

## Electronic Supplementary Information

### Hydration and dynamics of glutamate ion in aqueous solution

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## S1 RISM input

Table S1: Dihedral angles for glutamate ion from the literature and values of this work from structure optimization with GAUSSIAN 09.<sup>1</sup>

$C\alpha-C\beta-C\gamma-C2$	$N-C\alpha-C\beta-C\gamma$	$C1-C\alpha-C\beta-C\gamma$	source
$0^\circ$ to $100^\circ$	$180^\circ$ to $-100^\circ$	$0^\circ$ to $100^\circ$	2
$\sim 60^\circ, -70^\circ$ (1.57 M)	$-160^\circ, -90^\circ$	$(90 \pm 30)^\circ, 50^\circ$	3
$65.4^\circ$	$-174.2^\circ$	$68.9^\circ$	this work

Table S2: Atom coordinates,  $x$ ,  $y$  and  $z$ , van der Waals parameters,  $\sigma$  and  $\epsilon$ , and partial charges,  $q$  (as fraction of the elementary charge,  $e_0$ ), for the glutamate anion. For atom labelling see Fig. 1 of the Main Article.

Atom	$x / \text{nm}$	$y / \text{nm}$	$z / \text{nm}$	$\sigma / \text{nm}$	$\epsilon / \text{kcal mol}^{-1}$	$q / e_0$
O21	0.214	0.102	-0.086	0.296	0.210	-0.862
C2	0.227	0.003	-0.010	0.340	0.086	0.851
Cg	0.124	-0.016	0.103	0.340	0.109	-0.212
Cb	0.002	0.076	0.097	0.340	0.109	0.206
Ca	-0.088	0.051	-0.025	0.340	0.109	0.255
C1	-0.163	-0.086	-0.019	0.340	0.086	0.690
O11	-0.283	-0.079	0.02	0.296	0.210	-0.774
O12	-0.097	-0.186	-0.050	0.296	0.210	-0.780
N	-0.197	0.156	-0.029	0.325	0.170	-0.609
O22	0.319	-0.083	-0.015	0.296	0.210	-0.894
Hg1	0.093	-0.120	0.104	0.265	0.016	0.051
Hg2	0.176	0.002	0.197	0.265	0.016	0.037
Hb1	-0.058	0.065	0.188	0.265	0.016	-0.048
Hb2	0.036	0.179	0.092	0.265	0.016	-0.025
Ha	-0.030	0.059	-0.116	0.196	0.016	0.024
Hn1	-0.280	0.104	0.009	0.107	0.016	0.350
Hn2	-0.176	0.238	0.027	0.107	0.016	0.355
Hn3	-0.219	0.186	-0.123	0.107	0.016	0.385

## S2 Densities, Dynamic Viscosities and Electrical Conductivities

Table S3: Molar concentrations,  $c$ , densities,  $\rho$ , dynamic viscosities,  $\eta$ , and electrical conductivities,  $\kappa$ , of the investigated aqueous sodium glutamate solutions at 25 °C.

$c / \text{M}$	$\rho / \text{g}\cdot\text{cm}^{-3}$	$\eta / \text{mPa}\cdot\text{s}$	$\kappa / \text{S}\cdot\text{m}^{-1}$
0.101	1.005502	0.9921	0.571
0.206	1.014738	1.1115	1.087
0.406	1.031564	1.2395	1.885
0.601	1.047664	1.397	2.47
0.783	1.062868	1.552	2.93
0.965	1.074612	1.556	3.29
1.14	1.090961	1.738	3.563
1.30	1.103343	1.943	3.722
1.44	1.115383	2.166	3.847
1.60	1.128067	2.454	3.898
1.75	1.140130	2.715	3.88
1.90	1.150388	3.058	3.909

## S3 Dielectric Relaxation Spectroscopy

### S3.1 Relaxation time distribution functions

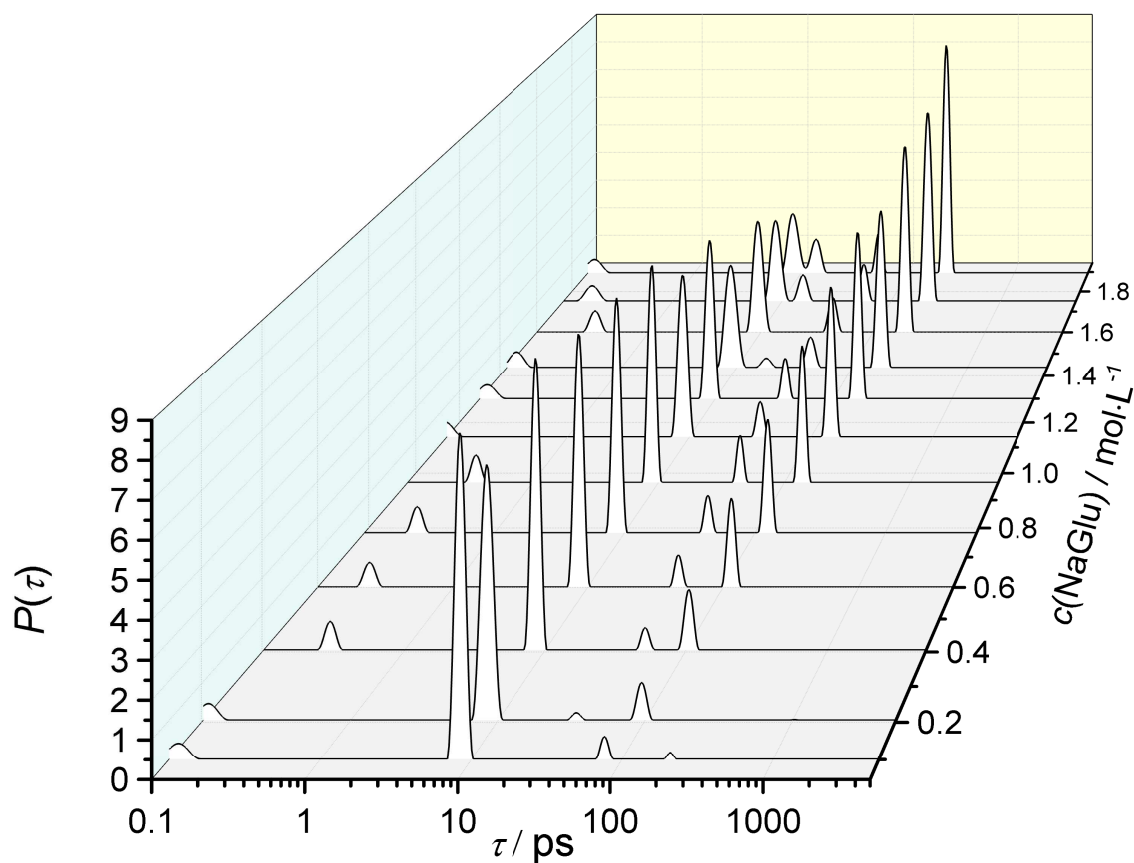


Figure S1: Relaxation-time distribution functions,  $P(\tau)$ , of the dielectric spectra of aqueous NaGlu solutions at 25 °C.<sup>4</sup>

### S3.2 Fit parameters of the dielectric spectra

Table S4: Static permittivity,  $\epsilon$ , relaxation amplitudes,  $S_j$ , and relaxation times,  $\tau_j$  of the resolved modes  $j = 1 \dots 3$ , and infinite-frequency permittivity,  $\epsilon_\infty$ , obtained from the D+D+D fit of dielectric spectra of NaGlu(aq) solutions of concentration  $c$  at 25 °C.<sup>a</sup>

$c / \text{M}$	$\epsilon$	$S_1$	$\tau_1 / \text{ps}$	$S_2$	$\tau_2 / \text{ps}$	$S_3$	$\tau_3 / \text{ps}$	$\epsilon_\infty$
0.101	80.01	3.96	90F	3.63	13.9	66.73	8.14	5.70
0.206	81.48	7.72	93.9	3.89	17.6	64.19	8.12	5.68
0.406	85.18	14.37	98.1	5.18	21.2	59.50	8.13	6.12
0.601	88.65	20.16	109	7.20	24.0	55.12	8.10	6.17
0.783	92.08	25.52	121	8.73	26.7	51.45	8.16	6.39
0.965	95.56	30.41	134	10.48	29.8	48.20	8.17	6.47
1.14	98.46	36.41	144	9.65	29.6	45.71	8.38	6.69
1.30	102.17	41.53	158	11.43	29.2	42.33	8.34	6.87
1.44	106.66	45.96	176	11.66	34.3	41.12	8.64	6.91
1.60	109.25	51.81	190	12.70	32.5	37.76	8.53	6.98
1.75	113.46	56.74	212	12.86	38.4	36.73	8.83	7.13
1.90	116.48	61.38	227	12.81	40.1	35.00	9.04	7.30

<sup>a</sup> Parameter values followed by "F" were fixed during fitting.

### S3.3 Correction for kinetic depolarization

Ions moving in an applied electric field,  $\vec{E}$ , exert a torque on neighboring dipolar solvent molecules. This additional force opposes the reorienting force of the applied field, resulting in a depolarization of the bulk solvent molecules. Experimentally, this depolarization is expressed as a reduction of the apparent bulk solvent amplitude,  $S_{\text{H}_2\text{O}, \text{bulk}}$ , by a kinetic dielectric decrement,  $\Delta\epsilon_{\text{kd}}$ . Thus, the corrected equilibrium solvent amplitude,  $S_{\text{H}_2\text{O}, \text{bulk}}^{\text{eq}}$ , is given by

$$S_{\text{H}_2\text{O}, \text{bulk}}^{\text{eq}} = S_{\text{H}_2\text{O}, \text{bulk}} + \Delta\epsilon_{\text{kd}} \quad (1)$$

The continuum model of Hubbard and Onsager<sup>5-7</sup> (HO) is frequently used to correct experimental DRS data for this effect. In the HO approach the dielectric increment can be written as

$$\Delta\epsilon_{\text{kd}}^{\text{HO}} = p \cdot \frac{\epsilon(0) - \epsilon_{\infty}(0)}{\epsilon(0)} \cdot \frac{\tau(0)}{\epsilon_0} \cdot \kappa \quad (2)$$

where  $\epsilon_0$  is the permittivity of free space,  $\epsilon(0)$  and  $\epsilon_{\infty}(0)$  are the static and infinite-frequency permittivities of the neat solvent,  $\tau(0)$  is the relaxation time of the solvent dispersion step,  $\kappa$  is the solution electrical conductivity, and  $p$  is a hydrodynamic parameter which describes the coupling of translational ion motions to the macroscopic viscosity. For  $p = 1$ , so-called *stick*, and for  $p = 2/3$  *slip* boundary conditions apply. Generally, *slip* conditions are considered more physically realistic<sup>8,9</sup> and so were chosen for further analysis. The HO theory is valid only at infinite dilution of the electrolyte and thus its application to concentrated solutions is problematic. Recently, Segal *et al.* introduced a modification of the HO equation to account for finite salt concentrations<sup>10</sup>

$$\Delta\epsilon_{\text{kd}}^{\text{Segal}} = \Delta\epsilon_{\text{kd}}^{\text{HO}} \cdot \exp(\sigma R) \cdot (\sigma R + 2)/2 \quad (3)$$

where  $\sigma$  is the reciprocal Debye length and  $R$  is the effective ion radius. Whereas  $\sigma$  can be calculated readily, the determination of  $R$  is not straightforward. In this work, the mean radius of anion and cation was used for  $R$ , with the value for  $\text{Na}^+$  taken from Marcus<sup>11</sup> while for  $\text{Glu}^-$  the equivalent sphere radius from DFT calculations was taken (Gaussian 09 at the B3LYP/6-31++G(d,p) level with the PCM solvation model).<sup>1</sup>

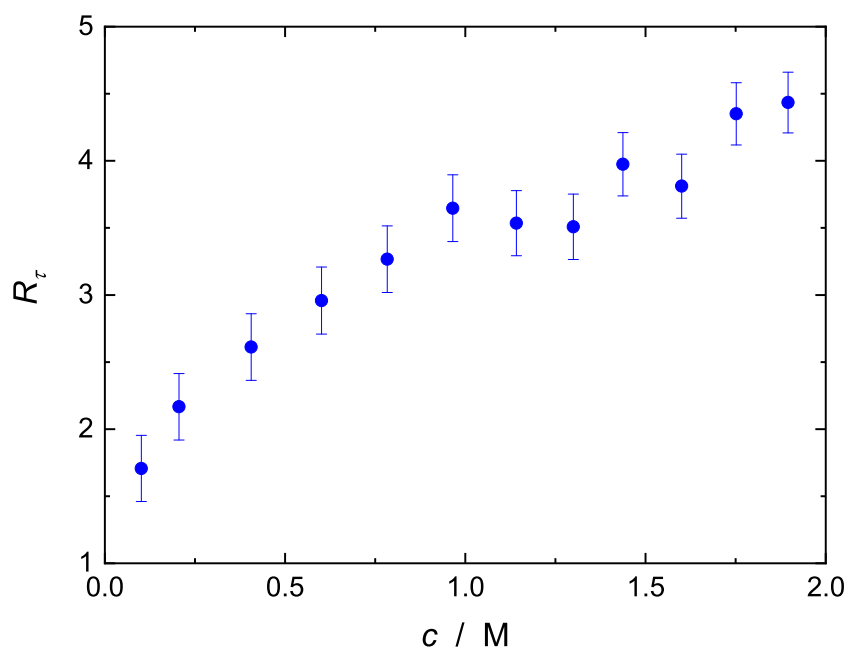


Figure S2: Slow-water retardation factor,  $R_\tau = \tau_3/\tau_2$  (●), of aqueous NaGlu solutions as function of solute concentration,  $c$ .

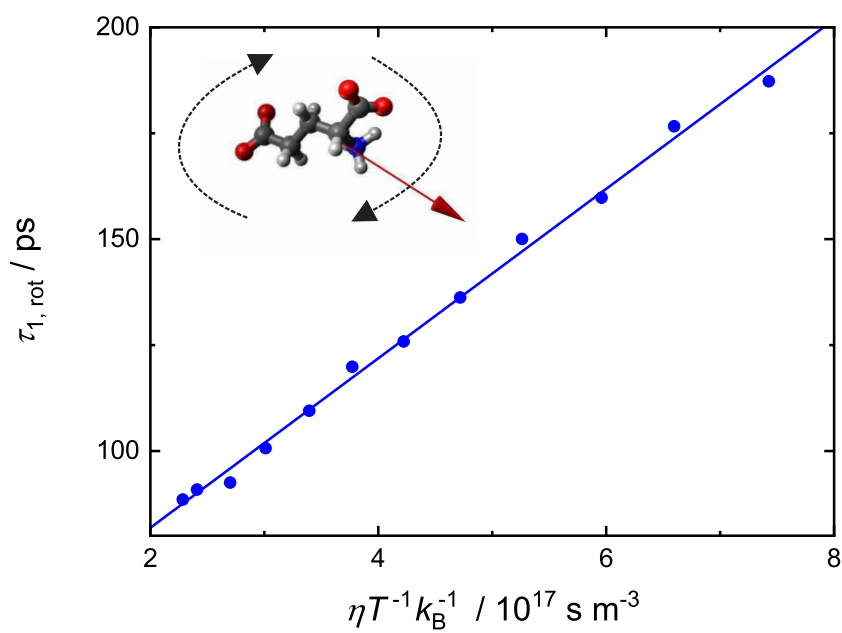


Figure S3: Rotational correlation time of the  $\text{Glu}^-$  anion,  $\tau_{1,\text{rot}}$  (●), as a function of  $\eta T^{-1} k_B^{-1}$ . The line denotes the Stokes-Einstein-Debye fit; the red arrow of the inset indicates the direction of the  $\text{Glu}^-$  dipole moment.

## S4 Quantum-chemical calculations of $\text{Glu}^-$ hydrates

The minimum-energy geometries and the respective dipole moments shown in Fig. S4 were obtained by calculations with Gaussian 09<sup>1</sup> at the B3LYP/6-31++G(d,p) level with the PCM solvation model (using the center of mass for the pivot).

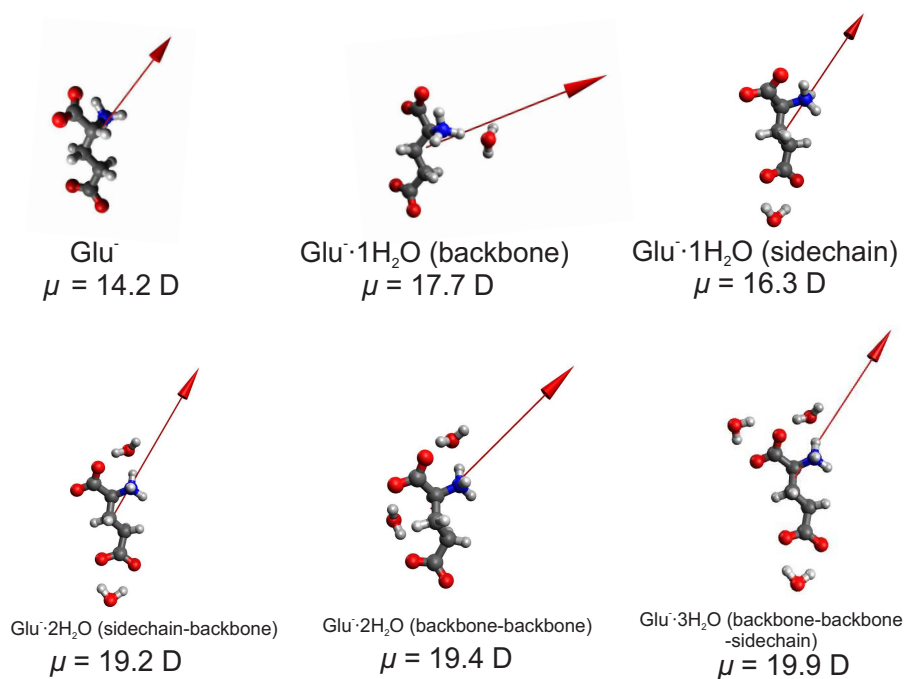


Figure S4: Structures of  $\text{Glu}^-$  and its hydrates obtained from DFT calculations. The arrows indicate the dipole moments of the aggregates. Blue: nitrogen, red: oxygen, dark-gray: carbon, light-gray: hydrogen.



## S5 RISM results

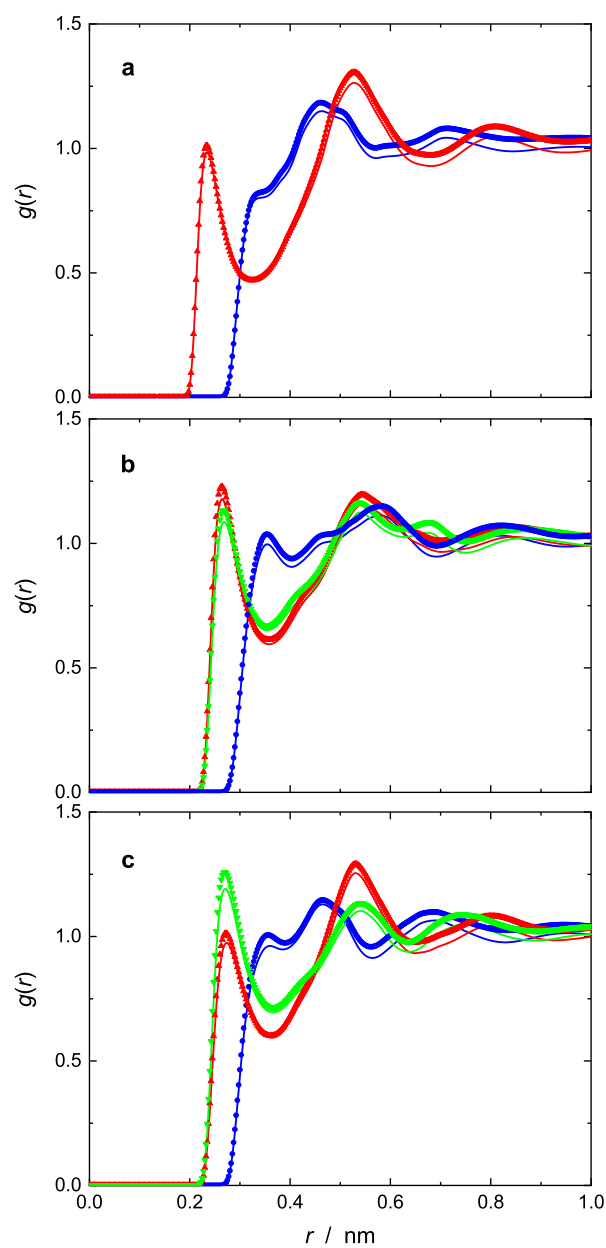


Figure S5: Radial distribution functions characterizing the hydration of the hydrophobic moiety of  $\text{Glu}^-$ : (a)  $g_{\text{C}\alpha\text{-Ow}}(r)$  (blue) and  $g_{\text{H}\alpha\text{-Hw}}(r)$  (red); (b)  $g_{\text{C}\beta\text{-Ow}}(r)$  (blue),  $g_{\text{H}\beta 1\text{-Ow}}(r)$  (red) and  $g_{\text{H}\beta 2\text{-Ow}}(r)$  (green); (c)  $g_{\text{C}\gamma\text{-Ow}}(r)$  (blue),  $g_{\text{H}\gamma 1\text{-Ow}}(r)$  (red) and  $g_{\text{H}\gamma 2\text{-Ow}}(r)$  (green). Lines show data for infinite dilution and symbols those for  $c = 1.90 \text{ M}$ .

Table S5: Values,  $g_{i-j}(r_{M1})$ , of the first maximum and its location,  $r_{M1}$  (brackets, in nm), of 1D-RISM site  $i$ -site  $j$  RDFs and associated coordination numbers,  $n$ , for NaGlu(aq) at “infinite dilution” ( $c \rightarrow 0$ ) and at  $c = 1.90$  M.

sites $i-j$	$g_{i-j}(r_{M1})$		CN	
	$c \rightarrow 0$	1.90 M	$c \rightarrow 0$	1.90 M
ammonium group hydration				
N-Ow	2.09 (0.290)	2.15 (0.290)	5.32	4.6
N-Hw	1.24 (0.358)	1.29 (0.352)	–	–
Hn1-Ow	0.45 (0.188)	0.45 (0.188)	0.3	0.25
Hn2-Ow	1.20 (0.180)	1.21 (0.180)	0.91	0.78
Hn3-Ow	1.42 (0.177)	1.42 (0.177)	0.99	0.85
backbone carboxylate group hydration				
O11-Ow	1.91 (0.295)	1.94 (0.295)	6.33	5.45
O11-Hw	2.35 (0.170)	2.36 (0.170)	2.46	2.06
O12-Ow	1.93 (0.292)	1.96 (0.292)	6.02	5.16
O12-Hw	2.58 (0.170)	2.57 (0.170)	2.65	2.19
side-chain carboxylate group hydration				
O21-Ow	1.92 (0.292)	1.94 (0.292)	5.91	5.04
O21-Hw	2.95 (0.168)	2.96 (0.168)	2.97	2.46
O22-Ow	2.06 (0.295)	2.08 (0.295)	6.77	5.77
O22-Hw	3.30 (0.168)	3.27 (0.168)	3.34	2.71
hydration of hydrophobic groups				
C $\alpha$ -Ow	1.15 (0.463)	1.18 (0.463)	22.72	19.21
H $\alpha$ -Ow	0.99 (0.235)	1.01 (0.235)	2.28	1.92
C $\beta$ -Ow	1.00 (0.355)	1.04 (0.355)	4.86	4.2
H $\beta$ 1-Ow	1.18 (0.265)	1.23 (0.263)	3.67	3.17
H $\beta$ 2-Ow	1.09 (0.267)	1.13 (0.267)	3.56	2.99
C $\gamma$ -Ow	0.96 (0.360)	1.01 (0.358)	3.83	3.59
H $\gamma$ 1-Ow	0.97 (0.273)	1.01 (0.273)	3.49	2.98
H $\gamma$ 2-Ow	1.19 (0.270)	1.26 (0.270)	4.31	3.75
Na <sup>+</sup> hydration				
Na-Ow	3.83 (0.235)	3.73 (0.235)	4.81	4.00
Na <sup>+</sup> binding				
O11-Na	6.61 (0.230)	4.80 (0.230)		0.22
O12-Na	8.52 (0.230)	5.59 (0.230)		0.27
O21-Na	8.57 (0.227)	6.17 (0.227)		0.29
O22-Na	11.42 (0.227)	7.66 (0.227)		0.41

## References

- [1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision E.01*, 2010, Gaussian Inc. Wallingford CT 2009.
- [2] S. E. McLain, A. K. Soper and A. Watts, *J. Phys. Chem. B*, 2006, **110**, 21251–21258.
- [3] C. D. Daub, K. Leung and A. Luzar, *J. Phys. Chem. B*, 2009, **113**, 7687–7700.
- [4] A. Y. Zaslavsky and R. Buchner, *J. Phys.: Condens. Matter*, 2011, **23**, 025903.
- [5] J. Hubbard and L. Onsager, *J. Chem. Phys.*, 1977, **67**, 4850–4857.
- [6] J. B. Hubbard, *J. Chem. Phys.*, 1978, **68**, 1649–1664.
- [7] J. B. Hubbard, P. Colonomos and P. G. Wolynes, *J. Chem. Phys.*, 1979, **71**, 2652–2661.
- [8] R. Buchner, T. Chen and G. Heftner, *J. Phys. Chem. B*, 2004, **108**, 2365–2375.
- [9] S. Schrödle, W. W. Rudolph, G. Heftner and R. Buchner, *Geochim. Cosmochim. Acta*, 2007, **71**, 5287–5300.
- [10] M. Sega, S. Kantorovich and A. Arnold, *Phys. Chem. Chem. Phys.*, 2015, **17**, 130–133.
- [11] Y. Marcus, *Ion Properties*, CRC Press, Boca Raton, 1997.