Supporting Information
A General Hydrogen-Bond Connectivity Descriptor Based on Graph Theory

Nico Di Fonte[1], Isabella Daidone[1], Laura Zanetti-Polzi[2]

[1]Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila 67100, Italy.
[2]Center S3, CNR-Institute of Nanoscience, Modena 41125, Italy.

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1 MD details

Table S1: Density, corrected diffusion coefficients, and D/D_0 ratios, where D_0 represents the diffusion coefficient of pure water.

MD	Density (kg/m^3)	Diffusion ($10^{-9} m^2/s$)	D/D_0
0 molal	996.4 ± 0.1	2.27 ± 0.01	1.000 ±0.006
0.4 molal	1010.5 ± 0.1	2.18 ± 0.01	0.960 ±0.006
2 molal	1069.1 ± 0.1	1.86 ± 0.01	0.819 ±0.006
4 molal	1134.2 ± 0.1	1.52 ± 0.01	0.669 ±0.006

Across all simulations of binary systems, sodium exhibits a coordination number of ≈ 4.7, while chloride exhibits a coordination number of ≈ 6.4.

2 Hydrogen Bond Definition Criteria

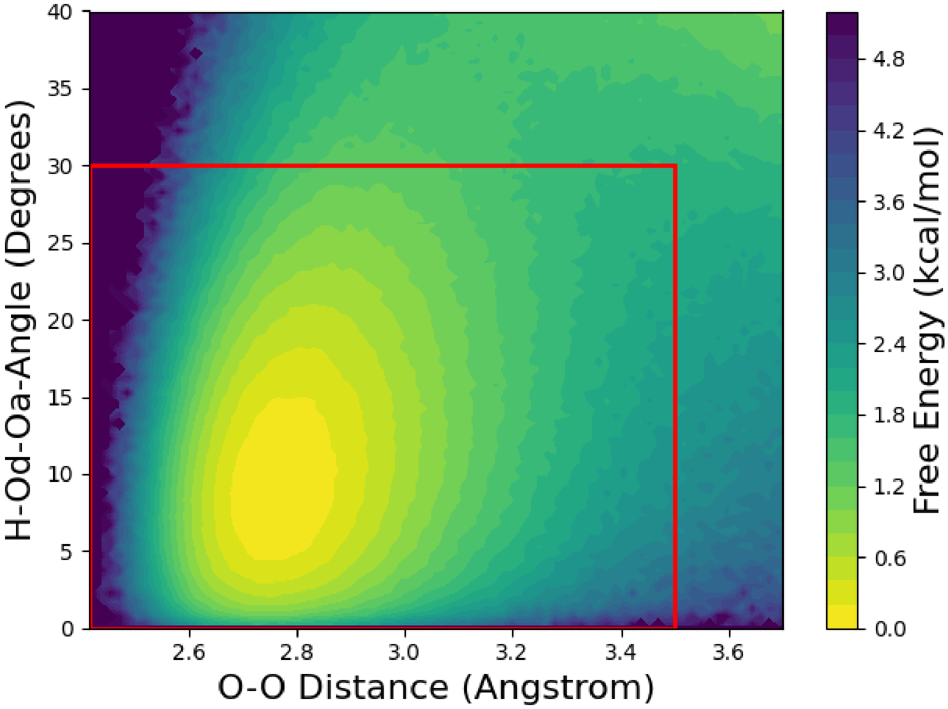

Figure S1: Two-dimensional free-energy landscape of the Oxygen-Oxygen distance and the H-Odonor-Oacceptor angle calculated for the pure water MD simulation. The red square indicates the geometric threshold adopted in this work.

The geometric criterion adopted in this work to define a hydrogen bond (HB), an O–O distance ≤ 0.35 nm and H-D-A angle $\leq 30°$, is standard and widely employed in the literature for the definition of hydrogen bonds.[1] To assess the sensitivity of our results to this choice, we also considered an energetic criterion based on the two-dimensional free-energy landscape computed along the H-bond distance and angle coordinates, classifying as hydrogen-bonded only those molecular pairs that fall within the main free-energy basin (using a 1.6 kcal/mol cutoff, see Fig. S1). As shown here, the geometric thresholds commonly adopted in the literature (highlighted in red) capture the vast majority of the basin. The geometric criterion introduces borderline cases near the cutoff boundary, corresponding to a population of molecular pairs at short O–O distances but large H–D–A angles (30–40°). To quantify the impact of this ambiguity, we recomputed the distribution of the HB-NTC (namely the NTC in which the edges are defined with the hydrogen bond criterium) for pure water and for the highest-concentration solution (4 molal) using both criteria. The two distributions (see Fig. S2) are nearly indistinguishable, demonstrating that the precise choice of hydrogen-bond criterion does not significantly affect our results, and that the conclusions drawn in this work are robust with respect to this methodological detail.

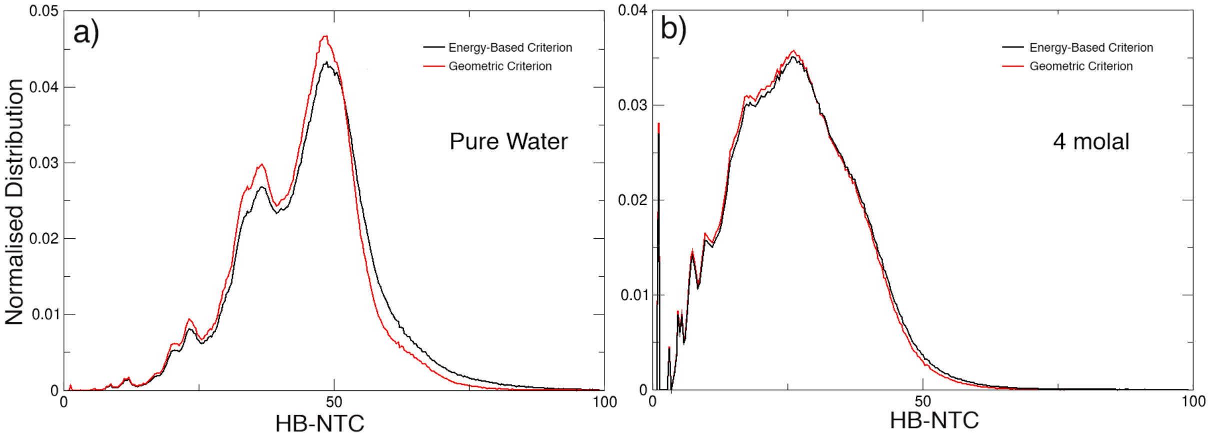

Figure S2: HB-NTC distributions computed using both the geometric-based cutoff adopted in this work and the energy-based cutoff for comparison for pure water (panel a) and the 4 molal solution (panel b).

3 Broadcaster and Receiver walks

The directed matrix constructed using the hydrogen-bond constraint presents a connectivity issue when considering walks that include edges pointing in opposite directions (Fig. S3).

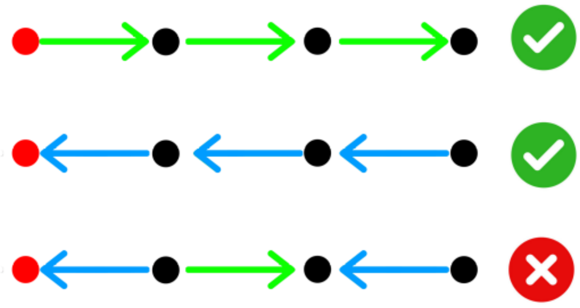

Figure S3: Example of correctly detected and undetected walks starting from a generic reference node (red dot). Walks in which the edges point toward each other are undetected, regardless of the value of k at which the interruption occurs; from that point onward, no further walks are considered for that branch.

Specifically, examining the adjacency matrix (A_{br} by rows captures the broadcaster contribution of each node. To account for the receiver contribution, one can either consider the corresponding columns or transpose the matrix$A_{re} = A_{br}^T$ and then analyze the elements by row. This issue, however, is easily resolved. If the direction of the edges is not of interest, information about the overall connectivity can be directly obtained from the undirected adjacency matrix of the graph constructed using the hydrogen-bond criteria (A_{und}). To capture all information regarding the orientation of the hydrogen bonds, the differences between A_{und}^k and $A_{br}^k + A_{re}^k$ must be considered. In particular, for walks of a generic length k starting from node i, all ending nodes j must be checked in all matrices. Any neighbours (l) present in the undirected matrix but missing from the broadcaster or receiver matrices must be included. To determine the direction of the edge, all neighbours (n) of node i at a distance $k-1$ should be examined, and it should then be assessed whether the edges are $n \to l$ (broadcaster) or $l \to n$ (receiver) as shown in Fig. S4.

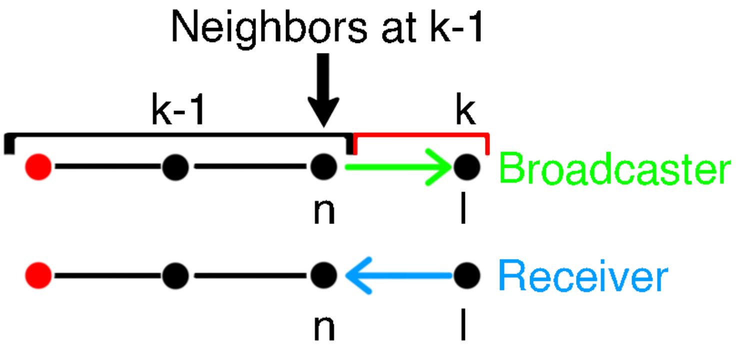

Figure S4: For walks of length k from node i, ending nodes j are checked across matrices. Missing neighbours l are added, and edge direction is determined via neighbours n at distance $k-1$.

4 Hydrogen Bond Network Analyses

Fig. S5 shows the Oxygen-Oxygen radial distribution function computed for the highest molality simulation, and the average distance value of molecules found at a chemical distance up to $k = 5$.

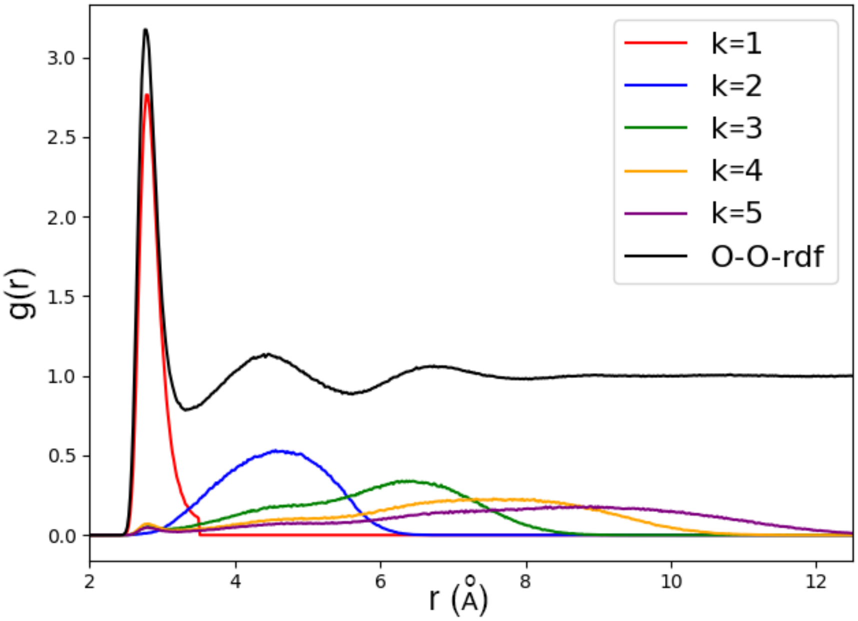

Figure S5: Oxygen–Oxygen radial distribution function for the 4 molal NaCl solution, showing the average distances of molecules at chemical distances up to $k = 5$.

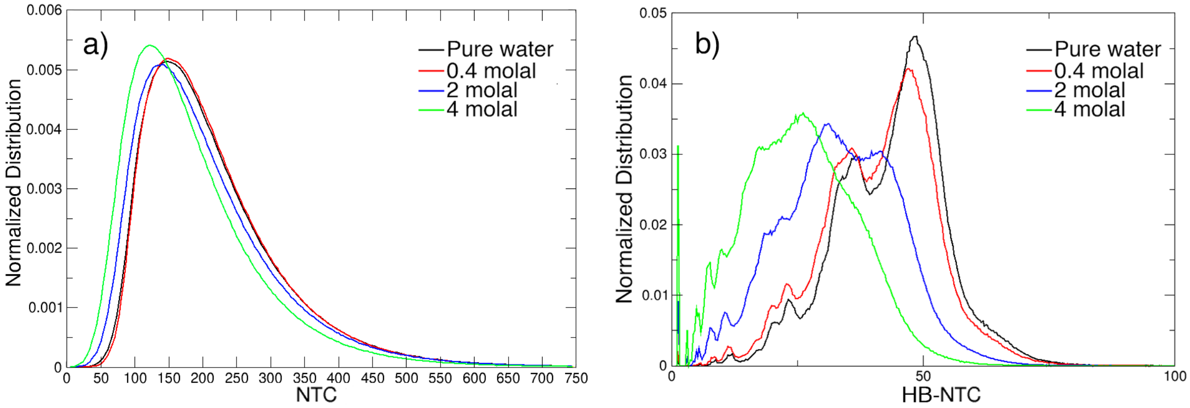

Figure S6: Panel a): NTC distributions for the pure system and NaCl solutions. Panel b): HB-NTC distributions for the pure system and NaCl solutions.

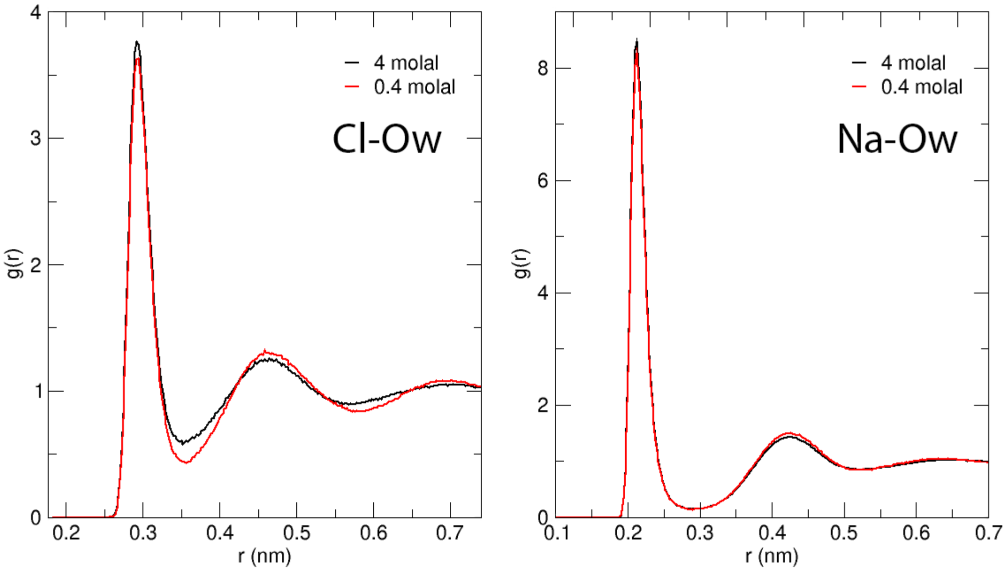

Figure S7: Ion-Oxygen radial distribution functions for the 0.4 molal (lowest molality) and 4 molal (highest molality) solutions, left panel: oxygen-chloride rdf, right panel: oxygen-sodium rdf.

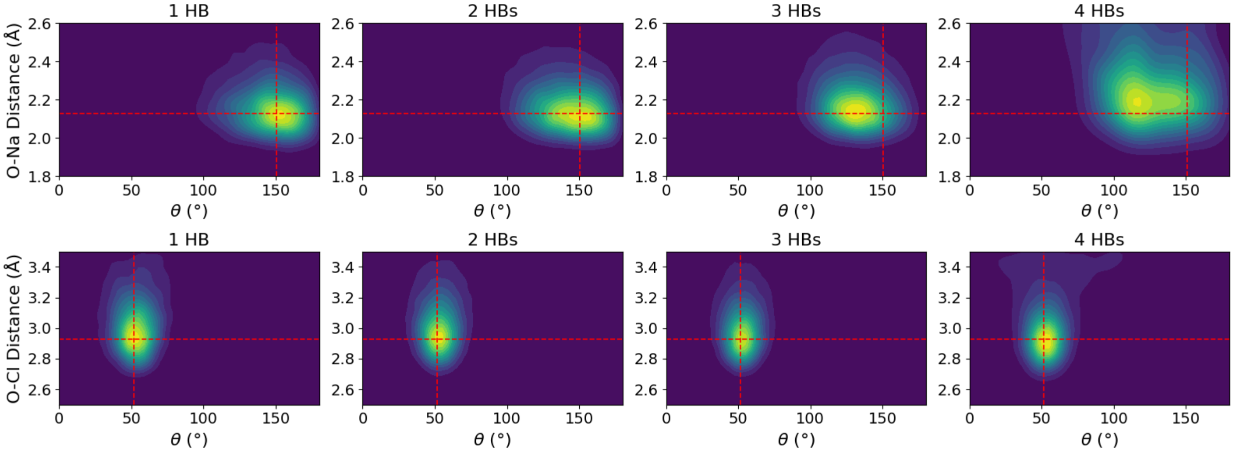

Figure S8: Two-dimensional distributions of the ion–oxygen distance and the θ angle. The upper four panels correspond to Na^+ and the lower four panels correspond to Cl^-. In each subplot, water molecules are classified according to the number of water–water hydrogen bonds they participate in. The red dashed lines represent the coordinates of the most populated bin of the 1HB distribution for each ion. Probabilities are normalized independently for each subplot such that the most populated bin has a value of 1.

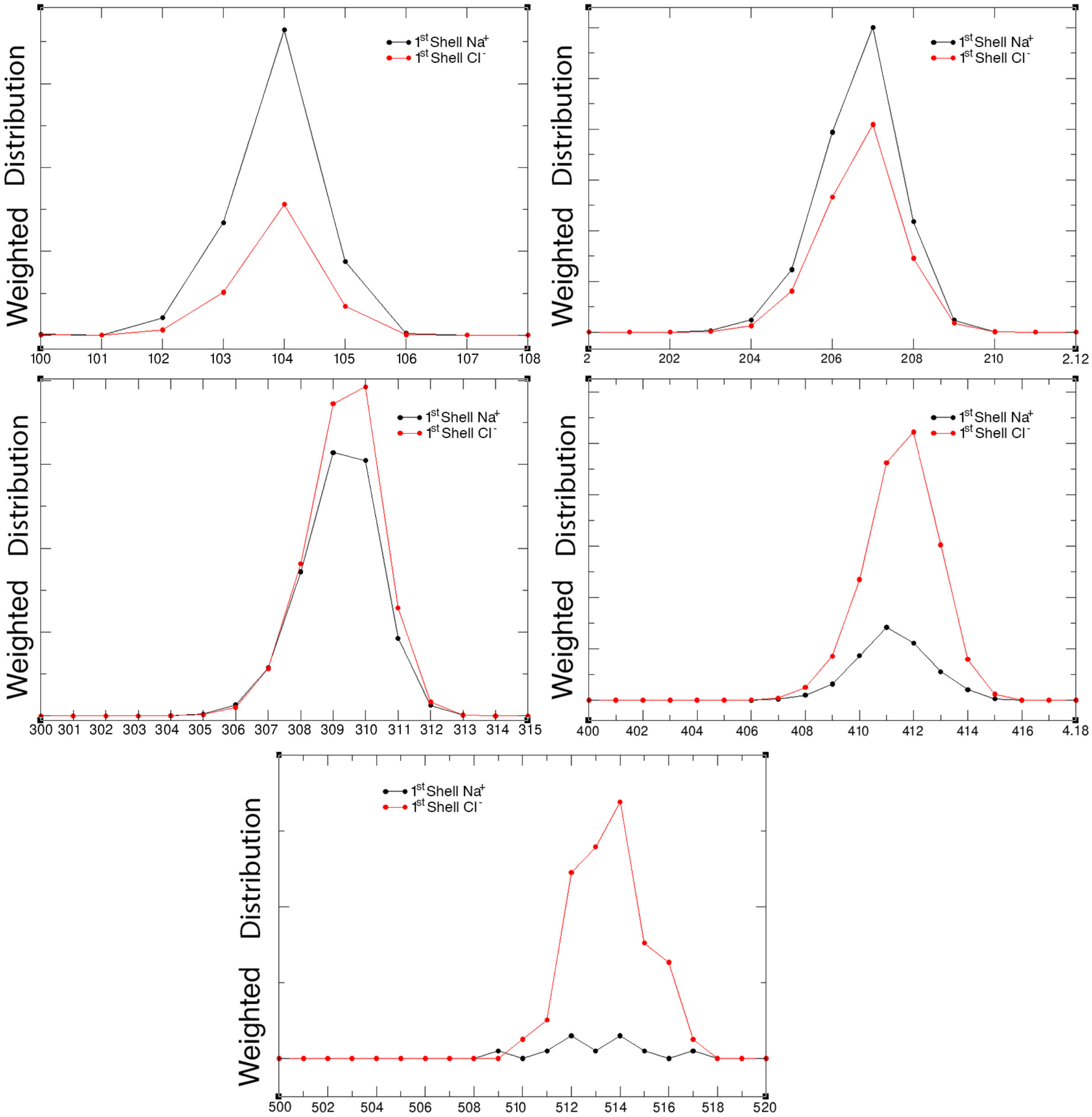

Figure S9: Weighted Hydrogen bond distributions for hydrogen bonds at $k = 2$. The x-axis is a three-digit HB score: the first digit indicates the number of hydrogen bonds at $k = 1$, and the last two digits indicate the number of hydrogen bonds at $k = 2$.

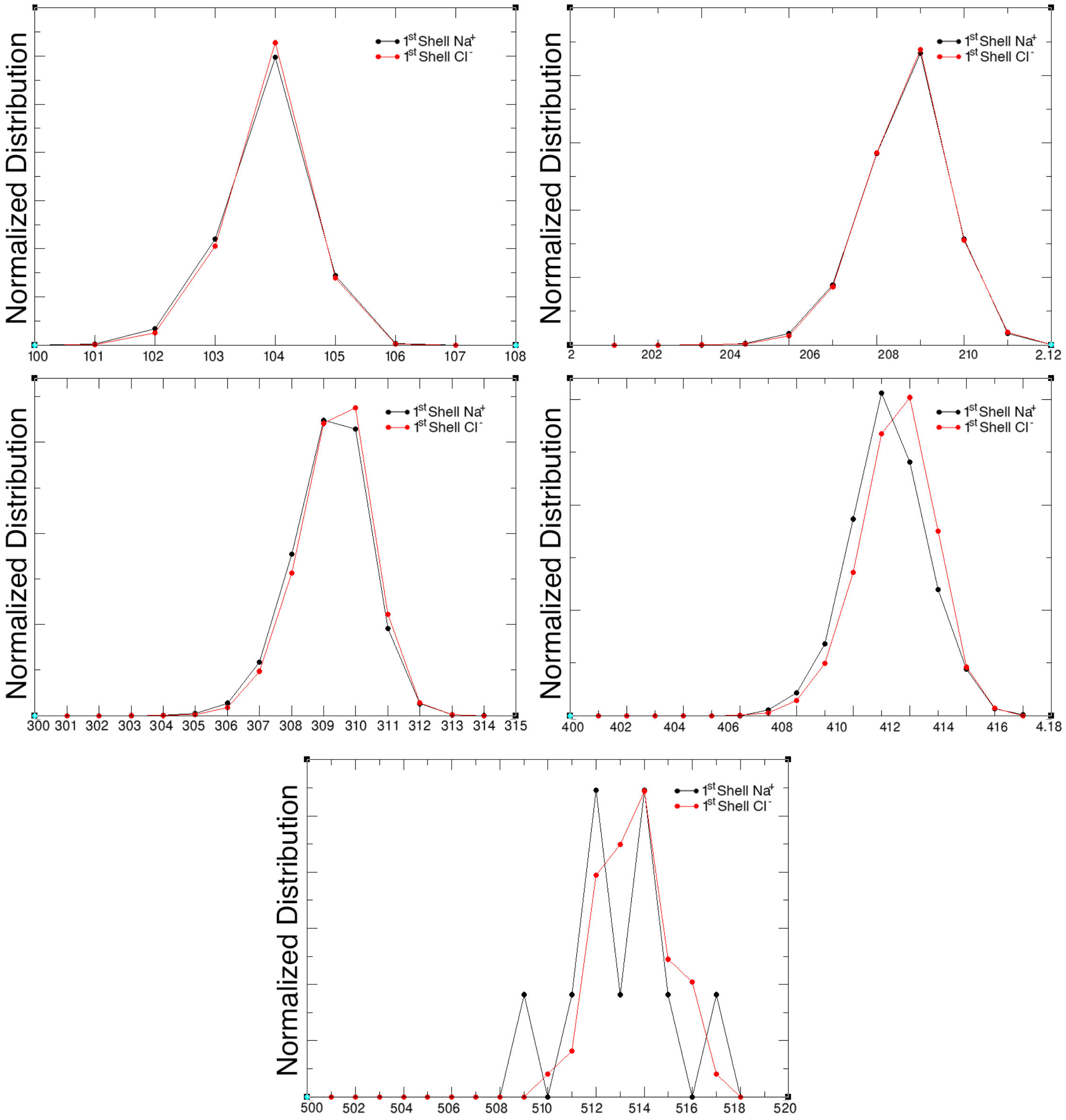

Figure S10: Normalized Hydrogen bond distributions for hydrogen bonds at $k = 2$. The x-axis is a three-digit HB score: the first digit indicates the number of hydrogen bonds at $k = 1$, and the last two digits indicate the number of hydrogen bonds at $k = 2$.

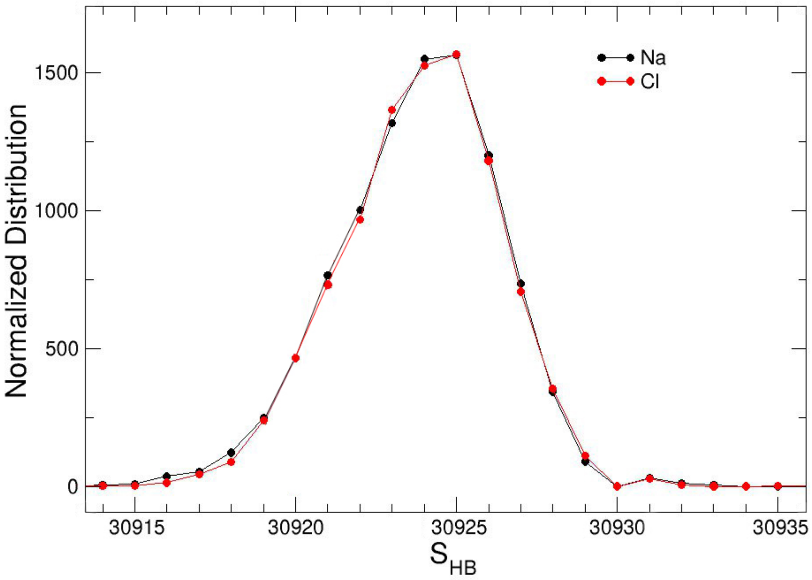

Figure S11: Normalized Hydrogen bond distributions for hydrogen bonds at $k = 3$ with $n_1 = 3$ and $n_2 = 9$.

References

[1] Alenka Luzar and David Chandler. Hydrogen-bond kinetics in liquid water. *Nature*, 379(6560):55–57, 1996.