Supporting Information for

Photoelectron Spectroscopy and Density Functional Theory Studies of $(fructose+(H_2O)_n)^-$ (n = 1-5) Anionic Clusters

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More low lying isomers of (fructose+$(H_2O)_n$)$^-$, n = 1-5 anions, as well as their corresponding neutrals, are summarized in Figures S4, S6 to S9 as well as Figures S11 to S15 in the Supporting Information. Note that the figure numbers in the S.I. document are related to those of the text figures, as for example Figure S4 ⇔ Figure 4.

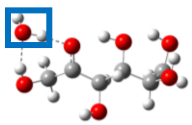
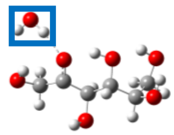
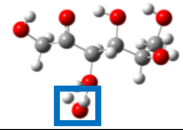
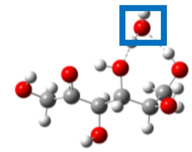
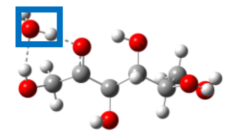
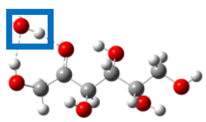
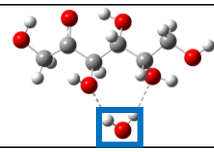
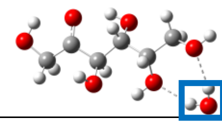
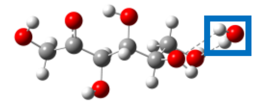
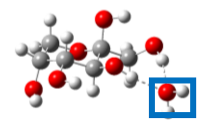
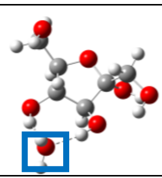
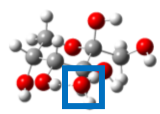
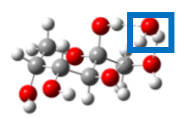
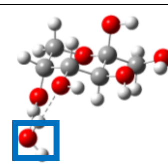
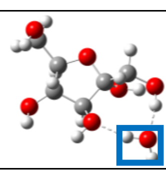
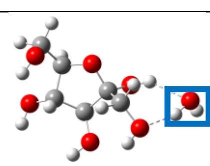
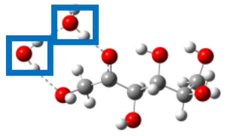
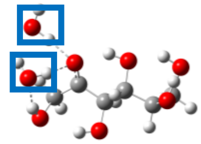
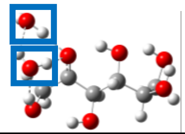
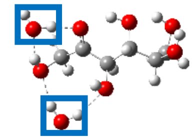
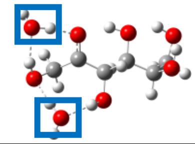
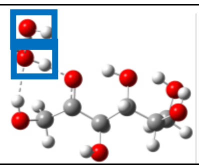
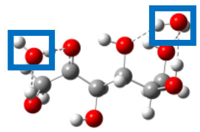
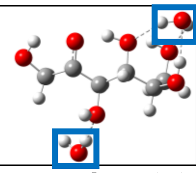
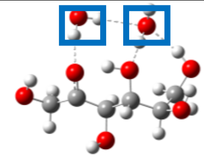
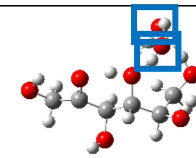
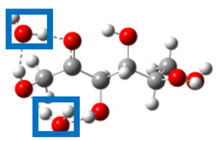
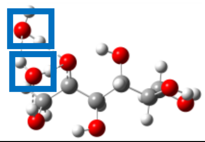
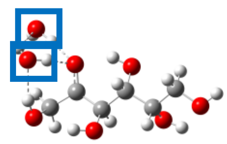
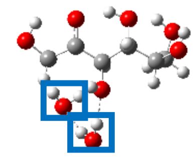
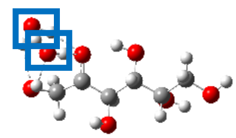
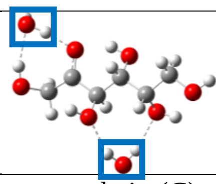
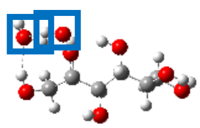
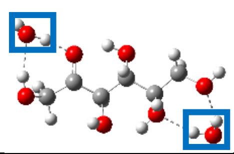
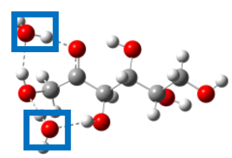
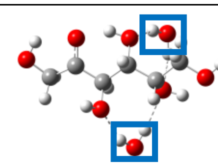
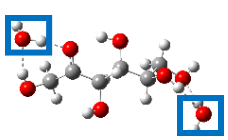
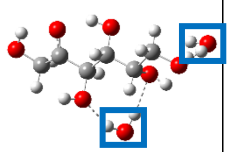
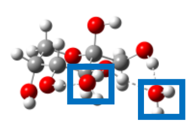
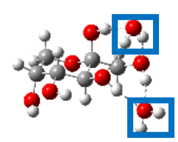
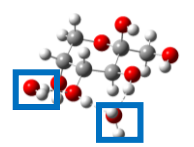
Optimized Anionic structure					
Structural Polymorphism	Open chain (A) +(1)(2)H_2O	Open chain (A) +(2)H_2O	Open chain (A) +(3)H_2O	Open chain (A) +(4)(6)H_2O	Open chain (B) +(1)(2)H_2O
ΔE (eV)	0.00	0.06	0.13	0.24	0.34
VDE (eV)	**2.24**	**2.36**	**2.17**	**1.99**	**1.98**
Optimized Anionic structure					
Structural Polymorphism	Open chain (C) +(1)(2)H_2O	Open chain (C) +(3)(5)H_2O	Open chain (C) +(5)(6)H_2O	Open chain (B) +(5)(6)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O
ΔE (eV)	0.34	0.44	0.45	0.55	0.79
VDE (eV)	**1.86**	**1.76**	**1.83**	**1.76**	**0.40**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(3)(4)H_2O	β-pyranose ($^2C_5$-chair) +(3)(4)H_2O	β-pyranose ($^2C_5$-chair) +(1)(2)H_2O	β-pyranose ($^2C_5$-chair) +(4)(5)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O
ΔE (eV)	0.92	0.97	0.97	0.97	1.01
VDE (eV)	**0.47**	**0.34**	**0.40**	**0.31**	**0.45**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(1)(3)H_2O	α- furanose (C_4-endo) +(1)(2)H_2O			
ΔE (eV)	1.17	1.20			
VDE (eV)	**0.31**	**0.21**			

Figure S4 Optimized geometries of the typical low lying anionic isomers of (fructose+H_2O)$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O	open chain (A) +(1)(2)H_2O+(2)H_2O	open chain (A) +(1)(2)H_2O+(2)(intra)H_2O	open chain (A) +(1)(2)H_2O+(1)(3)H_2O	open chain (A) +(1)(2)H_2O+(1)(3)H_2O
ΔE	0.00	0.00	0.01	0.01	0.02
VDE	**2.76**	**2.49**	**2.54**	**2.48**	**2.14**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)H_2O+(intra)H_2O	open chain (A) +(1)(2)H_2O+(4)(5)(6)H_2O	open chain (A) +(3)H_2O+(4)(5)(6)H_2O	open chain (A) +(4)(6)H_2O+(2)(intra)H_2O	open chain (A) +(4)(6)H_2O+(4)(intra)H_2O
ΔE	0.02	0.08	0.19	0.24	0.28
VDE	**2.59**	**2.36**	**2.47**	**2.42**	**2.31**
Optimized Anionic structure					
Structural Polymorphism	open chain (B) +(1)(2)H_2O+(1)(3)H_2O	open chain (B) +(1)(2)H_2O+(2)(intra)H_2O	open chain (C) +(1)(2)H_2O+(2)(intra)H_2O	open chain (A) +(3)H_2O+(intra)H_2O	open chain (C) +(1)(2)H_2O+(1)(2)H_2O
ΔE	0.32	0.33	0.35	0.35	0.36
VDE	**1.97**	**2.27**	**2.24**	**2.33**	**2.39**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) +(3)(5)H_2O+(1)(2)H_2O	open chain (B) +(1)(2)H_2O+(2)(intra)H_2O	open chain (C) +(1)(2)H_2O+(5)(6)H_2O	open chain (C) +(1)(2)H_2O+(1)(3)H_2O	open chain (C) +(3)(5)H_2O+(4)(5)H_2O
ΔE	0.36	0.37	0.38	0.38	0.42
VDE	**2.12**	**2.39**	**2.23**	**1.80**	**2.10**
Optimized Anionic structure					
Structural Polymorphism	open chain (B) +(1)(2)H_2O+(5)(6)H_2O	open chain (C) +(3)(5)H_2O+(6)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O+(3)(4)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O+(1)(2)(3)H_2O	β-pyranose ($^2C_5$-chair) +(3)(4)H_2O+(3)H_2O
ΔE	0.47	0.64	0.79	0.82	0.82
VDE	**2.03**	**1.93**	**0.61**	**0.58**	**0.73**

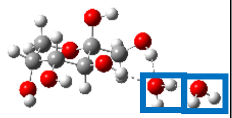
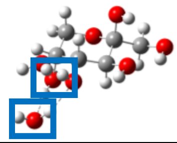
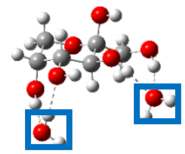
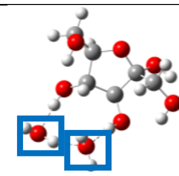
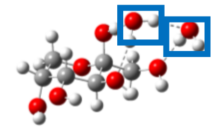
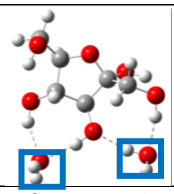
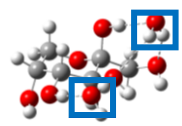
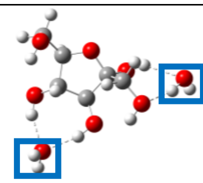
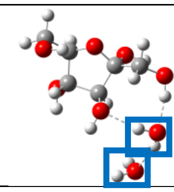
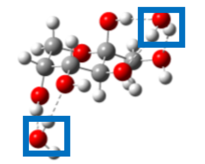
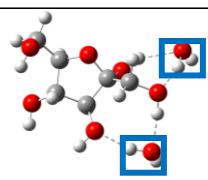
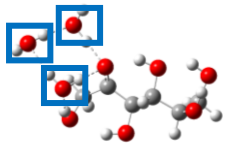
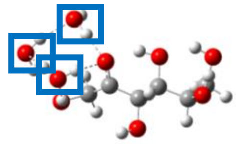
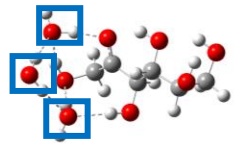
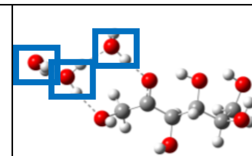
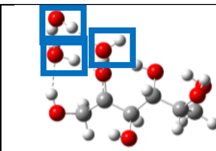
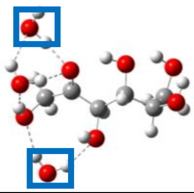
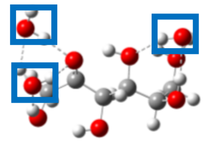
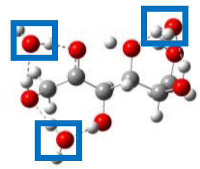
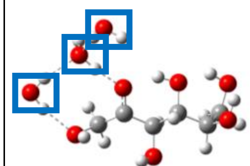
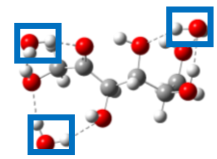
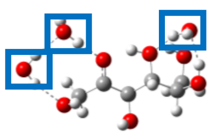
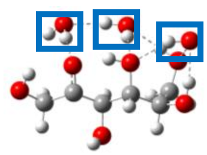
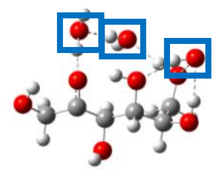
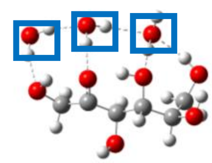
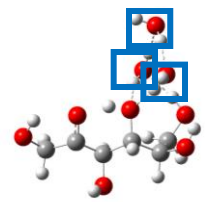
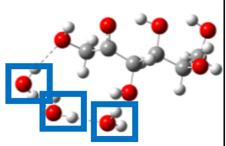
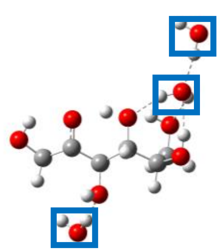
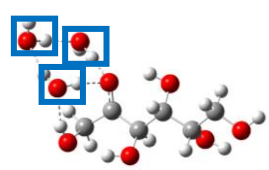
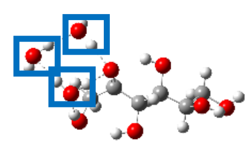
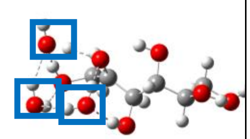
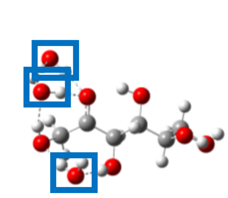
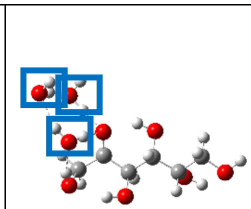
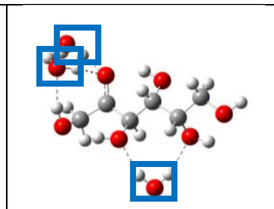
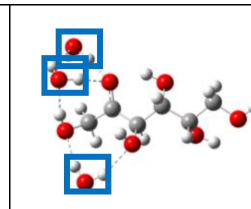
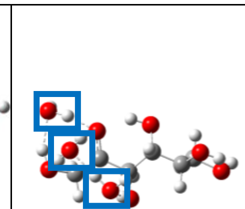
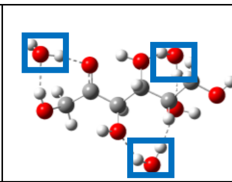
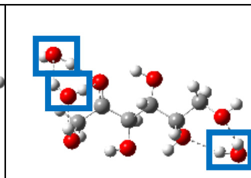
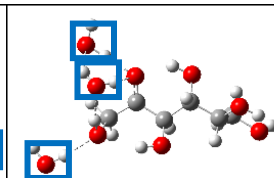
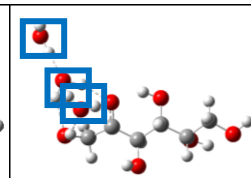
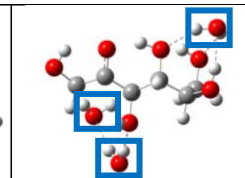
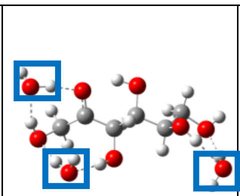
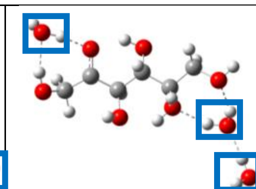
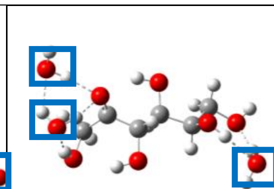
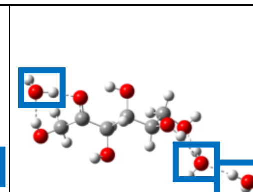
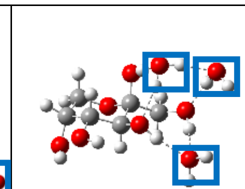
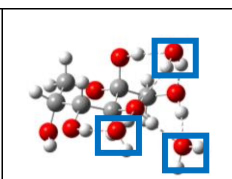
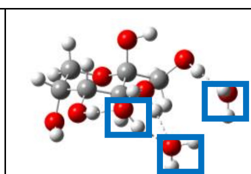
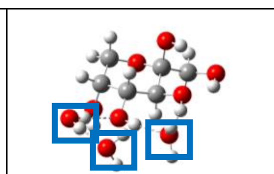
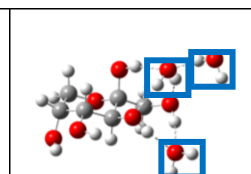
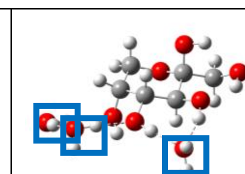
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^{2}C_{5}$-chair) +(1)(3)H_2O+(intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) +(4)(5)H_2O+(4)H_2O	β-pyranose ($^{2}C_{5}$-chair) +(1)(3)H_2O+(4)(5)H_2O	α- furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) +(2)(3)H_2O+(1)(intra)H_2O
ΔE	0.83	0.88	0.89	0.97	0.97
VDE	**0.53**	**0.58**	**0.60**	**0.77**	0.63
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(3)(4)H_2O+(1)(3)H_2O	β-pyranose ($^{2}C_{5}$-chair) +(1)(2)(3)H_2O+(3)(4)H_2O	α- furanose (C_4-endo) +(1)(2)H_2O+(3)(4)H_2O	α- furanose (C_4-endo) +(1)(3)H_2O+(intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) +(1)(2)(3)H_2O+(4)(5)H_2O
ΔE	0.97	1.00	1.02	1.06	1.07
VDE	**0.60**	**0.64**	**0.50**	**0.70**	**0.54**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(1)(2)H_2O+(1)(3)H_2O				
ΔE	1.29				
VDE	**0.35**				

Figure S6 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_2)^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure					
Structural Polymorphism	open chain (A)+(1)(2)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(2)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(2)H_2O+(1)(3)H_2O+(intra)H_2O	open chain (A)+(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(2)H_2O+(2)(intra)H_2O+(intra)H_2O
ΔE	0.00	0.03	0.05	0.08	0.08
VDE	**2.64**	**2.94**	**2.39**	**3.00**	**3.00**
Optimized Anionic structure					
Structural Polymorphism	open chain (A)+(1)(2)H_2O+(1)(3)H_2O+(2)(intra)H_2O	open chain (A)+(1)(2)$H_2$2O+(2)(intra)H_2O+(4)(5)(6)H_2O	open chain (A)+(1)(2)H_2O+(1)(3)H_2O+(4)(5)H_2O	open chain (A)+(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(2)H_2O+(1)(3)H_2O+(4)(5)(6)H_2O
ΔE	0.09	0.11	0.13	0.13	0.13
VDE	**2.86**	**2.75**	**2.41**	**3.09**	**2.75**
Optimized Anionic structure					
Structural Polymorphism	open chain (A)+(1)(intra)H_2O+(2)(intra)H_2O+(4)(5)H_2O	open chain (A)+(4)(5)(6)H_2O+(4)(6)(intra)H_2O+(2)(intra)H_2O	open chain (A)+(4)(5)(6)H_2O+(6)(intra)H_2O+(2)(intra)H_2O	open chain (A)+(4)(6)(intra)H_2O+(2)(intra)H_2O+(1)(intra)H_2O	open chain (A)+(4)(6)(intra)H_2O+(4)(intra)H_2O+(intra)H_2O
ΔE	0.17	0.21	0.23	0.26	0.32
VDE	**3.08**	**2.84**	**2.64**	**2.78**	**2.40**
Optimized Anionic structure					
Structural Polymorphism	open chain (A)+(1)(intra)H_2O+(3)(intra)H_2O+(intra)H_2O	open chain (A)+(4)(5)(6)(intra)H_2O+(3)H_2O+(intra)H_2O	open chain (C)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (B)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (B)+(1)(2)(intra)H_2O+(1)(intra)H_2O+(2)(3)(intra)H_2O
ΔE	0.36	0.36	0.36	0.37	0.38
VDE	**2.43**	**2.70**	**2.40**	**2.51**	**2.32**

Optimized Anionic structure					
Structural Polymorphism	open chain (B)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(1)(3)H_2O	open chain (C)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (C)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(3)(5)H_2O	open chain (C)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(1)(3)H_2O	open chain (B)+(1)(2)H_2O+(1)(2)H_2O+(3)(intra)H_2O
ΔE	0.38	0.38	0.39	0.41	0.42
VDE	**2.36**	**2.36**	**2.51**	**2.58**	**2.18**
Optimized Anionic structure					
Structural Polymorphism	open chain (C)+(1)(2)H_2O+(3)(5)H_2O+(4)(5)H_2O	open chain (C)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(5)(6)H_2O	open chain (B)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(1)(intra)H_2O	open chain (C)+(1)(2)(intra)H_2O+(1)(2)(intra)H_2O+(intra)H_2O	open chain (A)+(4)(5)(6)H_2O+(3)(intra)H_2O+(intra)H_2O
ΔE	0.42	0.44	0.45	0.45	0.49
VDE	**2.38**	**2.48**	**2.56**	**2.63**	**2.65**
Optimized Anionic structure					
Structural Polymorphism	open chain (B)+(1)(2)H_2O+(1)(3)H_2O+(5)(6)H_2O	open chain (C)+(1)(2)H_2O+(5)(6)(intra)H_2O+(intra)H_2O	open chain (B)+(1)(2)(intra)H_2O+(2)(intra)H_2O+(5)(6)H_2O	open chain (B)+(1)(2)H_2O+(5)(6)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(1)(3)H_2O+(2)(3)(intra)H_2O+(1)(intra)H_2O
ΔE	0.52	0.52	0.53	0.72	0.73
VDE	**2.02**	**2.38**	**2.34**	**2.14**	**0.87**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(1)(3)H_2O+(1)(2)(3)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)(intra)H_2O+(3)(intra)H_2O+(1)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(4)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(1)(2)(3)(intra)H_2O+(1)(3)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(4)(intra)H_2O+(5)(intra)H_2O
ΔE	0.79	0.82	0.82	0.84	0.85
VDE	**0.87**	**1.10**	**1.25**	**0.86**	**0.84**

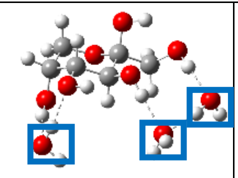
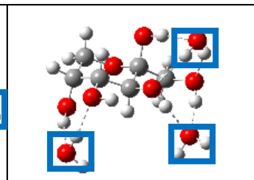
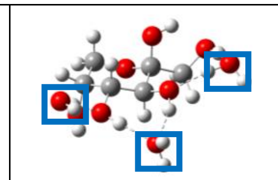
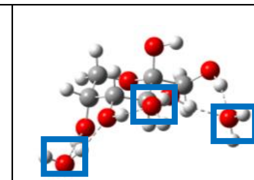
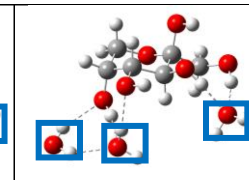
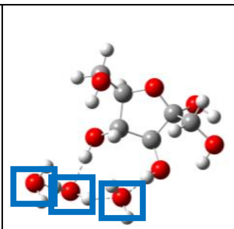
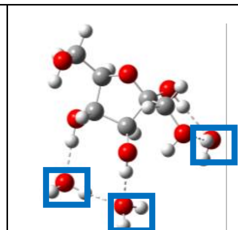
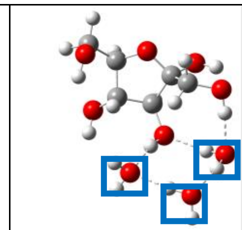
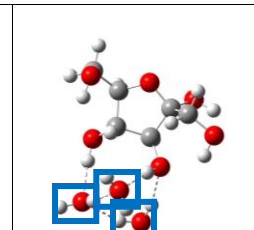
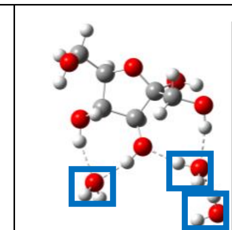
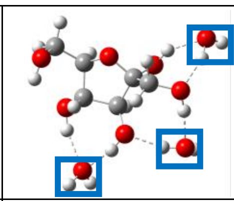
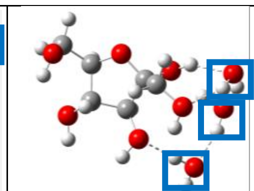
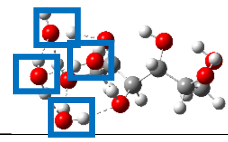
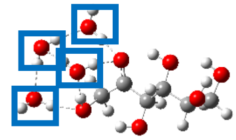
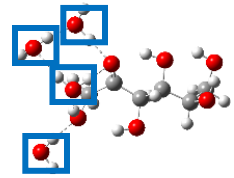
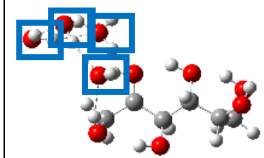
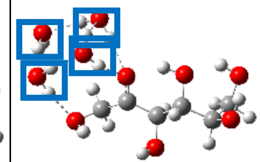
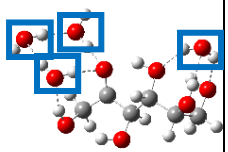
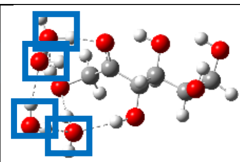
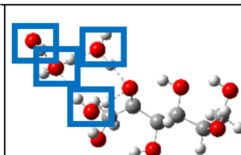
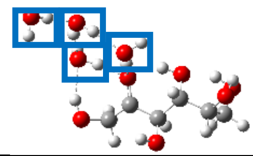
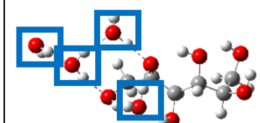
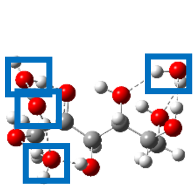
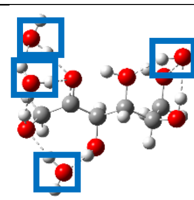
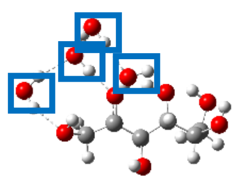
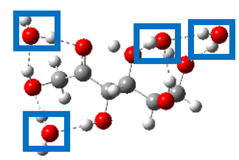
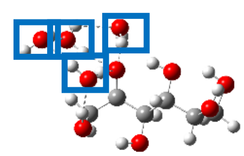
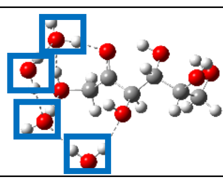
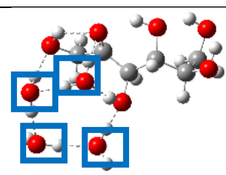
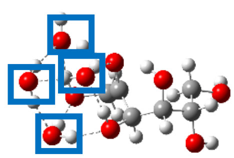
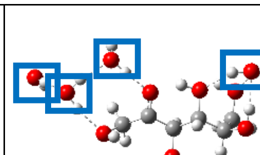
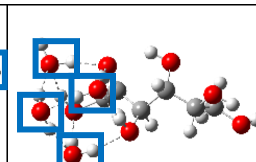
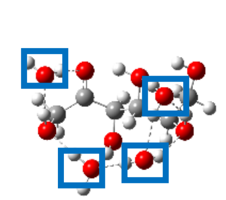
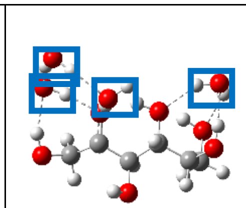
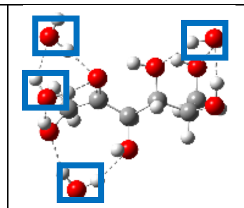
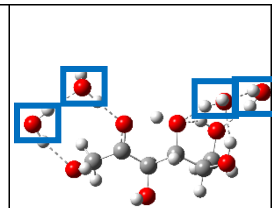
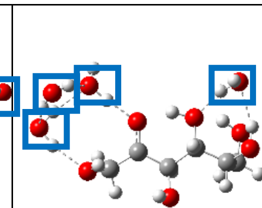
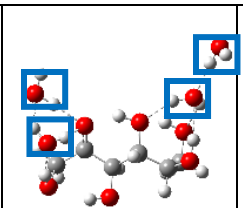
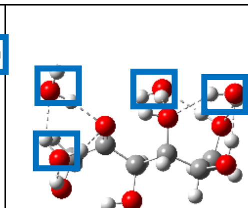
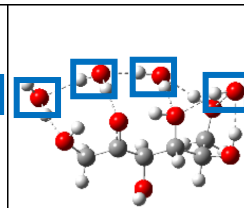
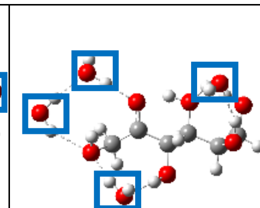
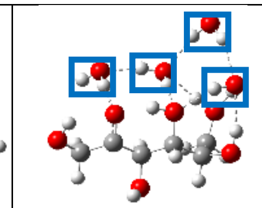
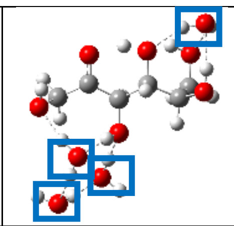
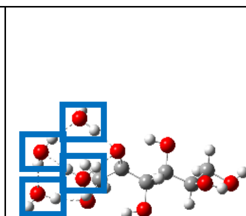
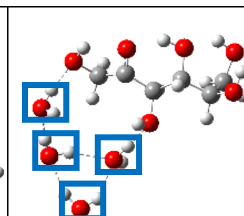
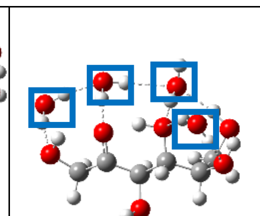
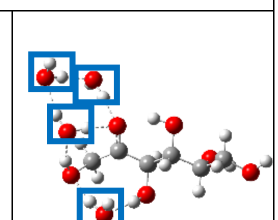
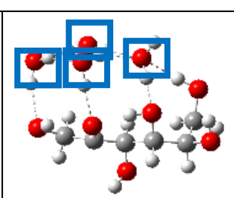
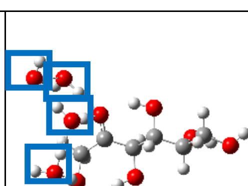
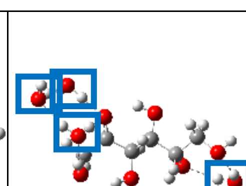
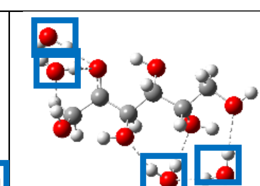
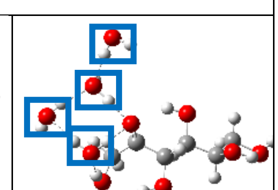
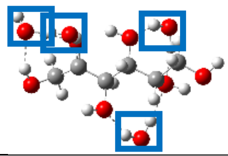
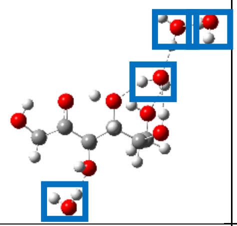
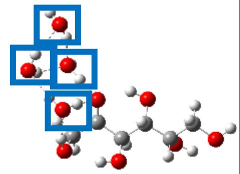
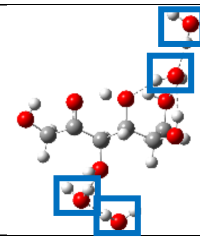
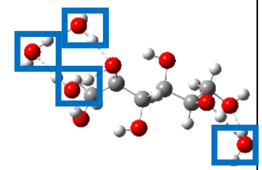
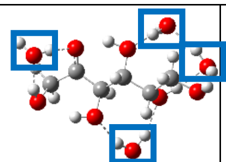
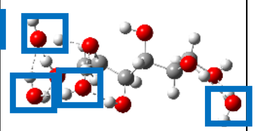
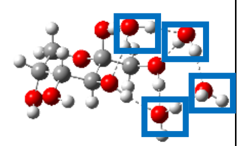
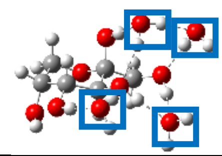
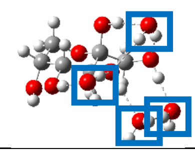
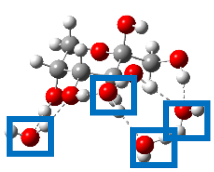
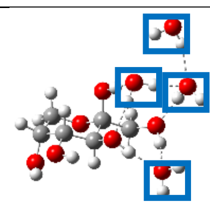
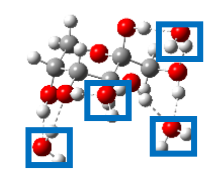
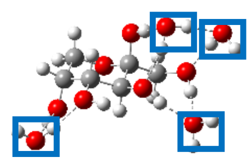
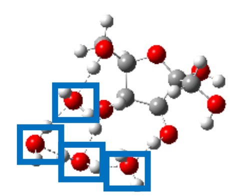
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + +(1)(intra)H_2O+(3)(intra)H_2O+(4)(5)H_2O	β-pyranose ($^2C_5$-chair) + +(1)(2)(3)H_2O+(1)(3)H_2O+(4)(5)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(1)(3)H_2O+(4)(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(1)(3)H_2O+(4)(5)H_2O	β-pyranose ($^2C_5$-chair) + +(4)(5)(intra)H_2O +(1)(3)H_2O+(5)(intra)H_2O
ΔE	0.85	0.85	0.87	0.89	0.95
VDE	**0.89**	**0.84**	**0.82**	**0.65**	**0.94**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O+(intra)H_2O	α-furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O+(1)(2)H_2O	α-furanose (C_4-endo) +(1)(3)(intra)H_2O+(3)(intra)H_2O+(intra)H_2O	α-furanose (C_4-endo) +(3)(intra)H_2O+(3)(intra)H_2O+(4)(intra)H_2O	α-furanose (C_4-endo) +(1)(3)(intra)H_2O +(intra)H_2O+(3)(4)H_2O
ΔE	0.96	0.97	0.97	1.01	1.06
VDE	**1.23**	**0.98**	**1.07**	**0.97**	**0.86**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_4-endo) +(1)(2)H_2O+(1)(3)H_2O+(3)(4)H_2O	α-furanose (C_4-endo) +(1)(2)(intra)H_2O +(2)(intra)H_2O+(3)(intra)H_2O			
ΔE	1.07	1.17			
VDE	**0.64**	**0.78**			

Figure S7 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_3$)$^-$ based on B3LYP/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O
ΔE	0.00	0.12	0.19	0.21	0.21
VDE	**2.88**	**2.74**	**2.87**	**3.18**	**3.10**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O
ΔE	0.21	0.22	0.23	0.23	0.25
VDE	**2.86**	**2.67**	**2.83**	**3.20**	**3.14**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(3)H_2O + (2)(intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)H_2O + (1)(3)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O
ΔE	0.26	0.26	0.27	0.27	0.27
VDE	**2.62**	**2.70**	**3.45**	**2.60**	**2.85**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(5)(6)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O
ΔE	0.28	0.28	0.29	0.30	0.30

VDE	**2.87**	**2.39**	**2.68**	**3.25**	**2.64**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)H_2O + (1)(3)(intra)H_2O + (4)(5)(intra)H_2O + (5)(intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (1)(3)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(5)H_2O + (intra)H_2O
ΔE	0.30	0.32	0.32	0.33	0.34
VDE	**2.41**	**3.22**	**3.09**	**3.28**	**3.29**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (4)(5)(6)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (4)(6)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(6)(intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(3)(intra)H_2O + (4)(5)H_2O	open chain (A) + (2)(intra)H_2O + (4)(6)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O
ΔE	0.36	0.37	0.38	0.40	0.41
VDE	**2.89**	**3.03**	**2.91**	**2.83**	**3.09**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(6)(intra)H_2O + (4)(5)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O
ΔE	0.44	0.46	0.48	0.49	0.51
VDE	**2.24**	**2.59**	**2.77**	**3.06**	**2.36**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O +	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O +	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O +	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O +	open chain (B) + (1)(2)(intra)H_2O + (2)(intra)H_2O +

	(4)(6)(intra)H_2O + (intra)H_2O	(2)(intra)H_2O + (intra)H_2O	(5)(6)H_2O + (intra)H_2O	(3)(5)(intra)H_2O + (6)(intra)H_2O	(intra)H_2O + (intra)H_2O
ΔE	0.51	0.52	0.53	0.59	0.59
VDE	**2.85**	**2.27**	**2.61**	**2.69**	**2.84**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (3)(5)H_2O + (4)(6)H_2O	open chain (A) + (3)H_2O + (4)(5)(6)H_2O + (intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (3)H_2O + (4)(5)(6)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (5)(6)H_2O
ΔE	0.60	0.60	0.61	0.61	0.65
VDE	**2.78**	**2.83**	**2.57**	**2.88**	**2.55**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) + (1)(2)H_2O + (3)(5)H_2O + (5)(6)(intra)H_2O + (4)(intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(3)(intra)H_2O + (5)(6)H_2O	β-pyranose ($^{2}C_{5}$-chair) + (1)(3)(intra)H_2O + (2)(3)(intra)H_2O + (1)(intra)H_2O + (intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) + (3)(4)H_2O + (2)(3)(intra)H_2O + (1)(3H_2O + (1)(intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) + (1)(2)(3)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (3)(4)H_2O
ΔE	0.66	0.66	0.87	0.96	0.98
VDE	**2.41**	**2.36**	**0.92**	**1.07**	**1.08**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^{2}C_{5}$-chair) + (1)(3)H_2O + (3)(4)(intra)H_2O + (4)(5)H_2O + (intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)H_2O + (intra)H_2O	β-pyranose ($^{2}C_{5}$-chair) + (1)(2)H_2O + (1)(3)H_2O + (3)(4)H_2O + (4)(5)H_2O	β-pyranose ($^{2}C_{5}$-chair) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)H_2O + (4)(5)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O
ΔE	0.99	1.00	1.03	1.05	1.05
VDE	**1.18**	**1.03**	**1.00**	**0.87**	**1.45**

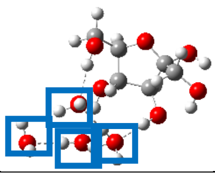
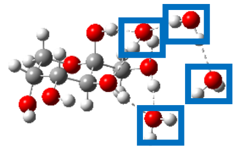
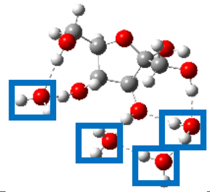
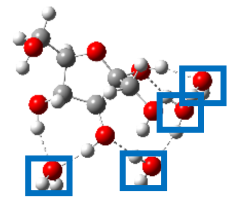
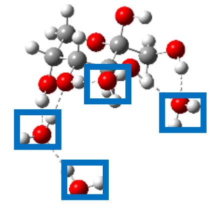
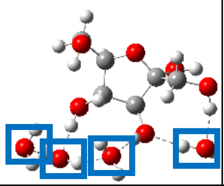
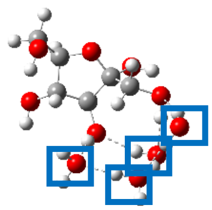
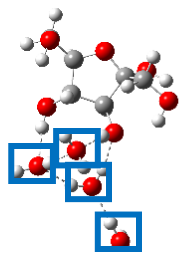
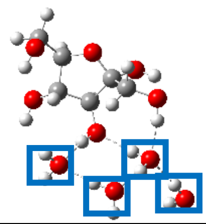
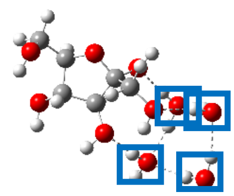
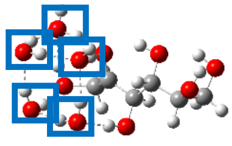
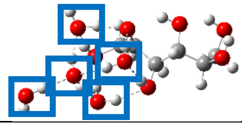
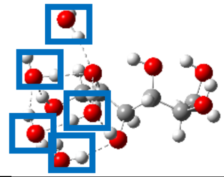
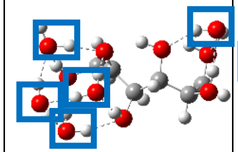
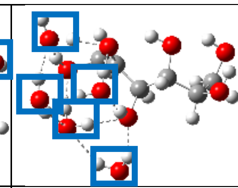
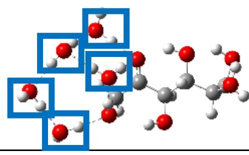
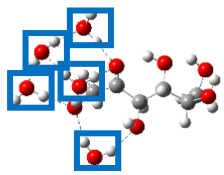
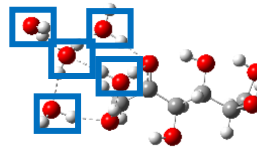
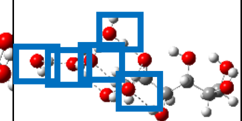
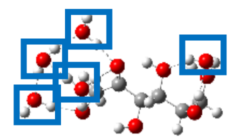
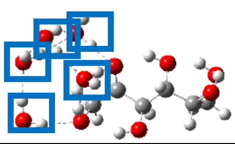
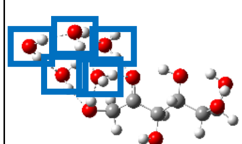
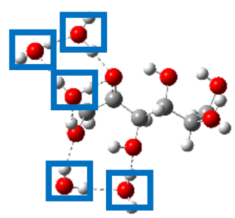
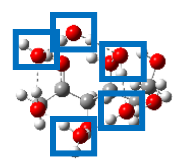
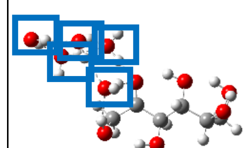
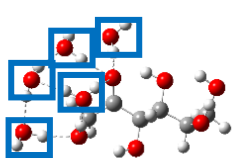
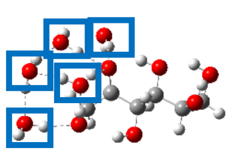
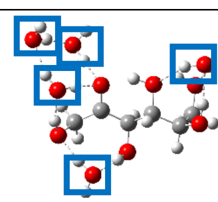
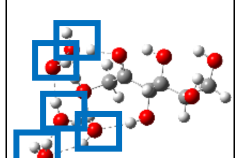
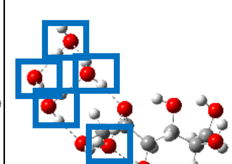
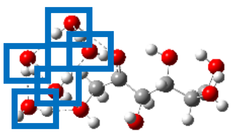
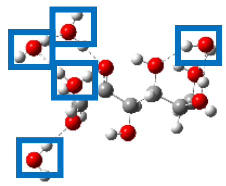
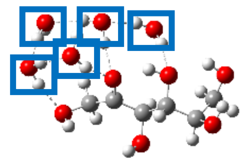
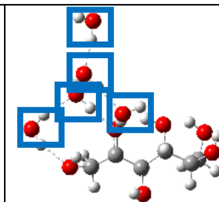
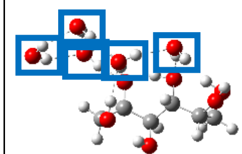
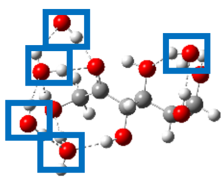
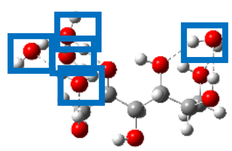
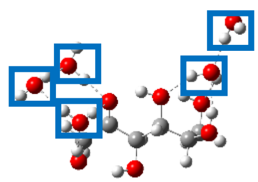
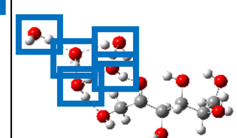
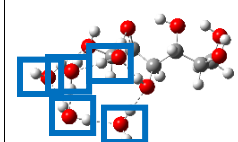
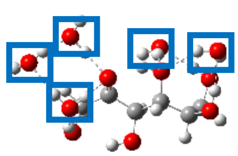
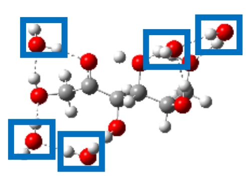
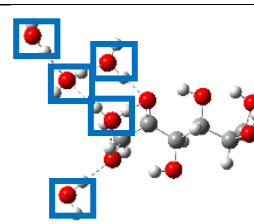
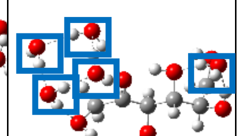
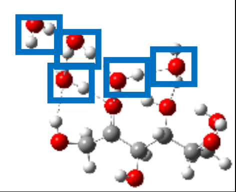
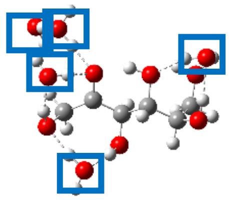
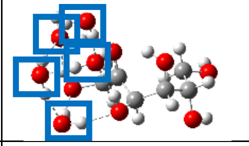
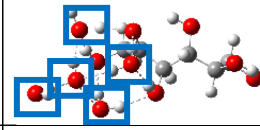
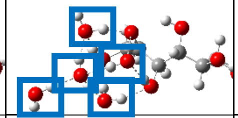
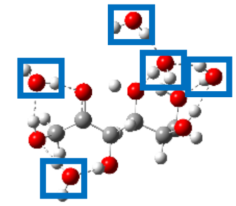
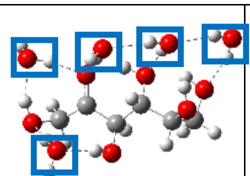
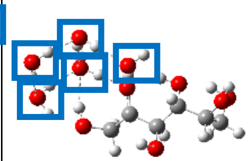
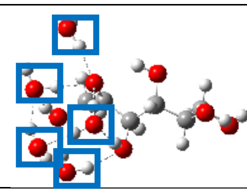
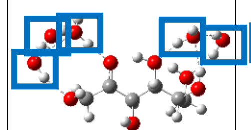
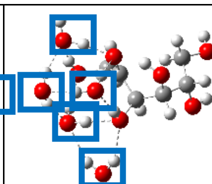
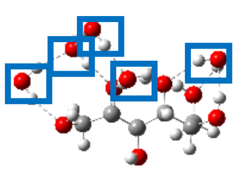
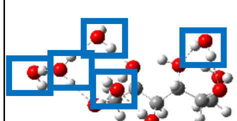
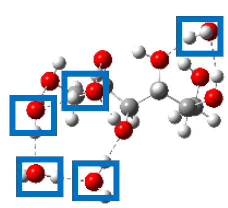
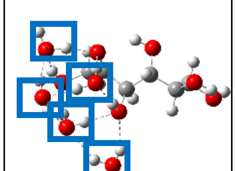
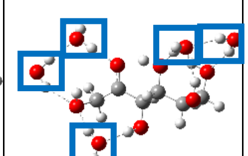
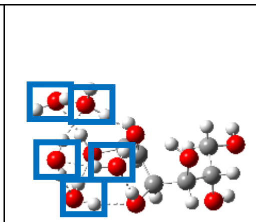
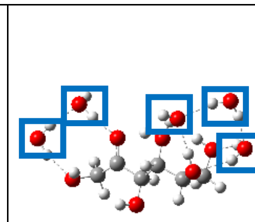
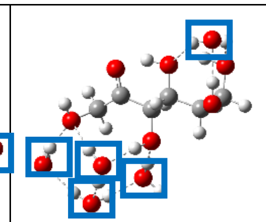
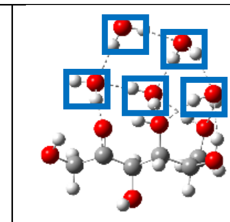
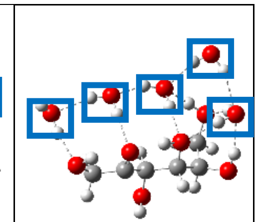
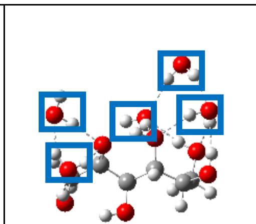
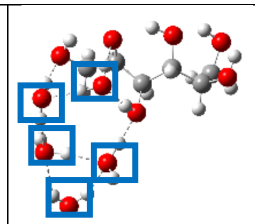
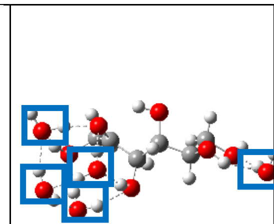
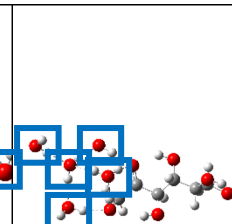
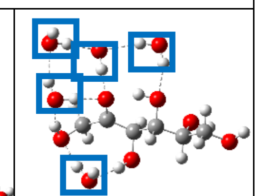
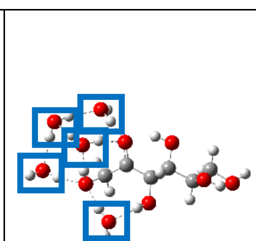
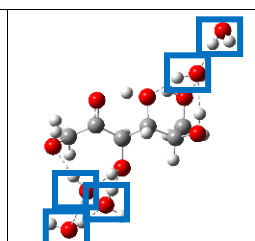
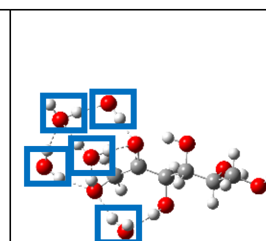
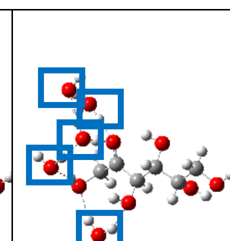
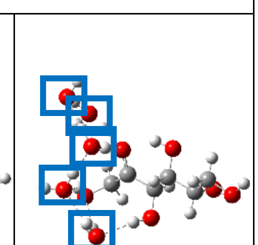
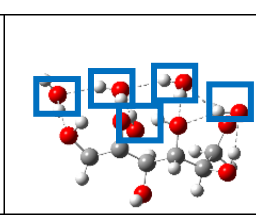
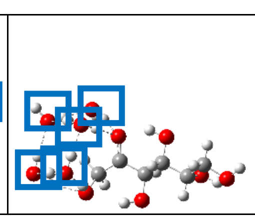
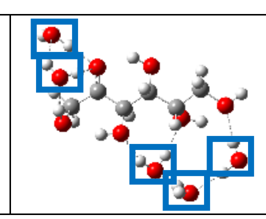
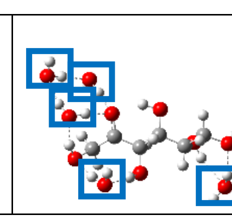
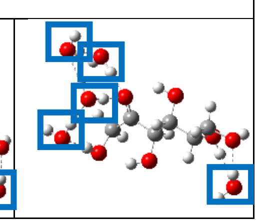
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (1)(2)(3)H_2O + (1)(3)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(3)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(6)H_2O	α-furanose (C_4-endo) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (3)(4)H_2O	β-pyranose ($^2C_5$-chair) + (1)(3)H_2O + (3)(4)H_2O + (4)(5)H_2O + (intra)H_2O
ΔE	1.07	1.07	1.07	1.11	1.15
VDE	**1.35**	**1.28**	**1.37**	**0.98**	**0.86**
Optimized Anionic structure					
WStructural Polymorphism	α-furanose (C_4-endo) + (1)(3)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O
ΔE	1.20	1.22	1.22	1.22	1.45
VDE	**1.23**	**1.16**	**1.08**	**1.23**	**0.98**

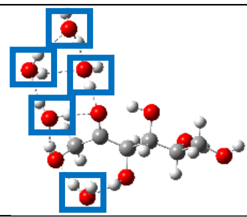
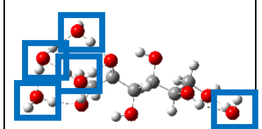
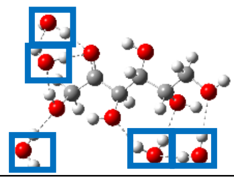
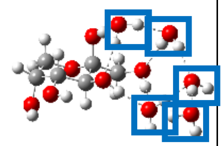
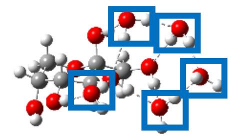
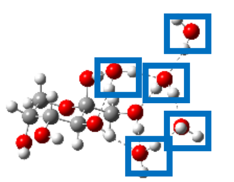
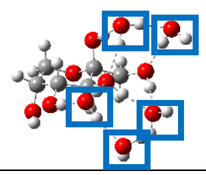
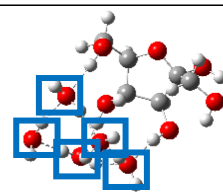
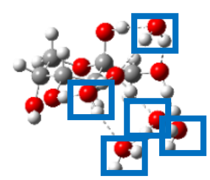
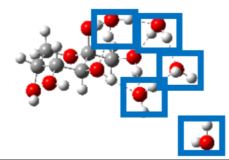
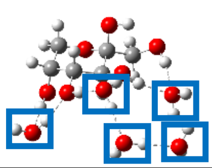
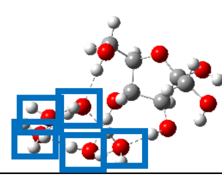
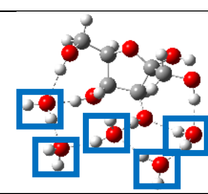
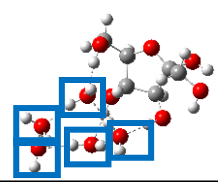
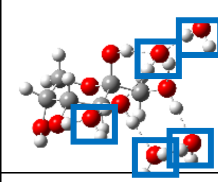
Figure S8 Optimized geometries of the typical low lying anionic isomers of $(fructose+(H_2O)_4)^-$ based on B3LYP/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of $fructose^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (2)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (3)(intra)H_2O
ΔE	0.00	0.06	0.08	0.10	0.10
VDE	**2.97**	**3.09**	**3.22**	**3.12**	**3.14**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(2)(3)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O
ΔE	0.15	0.15	0.17	0.18	0.20
VDE	**2.77**	**3.16**	**2.93**	**3.17**	**2.95**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (3)(intra)H_2O + (5)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O
ΔE	0.20	0.21	0.23	0.23	0.23
VDE	**3.44**	**3.61**	**3.11**	**2.63**	**3.44**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O +	open chain (A) + (1)(2)(intra)H_2O +	open chain (A) + (1)(2)(intra)H_2O +	open chain (A) +	open chain (A) + (1)(intra)H_2O +

	(1)(intra)H_2O + (2)(intra)H_2O + (2)H_2O + (intra)H_2O	(1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	(2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (4)(5)(6)H_2O	(1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	(2)(intra)H_2O + (1)(2)(3)H_2O + (intra)H_2O + (intra)H_2O
ΔE	0.25	0.25	0.26	0.26	0.26
VDE	**2.93**	**3.03**	**2.80**	**2.67**	**2.94**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O + (intra)H_2O
ΔE	0.27	0.27	0.29	0.29	0.30
VDE	**3.06**	**3.07**	**3.32**	**3.60**	**3.14**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O +(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O
ΔE	0.31	0.31	0.32	0.32	0.32
VDE	**2.98**	**3.24**	**2.98**	**3.26**	**2.58**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O + (4)(6)H_2O	open chain (A) + (1)(2)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O + (intra)H_2O
ΔE	0.32	0.33	0.33	0.33	0.33
VDE	**3.15**	**2.78**	**3.09**	**3.36**	**3.35**

Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (4)(5)(6)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)H_2O + (1)(3)H_2O + (4)(intra)H_2O + (5)(6)(intra)H_2O + (intra)H_2O
ΔE	0.33	0.34	0.34	0.35	0.35
VDE	**2.97**	**2.91**	**2.85**	**2.86**	**2.72**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)H_2O + (1)(3)H_2O + (2)(intra)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (2)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (3)(intra)H_2O
ΔE	0.35	0.36	0..37	0.37	0.37
VDE	**2.97**	**3.50**	**2.99**	**3.48**	**2.94**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(2)(3)H_2O + (intra)H_2O + (4)(5)H_2O	open chain (A) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O + (4)(5)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (3)(intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(3)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O
ΔE	0.38	0.38	0.38	0.39	0.40
VDE	**3.67**	**3.38**	**2.67**	**2.91**	**2.99**

Optimized Anionic structure					
Structural Polymorphism	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(5)(intra)H_2O + (5)(6)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(3)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(5)(6)H_2O	open chain (A) + (2)(intra)H_2O + (4)(6)(intra)H_2O + (4)(5)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(6)(intra)H_2O + (4)(5)(6)(intra)H_2O + (intra)H_2O
ΔE	0.39	0.40	0.42	0.43	0.44
VDE	**2.71**	**3.50**	**2.44**	**3.21**	**3.14**
Optimized Anionic structure					 E=-1069.105750
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (4)(5)(6)(intra)H_2O + (4)(6)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (5)(6)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O + (1)(3)H_2O
ΔE	0.45	0.46	0.48	0.51	0.52
VDE	**3.22**	**2.66**	**2.68**	**2.76**	**2.72**
Optimized Anionic structure					
Structural Polymorphism	open chain (B) + (1)(2)(intra)H_2O + (1)(3)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(5)(6)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)(intra)H_2O
ΔE	0.53	0.53	0.55	0.55	0.55
VDE	**2.56**	**2.42**	**2.61**	**2.73**	**2.45**
Optimized Anionic structure					

Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (4)(6)(intra)H_2O + (4)(5)(6)H_2O	open chain (C) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (3)(5)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (5)(6)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (5)(6)H_2O
ΔE	0.56	0.56	0.57	0.59	0.61
VDE	**3.11**	**2.54**	**2.84**	**2.51**	**2.44**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) + (1)(2)(intra)H_2O + (2)(intra)H_2O +(intra)H_2O + (intra)H_2O + (1)(3)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (5)(6)H_2O	open chain (C) + (1)(2)(intra)H_2O +(2)(intra)H_2O + (3)(5)(intra)H_2O + (6)(intra)H_2O + (1)H_2O	β-pyranose ($^2C_5$-chair) + (1)(3)(intra)H_2O + (2)(3)(intra)H_2O + (1)(intra)H_2O + (intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (3)(4)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)(intra)H_2O + (1)(intra)H_2O + (intra)H_2O
ΔE	0.62	0.64	0.65	0.95	0.96
VDE	**2.51**	**2.64**	**2.94**	**1.09**	**1.08**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + (2)(3)(intra)H_2O + (1)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (2)(3)(intra)H_2O + (1)(intra)H_2O + (1)(3)(intra)H_2O + (3)(4)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O + (intra)H_2O	-pyranose ($^2C_5$-chair) + (1)(2)(3)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (3)(4)(intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (2)(3)(intra)H_2O + (1)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (free)H_2O
ΔE	0.96	0.97	0.98	1.01	1.01
VDE	**1.04**	**1.49**	**1.38**	**1.05**	**1.39**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + (1)(3)(intra)H_2O + (3)(4)(intra)H_2O + (intra)H_2O + (intra)H_2O + (4)(5)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (4)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (1)(2)(3)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O +

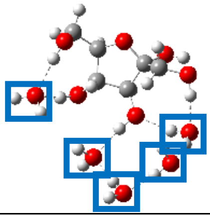
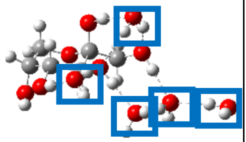
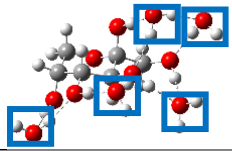
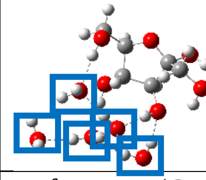
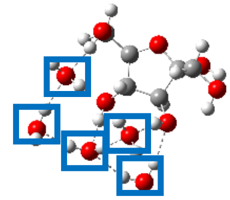
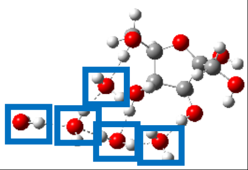
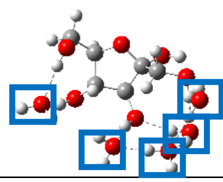
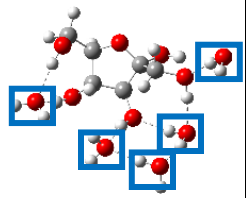
					(intra)H_2O + (3)(4)H_2O
ΔE	1.02	1.04	1.04	1.04	1.08
VDE	**1.38**	**1.43**	**1.24**	**1.33**	**1.24**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O + (4)(6)H_2O	β-pyranose ($^2C_5$-chair) + (1)(2)(3)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (3)(4)H_2O	β-pyranose ($^2C_5$-chair) + (2)(3)H_2O + (1)(intra)H_2O + (1)(3)H_2O + (3)(4)H_2O + (4)(5)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O
ΔE	1.11	1.11	1.12	1.13	1.15
VDE	**1.54**	**1.32**	**1.06**	**1.48**	**1.56**
Optimized Anionic structure	W 				
Structural Polymorphism	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(6)H_2O	α-furanose (C_4-endo) + (1)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(6)H_2O		
ΔE	1.18	1.18	1.19		
VDE	**1.64**	**1.50**	**1.48**		

Figure S9 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_5$)$^-$ based on B3LYP/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

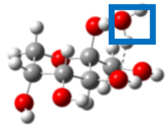
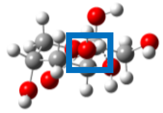
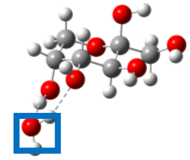
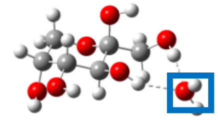
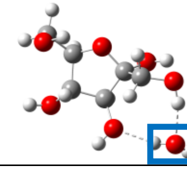
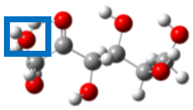
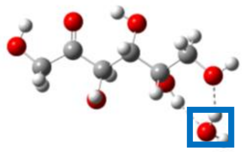
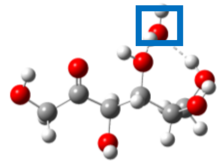
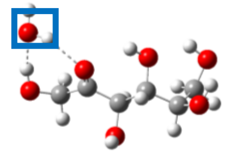
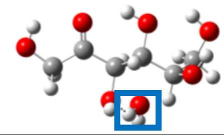
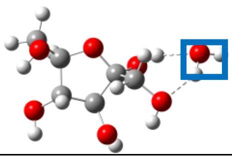
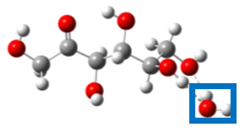
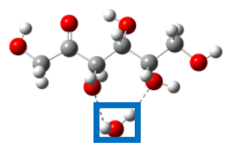
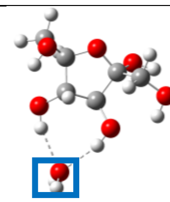
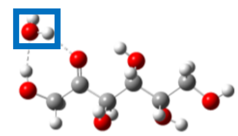
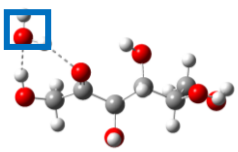
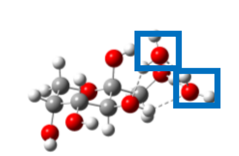
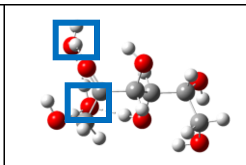
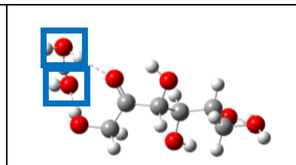
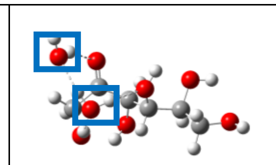
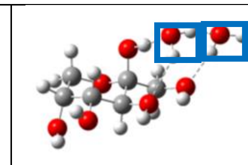
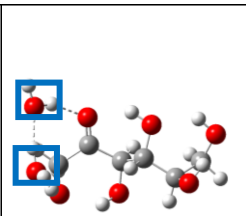
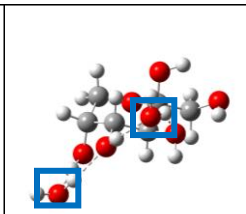
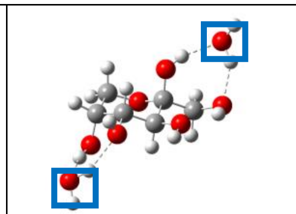
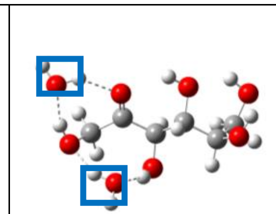
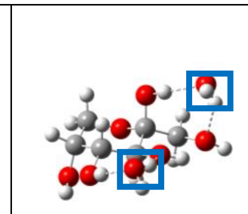
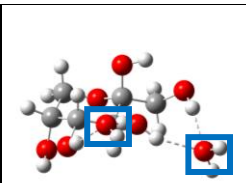
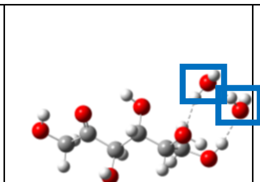
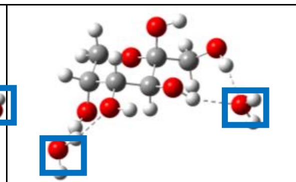
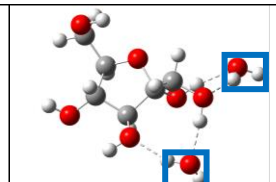
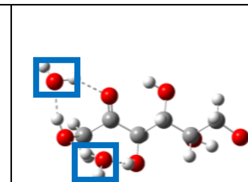
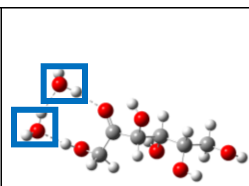
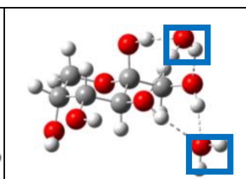
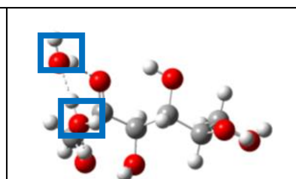
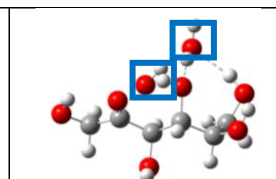
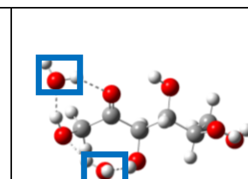
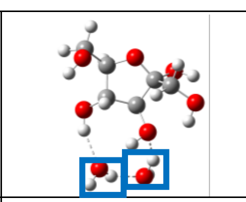
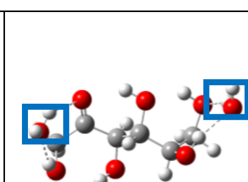
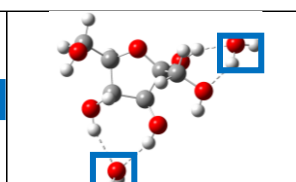
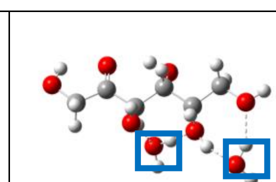
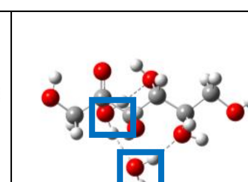
Optimized Neutral structure					
Structural Polymorphism	β-pyranose (${}^{2}C_5$-chair) +(2)(3)H_2O	β-pyranose (${}^{2}C_5$-chair) +(3)(4)H_2O	β-pyranose (${}^{2}C_5$-chair) +(4)(5)H_2O	β-pyranose (${}^{2}C_5$-chair) +(1)(3)H_2O	α- furanose (C_4-endo) +(1)(3)H_2O
ΔE (eV)	0.00	0.01	0.05	0.08	0.12
Optimized Neutral structure					
Structural Polymorphism	Open chain (A) +(1)(2)H_2O	Open chain (C) +(5)(6)H_2O	Open chain (A) +(4)(6)H_2O	Open chain (A) +(1)(2)H_2O	Open chain (A) +(3)H_2O
ΔE (eV)	0.15	0.16	0.18	0.20	0.21
Optimized Neutral structure					
Structural Polymorphism	α- furanose (C_4-endo) +(1)(2)H_2O	Open chain (B) +(5)(6)H_2O	Open chain (C) +(3)(5)H_2O	α- furanose (C_4-endo) +(3)(4)H_2O	Open chain (C) +(1)(2)H_2O
ΔE (eV)	0.22	0.23	0.24	0.25	0.25
Optimized Neutral structure					
Structural Polymorphism	Open chain (B) +(1)(2)H_2O				
ΔE (eV)	0.30				

Figure S11 Optimized geometries of the typical low lying neutral isomers of (fructose+H_2O) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^{2}C_5$-chair) +(1)(3)(intra)H_2O +(3)(intra)H_2O	open chain (A) +(2)(intra)H_2O+(1)(4)(intra)H_2O	open chain (B) +(1)(intra)H_2O+(2)(intra)H_2O	open chain (C) +(2)(intra)H_2O+(1)(4)(intra)H_2O	β-pyranose ($^{2}C_5$-chair) +(2)(3)(intra)H_2O +(1)(intra)H_2O
ΔE (eV)	0.00	0.05	0.06	0.07	0.08
Optimized Neutral structure					
Structural Polymorphism	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O	β-pyranose ($^{2}C_5$-chair) +(4)(5)H_2O+(3)(4)H_2O	β-pyranose ($^{2}C_5$-chair) +(1)(2)H_2O+(4)(5)H_2O	open chain (A) +(1)(2)H_2O+(1)(3)H_2O	β-pyranose ($^{2}C_5$-chair) +(1)(2)H_2O+(3)(4)H_2O
ΔE (eV)	0.11	0.12	0.14	0.16	0.18
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^{2}C_5$-chair) +(1)(3)H_2O+(3)(4)H_2O	open chain (A) +(6)(intra)H_2O+(4)(intra)H_2O	β-pyranose ($^{2}C_5$-chair) +(1)(3)H_2O+(4)(5)H_2O	α- furanose (C_4-endo) +(1)(2)H_2O+ (1)(3)H_2O	open chain (C) +(1)(2)H_2O+(1)(3)H_2O
ΔE (eV)	0.21	0.21	0.21	0.21	0.23
Optimized Neutral structure					
Structural Polymorphism	open chain (C) +(1)(intra)H_2O+(2)(intra)H_2O	β-pyranose ($^{2}C_5$-chair) +(1)(3)H_2O+(1)(2)(3)H_2O	open chain (B) +(1)(intra)H_2O+(2)(intra)H_2O	open chain (A) +(4)(6)(intra)H_2O+(intra)H_2O	open chain (B) +(1)(2)H_2O+(1)(3)H_2O
ΔE (eV)	0.23	0.24	0.25	0.27	0.29
Optimized Neutral structure					
Structural Polymorphism	α- furanose (C_4-endo) +(3)(intra)H_2O+ (4)(intra)H_2O	open chain (A) +(1)(2)H_2O+(5)(6)H_2O	α- furanose (C_4-endo) +(1)(2)H_2O+ (3)(4)H_2O	open chain (C) +(3)(5)H_2O+(5)(6)H_2O	open chain (C) +(5)(intra)H_2O+(4)(intra)H_2O

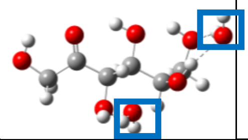
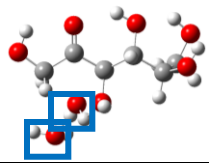
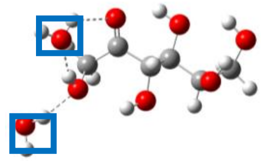
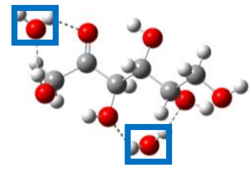
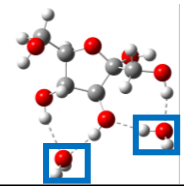
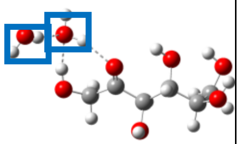
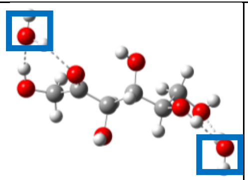
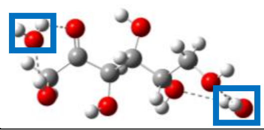
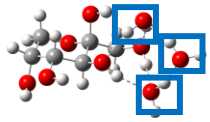
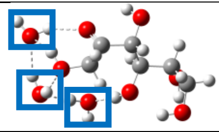
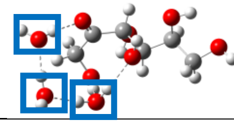
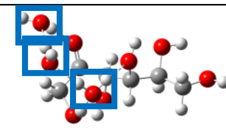
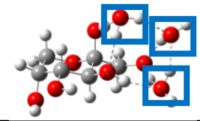
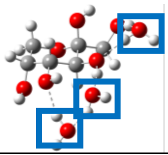
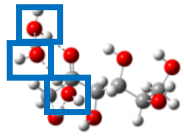
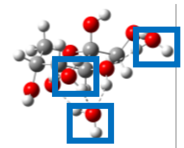
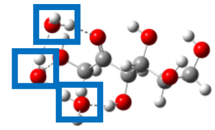
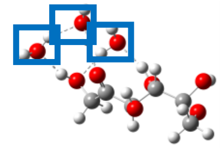
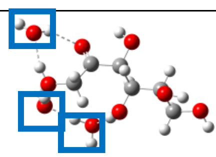
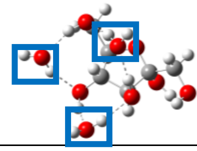
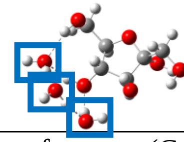
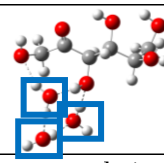
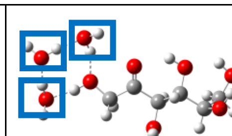
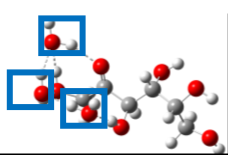
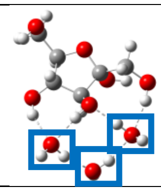
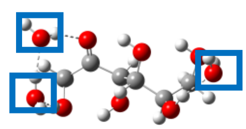
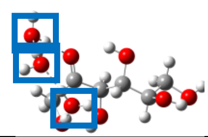
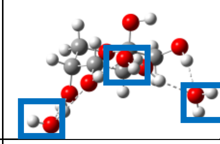
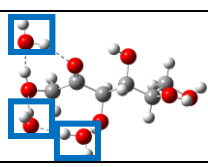
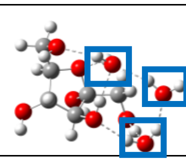
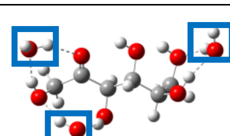
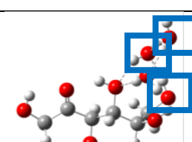
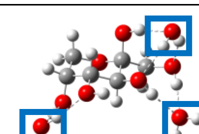
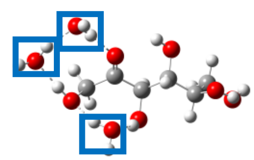
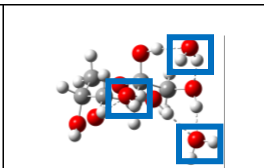
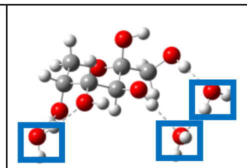
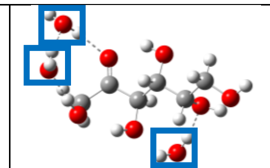
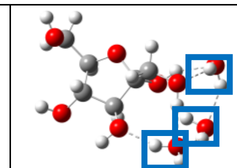
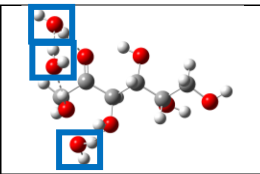
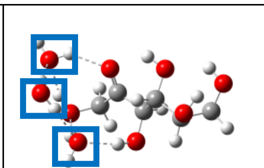
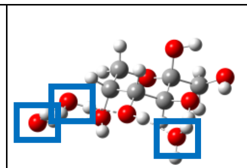
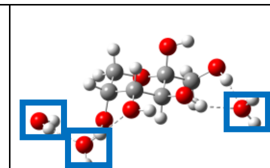
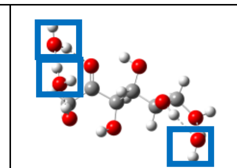
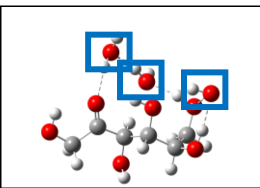
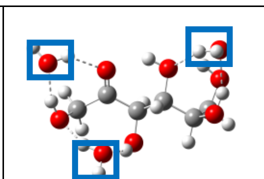
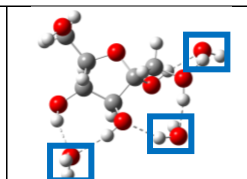
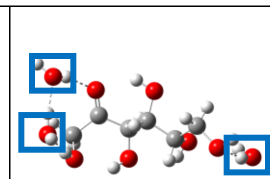
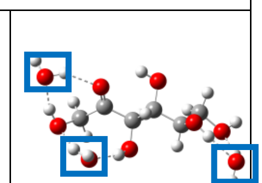
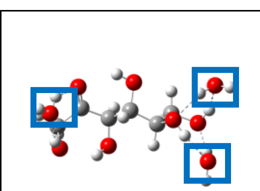
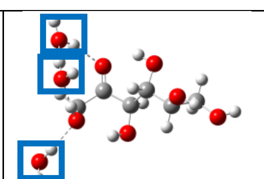
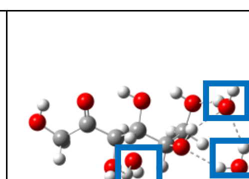
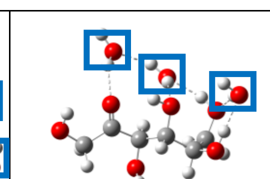
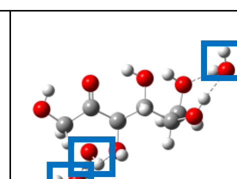
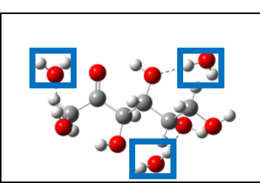
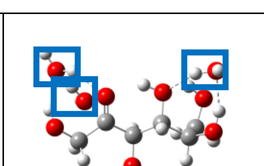
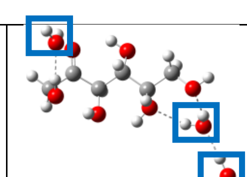
ΔE (eV)	0.30	0.31	0.32	0.33	0.34
Optimized Neutral structure					
Structural Polymorphism	open chain (A) +(3)H_2O+(5)(6)H_2O	open chain (A) +(3)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)H_2O+(1)H_2O	open chain (C) +(3)(5)H_2O+(1)(2)H_2O	α- furanose (C_4-endo) +(3)(4)H_2O+ (1)(3)H_2O
ΔE (eV)	0.35	0.38	0.39	0.39	0.40
Optimized Neutral structure					
Structural Polymorphism	open chain (A) +(1)(intra)H_2O+(intra)H_2O	open chain (B) +(1)(2)H_2O+(5)(6)H_2O	open chain (C) +(1)(2)H_2O+(5)(6)H_2O		
ΔE (eV)	0.43	0.43	0.47		

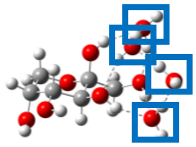
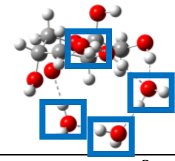
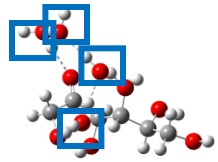
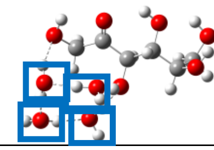
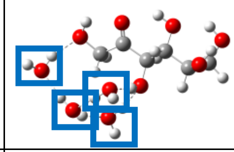
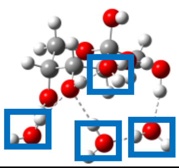
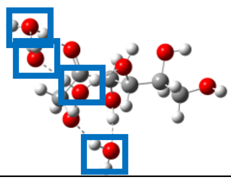
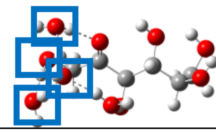
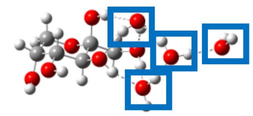
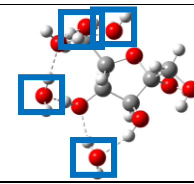
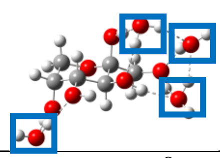
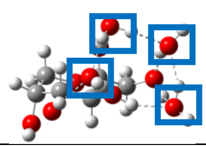
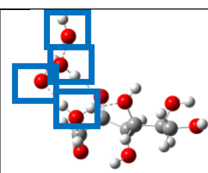
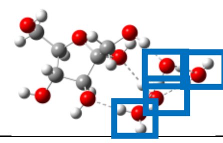
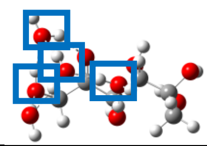
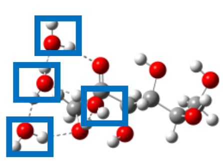
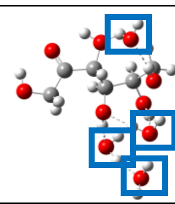
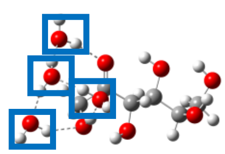
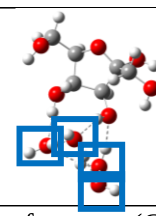
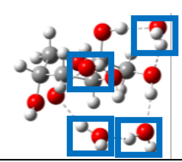
Figure S12 Optimized geometries of the typical low lying neutral isomers of (fructose+$(H_2O)_2$) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

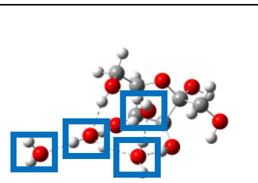
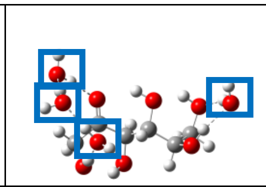
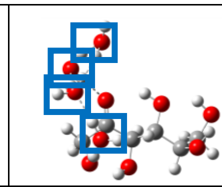
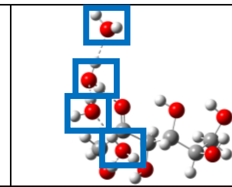
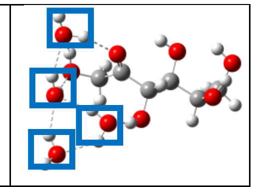
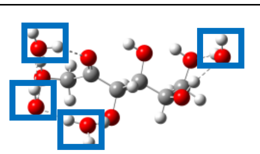
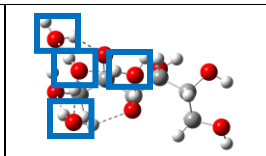
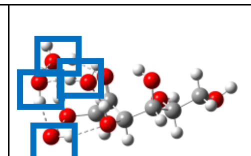
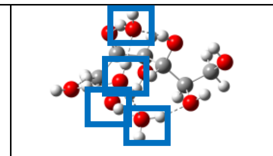
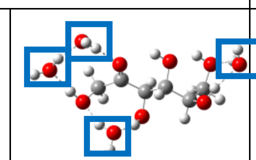
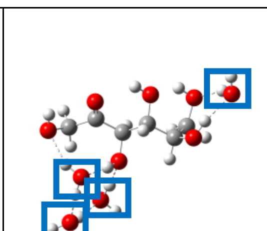
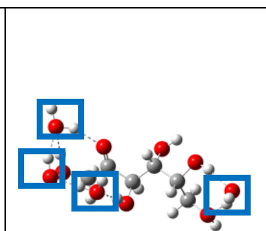
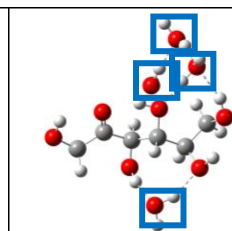
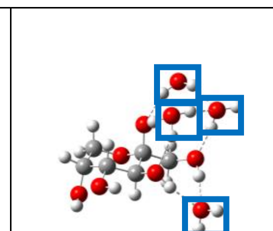
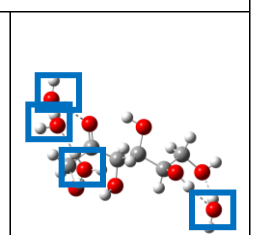
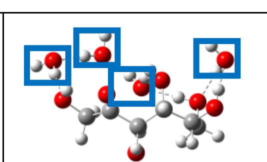
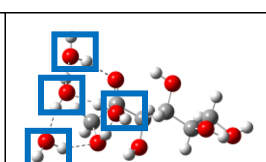
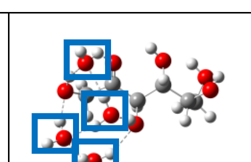
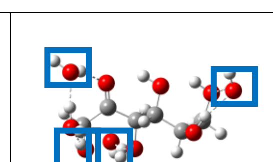
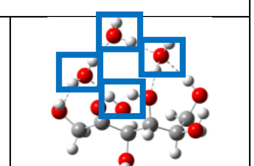
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + +(1)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(2)(intra)H_2O+(1)(intra)H_2O+(4)(intra)H_2O	open chain (C)+(1)(4)(intra)H_2O+(2)(intra)H_2O +(intra)H_2O	open chain (C)+(1)(4)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(2)(3)(intra)H_2O +(1)(intra)H_2O+(1)(3)(intra)H_2O
ΔE (eV)	0.00	0.05	0.08	0.08	0.09
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + +(1)(3)(intra)H_2O+(3)(intra)H_2O+(4)(intra)H_2O	open chain (A)+(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(1)(3)(intra)H_2O +(3)(4)(intra)H_2O +(1)H_2O	open chain (A)+(1)(intra)H_2O+(2)(intra)H_2O+(3)(intra)H_2O	open chain (A)+(1)(intra)H_2O+(2)(intra)H_2O +(1)(4)H_2O
ΔE (eV)	0.14	0.14	0.14	0.15	0.16
Optimized Neutral structure					
Structural Polymorphism	open chain (C)+(1)(2)H_2O+(1)(intra)H_2O+(4)(intra)H_2O	α-furanose (C_4-endo) +(3)(4)H_2O+(4)(6H_2O+(3)(6)H_2O	α-furanose (C_4-endo) +(4)(intra)H_2O+(4)(6)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(3)(intra)H_2O+ (3)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(intra)H_2O+(1)(intra)H_2O +(intra)H_2O
ΔE (eV)	0.16	0.17	0.21	0.23	0.24
Optimized Neutral structure					
Structural Polymorphism	open chain (B)+(1)(2)(intra)H_2O+(1)(intra)H_2O+(3)(intra)H_2O	α-furanose (C_4-endo) +(1)(3)(intra)H_2O+(3)(4)(intra)H_2O+(intra)H_2O	open chain (A)+(1)(intra)H_2O +(2)(intra)H_2O+(5)(6)H_2O	open chain (B)+(1)(intra)H2O+(2)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(1)(3)H_2O+(4)(5)H_2O
ΔE (eV)	0.26	0.26	0.29	0.30	0.30
Optimized Neutral structure					
Structural Polymorphism	open chain (B)+(1)(2)H_2O+(1)(intra)H_2O+(3)(intra)H_2O	α-furanose (C_4-endo) +(1)(3)(intra)H_2O+(	open chain (A)+(1)(2)H_2O+(1)(3)H_2O+(4)(5)(6)H_2O	open chain (A)+(4)(6)(intra)H_2O+(4)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(1)(2)(3)H_2O+(

		3)(6)(intra)H_2O+(intra)H_2O			1)(3)H_2O+(4)(5)H_2O
ΔE (eV)	0.31	0.32	0.34	0.35	0.35
Optimized Neutral structure					
Structural Polymorphism	open chain (B)+(1)(intra)H_2O+(2)(intra)H_2O+(1)(3)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(1)(3)H_2O+(1)(2)(3)H_2O	β-pyranose ($^2C_5$-chair) + +(1)(intra)H_2O+(3)(intra)H_2O+(4)(5)H_2O	open chain (C)+(1)(intra)H_2O+(2)(intra)H_2O+(3)(5)H_2O	α-furanose (C_4-endo) +(1)(2)(intra)H_2O +(1)(3)(intra)H_2O +(3)(intra)H_2O
ΔE (eV)	0.37	0.37	0.39	0.39	0.39
Optimized Neutral structure					
Structural Polymorphism	open chain (C)+(1)(intra)H_2O+(2)(intra)H_2O+(1)(3)H_2O	open chain (A)+(1)(2)(intra)H_2O+(1)(3)(intra)H_2O +(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(3)(4)H_2O+(4)(intra)H_2O+(5)(intra)H_2O	β-pyranose ($^2C_5$-chair) + +(4)(5)(intra)H_2O+(1)(3)H_2O+(intra)H_2O	open chain (B)+(1)(intra)H_2O+(2)(intra)H_2O +(5)(6)H_2O
ΔE (eV)	0.40	0.42	0.42	0.42	0.42
Optimized Neutral structure					
Structural Polymorphism	open chain (A)+(5)(6)H_2O+(6)(intra)H_2O+(2)(intra)H_2O	open chain (A)+(1)(2)H_2O+(1)(3)H_2O+(4)(5)H_2O	α-furanose (C_4-endo) +(1)(2)H_2O+(1)(3)H_2O+(3)(4)H_2O	open chain (C)+(1)(intra)H_2O+(2)(intra)H_2O+(5)(6)H_2O	open chain (B)+(1)(2)H_2O+(1)(3)H_2O+(5)(6)H_2O
ΔE (eV)	0.45	0.45	0.46	0.47	0.47
Optimized Neutral structure					
Structural Polymorphism	open chain (B)+(1)(2)H_2O+(5)(6)(intra)H_2O+(5)(6)(intra)H_2O	open chain (B)+(1)(intra)H_2O+(2)(intra)H_2O+(1)(intra)H_2O	open chain (A)+(5)(6)(intra)H_2O+(5)(intra)H_2O +(3)H_2O	open chain (A)+(5)(6)(intra)H_2O+(4)(6)(intra)H_2O +(2)(intra)H_2O	open chain (A)+(4)(6)H_2O+(3)H_2O+(intra)H_2O
ΔE (eV)	0.47	0.53	0.57	0.58	0.60
Optimized Neutral structure					

Structural Polymorphism	open chain (C)+(1)(2)H_2O+(4)H_2O+(5)H_2O	open chain (A)+(1)(2)(intra)H_2O+(intra)H_2O+(4)(5)H_2O	open chain (C)+(1)(2)H_2O+(5)(6)H_2O+(intra)H_2O		
ΔE (eV)	0.61	0.61	0.66		

Figure S13 Optimized geometries of the typical low lying neutral isomers of (fructose+$(H_2O)_3$) based on B3LYP/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^{2}C_5$-chair) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (1)(2)(intra)H_2O	β-pyranose ($^{2}C_5$-chair) + (1)(3)(intra)H_2O + (3)(4)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.00	0.14	0.19	0.25	0.25
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^{2}C_5$-chair) + (1)(intra)H_2O + (3)(4)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(4)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	β-pyranose ($^{2}C_5$-chair) + (1)(2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(4)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)(intra)H_2O
ΔE (eV)	0.26	0.27	0.31	0.31	0.32
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^{2}C_5$-chair) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)(intra)H_2O + (4)(5)H_2O	β-pyranose ($^{2}C_5$-chair) + (1)(intra)H_2O + (1)(3)(intra)H_2O + (2)(intra)H_2O + (3)(4)(intra)H_2O	open chain (C) + (1)(4)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.36	0.37	0.39	0.40	0.42
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (1)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (3)(6)H_2O + (4)(5)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	β-pyranose ($^{2}C_5$-chair) + (1)(2)H_2O + (1)(intra)H_2O + (4)(intra)H_2O + (3)(4)H_2O
ΔE (eV)	0.42	0.42	0.42	0.43	0.43

Optimized Neutral structure					
Structural Polymorphism	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(6)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.44	0.44	0.45	0.46	0.48
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (5)(6)H_2O	open chain (B) + (1)(2)(intra)H_2O + (3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(4)(intra)H_2O + (1)(5)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(3)H_2O + (5)(6)H_2O
ΔE (eV)	0.49	0.49	0.50	0.51	0.53
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (5)(6)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (5)(6)H_2O	open chain (A) + (3)(5)H_2O + (4)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (1)(intra)H_2O + (2)(3)(intra)H_2O + (1)(3)H_2O + (2)(intra)H_2O	open chain (B) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (5)(6)H_2O
ΔE (eV)	0.54	0.54	0.56	0.56	0.57
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (intra)H_2O + (4)(6)(intra)H_2O + (5)(6)H_2O	open chain (B) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (3)H_2O + (5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (4)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O
ΔE (eV)	0.57	0.58	0.59	0.61	0.63

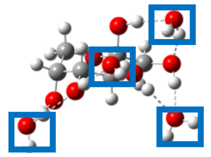
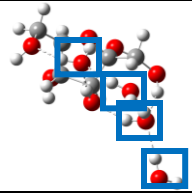
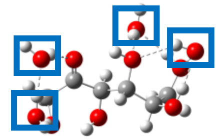
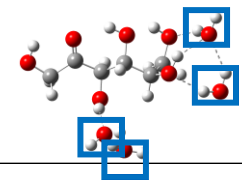
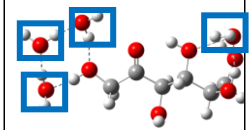
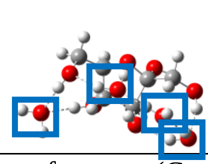
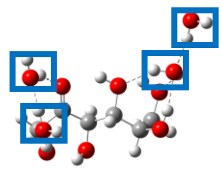
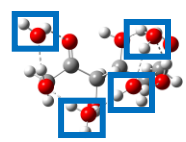
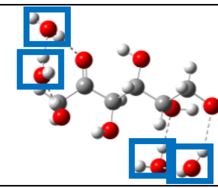
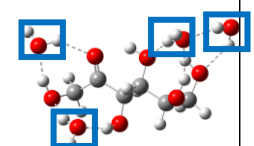
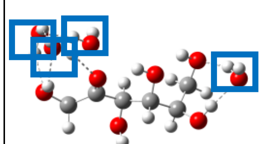
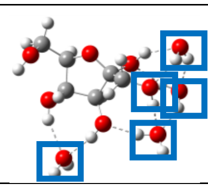
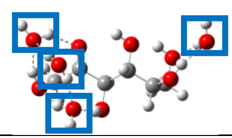
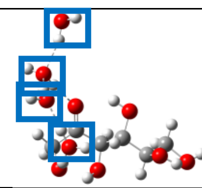
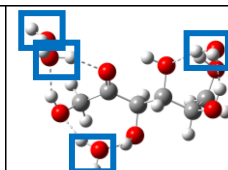
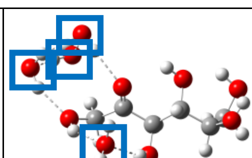
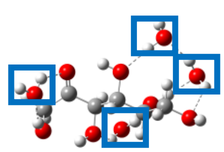
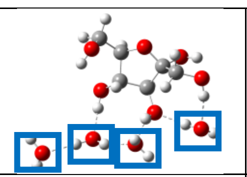
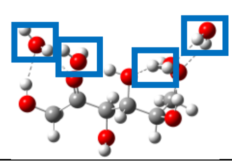
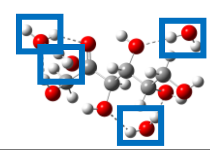
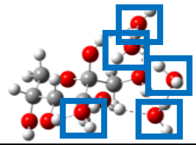
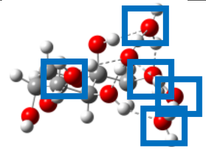
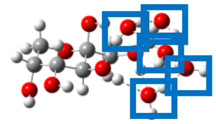
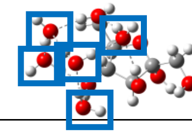
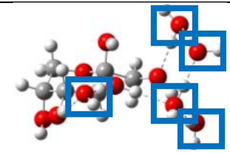
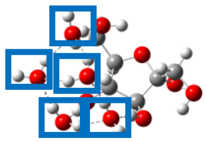
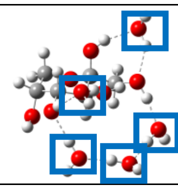
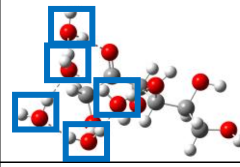
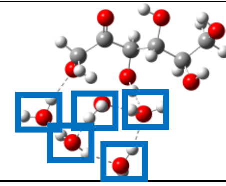
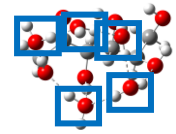
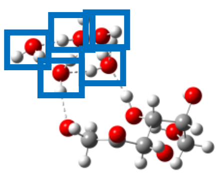
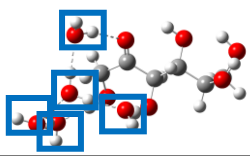
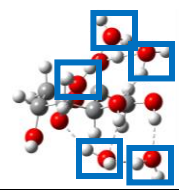
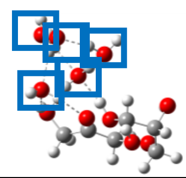
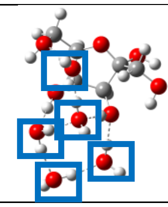
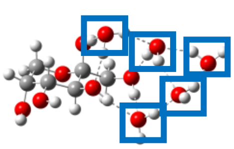
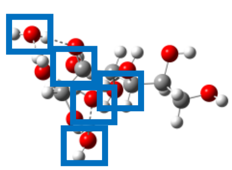
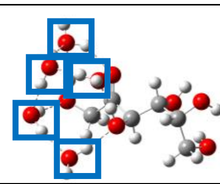
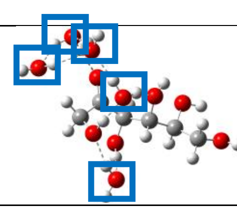
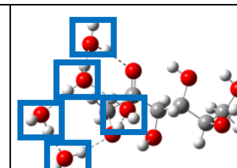
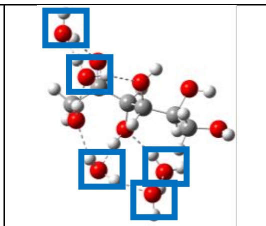
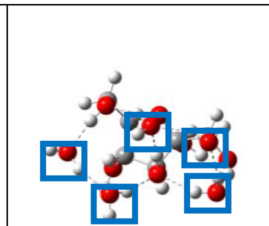
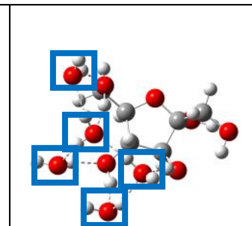
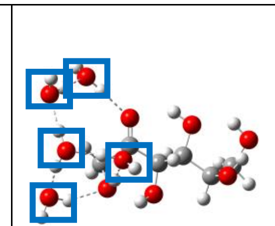
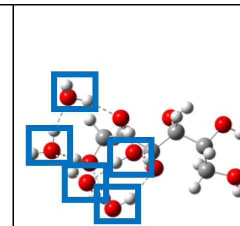
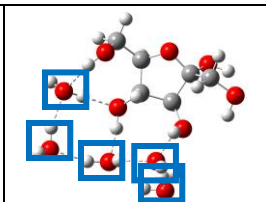
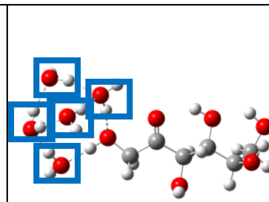
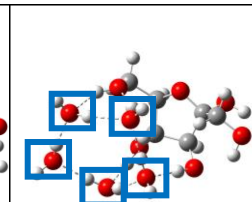
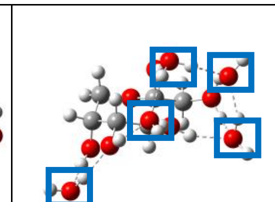
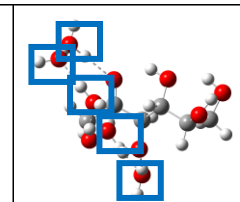
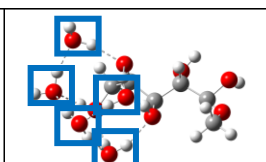
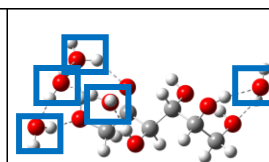
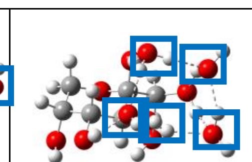
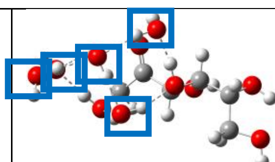
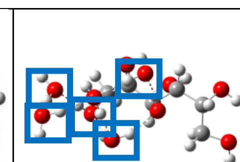
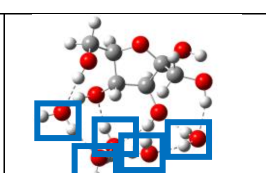
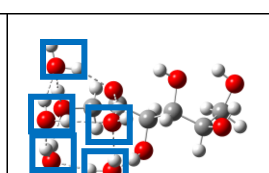
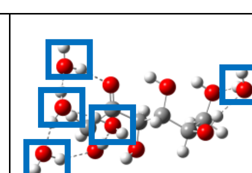
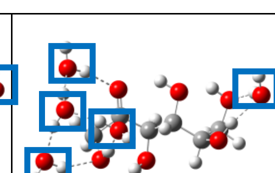
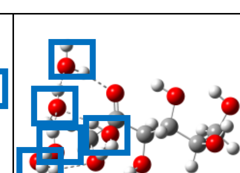
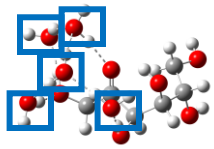
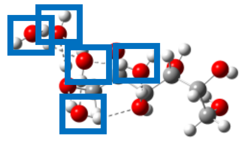
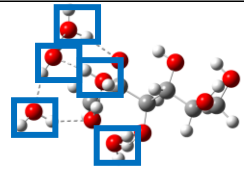
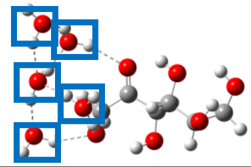
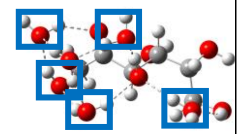
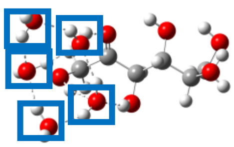
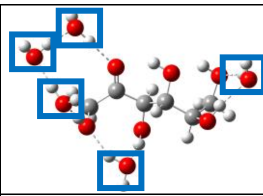
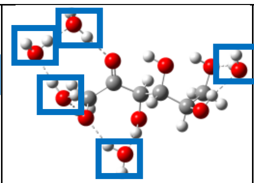
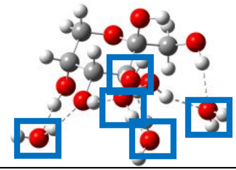
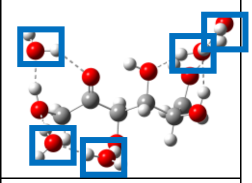
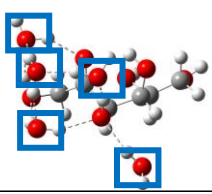
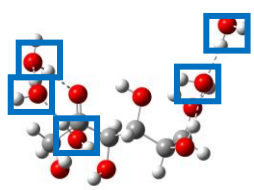
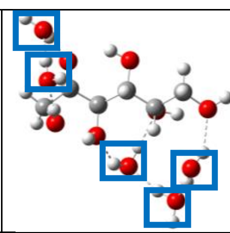
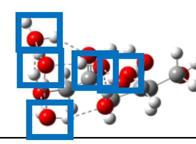
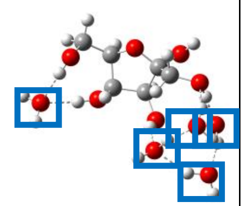
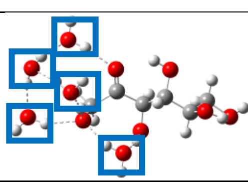
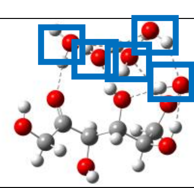
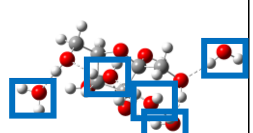
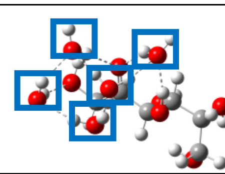
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^{2}C_5$-chair) + (1)(2)H_2O + (1)(3)H_2O + (3)(4)H_2O + (4)(5)H_2O	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (3)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(6)H_2O + (4)(5)(6)H_2O	open chain (A) + (3)H_2O + (5)(6)H_2O + (intra)H_2O + (5)(intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (4)(5)H_2O + (intra)H_2O
ΔE (eV)	0.64	0.65	0.65	0.65	0.66
Optimized Neutral structure					
Structural Polymorphism	α-furanose (C_4-endo) + (1)(3)H_2O + (3)(6)(intra)H_2O + (intra)H_2O + (4)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(5)(6)H_2O + (intra)H_2O	open chain (A) + (1)(2)H_2O + (1)(3)(intra)H_2O + (4)(5)(intra)H_2O + (5)(intra)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (5)(intra)H_2O + (6)(intra)H_2O	open chain (A) + (1)(2)H_2O + (1)(3)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O
ΔE (eV)	0.67	0.67	0.70	0.70	0.72
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (5)(6)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(2)(intra)H_2O + (2)(intra)H_2O + (1)(3)(intra)H_2O + (3)(4)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (5)(6)H_2O	open chain (B) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (4)(5)H_2O
ΔE (eV)	0.72	0.72	0.73	0.73	0.78
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(3)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)H_2O + (3)(5)H_2O + (5)(6)(intra)H_2O + (4)(intra)H_2O	α-furanose (C_4-endo) + (1)(3)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (intra)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (intra)H_2O + (3)(5)H_2O + (4)H_2O
ΔE (eV)	0.81	0.82	0.82	0.88	0.95

Figure S14 Optimized geometries of the typical low lying neutral isomers of (fructose+$(H_2O)_4$) based on B3LYP/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose^{-} parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O + (1)(2)(intra)H_2O + (3)(4)H_2O	β-pyranose ($^2C_5$-chair) + (1)(2)(intra)H_2O + (3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (4)(intra)H_2O	β-pyranose ($^2C_5$-chair) + (1)(3)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (4)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (3)(6)(intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (1)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (3)(4)H_2O
ΔE (eV)	0.00	0.02	0.02	0.05	0.09
Optimized Neutral structure					
Structural Polymorphism	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O + (intra)H_2O	pyranose ($^2C_5$-chair) + (1)(2) H_2O + (1)(intra)H_2O + (4)(intra)H_2O + (3)(4)H_2O + (intra)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(3)(intra)H_2O + (1)(intra)H_2O + (4)(intra)H_2O + (5)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.10	0.10	0.11	0.12	0.12
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (2)(3)(intra)H_2O + (1)(intra)H_2O + (3)(4)(intra)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(4)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.14	0.15	0.19	0.20	0.23
Optimized Neutral structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) + (1)(3)(intra)H_2O + (1)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (3)H_2O + (4)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (3)(intra)H_2O	open chain (C) + (1)(4)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O + (1)(3)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O

ΔE (eV)	0.23	0.23	0.26	0.26	0.26
Optimized Neutral structure					
Structural Polymorphism	open chain (C) + (1)(4)(intra)H_2O + (1)(3)(intra)H_2O +(2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (3)(intra)H_2O + (3)(6)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.27	0.27	0.29	0.31	0.33
Optimized Neutral structure					
Structural Polymorphism	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (4)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (3)(intra)H_2O + (4)(intra)H_2O + (6)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	β-pyranose ($^2C_5$-chair) + (2)(3)(intra)H_2O + (1)(intra)H_2O + (1)(3)(intra)H_2O + (3)(4)(intra)H_2O + (4)(5)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (3)(intra)H_2O + (intra)H_2O
ΔE (eV)	0.33	0.34	0.34	0.35	0.37
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (5)(6)H_2O	β-pyranose ($^2C_5$-chair) + (2)(3)(intra)H_2O + (1)(intra)H_2O + (1)(3)H_2O + (3)(4)(intra)H_2O + (intra)H_2O	open chain (B) + (1)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(intra)H_2O + (1)(3)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O
ΔE (eV)	0.37	0.39	0.40	0.40	0.40
Optimized Neutral structure					
Structural Polymorphism	α-furanose (C_4-endo) + (1)(3)(intra)H_2O + (3)(4)(intra)H_2O +	open chain (A) + (1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O +	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O +	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O +	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O +

	(4)(6)(intra)H_2O + (intra)H_2O + (intra)H_2O	(3)(intra)H_2O + (intra)H_2O	(intra)H_2O + (5)(6)H_2O	(intra)H_2O + (5)(6)H_2O	(intra)H_2O + (intra)H_2O
ΔE (eV)	0.42	0.43	0.43	0.43	0.43
Optimized Neutral structure					
Structural Polymorphism	open chain (C) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (3)H_2O	open chain (A) + (1)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (B) + (1)(2)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (3)(6)(intra)H_2O
ΔE (eV)	0.44	0.45	0.45	0.45	0.45
Optimized Neutral structure					
Structural Polymorphism	open chain (A) + (1)(3)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O + (intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (5)(6)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (5)(6)H_2O	β-pyranose ($^{2}C_5$-chair) + (1)(3)H_2O + (3)(4)(intra)H_2O + (intra)H_2O + (intra)H_2O + (4)(5)H_2O	open chain (A) + (1)(2)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (4)(5)(intra)H_2O + (6)(intra)H_2O
ΔE (eV)	0.46	0.47	0.47	0.48	0.52
Optimized Neutral structure					
Structural Polymorphism	open chain (C) + (1)(2)(intra)H_2O + ((3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (3)(intra)H_2O	open chain (A) + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (5)(6)H_2O + (intra)H_2O	open chain (C) + (1)(intra)H_2O + (2)(intra)H_2O + (3)(5)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	open chain (C) + (1)(2)(intra)H_2O + (3)(intra)H_2O + (1)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	α-furanose (C_4-endo) + (1)(intra)H_2O + (1)(intra)H_2O + (3)(intra)H_2O + (intra)H_2O + (4)(6)H_2O
ΔE (eV)	0.52	0.52	0.55	0.56	0.59
Optimized Neutral structure					
Structural Polymorphism	open chain (B) + (1)(intra)H_2O +	open chain (A) + (2)(intra)H_2O +	α-furanose (C_4-endo) +	open chain (A) + (1)(intra)H_2O +	

	(1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O	(4)(intra)H_2O + (4)(5)(6)(intra)H_2O + (6)(intra)H_2O + (intra)H_2O	(1)(intra)H_2O + (1)(3)(intra)H_2O + (3)(intra)H_2O + (6)(intra)H_2O + (4)(6)H_2O	(2)(intra)H_2O + (2)(3)(intra)H_2O + (intra)H_2O + (intra)H_2O	
ΔE (eV)	0.61	0.63	0.70	0.76	

Figure S15 Optimized geometries of the typical low lying neutral isomers of (fructose+$(H_2O)_5$) based on B3LYP/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

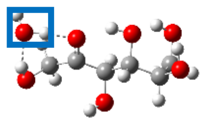
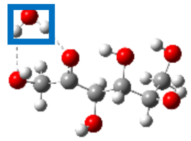
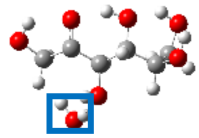
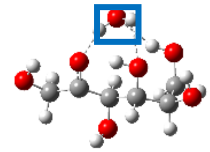
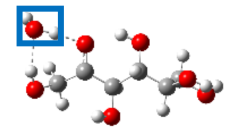
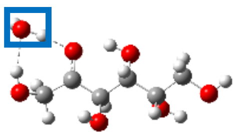
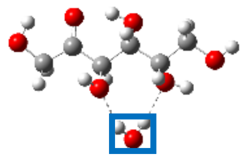
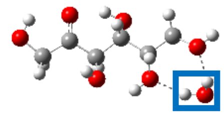
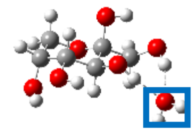
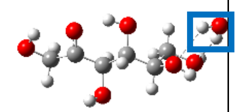
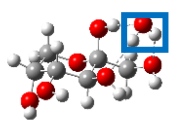
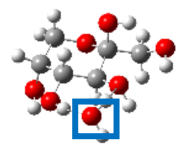
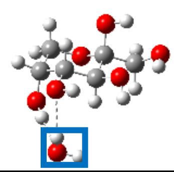
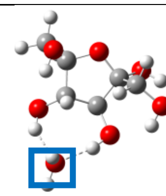
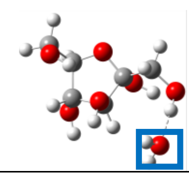
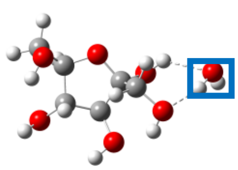
Optimized Anionic structure					
Structural Polymorphism	Open chain (A)+(1)(2)H_2O	Open chain (A) +(1)(2)H_2O	Open chain (A) +(3)H_2O	Open chain (A) +(2)(4)(6)H_2O	Open chain (B) +(1)(2)H_2O
ΔE (eV)	0.00	0.06	0.17	0.19	0.39
VDE (eV)	**2.24**	**2.33**	**2.16**	**2.30**	**1.90**
Optimized Anionic structure					
Structural Polymorphism	Open chain (C) +(1)(2)H_2O	Open chain (C) +(3)(5)H_2O	Open chain (C) +(5)(6)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O	Open chain (B) +(5)(6)H_2O
ΔE (eV)	0.42	0.48	0.48	0.53	0.61
VDE (eV)	**1.82**	**1.70**	**1.77**	**0.20**	**1.70**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) +(1)(2)(3)H_2O	β-pyranose ($^2C_5$-chair) +(3)(4)H_2O	β-pyranose ($^2C_5$-chair) +(4)(5)H_2O	α- furanose (C_4-endo) +(3)(4)H_2O	α- furanose (C_4-endo) +(1)H_2O
ΔE (eV)	0.63	0.69	0.69	0.76	0.89
VDE (eV)	**0.26**	**0.19**	**0.29**	**0.36**	**0.39**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(1)(2)H_2O				
ΔE (eV)	1.04				
VDE (eV)	**0.10**				

Figure S16 Optimized geometries of the typical low lying anionic isomers of (fructose+H_2O)$^-$ based on M062X/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

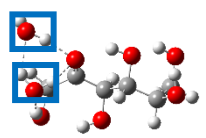
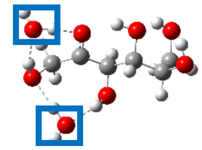
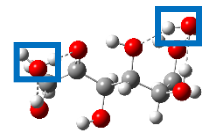
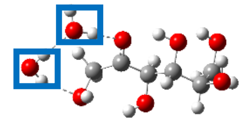
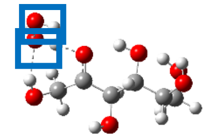
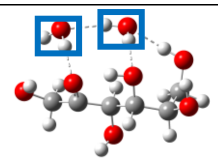
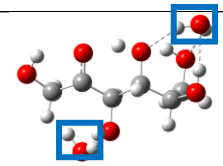
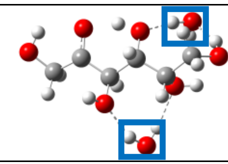
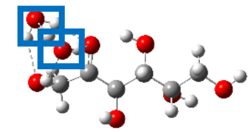
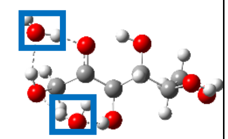
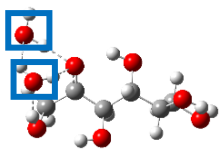
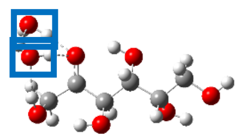
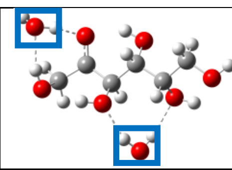
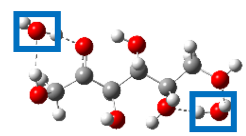
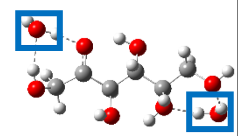
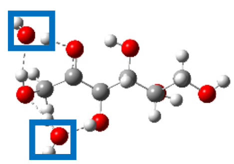
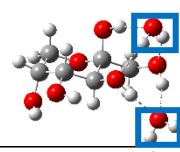
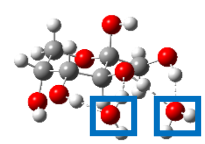
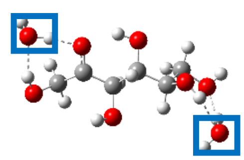
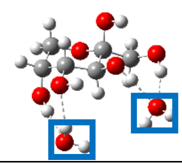
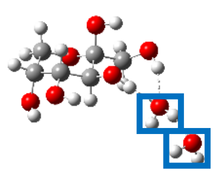
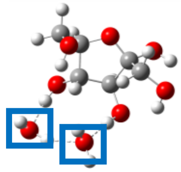
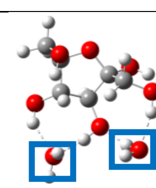
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O	open chain (A) +(1)(2)H_2O+(1)(3) H_2O	open chain (A) +(1)(2)H_2O+(4)(5)(6)H_2O	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O +(intra)H_2O
ΔE (eV)	0.00	0.03	0.07	0.08	0.13
VDE (eV)	**2.40**	**2.22**	**2.28**	**2.56**	**2.62**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(4)(6)H_2O+(2)(intra)H_2O	open chain (A) +(3)H_2O+(4)(5)(6) H_2O	open chain (C) +(3)(5)H_2O+(4)(6) H_2O	open chain (C) +(1)(2)(intra)H_2O+(1)(2)(intra)H_2O	open chain (B) +(1)(2)H_2O+(1)(3)H_2O
ΔE (eV)	0.14	0.23	0.33	0.35	0.37
VDE (eV)	**2.53**	**2.50**	**2.18**	**2.32**	**2.22**
Optimized Anionic structure					
Structural Polymorphism	open chain (B) +(1)(2)(intra)H_2O+(2)(intra)H_2O	open chain (C) +(1)(2)H_2O+(2)(intra)H_2O	open chain (C) +(3)(5)H_2O+(1)(2) H_2O	open chain (B) +(1)(2)H_2O+(5)(6)H_2O	open chain (C) +(1)(2)H_2O+(5)(6)H_2O
ΔE (eV)	0.37	0.40	0.41	0.43	0.46
VDE (eV)	**2.18**	**2.16**	**2.04**	**2.31**	**2.17**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) +(1)(2)H_2O+(1)(3) H_2O	β-pyranose ($^2C_5$-chair) +(1)(2)(3)H_2O+(1)(3)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O+(3)(4) H_2O	open chain (B) +(1)(2)H_2O+(5)(6)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O+(4)(5)H_2O
ΔE (eV)	0.46	0.54	0.56	0.57	0.61
VDE (eV)	**1.84**	**0.39**	**0.60**	**1.98**	**0.59**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O+(intra) H_2O	α- furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O	α- furanose (C_4-endo) +(1)(3)H_2O+(3)(4) H_2O		
ΔE (eV)	0.73	0.86	0.88		
VDE (eV)	**0.37**	**0.76**	**0.70**		

Figure S17 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_2$)$^-$ based on M062X/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

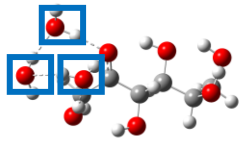
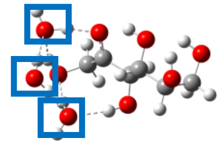
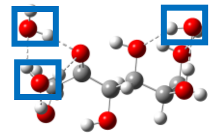
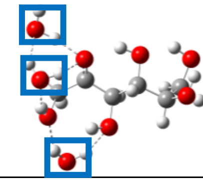
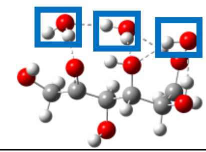
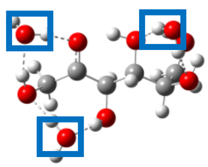
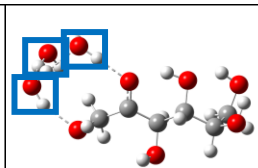
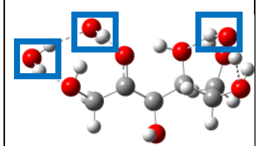
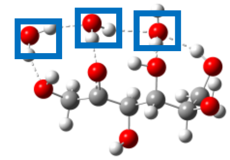
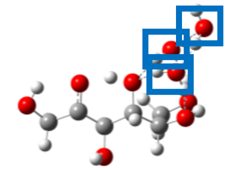
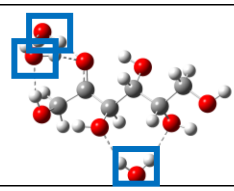
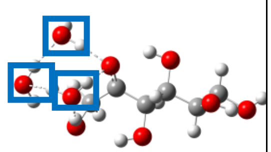
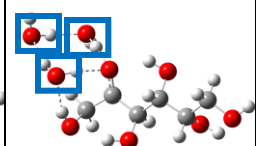
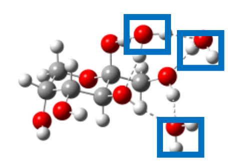
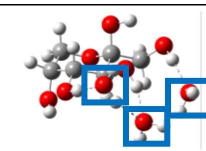
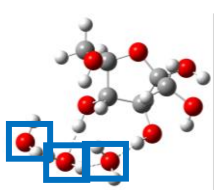
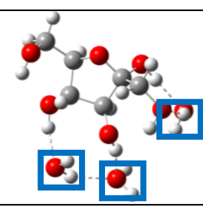
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)H_2O+(1)(3)H_2O+(intra)H_2O	open chain (A) +(1)(2)H_2O+(2)(intra)H_2O+(4)(5)(6)H_2O	open chain (A) +(1)(2)H_2O+(1)(3)H_2O+(2)(intra)H_2O	open chain (A) +(4)(5)(6)H_2O+(4)(6)(intra)H_2O+(2)(intra)H_2O
ΔE (eV)	0.00	0.03	0.04	0.05	0.08
VDE (eV)	**2.61**	**2.50**	**2.57**	**2.67**	**2.76**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)H_2O+(1)(3)H_2O+(4)(5)H_2O	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O+(4)(5)H_2O	open chain (A) +(4)(6)(intra)H_2O+(2)(intra)H_2O+(1)(intra)H_2O	open chain (A) +(4)(6)(intra)H_2O+(4)(5)(intra)H_2O+(intra)H_2O
ΔE (eV)	0.12	0.21	0.22	0.23	0.25
VDE (eV)	**2.41**	**2.76**	**3.00**	**2.76**	**2.39**
Optimized Anionic structure					 E=-915.871697
Structural Polymorphism	open chain (C) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(3)(5)H_2O	open chain (B) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (C) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)H_2O+(2)(3)(intra)H_2O+(1)(intra)H_2O	β-pyranose ($^2C_5$-chair) +(3)(4)H_2O+(3)(3)(intra)H_2O+(1)H_2O
ΔE (eV)	0.36	0.38	0.43	0.47	0.53
VDE (eV)	**2.44**	**2.49**	**2.38**	**0.71**	**0.95**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O+(intra)H_2O	α- furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O+(1)(2)H_2O			
ΔE (eV)	0.80	0.84			
VDE (eV)	**1.26**	**0.85**			

Figure S18 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_3)^-$ based on M062X/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures

(1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

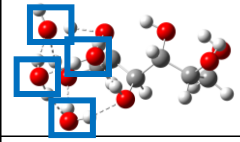
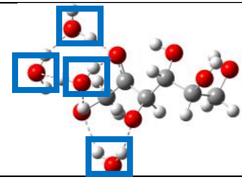
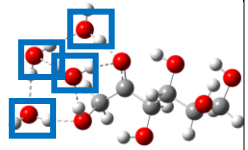
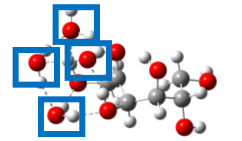
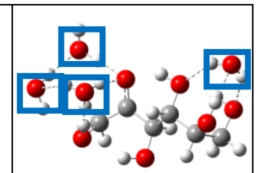
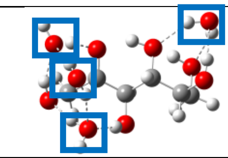
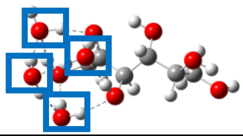
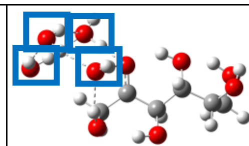
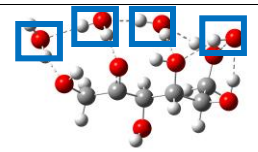
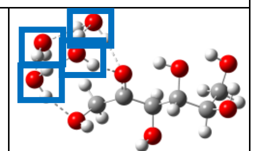
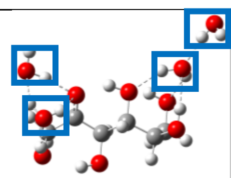
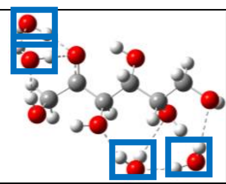
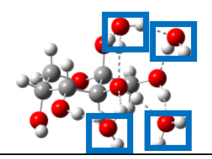
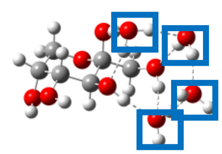
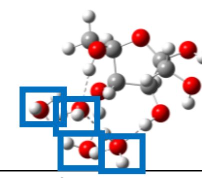
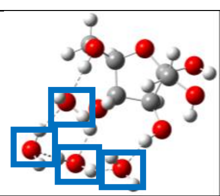
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O+(1)(3)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O+(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O	open chain (C) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O+(4)(5)(6)H_2O
ΔE (eV)	0.00	0.23	0.26	0.28	0.29
VDE (eV)	**2.89**	**3.09**	**2.60**	**2.67**	**2.81**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O+(4)(5)(6)H_2O	open chain (B) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O+(intra)H_2O	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O+(4)(6)(intra)H_2O+(4)(5)(6)H_2O	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O
ΔE (eV)	0.32	0.32	0.37	0.40	0.40
VDE (eV)	**2.68**	**2.67**	**3.07**	**2.85**	**3.07**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(4)(5)(6)H_2O+(intra)H_2O	open chain (C) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(3)(5)(intra)H_2O+(6)(intra)H_2O	β-pyranose ($^2C_5$-chair) +(3)(4)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(1)(intra)H_2O	β-pyranose ($^2C_5$-chair) +(1)(3)(intra)H_2O+(2)(3)(intra)H_2O+(1)(intra)H_2O+(intra)H_2O	α- furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O+(6)(intra)H_2O+(intra)H_2O
ΔE (eV)	0.47	0.54	0. 77	0.82	1.00
VDE (eV)	**2.71**	**2.59**	**1.12**	**0.73**	**1.10**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(3)(intra)H_2O+(4)(intra)H_2O+(6)(intra)H_2O+(intra)H_2O				
ΔE (eV)	1.05				
VDE (eV)	**1.48**				

Figure S19 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_4$)$^-$ based on M062X/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

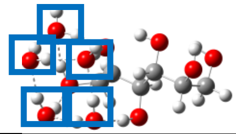
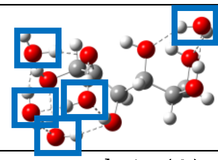
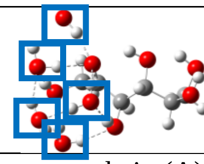
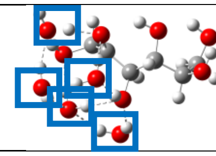
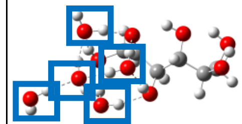
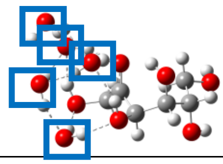
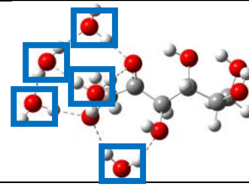
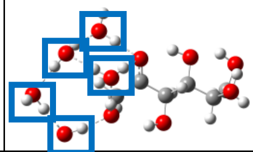
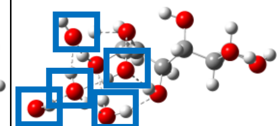
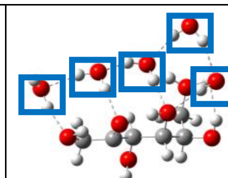
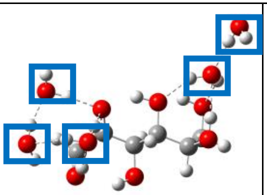
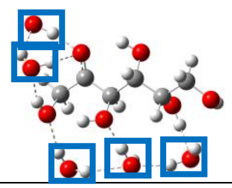
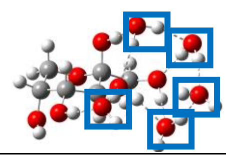
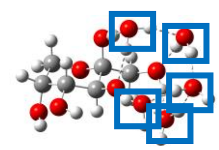
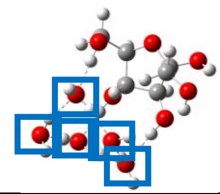
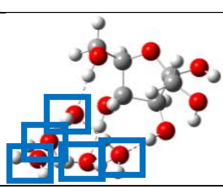
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(3)(intra)H_2O+(intra)H_2O +(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O +(intra)H_2O+(4)(5)(6)H_2O	open chain (A) +(1)(2)(intra)H_2O +(2)(3)(intra)H_2O +(1)(3)(intra)H_2O +(intra)H_2O+(2)H_2O	open chain (A) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O+(3)(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O +(2)(3)(intra)H_2O +(1)(3)(intra)H_2O +(intra)H_2O+(intra)H_2O
ΔE (eV)	0.00	0.06	0.08	0.09	0.14
VDE (eV)	**3.16**	**3.13**	**3.20**	**3.14**	**3.12**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O+(intra)H_2O	open chain (A) +(1)(2)(intra)H_2O+(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O +(1)(3)H_2O	open chain (A) +(1)(2)(intra)H_2O +(1)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O+(intra)H_2O	open chain (B) +(1)(2)(intra)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(intra)H_2O+(intra)H_2O	open chain (A) +(1)(intra)H_2O+(2)(intra)H_2O+(4)(6)(intra)H_2O+(4)(5)(6)(intra)H_2O+(intra)H_2O
ΔE (eV)	0.29	0.32	0.39	0.44	0.47
VDE (eV)	**2.77**	**3.08**	**2.64**	**2.89**	**3.09**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(intra)H_2O+(4)(5)(6)H_2O +(intra)H_2O	open chain (C) +(1)(2)(intra)H_2O+(2)(intra)H_2O+(3)(5)(intra)H_2O+(6)(intra)H_2O+(1)(intra)H_2O	β-pyranose ($^{2}C_5$-chair) +(3)(4)H_2O+(2)(3)(intra)H_2O+(1)(3)(intra)H_2O+(1)(intra)H_2O+(intra)H_2O	β-pyranose ($^{2}C_5$-chair) +(1)(3)(intra)H_2O+(2)(3)(intra)H_2O+(1)(intra)H_2O+(intra)H_2O+(3)(intra)H_2O	α- furanose (C_4-endo) +(3)(intra)H_2O+ (4)(intra)H_2O+(6)(intra)H_2O+(intra)H_2O+(intra)H_2O
ΔE (eV)	0.48	0.64	0.83	0.91	1.05
VDE (eV)	**2.95**	**2.81**	**1.12**	**0.82**	**1.21**
Optimized Anionic structure					
Structural Polymorphism	α- furanose (C_4-endo) +(3)(intra)H_2O+ (4)(intra)H_2O+(6)(intra)H_2O+(intra)H_2O				
ΔE (eV)	1.06				
VDE (eV)	**1.48**				

Figure S20 Optimized geometries of the typical low lying anionic isomers of (fructose+$(H_2O)_4$)$^-$ based on M062X/6-31++G(d) calculations. The relative energies and structural polymorphs are indicated. The blue squares indicate addition of H_2O units at the marked position. The C ordering is the same as that of fructose$^-$ parent anions. For open chain structures (1)C to (6)C is ordered from left to right. For both furanose and pyranose structures (1)C to (6)C is ordered from right to left in a clockwise direction.

Table S1 Solubility comparisons of different monosaccharides.

	pentoses			**hexoses**	
Aldo-	**ribose**	**arabinose**		**mannose**	**talose**
	100 g/L (25 °C)	834 g/L (25 °C)		2480 g/L (17 °C)	100 g/L
Keto-	**ribulose**			**fructose**	**tagatose**
	~678 g/L			3750 g/L (20 °C)	~100 g/L

More pentose (e.g., arabinose, ribulose…) and hexose (e.g., mannose, talose, tagatose…) aldo/keto-monosaccharides will be explored both experimentally and theoretically to compare comprehensively and systematically these uncovered behavioral differences. A few examples of such monosaccharide water cluster/solubility comparisons can be suggested that can help characterize the various monosaccharides: arabinose is an aldopentose, but with ~ 8 times greater solubility than that of ribose; tagatose, like fructose, is a ketohexose, however, it evidences similar solubility to that of ribose; ribulose (a ketopentose) whose solubility is greater than that of ribose; and mannose and talose (aldohexoses), which have solubilities of ~ 2×10^3 g/L and ~ 100g/L, respectively. And depending on what can be extracted from such systematic comparisons, we can anticipate a much deeper understanding of cluster vs solvation behavior. Perhaps these efforts will shed some light on the evolutionarily determined choices for various saccharides being employed for different biological applications.