Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Cation solvation with quantum chemical effects modeled by size-consistent multi-partitioning quantum mechanics/molecular mechanics method.

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Supplementary Information

Supplementary Figures

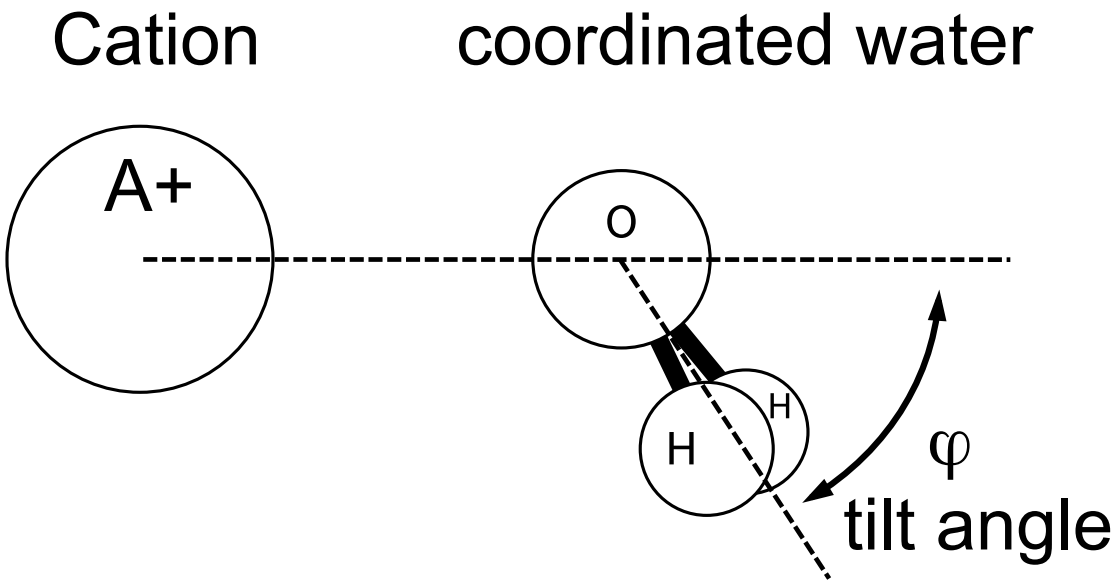

Figure S1. Definition of a tilt angle of a water molecule coordinated to a cation.

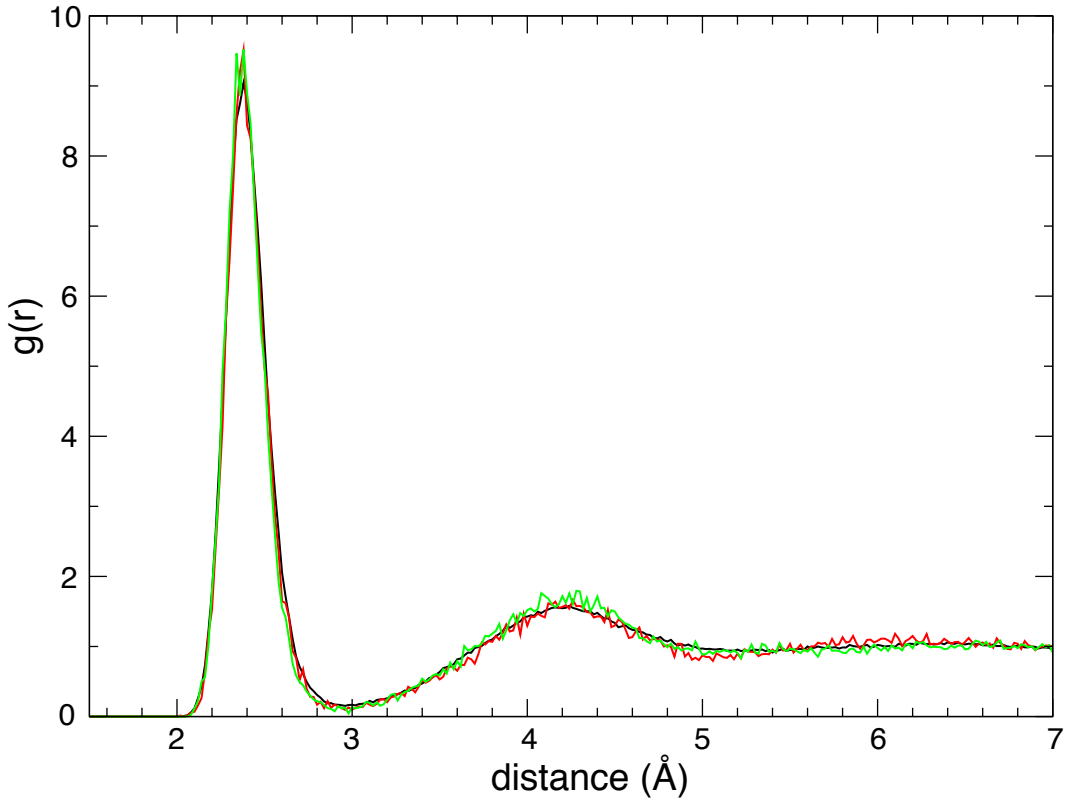

Figure S2. Cation-centered radial distribution functions of Na^+ solution obtained by SCMP method. The black line represents the result of 32 QM water molecules with 96 partitionings. The red line represents the result of 32 QM water molecules with 60 partitionings. The green line represents the result of 24 QM water molecules with 96 partitionings.

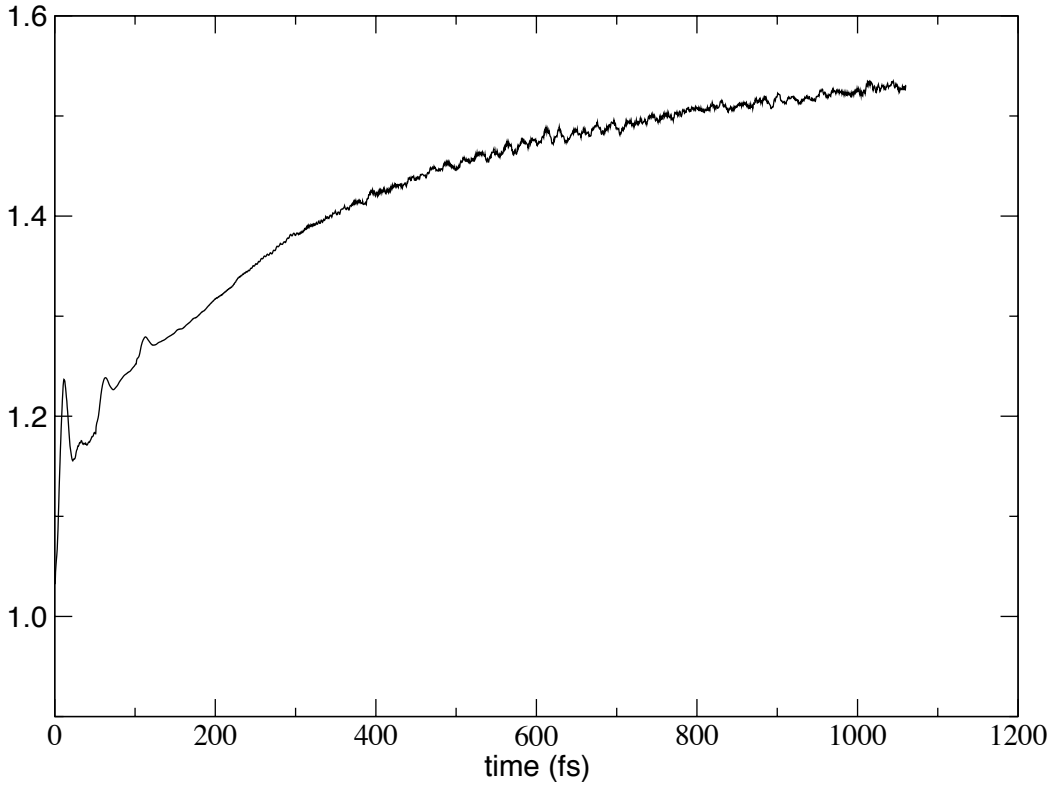

Figure S3. Density of pure 2048 DFTB3 water system in course of MD simulation time by full QM simulation under NPT condition.

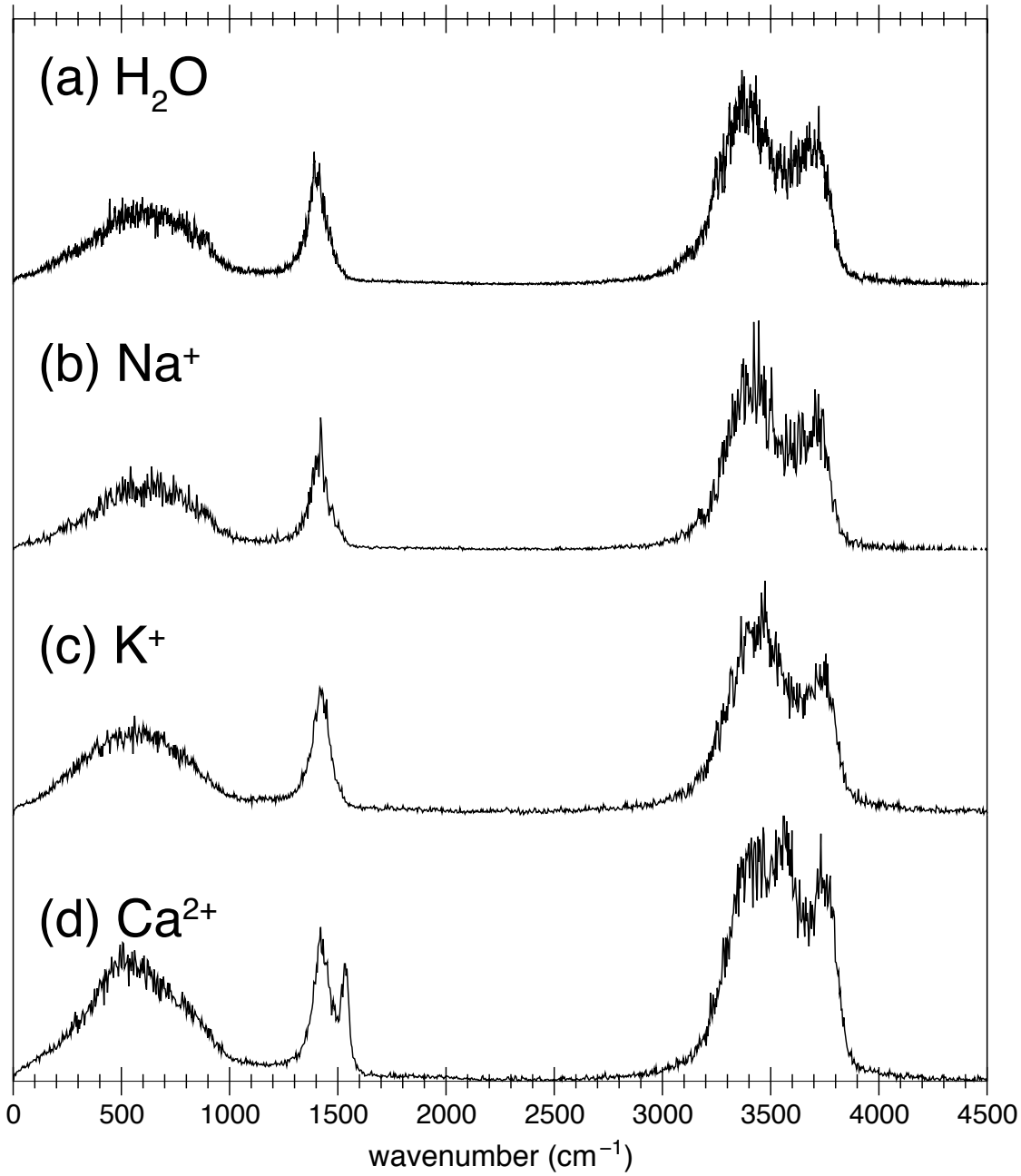

Figure S4. Raw IR spectra of (a) deionized water, (b) Na^+, (c) K^+, and (d) Ca^{2+} solutions.

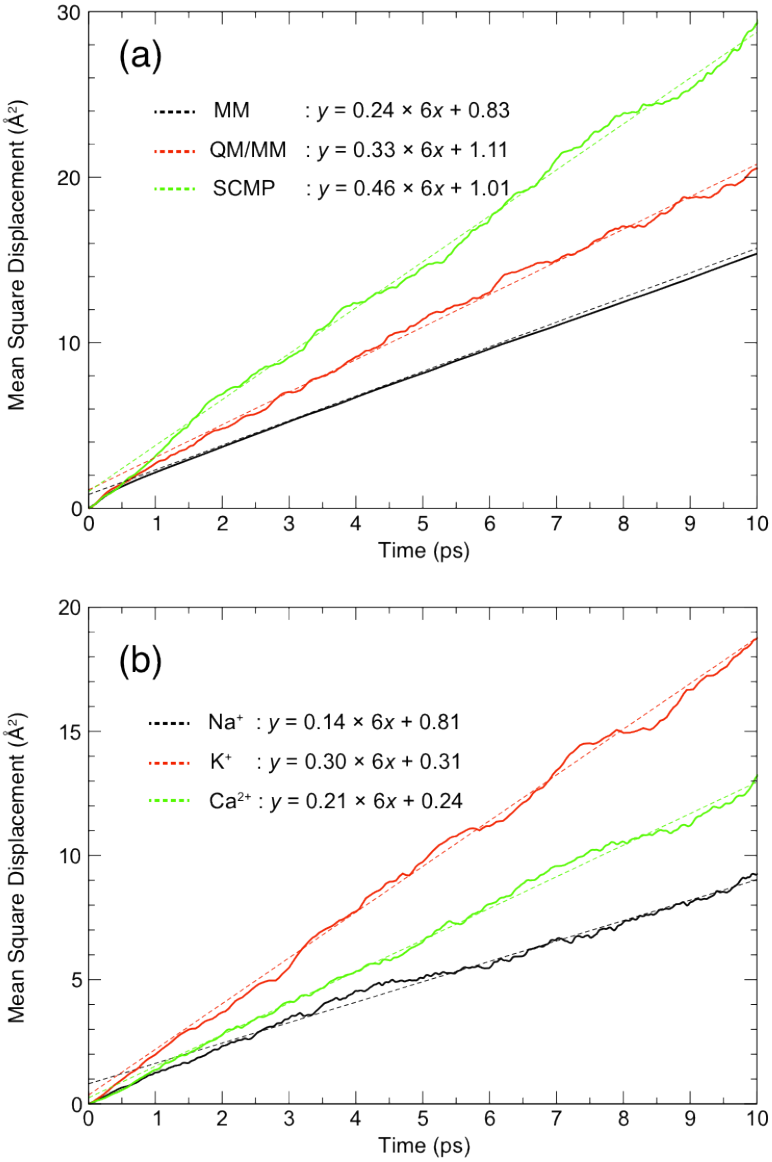

Figure S5. Mean square displacement as a function of MD simulation time. (a) The resulting functions of water obtained by MM, conventional QM/MM, and SCMP QM/MM methods colored black, red and green, respectively. (b) The SCMP results of Na^+, K^+, and Ca^{2+} are colored black, red and green, respectively. The functions are fitted by a straight line: $y = 6ax + b$, where the value of a is diffusion coefficient.

Supplementary Table 1. Transition parameters used in SCMP simulations (Å).

Solute	MM				QM			
	Fade-out		Fade-in		Fade-in		Fade-out	
	short	long	short	long	short	long	short	long
H_2O	3.30	5.80	5.80	8.80	3.30	5.80	5.80	8.80
Na^+	2.49	5.81	5.81	8.74	2.49	5.81	5.81	8.74
K^+	3.05	5.97	5.97	8.80	3.05	5.97	5.97	8.80
Ca^{2+}	2.45	5.85	5.85	8.78	2.45	5.85	5.85	8.78

Supplementary Table 2. Mulliken charges (*e*) on the cations obtained from DFT calculations for MD snapshots, which consist of the solute and the nearest 32 water molecules.

	PBE		B3LYP	
	STO-3G	def2-TZVP	STO-3G	def2-TZVP
Na^+	0.53	0.64	0.56	0.75
K^+	0.09	0.63	0.20	0.74
Ca^{2+}	0.47	1.28	0.59	1.53