Influence of Polarization on Carbohydrate Hydration: A Comparative Study using Additive and Polarizable Force Fields

Poonam Pandey and Sairam S. Mallajosyula*

Department of Chemistry, Indian Institute of Technology Gandhinagar, Simkheda, Gandhinagar, Gujarat, India

E-mail: msairam@iitgn.ac.in

Phone: +91 - 79 - 32454998. Fax: +91 - 79 - 2397 2324

Supporting Information

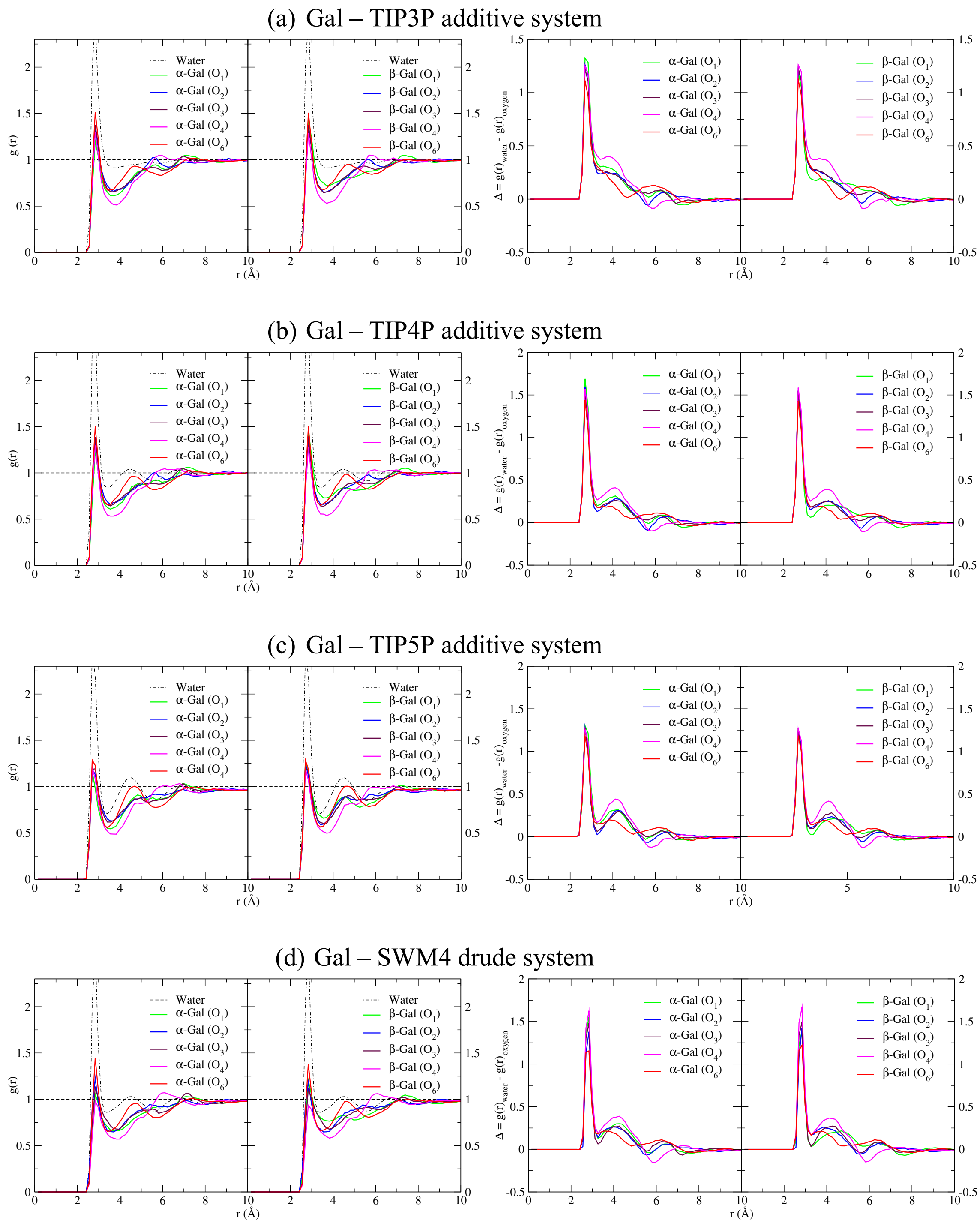

Figure S1: **Left Panel:** Selected oxygen (carbohydrate) - oxygen (water) radial distribution functions, *g(r)*, from 300 K simulations of carbohydrate (Gal) in four water models (a) TIP3P, (b) TIP4P, (c) TIP5P and (d) SWM4. **Right Panel:** Differences (Δ) between the radial distribution functions. Δ is calculated as the differences between *g(r)* of pure water and *g(r)* of selected oxygen carbohydrate (Gal) – oxygen (water) radial distribution from 300 K simulations.

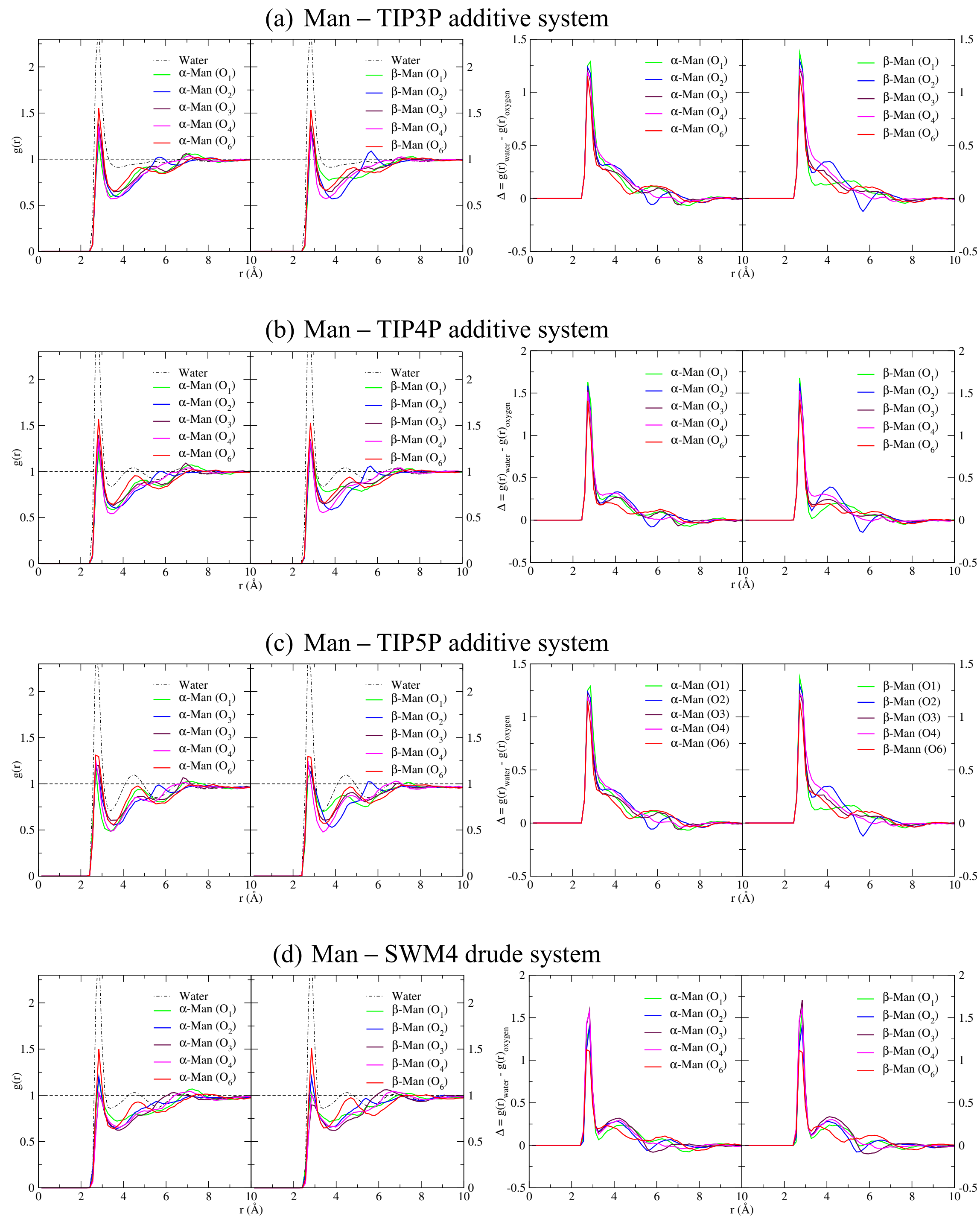

Figure S2: **Left Panel:** Selected oxygen (carbohydrate) - oxygen (water) radial distribution functions, *g(r)*, from 300 K simulations of carbohydrate (Man) in four water models (a) TIP3P, (b) TIP4P, (c) TIP5P and (d) SWM4. **Right Panel:** Differences (Δ) between the radial distribution functions. Δ is calculated as the differences between *g(r)* of pure water and *g(r)* of selected oxygen carbohydrate (Man) – oxygen (water) radial distribution from 300 K simulations.

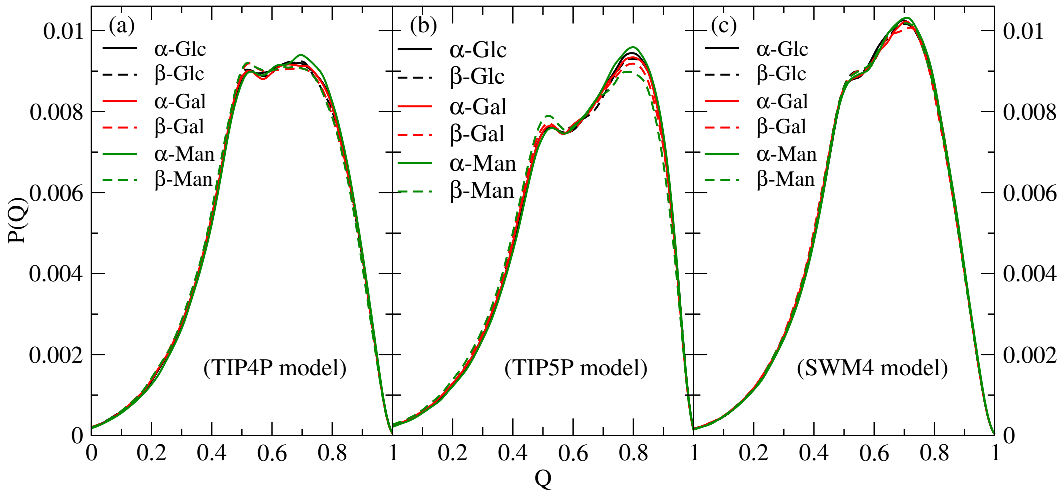

Figure S3: The *P(Q)* distribution of water molecules in the first solvation shell (less than 3.5 Å) around carbohydrates from the respective water model simulations (a) TIP4P, (b) TIP5P and (c) SWM4 simulations at 300 K.

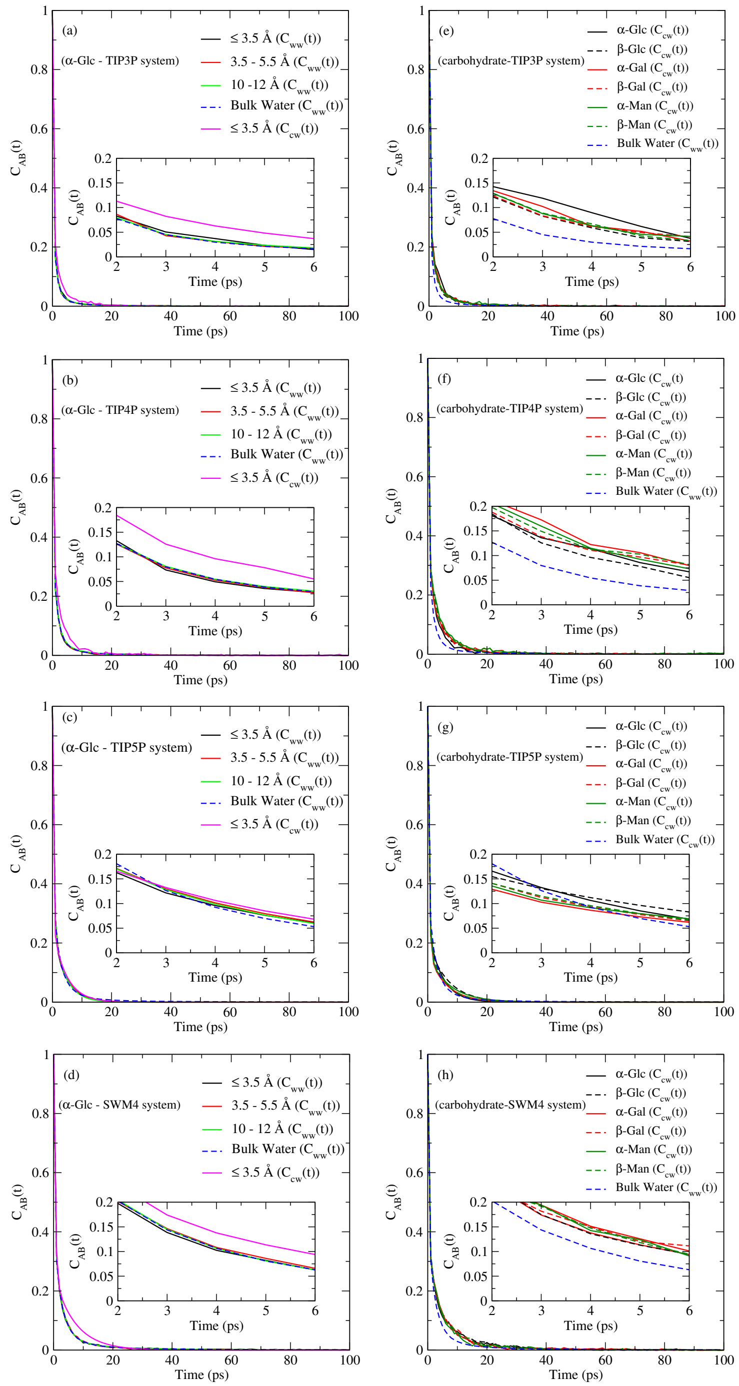

Figure S4: **Left Panel:** Comparison of intermittent H-bond autocorrelation function C_{ww} in the three hydration shells from (a) α–Glc – TIP3P, (b) α–Glc – TIP4P, (c) α–Glc – TIP5P, (d) α–Glc – SWM4 simulations at 300 K. The water-water (C_{ww}) autocorrelation function from bulk water simulations and the carbohydrate water intermittent H-bond autocorrelation function C_{cw} for the first hydration shell are also presented for comparison. **Right Panel:** Carbohydrate water intermittent H-bond autocorrelation function C_{cw} for the first hydration shell of the α and β anomers of Glc, Gal and Man from the (e) TIP3P, (f) TIP4P, (g) TIP5P and (h) SWM4 simulations. C_{ww} from bulk water simulations is also presented for comparison.

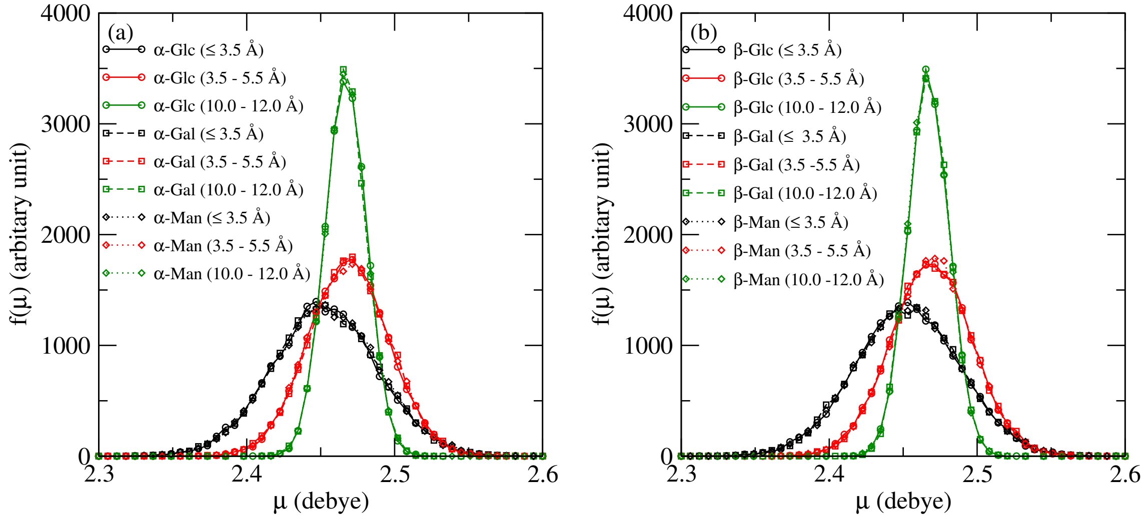

Figure S5: Dipole moment distribution of water molecules around the (a) α and (b) β anomers of carbohydrates from the carbohydrate water SWM4 simulations at 300 K.

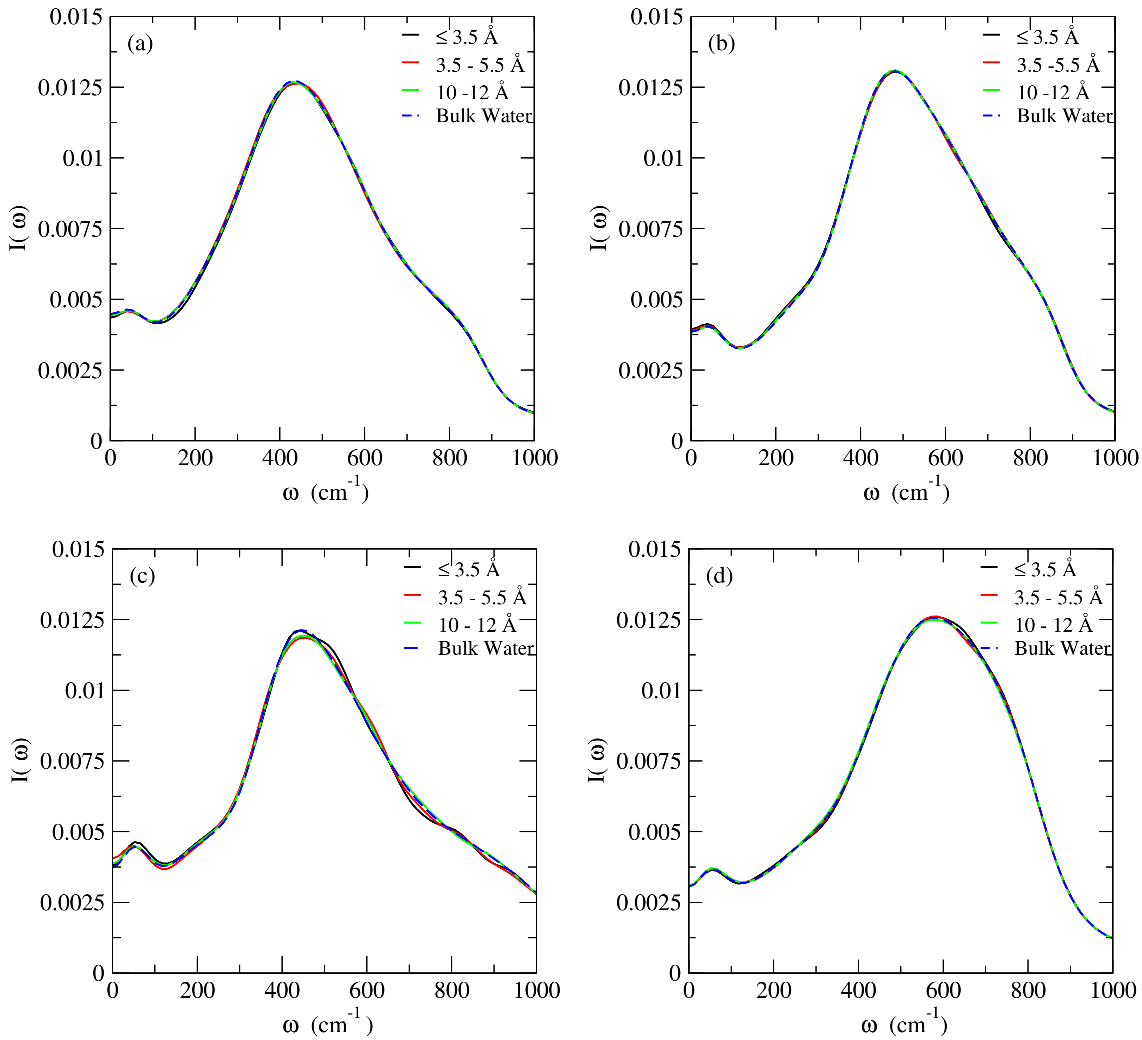

Figure S6: Vibrational spectra in the 0-1000 cm^{-1} range for hydrogen atoms of water molecules from the (a) α-Glc – TIP3P, (b) α-Glc – TIP4P, (c) α-Glc – TIP5P, (d) α-Glc – SWM4 simulations at 300K.

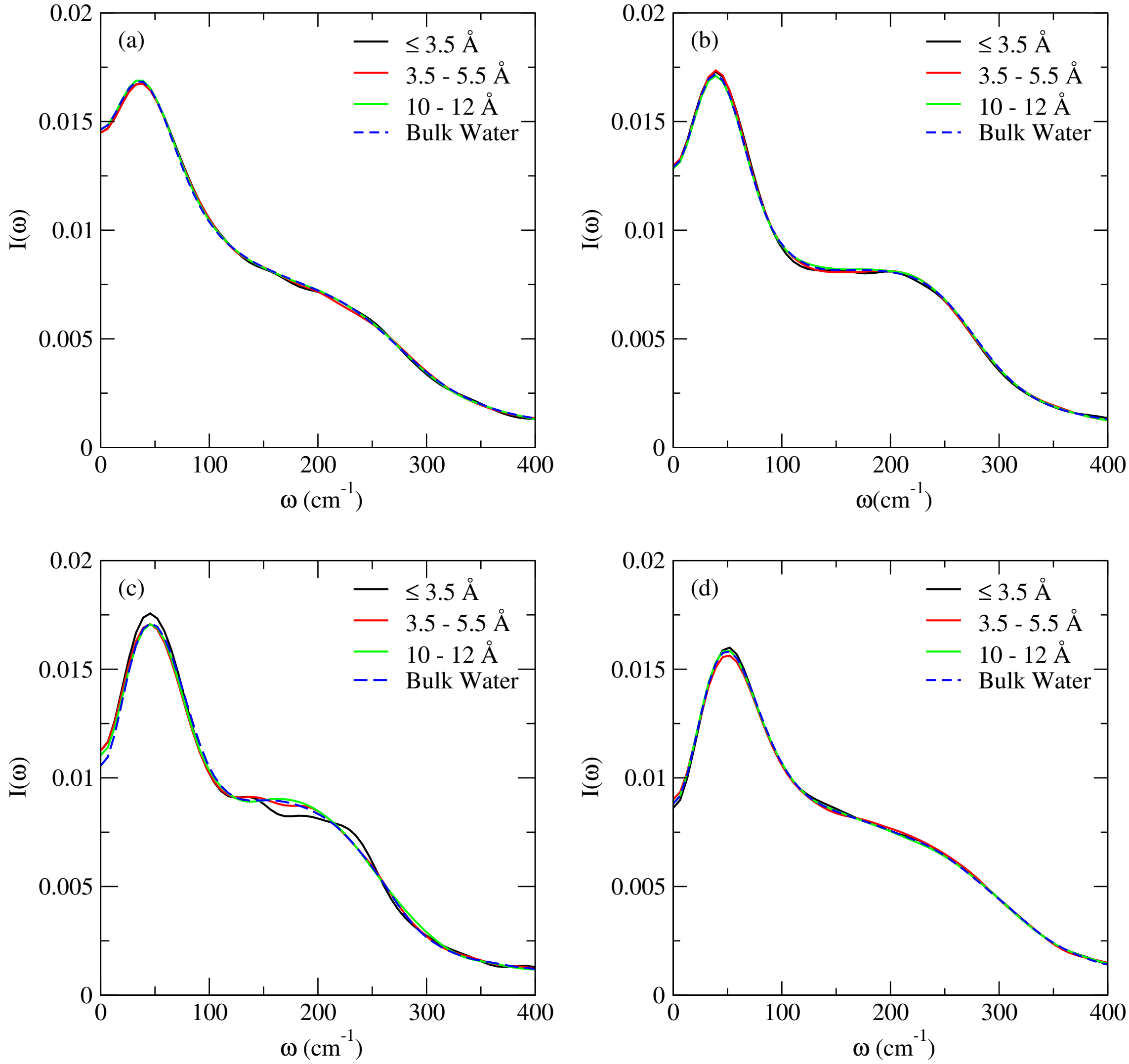

Figure S7: Vibrational spectra in the 0-400 cm^{-1} range for oxygen atoms of water molecules from the (a) α-Glc – TIP3P, (b) α-Glc – TIP4P, (c) α-Glc – TIP5P, (d) α-Glc – SWM4 simulations at 300K.

Table S1: Fractional Populations of the Conformers of the Exocyclic Torsion (O_5-C_5-C_6-O_6 = ω).

Carbohydrate-TIP3P system				
Conformers	Glucose		Galactose	
	MD	Experiments[a]	MD	Experiments[a]
GG (ω = -60°)	0.30	0.40	0.01	0.03
	0.05	0.31	0.01	0.03
GT (ω = 60°)	0.65	0.53	0.57	0.74
	0.87	0.61	0.53	0.72
TG (ω = 180°)	0.05	0.07	0.42	0.23
	0.08	0.08	0.46	0.25

Carbohydrate-TIP4P system				
Conformers	Glucose		Galactose	
	MD	Experiments[a]	MD	Experiments[a]
GG (ω = -60°)	0.48	0.40	0.07	0.03
	0.22	0.31	0.05	0.03
GT (ω = 60°)	0.45	0.53	0.49	0.74
	0.70	0.61	0.49	0.72
TG (ω = 180°)	0.10	0.07	0.44	0.23
	0.08	0.08	0.46	0.25

Carbohydrate-TIP5P system				
Conformers	Glucose		Galactose	
	MD	Experiments[a]	MD	Experiments[a]
GG (ω = -60°)	0.70	0.40	0.01	0.03
	0.53	0.31	0.02	0.03
GT (ω = 60°)	0.28	0.53	0.50	0.74
	0.45	0.61	0.38	0.72
TG (ω = 180°)	0.02	0.07	0.49	0.23
	0.14	0.08	0.60	0.25

Carbohydrate-SWM4 system				
Conformers	Glucose		Galactose	
	MD	Experiments[a]	MD	Experiments[a]
GG (ω = -60°)	0.18	0.40	0.16	0.03
	0.18	0.31	0.17	0.03
GT (ω = 60°)	0.71	0.53	0.68	0.74
	0.68	0.61	0.60	0.72
TG (ω = 180°)	0.11	0.07	0.16	0.23
	0.14	0.08	0.23	0.25

[a]Thibaudeau, C.; Stenutz, R.; Hertz, B.; Klepach, T.; Zhao, S.; Wu, Q. Q.; Carmichael, I.; Serianni, A. S. *J Am Chem Soc* **2004**, *126*, 15668.

Table S2: Coordination numbers of water oxygen (O_w) around the carbohydrate oxygen (O_n) by integrating the O_n – O_w radial distribution function to the first minima of the g(r) distribution.

Oxygen	Glucose							
	α				β			
	TIP3P	TIP4P	TIP5P	SWM4	TIP3P	TIP4P	TIP5P	SWM4
O_1	2.65	2.28	2.15	3.12	3.17	3.12	2.59	3.09
O_2	3.35	2.50	2.82	2.87	2.90	2.86	2.41	2.42
O_3	2.90	2.11	2.12	3.33	2.50	2.43	2.41	3.34
O_4	2.25	1.93	1.89	2.67	2.23	1.90	1.87	3.50
O_6	2.68	2.23	2.11	2.24	2.68	2.25	2.14	2.54

Oxygen	Galactose							
	α				β			
	TIP3P	TIP4P	TIP5P	SWM4	TIP3P	TIP4P	TIP5P	SWM4
O_1	2.67	2.28	2.19	2.71	3.20	2.74	2.61	3.58
O_2	2.94	2.50	2.88	2.82	2.53	2.48	2.10	2.43
O_3	2.93	2.46	2.15	3.78	2.52	2.45	2.80	3.34
O_4	2.88	2.20	2.79	2.82	2.56	2.52	2.51	2.83
O_6	2.29	2.57	2.11	2.18	2.63	2.20	2.08	2.14

Oxygen	Mannose							
	α				β			
	TIP3P	TIP4P	TIP5P	SWM4	TIP3P	TIP4P	TIP5P	SWM4
O_1	1.89	2.18	1.71	2.98	3.17	3.13	2.19	2.87
O_2	2.75	2.71	2.33	2.80	3.22	3.16	3.22	2.85
O_3	2.53	2.44	2.14	2.99	3.30	2.45	2.45	3.38
O_4	1.99	1.91	1.88	3.06	2.26	1.92	1.87	3.51
O_6	2.67	2.63	2.51	2.53	2.68	2.62	2.49	2.22

Table S3: Variation of dipole moment of water molecules in the hydration shell of six hexopyranose-water system.

Molecule	Hydration shell	Mean dipole value	Standard daviation
α-Glc	≤ 3.5 Å	2.45	0.04
	3.5-5.5 Å	2.47	0.03
	10.0-12.0 Å	2.46	0.01
β-Glc	≤ 3.5 Å	2.45	0.04
	3.5-5.5 Å	2.47	0.03
	10.0-12.0 Å	2.46	0.01
α-Gal	≤ 3.5 Å	2.45	0.04
	3.5-5.5 Å	2.47	0.03
	10.0-12.0 Å	2.46	0.01
β-Gal	≤ 3.5 Å	2.45	0.04
	3.5-5.5 Å	2.47	0.03
	10.0-12.0 Å	2.46	0.01
α-Man	≤ 3.5 Å	2.45	0.04
	3.5-5.5 Å	2.47	0.03
	10.0-12.0 Å	2.46	0.01
β-Man	≤ 3.5 Å	2.45	0.04
	3.5-5.5 Å	2.47	0.03
	10.0-12.0 Å	2.46	0.01