minimum of $g_{\text{MO}}(r)$, which is normally used to evaluate the coordination number (CN), cannot be unambiguously determined for both ions, as seen in Fig. 1. Therefore, hydration water molecules are identified in this work by adopting three different geometrical cutoff distances between each cation and the O atoms of solvating water molecules around in the range after the first peak where the RDF decreases and flattens. These distances were 3.7, 3.8, and 3.9 Å for Rb^+ and 3.8, 3.9, and 4.0 Å for Cs^+ and the corresponding distributions of the instantaneous CNs for Rb^+ and Cs^+ are shown in Fig. 2. We found that the in-

FIG. 1. Radial distribution functions $g_{\text{MO}}(r)$ (upper) and $g_{\text{MH}}(r)$ (lower) for $M = \text{Rb}$ and Cs in liquid water. For comparison, $g_{\text{MO}}(r)$ and $g_{\text{MH}}(r)$ of lighter alkali ions from Ref. 10 are also included in each panel.

FIG. 2. Dependence of the instantaneous coordination numbers (CNs) of Rb^+ (upper) and Cs^+ (lower) on the choice of the cut-off distance (see text for details).

stantaneous CNs of Cs^+ show a much broader distribution in comparison with other alkali ions. Interestingly, even the tetra-coordination, which is missing for K^+ and Rb^+ , is re-observed for Cs^+ , suggesting that the hydration ability of Cs^+ is significantly weaker than that of the other alkali ions. The averaged CN estimated as 7.0 $\sim$ 8.0 (7.0 $\sim$ 8.2) for Rb^+ (Cs^+) falls into the available experimental data ranging from 6 to 8.^{4,6,27}

The distribution of the tilt angle ψ is shown in Fig. 3;³⁵ here ψ is defined as sketched in the inset, namely the angle between the dipole vector of a hydrating H_2O molecule and the vector pointing from the O atom of H_2O to the cation. This angle is determined by a subtle balance between the ion-water interactions and the H-bonds formed by H_2O molecules belonging to the first and to the second solvation shells. The tendency of ψ to decrease from Li^+ to K^+ , noticed in previous works, still holds for Rb^+ and Cs^+ , and its average value is 121° and 119° for Rb^+ and Cs^+ , respectively.

The average molecular dipole moment μ of H_2O molecules in the first hydration shell of the alkali ions was computed via maximally localized Wannier function centers (WFCs)^{36,37} (Fig. 4). We found that μ of hydration waters decreases going from Li^+ to K^+ , but increases slightly going from K^+ to Cs^+ . This increase is accompanied by the increase of acceptor H bonds of hydration water molecules at the border of the first hydration shell of heavy alkali ions. In fact, the average number of acceptor H bonds, counted based on the local geometry,¹¹ turns out to be 1.06, 1.14, and 1.18 when a cutoff distance of 3.7, 3.8, and 3.9 Å is adopted for K^+ , Rb^+ , and Cs^+ , respectively. The further increase of cutoff distance by 0.1 Å leads to the increase of the number of acceptor H bonds per hydration H_2O molecule by 0.03 on average while keeping the number of donor H bonds constant. Considering that a large amount of hydration waters having $\psi < 90^\circ$ are

FIG. 3. Distribution of the cosine of the tilt angle ψ between the dipole vector of hydration water molecules and the vector pointing from the O atom of water to the alkali ion. For comparison, distributions for the light alkali ions of Ref. 10 are also shown.

also observed for K^+ , Rb^+ , and Cs^+ and that their population increases in this order, the formation of the acceptor H bonds at the border of the solvation shell is expected to result in an enhancement of water exchange reactions. Indeed, our estimated residence time of hydration H_2O molecules for Rb^+ and Cs^+ is about half of the corresponding estimate for Na^+ and K^+ .³⁸ This indicates that water exchange occurs more frequently for these heavier ions than for the lighter ones.

According to the Pearson's hard and soft acids and bases (HSAB) concept,³⁹ alkali ions are considered typical hard acids characterized by low polarizability. This is true for Li^+ and Na^+ , for which we estimated a net dipole moment negligibly small.⁴⁰ However, as shown in the inset of Fig. 5, heavy alkali ions, in water, have a net dipole moment reaching 0.4, 0.6, and 0.8 Debye for K^+ , Rb^+ , and Cs^+ , respectively. This is mainly due to polarizable shallow core orbitals, which are included explicitly in our plane-wave pseudopotential approach. If the net dipole moment is not vanishing, as in the cases indicated above, the hydration shell is prone to variations and, as a consequence, the ion-water complex can become more stable. A special (and extreme) case is represented by surface solvation which can be realized depending on a delicate bal-

FIG. 4. Average molecular dipole moment μ of water molecules belonging to the first hydration shell computed from Wannier function centers (WFCs).

FIG. 5. Distribution of the correlation function ϕ between dipole vectors of ions μ_{M^+} and the vector $\mathbf{R}_{cage}$ defined as in the text. The inset shows the distribution of μ_{M^+} for K^+ , Rb^+ , and Cs^+ in solution calculated from WFCs.

ance among the stabilization of the first solvation shell, the destabilization of the second shell, and longer distance interactions. This subtle interplay among different factors can determine whether or not an asymmetric hydration shell, such as the one realized at surfaces, can appear.

To examine the possibilities of forming such an asymmetric shell for alkali ions, we introduce a vector given by $\mathbf{R}_{cage} = \sum_{i=1}^{CN} (\mathbf{R}_{O_i} - \mathbf{R}_{M^+}) / |\mathbf{R}_{O_i} - \mathbf{R}_{M^+}|$. Here the sum for the oxygen positions $\mathbf{R}_{O_i}$ runs over the O atoms in the solvation shell at a given moment for a cation located at $\mathbf{R}_{M^+}$. The distribution of the modulus $|\mathbf{R}_{cage}|$ (not shown) indicates that for Li^+ and Na^+ the hydration shell is highly symmetric ($|\mathbf{R}_{cage}| \leq 0.5$) while for heavy alkali ions it tends to be asymmetric. In particular for Cs^+ the predominant structure is indeed asymmetric ($|\mathbf{R}_{cage}| \simeq 1.2$).

An order parameter ϕ can be defined as $\phi = \mu_{M^+} \cdot \mathbf{R}_{cage}$ which rationalizes the possible correlation between a net cation dipole μ_{M^+} and the asymmetry of the solvation shell measured with respect to the reference $\mathbf{R}_{cage}$. The strong asymmetric distribution of ϕ observed for Cs^+ (Fig. 5) evidences that the polarization of Cs^+ is strongly correlated with its asymmetric first hydration shell, thus making Cs^+ a peculiar case among the other alkali ions.

Summarizing, we studied hydration structure and polarization of Rb^+ and Cs^+ in liquid water at ambient conditions by first principles molecular dynamics. Our systematic analysis of the hydration structure and the related electronic structure peculiarities, based on maximally localized Wannier functions and their centers, revealed close relationships among molecular orientation, H-bond formation, and polarization of water molecules around the hydrated cations. Furthermore, we found that the polarization of heavy alkali ions, especially Cs^+ , tends to stabilize an asymmetric hydration structure. All these findings indicate rather clearly that Cs^+ possesses an intrinsic instability toward forming surface solvation states which would be a key step to adsorption of hydrated Cs^+ and in this peculiarity, along with the specific Cs^+ -clay interactions, resides the difficulty in the extraction of ^{137}Cs from clay minerals.

The calculations reported in this paper were performed at the JAEA supercomputer facility. We wish to dedicate this paper to the victims of Fukushima.

- ¹B. E. Conway, *Ionic Hydration in Chemistry and Biophysics, Studies in Physical and Theoretical Chemistry 12* (Elsevier, Amsterdam, 1981).
- ²Y. Marcus, *Ion Solvation* (Wiley, Chichester, 1986).
- ³J. Burgess, *Metal Ions in Solution* (Ellis Horwood, New York, 1978).
- ⁴D. T. Richens, *The Chemistry of Aqua Ions* (Wiley, Chichester, 1997).
- ⁵Y. Marcus, *Chem. Rev.* **88**, 1475 (1988).
- ⁶H. Ohtaki and T. Radnai, *Chem. Rev.* **93**, 1157 (1993).
- ⁷J. Smith, *Nature (London)* **472**, 7 (2011).
- ⁸G. Brumfiel, *Nature (London)* **478**, 435 (2011).
- ⁹W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 3rd ed. (Wiley, New York, 1996).
- ¹⁰T. Ikeda, M. Boero, and K. Terakura, *J. Chem. Phys.* **126**, 034501 (2007).
- ¹¹R. Scipioni, D. A. Schmidt, and M. Boero, *J. Chem. Phys.* **130**, 024502 (2009).
- ¹²D. A. Schmidt, R. Scipioni, and M. Boero, *J. Phys. Chem. A* **113**, 7725 (2009).
- ¹³R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ¹⁴CPMD, Copyright IBM Corp 1990-2008, MPI für Festkörperforschung Stuttgart 1997-2001, see <http://www.cpmd.org/>.
- ¹⁵W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹⁶F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, *J. Chem. Phys.* **109**, 6264 (1998).
- ¹⁷T. Ikeda, M. Boero, and K. Terakura, *J. Chem. Phys.* **127**, 074503 (2007).
- ¹⁸T. Ikeda, M. Hirata, and T. Kimura, *J. Chem. Phys.* **122**, 244507 (2005).
- ¹⁹J. M. Park and M. Boero, *J. Phys. Chem. B* **114**, 11102 (2010).
- ²⁰See M. Sprik, J. Hutter, and M. Parrinello, *J. Chem. Phys.* **105**, 1142 (1996).
- ²¹N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ²²S. Goedecker, M. Teter, and J. Hutter, *Phys. Rev. B* **54**, 1703 (1996).
- ²³C. Hartwigsen, S. Goedecker, and J. Hutter, *Phys. Rev. B* **58**, 3641 (1998).
- ²⁴J. C. Grossman, E. Schwegler, E. W. Draeger, F. Gygi, and G. Galli, *J. Chem. Phys.* **120**, 300 (2004).
- ²⁵E. Schwegler, J. C. Grossman, F. Gygi, and G. Galli, *J. Chem. Phys.* **121**, 5400 (2004).
- ²⁶F. A. Bornemann and C. Schütte, *Numer. Math.* **78**, 359 (1998).
- ²⁷M. J. San-Román, J. Hernández-Cobos, H. Saint-Martin, and I. Ortega-Blake, *Theor. Chem. Acc.* **126**, 197 (2010).
- ²⁸M. Kołaski, H. M. Lee, Y. C. Choi, K. S. Kim, P. Tarakeshwar, D. J. Miller, and J. M. Lisy, *J. Chem. Phys.* **126**, 074302 (2007).
- ²⁹G. Makov and M. C. Payne, *Phys. Rev. B* **51**, 4014 (1995).
- ³⁰S. Nosé, *Mol. Phys.* **52**, 255 (1984); S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
- ³¹W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- ³²S. Ramos, G. W. Neilson, A. C. Barnes, and P. Buchanan, *J. Chem. Phys.* **123**, 214501 (2005).
- ³³P. R. Smirnov and V. N. Trostin, *Russ. J. Gen. Chem.* **77**, 2101 (2007).
- ³⁴J. Mähler and I. Persson, *Inorg. Chem.* **51**, 425 (2012).
- ³⁵For subsequent analyses of hydration of Rb^+ and Cs^+ , we used the cutoff distance of 3.8 and 3.9 Å, respectively, unless otherwise mentioned.
- ³⁶P. L. Silvestrelli and M. Parrinello, *Phys. Rev. Lett.* **82**, 3308 (1999).
- ³⁷N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997).
- ³⁸The residence time of water molecules in the first shell, estimated according to the prescription of Impey *et al.* [*J. Phys. Chem.* **87**, 5071 (1983)], are 7 and 9 ps for Rb^+ and Cs^+ , respectively.
- ³⁹R. G. Pearson, *J. Am. Chem. Soc.* **85**, 3533 (1963).
- ⁴⁰J. J. Molina, S. Lectez, S. Tazi, M. Salanne, J.-F. Dufrêche, J. Roques, E. Simoni, P. A. Madden, and P. Turq, *J. Chem. Phys.* **134**, 014511 (2011).