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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  $\Leftrightarrow$  Figure 4.

	I				T
Optimized Anionic structure		P. Company	y y y		
Structural Polymorphism	Open chain (A) +(1)(2)H <sub>2</sub> O	Open chain (A) +(2)H <sub>2</sub> O	Open chain (A) +(3)H <sub>2</sub> O	Open chain (A) +(4)(6)H <sub>2</sub> O	Open chain (B) +(1)(2)H <sub>2</sub> O
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				7	
Structural Polymorphism	Open chain (C) +(1)(2)H <sub>2</sub> O	Open chain (C) +(3)(5)H <sub>2</sub> O	Open chain (C) +(5)(6)H <sub>2</sub> O	Open chain (B) +(5)(6)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O
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		- 4 - 4 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5			- 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3
Anionic structure	<b>19</b>	<b>∂</b> € €			90, 30,
Structural Polymorphism	α- furanose (C <sub>4</sub> - endo) +(3)(4)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(3)(4)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(2)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(4)(5)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O
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	$\alpha$ - furanose (C <sub>4</sub> -	$\alpha$ - furanose (C <sub>4</sub> -			
Polymorphism	endo) +(1)(3)H <sub>2</sub> O 1.17	endo) +(1)(2)H <sub>2</sub> O 1.20			
ΔE (eV)	0.31	0.21			
VDE (eV)	U.31	U. <b>41</b>			

Figure S4 Optimized geometries of the typical low lying anionic isomers of (fructose+ $H_2O$ )<sup>-</sup> 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<sup>-</sup> 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   Open chain (A)   Open chain (A)   (1)(2)H-O+(2)(in   (1)(2)H-O+(2)(in   (1)(2)H-O+(2)(in   (1)(2)H-O+(3)(in   (1)			7			
Structural Polymorphism   Open chain (A)	Optimized	<u>•</u>	<b>Q</b>	<b>9</b> .,		
Structural Polymorphism				· • • •		100 mg 100 mg
Structural Polymorphism		63			• • • • • • • • • • • • • • • • • • •	3
Structural Polymorphism					•	
Polymorphism	Ctm1atuma1	open chain (A)		open chain (A)		
AE   0.00   0.00   0.01   0.01   0.02		$+(1)(intra)H_2O+(2$	$+(1)(2)H_2O+(2)$	$+(1)(2)H_2O+(2)(in$	$+(1)(2)H_2O+(1)(3)H$	$+(1)(2)H_2O+(1)(3$
Optimized Anionic structure	Forymorphism	)(intra)H <sub>2</sub> O	$H_2O$	tra)H <sub>2</sub> O	$_2$ O	)H <sub>2</sub> O
Optimized Anionic structure	ΔΕ	0.00	0.00	0.01	0.01	0.02
Optimized Anionic structural Polymorphism   Open chain (A)   Open chain (A)   (1)(2)H <sub>2</sub> O+(intra   (1)(2)H <sub>2</sub> O+(i)(4)   (1)(3)H <sub>2</sub> O+(i)(5)(6)   (1)(4)(5)(6)   (1)(4)(5)(6)   (1)(4)(5)(6)   (1)(4)(5)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)   (1)(4)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)	VDE	2.76		2.54	2.48	2.14
Structural Polymorphism   Open chain (A)   +(1)(2)H-O+(4)(   +(3)H-O+(4)(5)(6)   +(3)H-O+(4)(1)(1)(1)   +(3)H-O+(4)(1)(1)   +(3)H-O+(4)(1)   +(3)H-O+(	,		_,,,		_,,,	
Structural Polymorphism   Open chain (A)   +(1)(2)H-O+(4)(   +(3)H-O+(4)(5)(6)   +(3)H-O+(4)(1)(1)(1)   +(3)H-O+(4)(1)(1)   +(3)H-O+(4)(1)   +(3)H-O+(				<b>J-</b>	<b>9</b> 🔏	4
Structural Polymorphism   Open chain (A)   +(1)(2)H-O+(4)(   +(3)H-O+(4)(5)(6)   +(3)H-O+(4)(1)(1)(1)   +(3)H-O+(4)(1)(1)   +(3)H-O+(4)(1)   +(3)H-O+(	Optimized					<b>7</b>
Structural Polymorphism   Open chain (A)						
Structural Polymorphism   H(1)(2)H-0+(intra   H(2)			2000	<b>4</b> 3 -	-30-39-35	3
Structural Polymorphism   H(1)(2)H-0+(intra   H(2)		2 7 2 3	• 3• 3		٠ 🛵	,
Structural Polymorphism   H(1)(2)H-0+(intra   H(2)	~ .	open chain (A)	open chain (A)	open chain (A)	open chain (A)	open chain (A)
Optimized Anionic structural Polymorphism   Open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2)   H <sub>2</sub> O   H <sub>2</sub> O   Open chain (C) +(1)(2)H <sub>2</sub> O+(2)(i   H <sub>2</sub> O   H <sub>2</sub> O			. ,			
ΔΕ         0.02         0.08         0.19         0.24         0.28           VDE         2.59         2.36         2.47         2.42         2.31           Optimized Anionic structural Polymorphism         open chain (B) +(1)(2)H <sub>2</sub> O+(2)(i) ntra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(2)(i) tra)H <sub>2</sub> O         open chain (A) +(1)(2)H <sub>2</sub> O+(1)(2) intra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(2)(in tra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(1)(2) intra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(2)(i) +(1)(2)H <sub>2</sub> O+(3)(i)         open chain (C) +(3)(5)H <sub>2</sub> O+(6)(i)         open chain (C) +(1)(2)H <sub>2</sub> O+(3)(i)         open chain (C) +(1)(2)H <sub>2</sub> O+(3)(i)         open chain (C) +(3)(5)H <sub>2</sub> O+(6)H <sub>2</sub> O         open chain (C) +(1)(3)H <sub>2</sub> O+(3)(4)         open chain (C) +(1)(3)H <sub>2</sub> O+(3)H <sub>2</sub> O         open chain (C) +(3)(5)H <sub>2</sub> O+(6)H <sub>2</sub> O         ope	Polymorphism				. , . ,	
VDE         2.59         2.36         2.47         2.42         2.31           Optimized Anionic structure         Open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3 +(1)(2)H <sub>2</sub> O+(2)(i ntra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(2)(i ntra)H <sub>2</sub> O         open chain (A) +(1)(2)H <sub>2</sub> O+(1)(2 h <sub>2</sub> O+(1)(2) (i ntra)H <sub>2</sub> O         open chain (A) +(1)(2)H <sub>2</sub> O+(1)(2 h <sub>2</sub> O+(1)(2) (i ntra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(1)(2 h <sub>2</sub> O+(2)(i ntra)H <sub>2</sub> O         open chain (C) h <sub>2</sub> O         open chain	ΔΕ					
Optimized Anionic structural Polymorphism         open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3) +(1)(2)H <sub>3</sub> O+(2)(i) +(1)(2)H <sub>2</sub> O+(5)(6) +(1)(2)H <sub>2</sub> O+(3)(3)H <sub>2</sub> O+(4)(5) +(1)(2)H <sub>2</sub> O+(3)(4) +(1)(3)H <sub>2</sub> O+(3)						
Anionic structural roll open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3   +(1)(2)H <sub>2</sub> O+(2)(i   tra)H <sub>2</sub> O   +(1)(2)H <sub>2</sub> O+(1)(1   tra)H <sub>2</sub> O   O   Open chain (C)   +(1)(2)H <sub>2</sub> O+(1)(1   O   O   Open chain (C)	·			<u> </u>	*	
Anionic structural roll open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3   +(1)(2)H <sub>2</sub> O+(2)(i   tra)H <sub>2</sub> O   +(1)(2)H <sub>2</sub> O+(1)(1   tra)H <sub>2</sub> O   O   Open chain (C)   +(1)(2)H <sub>2</sub> O+(1)(1   O   O   Open chain (C)					3 <b>4 3</b> 3	
Anionic structural roll open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3   +(1)(2)H <sub>2</sub> O+(2)(i   tra)H <sub>2</sub> O   +(1)(2)H <sub>2</sub> O+(1)(1   tra)H <sub>2</sub> O   O   Open chain (C)   +(1)(2)H <sub>2</sub> O+(1)(1   O   O   Open chain (C)	Optimized	• • • • • • • • • • • • • • • • • • •		9.		
Structural Polymorphism         open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3 +(1)(2)H <sub>2</sub> O+(2)(i ntra)H <sub>2</sub> O         open chain (C) +(1)(2)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O         open chain (A) +(3)H <sub>2</sub> O+(intra)H <sub>2</sub> +(1)(2)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O+(1)(3)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O+(1)(3)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O+(		Balana	9 9		7 7 7 7	• • •
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Polymorphism   Pol		<b>3</b>	8 3 3 °		<b>~</b>	2 2 2 2
Polymorphism   Pol	~ .	open chain (B)	open chain (B)	open chain (C)	open chain (A)	open chain (C)
Optimized Anionic structural Polymorphism   Optimized Anionic structure   Optimized Anionic Structural Polymorphism   Optimized Optimized Anionic Structural Polymorphism   Optimized Optimized Optimized Structural Polymorphism   Optimized O		. ,				
ΔΕ         0.32         0.33         0.35         0.35         0.36           VDE         1.97         2.27         2.24         2.33         2.39           Optimized Anionic structure           Polymorphism Polymorphism         open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2) (2) (2) (1) (2) (2) (2) (2) (2) (2) (2) (2) (2) (2	Polymorphism					
VDE         1.97         2.27         2.24         2.33         2.39           Optimized Anionic structure         Open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2) +(1)(2)H <sub>2</sub> O+(2)(i) ntra)H <sub>2</sub> O         open chain (B) +(1)(2)H <sub>2</sub> O+(5)(6) +(1)(2)H <sub>2</sub> O+(1)(3)H +(3)(5)H <sub>2</sub> O+(4)(5) +(1)(2)H <sub>2</sub> O+(4)(5)         open chain (C) +(3)(5)H <sub>2</sub> O+(4)(5) +(3)(5)H <sub>2</sub> O+(4)(5) +(3)(5)H <sub>2</sub> O+(4)(5)           VDE         2.12         2.39         2.23         1.80         2.10           Optimized Anionic structure         Open chain (B) +(1)(2)H <sub>2</sub> O+(5)(6) +(3)(5)H <sub>2</sub> O+(6)H +(3)(5)H <sub>2</sub> O+(6)H +(1)(3)H <sub>2</sub> O+(3)(4) +(1)(3)H <sub>2</sub> O+(1)(2)(10) +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O +(4)(5)H <sub>2</sub> O+(3)(4) +(1)(3)H <sub>2</sub> O+(1)(2)(10) +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O +(3)(4) +(1)(3)H <sub>2</sub> O+(1)(2)(10) +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O +(3)(4) +(3)(4)H <sub>2</sub> O+(3)(4)	ΔΕ				0.35	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						
Anionic structure         Anionic structural Polymorphism         open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2) $(2)$ $(2)$ $(2)$ $(2)$ $(2)$ $(3)$ $(2)$ $(2)$ $(3)$ $(3)$ $(2)$ $(3)$	·		·	·		
Anionic structure         Anionic structural Polymorphism         open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2) $(2)$ $(2)$ $(2)$ $(2)$ $(2)$ $(3)$ $(2)$ $(2)$ $(3)$ $(3)$ $(2)$ $(3)$		•,				2 32
Anionic structure         Anionic structural Polymorphism         open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2) $(2)$ $(2)$ $(2)$ $(2)$ $(2)$ $(3)$ $(2)$ $(2)$ $(3)$ $(3)$ $(2)$ $(3)$	Optimized	<b>3</b> 39 32	3 I a			
Structural Polymorphism         open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2 )(2) +(1)(2)H <sub>2</sub> O+(2)(i )(i )(1)(2)H <sub>2</sub> O+(5)(6)         open chain (C) +(1)(2)H <sub>2</sub> O+(1)(3)H +(3)(5)H <sub>2</sub> O+(4)(5) (6) (6) +(1)(2)H <sub>2</sub> O+(1)(3)H +(3)(5)H <sub>2</sub> O+(4)(5) (6) (6) (6) (7)(2)H <sub>2</sub> O           ΔΕ         0.36         0.37         0.38         0.38         0.42           VDE         2.12         2.39         2.23         1.80         2.10           Optimized Anionic structure           Polymorphism         open chain (B) +(1)(2)H <sub>2</sub> O+(5)(6) (6) (7)(6) (7)(6) (7)(6) (7)(7)(7)(7)(7)(7)(7)(7)(7)(7)(7)(7)(7)(				3. 4. 4. 4. 4.	و فر فر فر د	
Structural Polymorphism	structure	2200				•
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Structural Polymorphism		open chain (C)	open chain (B)	open chain (C)	open chain (C)	open chain (C)
Optimized Anionic structure						
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Polymorphism					
VDE         2.12         2.39         2.23         1.80         2.10           Optimized Anionic structure           Structural Polymorphism         open chain (B) +(1)(2)H <sub>2</sub> O+(5)(6 )H <sub>2</sub> O         open chain (C) +(3)(5)H <sub>2</sub> O+(6)H +(1)(3)H <sub>2</sub> O+(3)(4) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2)( +(3)(4)H <sub>2</sub> O+(3)H <sub>2</sub> O         γ-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(3)(4) +(3)(4)H <sub>2</sub> O+(3)(4) +(3)(4	ΔΕ	·				
Optimized Anionic structure         Applymorphism         β-pyranose (²C <sub>5</sub> -chair)         β-pyranose (²C						
Anionic structure  Anionic structure  Anionic structure  Anionic structure	<u> </u>				1	
Anionic structure  Anionic structure  Anionic structure  Anionic structure			- 4-			
Anionic structure  Anionic structure  Anionic structure  Anionic structure	Optimized	<b>6.</b> 40 5	🛂 🤰 💢 🚅 🚂	3 63	پ 😜 🥦	
structure         β-pyranose ( $^2$ C <sub>5</sub> -chair)         γ-pyranose ( $^$		22000	35 00	200	• •	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		-3 1 1 T				A)10 33
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			<b>~</b>	2-1-5		7
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$				β-pyranose ( <sup>2</sup> C <sub>5</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -
Polymorphism $+(1)(2)H_2O+(5)(6)$ $+(3)(5)H_2O+(6)H$ $+(1)(3)H_2O+(3)(4)$ $+(1)(3)H_2O+(1)(2)($ $+(3)(4)H_2O+(3)H_2$ ΔΕ $0.47$ $0.64$ $0.79$ $0.82$ $0.82$	Structural	open chain (B)	open chain (C)			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Polymorphism					
ΔE 0.47 0.64 0.79 0.82 0.82						
	ΔΕ					0.82
	VDE	2.03			0.58	
		•			•	

					I
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(1)(3)H <sub>2</sub> O+(intra )H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(4)(5)H <sub>2</sub> O+(4)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(4)(5) H <sub>2</sub> O	α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(2)(3)H <sub>2</sub> O+(1)(in tra)H <sub>2</sub> O
ΔΕ	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 <sub>4</sub> - endo) +(3)(4)H <sub>2</sub> O+ (1)(3)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(2)(3)H <sub>2</sub> O+( 3)(4)H <sub>2</sub> O	α- furanose (C <sub>4</sub> - endo) +(1)(2)H <sub>2</sub> O+ (3)(4)H <sub>2</sub> O	$\alpha$ - furanose (C <sub>4</sub> - endo) +(1)(3)H <sub>2</sub> O+ (intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(2)(3)H <sub>2</sub> O+(4)(5)H <sub>2</sub> O
ΔΕ	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 <sub>4</sub> - endo) +(1)(2)H <sub>2</sub> O+ (1)(3)H <sub>2</sub> O				
ΔΕ	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 <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O +(intra)H <sub>2</sub> O	open chain (A)+(1)(2)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O +(intra)H <sub>2</sub> O	open chain (A)+(1)(2)H <sub>2</sub> O+(1)( 3)H <sub>2</sub> O+(intra)H <sub>2</sub> O	open chain (A)+(1)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O	open chain (A)+(1)(2)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intr a)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O+( 1)(3)H <sub>2</sub> O+(2)(int ra)H <sub>2</sub> O	open chain (A)+(1)(2)H <sub>2</sub> 2O+( 2)(intra)H <sub>2</sub> O+(4)( 5)(6)H <sub>2</sub> O	open chain (A)+(1)(2)H <sub>2</sub> O+(1)( 3)H <sub>2</sub> O+(4)(5)H <sub>2</sub> O	open chain (A)+(1)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O	open chain (A)+(1)(2)H <sub>2</sub> O+( 1)(3)H <sub>2</sub> O+(4)(5)( 6)H <sub>2</sub> O
ΔΕ	0.09	0.11	0.13	0.13	0.13
VDE	2.86	2.75	2.41	3.09	2.75
Optimized Anionic structure					4 4 9 9 9 9
Structural Polymorphism	open chain (A)+(1)(intra)H <sub>2</sub>	open chain $(A)+(4)(5)(6)H_2O$	open chain $(A)+(4)(5)(6)H_2O+(6)(6)(6)H_2O+(6)(6)(6)H_2O+(6)(6)(6)H_2O+(6)(6)(6)(6)H_2O+(6)(6)(6)(6)H_2O+(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)(6)($	open chain (A)+(4)(6)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+	open chain (A)+(4)(6)(intra)
	O+(2)(intra)H <sub>2</sub> O +(4)(5)H <sub>2</sub> O	+(4)(6)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O	6)(intra) $H_2O+(2)$ (int ra) $H_2O$	$_2$ O+(2)(Intra)H <sub>2</sub> O+ (1)(intra)H <sub>2</sub> O	H <sub>2</sub> O+(4)(intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O
ΔΕ	+(4)(5)H <sub>2</sub> O 0.17	+(2)(intra)H <sub>2</sub> O 0.21	ra)H <sub>2</sub> O 0.23	(1)(intra)H <sub>2</sub> O 0.26	O+(intra)H <sub>2</sub> O 0.32
ΔE <b>VDE</b>	$+(4)(5)H_2O$	+(2)(intra)H <sub>2</sub> O	ra)H <sub>2</sub> O	(1)(intra)H <sub>2</sub> O	O+(intra)H <sub>2</sub> O
	+(4)(5)H <sub>2</sub> O 0.17	+(2)(intra)H <sub>2</sub> O 0.21	ra)H <sub>2</sub> O 0.23	(1)(intra)H <sub>2</sub> O 0.26	O+(intra)H <sub>2</sub> O 0.32
Optimized Anionic structure  Structural Polymorphism	+(4)(5)H <sub>2</sub> O 0.17 3.08 open chain (A)+(1)(intra)H <sub>2</sub> O+ (3)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O	+(2)(intra)H <sub>2</sub> O 0.21 2.84  open chain (A)+(4)(5)(6)(intr a)H <sub>2</sub> O+(3)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O	ra)H <sub>2</sub> O 0.23 2.64  open chain (C)+(1)(2)(intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O	(1)(intra)H <sub>2</sub> O 0.26 2.78 open chain (B)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+ (intra)H <sub>2</sub> O	O+(intra)H <sub>2</sub> O 0.32 2.40  open chain (B)+(1)(2)(intra) H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O+(2)(3)(intra)H <sub>2</sub> O
Optimized Anionic structure	+(4)(5)H <sub>2</sub> O 0.17 3.08 open chain (A)+(1)(intra)H <sub>2</sub> O+ (3)(intra)H <sub>2</sub> O+(i	+(2)(intra)H <sub>2</sub> O 0.21 2.84  open chain (A)+(4)(5)(6)(intr a)H <sub>2</sub> O+(3)H <sub>2</sub> O+(i	ra)H <sub>2</sub> O 0.23 2.64  open chain (C)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+(in	(1)(intra)H <sub>2</sub> O 0.26 2.78 open chain (B)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+	O+(intra)H <sub>2</sub> O 0.32 2.40  open chain (B)+(1)(2)(intra) H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O+(2)(3)(intra)H <sub>2</sub>

Polymorphism H <sub>2</sub>	3)+(1)(2)(intra)	open chain	open chain	open chain	open chain
ΔΕ	2O+(2)(intra)H 2O+(1)(3)H <sub>2</sub> O	(C)+(1)(2)(intra)H 2O+(2)(intra)H <sub>2</sub> O+ (intra)H <sub>2</sub> O	(C)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+(3 )(5)H <sub>2</sub> O	(C)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+ (1)(3)H <sub>2</sub> O	(B)+(1)(2)H <sub>2</sub> O+(1 )(2)H <sub>2</sub> O+(3)(intra )H <sub>2</sub> O
	0.38	0.38	0.39	0.41	0.42
VDE	2.36	2.36	2.51	2.58	2.18
1	1	•			
Optimized Anionic structure					
	open chain C)+(1)(2)H <sub>2</sub> O+( )(5)H <sub>2</sub> O+(4)(5) H <sub>2</sub> O	open chain (C)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+ (5)(6)H <sub>2</sub> O	open chain (B)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+(1 )(intra)H <sub>2</sub> O	open chain (C)+(1)(2)(intra)H <sub>2</sub> O+(1)(2)(intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O	open chain (A)+(4)(5)(6)H <sub>2</sub> O +(3)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O
ΔΕ	0.42	0.44	0.45	0.45	0.49
VDE	2.38	2.48	2.56	2.63	2.65
<u>.</u>					
Optimized Anionic structure					
	open chain 3)+(1)(2)H <sub>2</sub> O+( )(3)H <sub>2</sub> O+(5)(6) H <sub>2</sub> O	open chain (C)+(1)(2)H <sub>2</sub> O+(5 )(6)(intra)H <sub>2</sub> O+(in tra)H <sub>2</sub> O	open chain (B)+(1)(2)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O+(5 )(6)H <sub>2</sub> O	open chain (B)+(1)(2)H <sub>2</sub> O+(5 )(6)(intra)H <sub>2</sub> O+(in tra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(1)(3)H <sub>2</sub> O+(2)(3 )(intra)H <sub>2</sub> O+(1)(i ntra)H <sub>2</sub> O
$\Delta \mathrm{E}$	0.52	0.52	0.53	0.72	0.73
VDE	2.02	2.38	2.34	2.14	0.87
Optimized Anionic structure	3				
Structural Polymorphism +(3)	-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (3)(4)H <sub>2</sub> O+(1)( )H <sub>2</sub> O+(1)(2)(3) H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(3)(4)(intra)H <sub>2</sub> O +(3)(intra)H <sub>2</sub> O+(1 )H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(3)(4)H <sub>2</sub> O+(4)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(1)(2)(3)(intra)H <sub>2</sub> O+(1)(3)H <sub>2</sub> O+(int ra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(3)(4)H <sub>2</sub> O+(4)(i ntra)H <sub>2</sub> O+(5)(intr a)H <sub>2</sub> O
ΔΕ	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 ( <sup>2</sup> C <sub>5</sub> - chair) + +(1)(intra)H <sub>2</sub> O+( 3)(intra)H <sub>2</sub> O+(4) (5)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(1)(2)(3)H <sub>2</sub> O+(1) (3)H <sub>2</sub> O+(4)(5)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(3)(4)H <sub>2</sub> O+(1)(3)H <sub>2</sub> O+(4)(intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(3)(4)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O+(4)(5)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(4)(5)(intra)H <sub>2</sub> O +(1)(3)H <sub>2</sub> O+(5)(i ntra)H <sub>2</sub> O
ΔΕ	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 <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+( 4)(intra)H <sub>2</sub> O+(in tra)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+(4 )(intra)H <sub>2</sub> O+(1)(2) H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) +(1)(3)(intra)H <sub>2</sub> O+( 3)(intra)H <sub>2</sub> O+(intra) H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+(3 )(intra)H <sub>2</sub> O+(4)(in tra)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) +(1)(3)(intra)H <sub>2</sub> O +(intra)H <sub>2</sub> O+(3)(4 )H <sub>2</sub> O
ΔΕ	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 <sub>4</sub> - endo) +(1)(2)H <sub>2</sub> O+(1)( 3)H <sub>2</sub> O+(3)(4)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) +(1)(2)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O+(3 )(intra)H <sub>2</sub> O			
ΔΕ	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 <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
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	open chain (A) +	open chain (A) +	open chain (A) +	open chain (A) +	open chain (A) +
Structural Polymorphism	(1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O 0.26	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O 0.26	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.27	open chain (A) + (1)(2)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 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 <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.28	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.28	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.29	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.30	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.30

VDE	2.87	2.39	2.68	3.25	2.64
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O + (intra)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O +	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(6)H <sub>2</sub> O +	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O +	open chain (A) + (2)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +
	(intra)H <sub>2</sub> O	$(4)(5)(6)H_2O$	$+(4)(5)(6)H_2O$	$(4)(5)H_2O$	$(4)(5)(6)H_2O$
ΔΕ	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 <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	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 <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O
ΔΕ	0.44	0.46	0.48	0.49	0.51
VDE	2.24	2.59	2.77	3.06	2.36
Optimized Anionic structure			GP.		
Structural Polymorphism	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +	open chain (C) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +

	(4)(6)(intra)H <sub>2</sub> O	(2)(intra)H <sub>2</sub> O +	(5)(6)H <sub>2</sub> O +	(3)(5)(intra)H <sub>2</sub> O +	(intra)H <sub>2</sub> O +
	+ (intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(6)(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(5)H <sub>2</sub> O + (4)(6)H <sub>2</sub> O	open chain (A) + (3)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (3)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O
ΔΕ	0.60	0.60	0.61	0.61	0.65
VDE	2.78	2.83	2.57	2.88	2.55
Optimized Anionic structure					9
Structural Polymorphism	open chain (C) + (1)(2)H <sub>2</sub> O + (3)(5)H <sub>2</sub> O + (5)(6)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(3)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (3)(4)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(2)(3)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O
ΔΕ	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 ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(3)H <sub>2</sub> O + (3)(4)(intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O + (intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(2)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) + (3)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
ΔΕ	0.99	1.00	1.03	1.05	1.05
VDE	1.18	1.03	1.00	0.87	1.45
1					

Optimized Anionic structure					
Structural Polymorphism	α-furanose (C <sub>4</sub> - endo) + (3)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 1.07	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(2)(3)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) + (1)(3)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(6)H <sub>2</sub> O 1.07	α-furanose (C <sub>4</sub> - endo) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(3)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O + (intra)H <sub>2</sub> O
VDE	1.35	1.28	1.37	0.98	0.86
Optimized Anionic structure					
WStructural Polymorphism	α-furanose (C <sub>4</sub> - endo) + (1)(3)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) + (1)(3)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	$\begin{array}{c} \alpha\text{-furanose} \ (C_4\text{-}\\ \text{endo}) \ + \\ (3)(\text{intra})H_2O \ + \\ (3)(\text{intra})H_2O \ + \\ (4)(\text{intra})H_2O \ + \\ (\text{intra})H_2O \end{array}$	$\begin{array}{c} \alpha\text{-furanose} \ (C_4\text{-}\\ \text{endo}) \ +\\ (1)(3)(\text{intra})H_2O \ +\\ (3)(\text{intra})H_2O \ +\\ (\text{intra})H_2O \ +\\ (\text{intra})H_2O \end{array}$	$\begin{array}{c} \alpha\text{-furanose} \ (C_4\text{-}\\ \text{endo}) \ + \\ (1)(\text{intra})H_2O \ + \\ (2)(\text{intra})H_2O \ + \\ (3)(\text{intra})H_2O \ + \\ (\text{intra})H_2O \end{array}$
ΔE <b>VDE</b>	1.20 1.23	1.22 <b>1.16</b>	1.22 <b>1.08</b>	1.22 1.23	1.45 <b>0.98</b>

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 <u>AE</u>	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (2)H <sub>2</sub> O 0.08	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O 0.10	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O
VDE	2.97	3.09	3.22	3.12	3.14
Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(3)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O +	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +
Polymorphism	(1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	+ (1)(2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
Polymorphism	(1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	$(1)(2)(intra)H_2O + (1)(intra)H_2O + (2)(intra)H_2O + (intra)H_2O + (intra)H_2O$	(1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	+ (1)(2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
Polymorphism $\Delta E$	(1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	+ (1)(2)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O

	(1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	$(2)(intra)H_2O + (intra)H_2O + (1)(3)H_2O + (4)(5)(6)H_2O$	(1)(2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +	$(2)(intra)H_2O +  (1)(2)(3)H_2O +  (intra)H_2O +  (intra)H_2O$
				(intra)H <sub>2</sub> O	
ΔΕ	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 <sub>2</sub> O + (1)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	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 <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(intra) $H_2O$ + (2)(intra) $H_2O$ + (4)(intra) $H_2O$ + (intra) $H_2O$ + (intra) $H_2O$
ΔΕ	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 <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O +	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O
	(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	$(intra)H_2O + (4)(5)(6)H_2O$	$(4)(5)(6)H_2O + (intra)H_2O$	+ (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	+ (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
ΔΕ	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 ΔE	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O + (4)(6)H <sub>2</sub> O 0.32	open chain (A) + (1)(2)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O 0.33	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.33	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O 0.33	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.33
ΔE <b>VDE</b>	3.15	2.78	3.09	3.36	3.35
VDE	3.13	4.10	3.03	3.30	3.33

Optimized Anionic structure					
Structural Polymorphism	open chain (A) + (1)(2)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (A) + (1)(2)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (5)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (2)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O
ΔΕ	0.35	0.36	037	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 <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(2)(3)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O
ΔΕ	0.38	0.38	0.38	0.39	0.40
	0.50	0.50	0.50	0.37	U. TU
VDE	3.67	3.38	2.67	2.91	2.99

Optimized Anionic structure					
Structural Polymorphism	open chain (C) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.39	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (5)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.40	open chain (A) + (1)(3)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O 0.42	open chain (A) + (2)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (4)(5)(6)(intra)H 2O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.43	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (4)(5)(6)(intra)H <sub>2</sub> O O + (intra)H <sub>2</sub> O 0.44
VDE	2.71	3.50	2.44	3.21	3.14
			<del></del>	<u>,</u>	
Optimized Anionic structure				<b>2 0 0 0 0 0 0 0 0 0 0</b>	E=-1069.105750
Structural Polymorphism	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(6)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	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 <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O
ΔΕ	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 <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.53	open chain (A) + (1)(3)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(6)(intra)H <sub>2</sub> O O + (intra)H <sub>2</sub> O 0.53	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O 0.55	open chain (C) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O 0.55	open chain (C) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O 0.55
VDE	2.56	2.42	2.61	2.73	2.45
Optimized Anionic structure					

Structural Polymorphism <u>AE</u> <b>VDE</b>	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O 0.56 3.11	open chain (C) + (1)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O  0.56  2.54	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (3)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O  0.57  2.84	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O 0.59 2.51	open chain (C) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O  0.61  2.44
Optimized Anionic structure					
Structural Polymorphism	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O	open chain (B) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O	open chain (C) + (1)(2)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O + (3)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O +	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(3)(intra)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (3)(4)H <sub>2</sub> O + (2)(3)(intra)H <sub>2</sub> O + (1)(3)(intra)(intra )H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O
ΔΕ	0.62	0.64	0.65	0.95	0.96
VDE	2.51	2.64	2.94	1.09	1.08
Optimized Anionic structure	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) + (2)(3)(intra)H <sub>2</sub> O +	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) + (2)(3)(intra)H <sub>2</sub> O +	α-furanose (C <sub>4</sub> - endo) + (3)(intra)H <sub>2</sub> O +	-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) + (1)(2)(3)H <sub>2</sub> O +	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) + (2)(3)(intra)H <sub>2</sub> O
Polymorphism $\Delta E$	(1)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (3)(4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(4)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (3)(4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	+ (1)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (free)H <sub>2</sub> O
VDE	1.04	1.49	1.38	1.05	1.39
Optimized Anionic					
Structure  Structural Polymorphism	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(3)(intra)H <sub>2</sub> O + (3)(4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) + (3)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) + (1)(3)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (4)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	α-furanose (C <sub>4</sub> - endo) + (3)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(2)(3)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O +

					(intra)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O
ΔΕ	1.02	1.04	1.04	1.04	1.08
VDE	1.38	1.43	1.24	1.33	1.24
Optimized Anionic structure					
	α-furanose (C <sub>4</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -		α-furanose (C <sub>4</sub> -	α-furanose (C <sub>4</sub> -
	endo) +	chair) +	$\beta$ -pyranose ( ${}^{2}C_{5}$ -	endo) +	endo) +
Structural	$(1)(3)(intra)H_2O +$	$(1)(2)(3)H_2O +$	chair) + $(2)(3)H_2O$	$(3)(intra)H_2O +$	$(3)(intra)H_2O +$
Polymorphism	$(3)(intra)H_2O +$	$(1)(intra)H_2O +$	$+(1)(intra)H_2O +$	$(3)(intra)H_2O +$	$(3)(intra)H_2O +$
Torymorphism	(intra)H <sub>2</sub> O +	$(3)(intra)H_2O +$	$(1)(3)H_2O +$	$(4)(intra)H_2O +$	$(4)(intra)H_2O +$
	(intra)H <sub>2</sub> O +	$(intra)H_2O +$	$(3)(4)H_2O +$	$(6)(intra)H_2O +$	$(6)(intra)H_2O +$
	$(4)(6)H_2O$	$(3)(4)H_2O$	$(4)(5)H_2O$	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔΕ	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				
	α-furanose (C <sub>4</sub> -	α-furanose (C <sub>4</sub> -	$\alpha$ -furanose (C <sub>4</sub> -		
	endo) +	endo) +	endo) +		
Structural	$(3)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$		
Polymorphism	$(4)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(1)(3)(intra)H_2O +$		
	$(6)(intra)H_2O +$	$(3)(intra)H_2O +$	$(3)(intra)H_2O +$		
	(intra)H <sub>2</sub> O +	$(intra)H_2O +$	$(intra)H_2O +$		
	(intra)H <sub>2</sub> O	$(4)(6)H_2O$	$(4)(6)H_2O$		
ΔΕ	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	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	α- furanose (C <sub>4</sub> -			
Polymorphism	chair) $+(2)(3)H_2O$	chair) $+(3)(4)H_2O$	chair) $+(4)(5)H_2O$	chair) $+(1)(3)H_2O$	endo) $+(1)(3)H_2O$
ΔE (eV)	0.00	0.01	0.05	0.08	0.12
Optimized Neutral structure					
Structural	Open chain (A)	Open chain (C)	Open chain (A)	Open chain (A)	Open chain (A)
Polymorphism	$+(1)(2)H_2O$	$+(5)(6)H_2O$	$+(4)(6)H_2O$	$+(1)(2)H_2O$	$+(3)H_2O$
$\Delta E (eV)$	0.15	0.16	0.18	0.20	0.21
Optimized Neutral structure					
Structural	α- furanose (C <sub>4</sub> -	Open chain (B)	Open chain (C)	α- furanose (C <sub>4</sub> -	Open chain (C)
Polymorphism	endo) $+(1)(2)H_2O$	$+(5)(6)H_2O$	$+(3)(5)H_2O$	endo) $+(3)(4)H_2O$	$+(1)(2)H_2O$
ΔE (eV)	0.22	0.23	0.24	0.25	0.25
Optimized Neutral structure					
Structural Polymorphism	Open chain (B) +(1)(2)H <sub>2</sub> O				
$\Delta E \text{ (eV)}$	0.30				
\ /	1				

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<sup>-</sup> 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.

	Т				T- 1
Optimized Neutral structure	5		9.33		
Structural Polymorphis m	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(1)(3)(intra)H <sub>2</sub> O +(3)(intra)H <sub>2</sub> O	open chain (A) +(2)(intra)H <sub>2</sub> O+(1 )(4)(intra)H <sub>2</sub> O	open chain (B) +(1)(intra)H <sub>2</sub> O+(2)(int ra)H <sub>2</sub> O	open chain (C) +(2)(intra)H <sub>2</sub> O+(1)( 4)(intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(2)(3)(intra)H <sub>2</sub> O +(1)(intra)H <sub>2</sub> O
ΔE (eV)	0.00	0.05	0.06	0.07	0.08
Optimized Neutral structure					96 (E)
Structural Polymorphis m  ΔE (eV)	open chain (A) +(1)(intra)H <sub>2</sub> O+(2 )(intra)H <sub>2</sub> O 0.11	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(4)(5)H <sub>2</sub> O+(3)(4 )H <sub>2</sub> O 0.12	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(2)H <sub>2</sub> O+(4)(5)H <sub>2</sub> O 0.14	open chain (A) +(1)(2)H <sub>2</sub> O+(1)(3)H <sub>2</sub> O 0.16	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(1)(2)H <sub>2</sub> O+(3)(4)  H <sub>2</sub> O 0.18
ΔE (ev)	0.11	0.12	0.14	0.10	0.16
Optimized Neutral structure				<u> </u>	
Structural Polymorphis m	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(1)(3)H <sub>2</sub> O+(3)(4 )H <sub>2</sub> O	open chain (A) +(6)(intra)H <sub>2</sub> O+(4 )(intra)H <sub>2</sub> O	β-pyranose ( ${}^2C_5$ -chair) +(1)(3)H $_2$ O+(4)(5)H $_2$ O	$\alpha$ - furanose (C <sub>4</sub> - endo) +(1)(2)H <sub>2</sub> O+ (1)(3)H <sub>2</sub> O	open chain (C) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O
ΔE (eV)	0.21	0.21	0.21	0.21	0.23
Optimized Neutral structure	<u>ڡ</u> ۿ؞؞ۣڎٷٷٷٷ؞؞				
Structural Polymorphis m ΔE (eV)	open chain (C) +(1)(intra)H <sub>2</sub> O+(2 )(intra)H <sub>2</sub> O 0.23	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(1)(2 )(3)H <sub>2</sub> O 0.24	open chain (B) +(1)(intra)H <sub>2</sub> O+(2)(int ra)H <sub>2</sub> O 0.25	open chain (A) +(4)(6)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O 0.27	open chain (B) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O 0.29
(CV)	1 0.20	··		0.27	
Optimized Neutral structure					
Structural Polymorphis m	α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O	open chain (A) +(1)(2)H <sub>2</sub> O+(5)(6 )H <sub>2</sub> O	α- furanose (C <sub>4</sub> -endo) +(1)(2)H <sub>2</sub> O+ (3)(4)H <sub>2</sub> O	open chain (C) +(3)(5)H <sub>2</sub> O+(5)(6)H <sub>2</sub> O	open chain (C) +(5)(intra)H <sub>2</sub> O+(4 )(intra)H <sub>2</sub> O

ΔE (eV)	0.30	0.31	0.32	0.33	0.34
Optimized					
Neutral structure	3 9		<u>•</u>	<b>6</b>	
Structural Polymorphis m	open chain (A) +(3)H <sub>2</sub> O+(5)(6)H <sub>2</sub> O	open chain (A) +(3)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O	open chain (A) +(1)(2)H <sub>2</sub> O+(1)H <sub>2</sub> O	open chain (C) +(3)(5)H <sub>2</sub> O+(1)(2)H <sub>2</sub> O	α- furanose (C <sub>4</sub> - endo) +(3)(4)H <sub>2</sub> O+ (1)(3)H <sub>2</sub> O
ΔE (eV)	0.35	0.38	0.39	0.39	0.40
Optimized Neutral structure					
Structural Polymorphis m	open chain (A) +(1)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O	open chain (B) +(1)(2)H <sub>2</sub> O+(5)(6 )H <sub>2</sub> O	open chain (C) +(1)(2)H <sub>2</sub> O+(5)(6)H <sub>2</sub>		
$\Delta E (eV)$	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<sup>-</sup> 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.

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Ontimizad				3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	s 4 🚰 🚁
Optimized Neutral				33 3 9 3 9 3	
structure	3 0	3	<b></b>	3	902.2.5
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -				β-pyranose ( <sup>2</sup> C <sub>5</sub> -
	chair) +	open chain	open chain	open chain	chair) +
	$+(1)(3)(intra)H_2O+($	$(A)+(1)(2)(intra)H_2$	(C)+(1)(4)(intra)H	$(C)+(1)(4)(intra)H_2$	+(2)(3)(intra)H2O
Structural	$1)(3)(intra)H_2O+(in$	$O+(1)(intra)H_2O+(4$	$_2O+(2)(intra)H_2O$	$O+(2)(intra)H_2O+(i$	+(1)(intra)H <sub>2</sub> O+(
Polymorphism	tra)H <sub>2</sub> O	)(intra)H <sub>2</sub> O	+(intra)H <sub>2</sub> O	ntra)H <sub>2</sub> O	1)(3)(intra)H <sub>2</sub> O
ΔE (eV)	0.00	0.05	0.08	0.08	0.09
	1				
	<b>9 9</b>	ě.	3. P 10		<b>4</b>
Optimized		<b>∞</b> • • • • • • • • • • • • • • • • • • •			3000
Neutral	9 🔨 🚱	3 76 30 32	9	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
structure		300		<b>6</b>	3 3 30
			'		
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -		β-pyranose ( <sup>2</sup> C <sub>5</sub> -		
	chair) +	open chain	chair) +	open chain	open chain
	$+(1)(3)(intra)H_2O+($	$(A)+(1)(intra)H_2O+$	$+(1)(3)(intra)H_2O$	$(A)+(1)(intra)H_2O+($	$(A)+(1)(intra)H_2$
Structural	$3)(intra)H_2O+(4)(in$	$(2)(intra)H_2O+(intr$	+(3)(4)(intra)H2O	$2)(intra)H_2O+(3)(int$	$O+(2)(intra)H_2O$
Polymorphism	tra)H <sub>2</sub> O	a)H <sub>2</sub> O	$+(1)H_2O$	ra)H <sub>2</sub> O	$+(1)(4)H_2O$
ΔE (eV)	0.14	0.14	0.14	0.15	0.16
				3- 3	
	•				•
Optimized		<b>79</b>			
Neutral		• • •			9 9 36
structure			<b>6</b>	<u>ه م</u>	• •
			α-furanose (C <sub>4</sub> -	open chain	
	open chain	$\alpha$ -furanose (C <sub>4</sub> -	endo)	$(A)+(1)(3)(intra)H_2$	open chain
	$(C)+(1)(2)H_2O+(1)($	endo)	$+(4)(intra)H_2O+(4$	O+	$(A)+(1)(intra)H_2$
Structural	intra) $H_2O+(4)$ (intra	$+(3)(4)H_2O+(4)(6H$	$)(6)(intra)H_2O+(in$	$(3)(intra)H_2O+(intra)$	$O+(1)(intra)H_2O$
Polymorphism	)H <sub>2</sub> O	<sub>2</sub> O+(3)(6)H <sub>2</sub> O	tra)H <sub>2</sub> O	)H <sub>2</sub> O	+(intra)H <sub>2</sub> O
ΔE (eV)	0.16	0.17	0.21	0.23	0.24
		-			T
		\$ 330	P	<u>.</u>	
Optimized		3 × 🚅			
Neutral			1 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	<b>10</b>	3
structure		To francisco (C			0,
	oman ahain	$\alpha$ -furanose (C <sub>4</sub> -	onan ahain	onan ahain	β-pyranose ( <sup>2</sup> C <sub>5</sub> -
	open chain (B)+(1)(2)(intra)H <sub>2</sub>	endo) +(1)(3)(intra)H <sub>2</sub> O+(	open chain (A)+(1)(intra)H <sub>2</sub> O	open chain (B)+(1)(intra)H2O+	chair) + +(3)(4)H <sub>2</sub> O+(1)(
CA	$O+(1)(2)(1ntra)H_2$ O+(1)(intra)H <sub>2</sub> O+(	$+(1)(3)(intra)H_2O+(intra)(3)(4)(intra)H_2O+(intra)(3)(4)(intra)(4)(4)(intra)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)$	$+(2)(intra)H_2O+(5)$	(B)+(1)(Intra)H2O+ (2)(intra)H <sub>2</sub> O+(intra	+(3)(4)H2O+(1)(3)H2O+(4)(5)H2
Structural Polymorphism	$3$ )(intra) $H_2O+($	tra)H <sub>2</sub> O+(III	$+(2)(IIIIa)H_2O+(3)$ $)(6)H_2O$	$(2)(\text{intra})H_2O+(\text{intra})H_2O$	0
$\Delta E (eV)$	0.26	0.26	0.29	0.30	0.30
<u> </u>	0.20	0.20	0.27	0.50	0.50
	2	•		<u> </u>	
	***************************************		🕶 👵 🤏 🍎	<b>.</b>	
Optimized				2 1 1 1 5 T	
Neutral	<b>1</b>	9	3	3 39 39	
structure	open chain	· [6]	open chain	open chain	
	open chain $(B)+(1)(2)H_2O+(1)($	α-furanose (C <sub>4</sub> -	open chain $(A)+(1)(2)H_2O+(1)$	open chain $(A)+(4)(6)(intra)H_2$	β-pyranose ( <sup>2</sup> C <sub>5</sub> -
Structural	$(B)+(1)(2)H_2O+(1)(1)$ intra)H <sub>2</sub> O+(3)(intra	endo)	$(A)+(1)(2)H_2O+(1)$ $)(3)H_2O+(4)(5)(6)$	$O+(4)(intra)H_2O+(i$	chair) +
Polymorphism	)H <sub>2</sub> O	$+(1)(3)(intra)H_2O+($	$H_2O$	$0+(4)(IIIIa)H_2O+(IIIIa)H_2O$	$+(1)(2)(3)H_2O+($
1 orymorphism	<i>)</i> 112O	- (1)(5)(IIIIa)H2O+(	1120	111111111111111111111111111111111111111	+(1)(2)(3)112O+(

		3)(6)(intra)H <sub>2</sub> O+(in			1)(3)H <sub>2</sub> O+(4)(5)
ΔE (eV)	0.31	tra)H <sub>2</sub> O 0.32	0.34	0.35	H <sub>2</sub> O 0.35
, ,	1		T		
Optimized Neutral structure					
Structural Polymorphism	open chain (B)+(1)(intra)H <sub>2</sub> O+ (2)(intra)H <sub>2</sub> O+(1)(3 )H <sub>2</sub> O 0.37	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) + +(3)(4)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O+(1)(2)(3)H <sub>2</sub> O 0.37	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(1)(intra)H <sub>2</sub> O+(3 )(intra)H <sub>2</sub> O+(4)(5) H <sub>2</sub> O 0.39	open chain (C)+(1)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) H <sub>2</sub> O 0.39	α-furanose (C <sub>4</sub> - endo) +(1)(2)(intra)H <sub>2</sub> O +(1)(3)(intra)H <sub>2</sub> O +(3)(intra)H <sub>2</sub> O 0.39
ΔE (eV)	0.57	0.57	0.39	0.39	0.39
Optimized Neutral structure					
Structural Polymorphism	open chain (C)+(1)(intra)H <sub>2</sub> O+ (2)(intra)H <sub>2</sub> O+(1)(3 )H <sub>2</sub> O	open chain (A)+(1)(2)(intra)H <sub>2</sub> O+(1)(3)(intra)H <sub>2</sub> O +(intra)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(3)(4)H <sub>2</sub> O+(4)(in tra)H <sub>2</sub> O+(5)(intra) H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + +(4)(5)(intra)H <sub>2</sub> O+( 1)(3)H <sub>2</sub> O+(intra)H <sub>2</sub> O	open chain (B)+(1)(intra)H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O +(5)(6)H <sub>2</sub> O
ΔE (eV)	0.40	0.42	0.42	0.42	0.42
Optimized Neutral structure			?		
Structural Polymorphism ΔE (eV)	open chain (A)+( 5)(6)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(2)(intr a)H <sub>2</sub> O 0.45	open chain (A)+(1)(2)H <sub>2</sub> O+(1)( 3)H <sub>2</sub> O+(4)(5)H <sub>2</sub> O 0.45	α-furanose (C <sub>4</sub> - endo) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O+(3)(4)H <sub>2</sub> O 0.46	open chain (C)+(1)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(5)(6) H <sub>2</sub> O 0.47	open chain (B)+(1)(2)H <sub>2</sub> O+( 1)(3)H <sub>2</sub> O+(5)(6) H <sub>2</sub> O 0.47
Optimized Neutral structure					
Structural Polymorphism ΔE (eV)	open chain (B)+(1)(2)H <sub>2</sub> O+(5)( 6)(intra)H <sub>2</sub> O+(5)(6) (intra)H <sub>2</sub> O 0.47	open chain (B)+(1)(intra)H <sub>2</sub> O+ (2)(intra)H <sub>2</sub> O+(1)(i ntra)H <sub>2</sub> O 0.53	open chain (A)+(5)(6)(intra)H <sub>2</sub> O+(5)(intra)H <sub>2</sub> O +(3)H <sub>2</sub> O 0.57	open chain (A)+(5)(6)(intra)H <sub>2</sub> O+(4)(6)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O 0.58	open chain (A)+(4)(6)H <sub>2</sub> O+( 3)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.60
Optimized Neutral structure					

		open chain	open chain	
	open chain	$(A)+(1)(2)(intra)H_2$	$(C)+(1)(2)H_2O+(5)$	
Structural	$(C)+(1)(2)H_2O+(4)$	$O+(intra)H_2O+(4)(5)$	)(6)H2O+(intra)H2	
Polymorphism	$H_2O+(5)H_2O$	)H <sub>2</sub> O	0	
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<sup>-</sup> 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.

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			<b>34</b>	و 🔞 🐧 م	2 • ° 0
0	•				
Optimized Neutral		9 0	300	<u>♦</u> • • • • • • • • • • • • • • • • • • •	300
structure	9 c 2 c 6	<u>•</u>			<b>9</b>
5414404410	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -			
	chair) +	chair) +	open chain (C) +	open chain (A) +	open chain (A) +
	$(1)(3)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$
	$(3)(intra)H_2O +$	$(3)(4)H_2O +$	$(2)(intra)H_2O +$	$(3)(intra)H_2O +$	$(3)(intra)H_2O +$
Structural	(intra)H <sub>2</sub> O +	$(4)(intra)H_2O +$	$(4)(intra)H_2O +$	$(3)(intra)H_2O +$	$(3)(intra)H_2O +$
Polymorphism	$(1)(2)(intra)H_2O$	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔE (eV)	0.00	0.14	0.19	0.25	0.25
	T		T		
	• <b>*</b>				<b>₃</b> 🍠 💣
			•	<b>△</b> ~ <b>△</b>	
Optimized		3 6 6			
Neutral		3		90.30	
structure		<u> </u>	<u> </u>		
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -			β-pyranose ( <sup>2</sup> C <sub>5</sub> -	α-furanose (C <sub>4</sub> -
	chair) +	open chain (C) +	open chain (A) +	chair) +	endo) +
	$(1)(intra)H_2O +$	$(1)(4)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(2)(3)(intra)H_2O$	$(3)(4)H_2O +$
	$(3)(4)(intra)H_2O +$	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$	$+ (1)(3)(intra)H_2O +$	$(4)(intra)H_2O +$
Structural	(4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	$(intra)H_2O +$	(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(6)(intra)H <sub>2</sub> O + (intra)(intra)H <sub>2</sub> O
Polymorphism ΔE (eV)	0.26	(1)(3)H <sub>2</sub> O 0.27	0.31	0.31	0.32
ΔΕ (ΕΥ)	0.20	0.27	0.31	0.31	0.32
			₹		
	A 4 19 1				
Optimized					
Neutral					
structure	> <b>6</b>	9 3 2	<b>5</b> 5	3 2	95 6 565
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -		α-furanose (C <sub>4</sub> -	
	chair) +	chair) +	open chain (C) +	endo) +	open chain (A) +
	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(4)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(2)(intra)H_2O$
	$(2)(3)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$	$+(1)(intra)H_2O +$
Structural	$(1)(3)(intra)H_2O +$	$(2)(intra)H_2O +$	(intra)H <sub>2</sub> O +	$(3)(intra)H_2O +$	$(3)(intra)H_2O +$
Polymorphism	$(4)(5)H_2O$	$(3)(4)(intra)H_2O$	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔE (eV)	0.36	0.37	0.39	0.40	0.42
			<u> </u>	•	
		• • • • • • • • • • • • • • • • • • •			
			<b>6</b>		9 9 7
Optimized		3			9
Neutral				<b>3</b> € <b>3</b> €	9 6 3 3
structure	<b>1</b> 2 2	<b>I</b>		<b>-</b>	<b>**</b> 9 • 9
				α-furanose (C <sub>4</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -
	open chain (A) +	open chain (A) +	open chain (A) +	endo) +	chair) +
	$(1)(intra)H_2O +$	$(3)(6)H_2O +$	$(1)(intra)H_2O +$	$(3)(intra)H_2O +$	$(1)(2)H_2O +$
	$(1)H_2O +$	$(4)(5)H_2O +$	$(1)(intra)H_2O +$	$(3)(intra)H_2O +$	$(1)(intra)H_2O +$
Structural	$(2)(intra)H_2O +$	$(4)(intra)H_2O +$	$(2)(intra)H_2O +$	$(4)(intra)H_2O +$	$(4)(intra)H_2O +$
Polymorphism	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(3)(4)H_2O$
$\Delta E (eV)$	0.42	0.42	0.42	0.43	0.43
i					

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

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Optimized Neutral structure					
Structural Polymorphism ΔE (eV)	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) + (1)(2)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O 0.64	α-furanose (C <sub>4</sub> - endo) + (1)(3)(intra)H <sub>2</sub> O + (3)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.65	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(6)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O 0.65	open chain (A) + (3)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O  0.65	open chain (A) + (1)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.66
Optimized Neutral structure					
Structural Polymorphism ΔE (eV)	α-furanose (C <sub>4</sub> - endo) + (1)(3)H <sub>2</sub> O + (3)(6)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(6)H <sub>2</sub> O  0.67	open chain (A) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (4)(5)(6)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.67	open chain (A) + (1)(2)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O 0.70	open chain (C) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O	open chain (A) + (1)(2)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O 0.72
Optimized Neutral structure					
Structural Polymorphism ΔE (eV)	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.72	α-furanose (C <sub>4</sub> - endo) + (1)(2)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (3)(4)H <sub>2</sub> O 0.72	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (1)(3)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (5)(6)H <sub>2</sub> O 0.73	open chain (B) + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.73	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (1)(3)H <sub>2</sub> O + (4)(5)H <sub>2</sub> O 0.78
Optimized Neutral structure					
Structural Polymorphism  ΔE (eV)	open chain (A) + (1)(3)(intra)H <sub>2</sub> O + (1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.81	open chain (C) + (1)(2)H <sub>2</sub> O + (3)(5)H <sub>2</sub> O + (5)(6)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O 0.82	α-furanose (C <sub>4</sub> - endo) + (1)(3)H <sub>2</sub> O + (3)(intra)H <sub>2</sub> O + (4)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O 0.82	open chain (A) + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (4)(5)(intra)H <sub>2</sub> O + (6)(intra)H <sub>2</sub> O 0.88	open chain (C) + (1)(2)(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O + (3)(5)H <sub>2</sub> O + (4)H <sub>2</sub> O 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<sup>-</sup> parent anions. For open chain structures (1)C to (6)C

is ordered from left to right.	. For both furanose a	nd pyranose structure	s (1)C to (6)C is ordere	d from right to left in a
clockwise direction.				

	T				
Optimized Neutral structure					
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -				
	chair) +	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	α-furanose (C <sub>4</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -
	$(1)(3)(intra)H_2O +$	chair) +	chair) +	endo) +	chair) +
	$(intra)H_2O +$	$(1)(2)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(4)(intra)H_2O +$	$(1)(intra)H_2O +$
	$(intra)H_2O +$ $(intra)H_2O +$	$(3)(intra)H_2O +$	$(1)(3)(11114)H_2O + (1)(11114)H_2O + (1)(11114)H_2O + (1)(1114)H_2O + (1)(114)H_2O + (1)(114)H$	$(4)(intra)H_2O + (4)(intra)H_2O +$	$(1)(intra)H_2O + (1)(intra)H_2O +$
		` ' ` '	` / ` /	, , , ,	` ' ' '
	$(1)(2)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(3)(intra)H_2O +$	$(6)(intra)H_2O +$	$(3)(intra)H_2O +$
Structural	$(3)(4)H_2O$	(intra)H <sub>2</sub> O +	(intra)H <sub>2</sub> O +	$(3)(6)(intra)H_2O +$	(intra)H <sub>2</sub> O +
Polymorphism		(4)(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(3)(4)H_2O$
ΔE (eV)	0.00	0.02	0.02	0.05	0.09
	T		T		Γ
Optimized Neutral structure					
	α-furanose (C <sub>4</sub> -				
	endo) +	pyranose ( <sup>2</sup> C <sub>5</sub> -	open chain (C) +	open chain (A) +	open chain (A) +
	$(3)(intra)H_2O +$	chair) + $(1)(2)$ H <sub>2</sub> O	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(3)(intra)H_2O$
	$(4)(intra)H_2O +$	$+ (1)(intra)H_2O +$	$(2)(intra)H_2O +$	$(3)(intra)H_2O +$	$+ (1)(intra)H_2O +$
	$(6)(intra)H_2O +$	$(4)(intra)H_2O +$	$(4)(intra)H_2O +$	$(intra)H_2O +$	$(4)(intra)H_2O +$
Structural	$(intra)H_2O +$	$(3)(4)H_2O +$	$(intra)H_2O +$	$(intra)H_2O + (intra)H_2O +$	$(5)(intra)H_2O +$
				, ,	
Polymorphism	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔE (eV)	0.10	0.10	0.11	0.12	0.12
	1		_		
Optimized Neutral structure					
			β-pyranose ( <sup>2</sup> C <sub>5</sub> -		α-furanose (C <sub>4</sub> -
	open chain (A) +	open chain (A) +	chair) +	open chain (A) +	endo) +
	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(2)(3)(intra)H_2O +$	$(1)(2)(intra)H_2O +$	$(3)(intra)H_2O +$
	$(4)(intra)H_2O +$	$(2)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(4)(intra)H_2O +$	$(3)(intra)H_2O +$
	(intra)H <sub>2</sub> O +	$(3)(intra)H_2O +$	$(3)(4)(intra)H_2O +$	$(intra)H_2O +$	$(4)(intra)H_2O +$
Structural	$(intra)H_2O +$	$(intra)H_2O +$	$(4)(intra)H_2O +$	$(intra)H_2O +$	$(6)(intra)H_2O +$
Polymorphism	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(intra)H_2O$	(intra)H <sub>2</sub> O
$\Delta E \text{ (eV)}$	0.14	0.15	0.19	0.20	0.23
ΔΕ (ΕΥ)	0.14	0.13	0.17	0.20	0.23
				40 2	
Optimized Neutral structure					
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -				
	chair) +	open chain (C) +	open chain (A) +	open chain (C) +	open chain (A) +
	$(1)(3)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(4)(intra)H_2O +$	$(1)(intra)H_2O +$
	$(1)(intra)H_2O +$	$(2)(intra)H_2O +$	$(1)(2)(intra)H_2O +$	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$
1			, , , , = , , , , , , , , , , , , , , ,	(=)(u,ı.12O	(2)(11111111111111111111111111111111111
				$(intra)H_2O +$	(intra)H₂O +
Stemature 1	$(2)(3)(intra)H_2O +$	$(3)H_2O +$	$(3)(intra)H_2O +$	$(intra)H_2O + (intra)H_2O +$	(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O +
Structural Polymorphism				$(intra)H_2O + (intra)H_2O + (1)(3)H_2O$	$(intra)H_2O +  (intra)H_2O +  (intra)H_2O$

ΔE (eV)	0.23	0.23	0.26	0.26	0.26
	<u>.</u>				
		3. a.			
Optimized					
Neutral structure					
Structure		α-furanose (C <sub>4</sub> -	α-furanose (C <sub>4</sub> -		
	open chain (C) +	endo) +	endo) +	open chain (A) +	open chain (B) +
	$(1)(4)(intra)H_2O + (1)(3)(intra)H_2O$	$(1)(3)(intra)H_2O + (3)(intra)H_2O +$	$(3)(intra)H_2O + (4)(intra)H_2O +$	$(1)(intra)H_2O + (1)(intra)H_2O +$	(1)(intra)H <sub>2</sub> O + (2)(intra)H <sub>2</sub> O +
	$+(2)(intra)H_2O +$	$(3)(6)(intra)H_2O +$	$(6)(intra)H_2O +$	(2)(intra)H2O +	$(1)(3)(intra)H_2O$
Structural	$(3)(intra)H_2O +$	$(6)(intra)H_2O +$	$(6)(intra)H_2O +$	(intra)H <sub>2</sub> O +	$+(3)(intra)H_2O +$
Polymorphism	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔE (eV)	0.27	0.27	0.29	0.31	0.33
			2	3 P. 3	Part of
		7 0 3			
Optimized Neutral				<b>1 1 1 1 1 1 1 1 1 1</b>	3 3 3 3
structure		3 7 300	10 (a)	•	<b>*</b>
	α-furanose (C <sub>4</sub> -		α-furanose (C <sub>4</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	
	endo) +	open chain (A) +	endo) +	chair) +	open chain (A) +
	$(3)(intra)H_2O + (4)(intra)H_2O +$	$(1)(intra)H_2O + (1)(intra)H_2O +$	$(3)(intra)H_2O + (4)(intra)H_2O +$	$(2)(3)(intra)H_2O + (1)(intra)H_2O +$	$(1)(intra)H_2O + (2)(intra)H_2O +$
	$(4)(6)(intra)H_2O +$	(1)(IIIIa)H2O + (intra)H2O +	$(4)(\ln(a)H_2O + (6)(intra)H_2O +$	$(1)(111113)H_2O + (1)(3)(11113)H_2O +$	$(2)(\text{intra})H_2O +$ $(\text{intra})H_2O +$
Structural	$(4)(0)(Intra)H_2O +$ $(intra)H_2O +$	$(intra)H_2O +$	$(6)(intra)H_2O +$	$(3)(4)(intra)H_2O +$	$(3)(intra)H_2O +$
Polymorphism	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(4)(5)H_2O$	(intra)H <sub>2</sub> O
ΔE (eV)	0.33	0.34	0.34	0.35	0.37
		<b>6.</b>	<u>ه</u> پ		· 📸 »
Optimized			30 2 2 3		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Neutral structure		The state of the s			
			β-pyranose ( <sup>2</sup> C <sub>5</sub> -		open chain (B) +
	open chain (A) +	open chain (A) +	chair) +	open chain (B) +	$(1)(intra)H_2O +$
	$(1)(intra)H_2O + (2)(intra)H_2O +$	$(1)(2)(intra)H_2O + (1)(intra)H_2O +$	$(2)(3)(intra)H_2O + (1)(intra)H_2O +$	$(1)(intra)H_2O + (1)(3)(intra)H_2O +$	(1)(3)(intra)H <sub>2</sub> O +
	$(1)(3)(intra)H_2O +$	$(3)(intra)H_2O +$	$(1)(3)H_2O +$	$(3)(intra)H_2O +$	$(2)(3)(intra)H_2O$
Structural	$(3)(intra)H_2O +$	(intra)H <sub>2</sub> O +	$(3)(4)(intra)H_2O +$	$(intra)H_2O +$	$+ (intra)H_2O +$
Polymorphism	(intra)H <sub>2</sub> O	$(5)(6)H_2O$	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O
ΔE (eV)	0.37	0.39	0.40	0.40	0.40
	3.				
		<b>5</b>	<u>.</u>		
Optimized					<b>I</b>
Neutral	3				
structure	or francisco (C	open shain (A)	onen chain (A)	onen shein (A)	onen chein (A)
	$\alpha$ -furanose (C <sub>4</sub> -endo) +	open chain $(A)$ + $(1)(2)(intra)H_2O$ +	open chain (A) + (1)(intra)H <sub>2</sub> O +	open chain (A) + (1)(intra)H <sub>2</sub> O +	open chain (A) + (1)(intra)H <sub>2</sub> O +
Structural	$(1)(3)(intra)H_2O +$	$(1)(2)(11112)H_2O + (1)(1112)H_2O + (1)(112)H_2O + ($	$(1)(\text{intra})H_2O + (2)(\text{intra})H_2O +$	$(1)(\ln(a)H_2O + (2)(intra)H_2O +$	$(1)(intra)H_2O + (1)(intra)H_2O +$
Polymorphism	$(3)(4)(intra)H_2O +$	$(2)(intra)H_2O +$	$(intra)H_2O +$	$(intra)H_2O +$	$(2)(intra)H_2O +$

	(4)(6)(intro)II () :	(2)(intro)[I] O +	(intro)II O	(intro)II O	(intro)II O
	$(4)(6)(intra)H_2O +$	$(3)(intra)H_2O +$	$(intra)H_2O +$	$(intra)H_2O +$	(intra)H <sub>2</sub> O +
	(intra)H <sub>2</sub> O + (intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(5)(6)H_2O$	$(5)(6)H_2O$	(intra)H <sub>2</sub> O
ΔE (eV)	0.42	0.43	0.43	0.43	0.43
ΔΕ (ΕΥ)	0.42	0.43	0.43	0.43	0.43
			Ż		
	5.00 P	- 2		<b>P</b> 5.	
		Name of the last o			
Optimized					
Neutral structure	7 353	<b>6</b>	•	<u> </u>	
structure					open chain (B) +
	open chain (C) +	open chain (A) +	open chain (A) +	open chain (A) +	$(1)(2)(intra)H_2O$
	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	+
	$(1)(intra)H_2O +$	$(3)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(3)(intra)H_2O$
	$(2)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$	+ (3)(intra)H <sub>2</sub> O +
Structural	$(3)(intra)H_2O +$	(intra)H <sub>2</sub> O +	(intra)H <sub>2</sub> O +	(intra)H <sub>2</sub> O +	(intra)H <sub>2</sub> O +
Polymorphism	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(3)H_2O$	(intra)H <sub>2</sub> O	$(3)(6)(intra)H_2O$
ΔE (eV)	0.44	0.45	0.45	0.45	0.45
,					
		<b>_</b>	i i	3 4	4
	<b>3</b> 5 3 3	3 3 3 3 X	9 30 34 3	****	6
				300	
Optimized			3		
Neutral structure			•	<b>6</b>	
structure	open chain (A) +	open chain (A) +	open chain (A) +	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	open chain (A) +
	$(1)(3)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	chair) + $(1)(3)H_2O$ +	$(1)(2)H_2O +$
	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$	$(3)(4)(intra)H_2O +$	$(1)(intra)H_2O +$
	$(intra)H_2O +$	$(intra)H_2O +$	$(intra)H_2O +$	$(intra)H_2O +$	$(3)(intra)H_2O +$
Structural	$(intra)H_2O +$	$(1)(3)H_2O +$	$(1)(3)H_2O +$	$(intra)H_2O +$	$(4)(5)(intra)H_2O$
Polymorphism	(intra)H <sub>2</sub> O	$(5)(6)H_2O$	$(5)(6)H_2O$	$(4)(5)H_2O$	+ (6)(intra)H <sub>2</sub> O
ΔE (eV)	0.46	0.47	0.47	0.48	0.52
			•		,
		<u>•</u>	7		
	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<b>6.</b>			
0 4 1		<b>→</b> • • •	3 3 3	<u> </u>	9 6b
Optimized Neutral		3 78 39 2	<b>36</b>		
structure	<u> </u>		•		
					α-furanose (C <sub>4</sub> -
	open chain (C) +	open chain (A) +	open chain (C) +	open chain (C) +	endo) +
	$(1)(2)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(intra)H_2O +$	$(1)(2)(intra)H_2O +$	$(1)(intra)H_2O +$
	$((3)(intra)H_2O +$	$(2)(intra)H_2O +$	$(2)(intra)H_2O +$	$(3)(intra)H_2O +$	$(1)(intra)H_2O +$
	$(1)(3)(intra)H_2O +$	(intra)H <sub>2</sub> O +	$(3)(5)(intra)H_2O +$	$(1)(3)(intra)H_2O +$	$(3)(intra)H_2O +$
Structural	(intra)H <sub>2</sub> O +	$(5)(6)H_2O +$	$(6)(intra)H_2O +$	(intra)H <sub>2</sub> O +	(intra)H <sub>2</sub> O +
Polymorphism	(3)(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	(intra)H <sub>2</sub> O	$(4)(6)H_2O$
ΔE (eV)	0.52	0.52	0.55	0.56	0.59
	<u> </u>			<b>T</b>	
	<b>•</b> • • ·				
Optimized					
Neutral		35			
structure		• • •		<b>%</b> >	
Structural	open chain (B) +	open chain (A) +	α-furanose (C <sub>4</sub> -	open chain (A) +	
Polymorphism	$(1)(intra)H_2O +$	$(2)(intra)H_2O +$	endo) +	$(1)(intra)H_2O +$	

	(1)(intra)H <sub>2</sub> O +	$(4)(intra)H_2O +$	$(1)(intra)H_2O +$	(2)(intra)H <sub>2</sub> O +	
	$(2)(intra)H_2O +$	$(4)(5)(6)(intra)H_2O$	$(1)(3)(intra)H_2O +$	$(2)(3)(intra)H_2O +$	
	(intra)H <sub>2</sub> O +	$+ (6)(intra)H_2O +$	$(3)(intra)H_2O +$	$(intra)H_2O +$	
	$(1)(3)H_2O$	(intra)H <sub>2</sub> O	$(6)(intra)H_2O +$	(intra)H <sub>2</sub> O	
			$(4)(6)H_2O$		
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<sup>-</sup> 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.

	ı		l I		1
Optimized Anionic structure					
Structural Polymorphism	Open chain (A)+(1)(2)H <sub>2</sub> O	Open chain (A) +(1)(2)H <sub>2</sub> O	Open chain (A) +(3)H <sub>2</sub> O	Open chain (A) +(2)(4)(6)H <sub>2</sub> O	Open chain (B) +(1)(2)H <sub>2</sub> O
$\Delta E (eV)$	0.00	0.06	0.17	0.19	0.39
VDE (eV)	2.24	2.33	2.16	2.30	1.90
(22 (61)					245 0
Optimized Anionic structure					
Structural Polymorphism	Open chain (C) +(1)(2)H <sub>2</sub> O	Open chain (C) +(3)(5)H <sub>2</sub> O	Open chain (C) +(5)(6)H <sub>2</sub> O	$\beta$ -pyranose ( $^2$ C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O	Open chain (B) +(5)(6)H <sub>2</sub> O
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			ă.		
Structural Polymorphism	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(1)(2)(3)H <sub>2</sub> O	$β$ -pyranose ( $^2$ C <sub>5</sub> -chair) +(3)(4)H <sub>2</sub> O	$β$ -pyranose ( $^2$ C <sub>5</sub> -chair) +(4)(5)H $_2$ O	$\alpha$ - furanose (C <sub>4</sub> - endo) +(3)(4)H <sub>2</sub> O	$\alpha$ - furanose (C <sub>4</sub> - endo) +(1)H <sub>2</sub> O
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	$\alpha$ - furanose (C <sub>4</sub> -				
Polymorphism	endo) +(1)(2)H <sub>2</sub> O 1.04				
ΔE (eV)					
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.

	1	<del></del>	T		
Optimized Anionic structure					
Structural	open chain (A) +(1)(2)(intra)H <sub>2</sub> O+	open chain (A) $+(1)(2)H_2O+(1)(3)$	open chain (A) $+(1)(2)H_2O+(4)(5)$	open chain (A) $+(1)(intra)H_2O+(2)($	open chain (A) +(1)(2)(intra)H <sub>2</sub> O
Polymorphism	(2)(intra)H <sub>2</sub> O	H <sub>2</sub> O	(6)H <sub>2</sub> O	intra)H <sub>2</sub> O	+(intra)H <sub>2</sub> O
$\Delta E (eV)$	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 <sub>2</sub> O+(2)(int ra)H <sub>2</sub> O	open chain (A) +(3)H <sub>2</sub> O+(4)(5)(6) H <sub>2</sub> O	open chain (C) +(3)(5)H <sub>2</sub> O+(4)(6) H <sub>2</sub> O	open chain (C) +(1)(2)(intra)H <sub>2</sub> O+( 1)(2)(intra)H <sub>2</sub> O	open chain (B) +(1)(2)H <sub>2</sub> O+(1)( 3)H <sub>2</sub> O
ΔE (eV)	0.14	0.23	0.33	0.35	0.37
VDE (eV)	2.53	2.50	2.18	2.32	2.22
(3.7)					<u> </u>
Optimized Anionic structure		35			
	open chain (B)	open chain (C)	open chain (C)	open chain (B)	open chain (C)
Structural	$+(1)(2)(intra)H_2O+$	$+(1)(2)H_2O+(2)(intr$	$+(3)(5)H_2O+(1)(2)$	$+(1)(2)H_2O+(5)(6)H$	$+(1)(2)H_2O+(5)($
Polymorphism	(2)(intra)H <sub>2</sub> O	$a)H_2O$	$H_2O$	$_{2}\mathrm{O}$	$6)H_2O$
$\Delta E (eV)$	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		<b>9</b>			<u> </u>
Structural Polymorphism	open chain (C) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(2)(3)H <sub>2</sub> O+(1)( 3)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(3)(4) H <sub>2</sub> O	open chain (B) +(1)(2)H <sub>2</sub> O+(5)(6)H <sub>2</sub> O	β-pyranose ( <sup>2</sup> C <sub>5</sub> -chair) +(1)(3)H <sub>2</sub> O+(4)( 5)H <sub>2</sub> O
$\Delta E (eV)$	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	R nyranasa (2C	a furances (C	a furances (C		
	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	α- furanose (C <sub>4</sub> -	α- furanose (C <sub>4</sub> -		
	chair)	endo)	endo)		
a -	1 (1)(2)II O (' )	(2)(!\TT A			1
Structural	$+(1)(3)H_2O+(intra)$	$+(3)(intra)H_2O+$	$+(1)(3)H_2O+(3)(4)$		
Polymorphism	$H_2O$	$(4)(intra)H_2O$	$H_2O$		

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.

			<u> </u>	<u> </u>	
Optimized Anionic structure					
Structural Polymorphism	open chain (A) +(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O 0.00	open chain (A) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.03	open chain (A) +(1)(2)H <sub>2</sub> O+(2)(in tra)H <sub>2</sub> O+(4)(5)(6) H <sub>2</sub> O 0.04	open chain (A) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O+(2)(intra)H <sub>2</sub> O 0.05	open chain (A) +(4)(5)(6)H <sub>2</sub> O+( 4)(6)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O 0.08
ΔE (eV)			2.57		
VDE (eV)	2.61	2.50	2.57	2.67	2.76
Optimized Anionic structure					
Structural Polymorphism ΔE (eV)	open chain (A) +(1)(2)H <sub>2</sub> O+(1)(3) H <sub>2</sub> O+(4)(5)H <sub>2</sub> O 0.12	open chain (A) +(1)(intra)H <sub>2</sub> O+(2)( intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O	open chain (A) +(1)(intra)H <sub>2</sub> O+(2 )(intra)H <sub>2</sub> O+(4)(5) H <sub>2</sub> O 0.22	open chain (A) +(4)(6)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(1)(int ra)H <sub>2</sub> O 0.23	open chain (A) +(4)(6)(intra)H <sub>2</sub> O +(4)(5)(intra)H <sub>2</sub> O +(intra)H <sub>2</sub> O 0.25
	2.41	2.76	3.00	2.76	2.39
VDE (eV)	2,41	2.70	3.00	2.10	2.39
Optimized Anionic structure					E=-915.871697
Structural Polymorphism ΔE (eV)	open chain (C) +(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) H <sub>2</sub> O 0.36	open chain (B) +(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O 0.38	open chain (C) +(1)(2)(intra)H <sub>2</sub> O +(2)(intra)H <sub>2</sub> O+(i ntra)H <sub>2</sub> O 0.43	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(1)(3)H <sub>2</sub> O+(2)(3)(i ntra)H <sub>2</sub> O+(1)(intra) H <sub>2</sub> O 0.47	β-pyranose ( <sup>2</sup> C <sub>5</sub> - chair) +(3)(4)H <sub>2</sub> O+(3)( 3)(intra)H <sub>2</sub> O+(1)  H <sub>2</sub> O  0.53
VDE (eV)	2.44	2.49	2.38	0.71	0.95
Optimized Anionic structure					
Structural Polymorphism ΔE (eV) VDE (eV)	α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(intr a)H <sub>2</sub> O 0.80 1.26	α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(1)(2 )H <sub>2</sub> O 0.84 <b>0.85</b>			
	1 76	11 84	Ť		İ

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

Optimized Optimized	
Anionic	
structure	3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3
open chain (A) open chain (A) open chain (	C) open chain (A)
$+(1)(2)(intra)H_2O+($ open chain (A) $+(1)(2)(intra)H_2O$ $+(1)(2)(intra)H$	$_{2}O+( +(1)(2)(intra)H_{2}O$
$2)(3)(intra)H_2O+(1) + (1)(2)(intra)H_2O+(1) + (1)(intra)H_2O+(2) + (2)(3)(intra)H_2O+(2)$	
Structural $(3)(intra)H_2O+(intr   1)(3)H_2O+(2)(intra) )(intra)H_2O+(intra   (3)(intra)H_2O+(2)(intra   (3)(intra)H_2O+(2)(intra)H_2O+(2)(intra   (3)(intra)H_2O+(2)(intra)H_2O+(2)(intra   (3)(intra)H_2O+(2)(intra)H_2O+(2)(intra   (3)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intra)H_2O+(2)(intr$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c} \text{(max)} & \text{(a)} & \text{(b)} & \text{(b)} & \text{(c)} & \text$
$\Delta E (eV)$ 0.00 0.23 0.26 0.28	0.29
VDE (eV)         2.89         3.09         2.60         2.67	2.81
100 2101	
Optimized Optimized	
Anionic	
structure	, <u> </u>
open chain (A) open chain (B) open chain (A) open chain (A)	A) open chain (A)
$+(1)(2)(intra)H_2O+( +(1)(2)(intra)H_2O+( +(1)(2)(intra)H_2O +(1)(intra)H_2O	$+(2)( +(1)(intra)H_2O+($
$1)(3)(intra)H_2O+(in   2)(3)(intra)H_2O+(1)   +(2)(intra)H_2O+(i   intra)H_2O+(4)(6)$	
Structural $tra)H_2O+(4)(5)(6)H$ $(3)(intra)H_2O+(intra)H_2O+(intra)H$ $ra)H_2O+(4)(5)(6)H$	
Polymorphism 2O a)H <sub>2</sub> O 2O O	$H_2O$
$\Delta E (eV)$ 0.32 0.32 0.37 0.40	0.40
VDE (eV) 2.68 2.67 3.07 2.85	3.07
<b>9 9</b> .	
Optimized	
Anionic	200
structure	
$\beta$ -pyranose ( ${}^{2}C_{5}$ - $\beta$ -pyranose ( ${}^{2}$	-
open chain (C) chair) chair)	endo)
open chain (A) $+(1)(2)(intra)H_2O+( +(3)(4)H_2O+(2)(3) +(1)(3)(intra)H_2O+(4)(3) +(1)(3)(intra)H_2O+(4)(3)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)(4)$	$I_2O+( +(3)(intra)H_2O+$
$+(1)(2)(intra)H_2O+(2)(intra)H_2O+(3)(5)$ (intra) $H_2O+(1)(3)(2)(3)(intra)H_2O$	$O+(1)$ (4)(intra) $H_2O+(6)$
Structural 2)(intra) $H_2O+(4)(5)$ (intra) $H_2O+(6)$ (intr   intra) $H_2O+(1)$ (intr   (intra) $H_2O+$ (intra)	tra)H (intra)H <sub>2</sub> O+(intra
Polymorphism $(6)H_2O+(intra)H_2O$ $a)H_2O$ $a)H_2O$ $2O$	$)\mathrm{H}_{2}\mathrm{O}$
$\Delta E (eV)$ 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	
α- furanose (C <sub>4</sub> -	
endo)	
+(3)(intra)H <sub>2</sub> O+	
$(4)(intra)H_2O+(6)(i$	
Structural ntra)H <sub>2</sub> O+(intra)H <sub>2</sub>	
Polymorphism O	
Polymorphism O $\Delta E (eV)$ 1.05	

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<sup>-</sup> 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.

	7	P			
Optimized			🍻 🔅 😘		
Anionic	33 33				
structure		11. (1)			
	aman ahain (A)	open chain (A)	open chain (A)	aman ahain (A)	open chain (A)
	open chain (A) +(1)(2)(intra)H <sub>2</sub> O+(	+(1)(2)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1)	+(1)(2)(intra)H <sub>2</sub> O +(2)(3)(intra)H <sub>2</sub> O	open chain (A) $+(1)(2)(intra)H_2O+($	+(1)(2)(intra)H <sub>2</sub> O +(2)(3)(intra)H <sub>2</sub> O
	$+(1)(2)(\ln(a)H_2O+(3)(in + (1)(2)(in + (1$	$(3)(intra)H_2O$	$+(2)(3)(intra)H_2O$ +(1)(3)(intra)H <sub>2</sub> O	$2)(3)(intra)H_2O+(1)$	$+(2)(3)(intra)H_2O$ +(1)(3)(intra)H <sub>2</sub> O
Structural	$tra)H_2O+(intra)H_2O$	$+(intra)H_2O+(4)(5)($	$+(intra)H_2O+(2)H$	$(3)(intra)H_2O+(intra)$	$+(intra)H_2O+(intra)H_2O$
Polymorphism	+(intra)H <sub>2</sub> O	6)H <sub>2</sub> O	2O	)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O	$a)H_2O$
ΔE (eV)	0.00	0.06	0.08	0.09	0.14
VDE (eV)	3.16	3.13	3.20	3.14	3.12
		<b>.</b>			<b></b>
			<b>6</b>	<b>7</b> • • • • • •	30 <sup>20</sup> 34 0
Optimized	900				3 3 3 3 3
Anionic			3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3		<del>- 33 - 33 - 4</del>
structure		<b>0</b> 1	• • • • • • • • • • • • • • • • • • • •		aman ahain (A)
	open chain (C)	open chain (A)	open chain (A)	open chain (B)	open chain (A) +(1)(intra)H <sub>2</sub> O+(
	$+(1)(2)(intra)H_2O+($	$+(1)(2)(intra)H_2O+($	$+(1)(2)(intra)H_2O$	+(1)(2)(intra)H2O+(	$+(1)(IIIIa)H_2O+(4)($ 2)(intra) $H_2O+(4)($
	$(1)(2)(\text{intra})H_2O+(1)$ 2)(3)(intra)H <sub>2</sub> O+(1)	1)(intra) $H_2O+(2)$ (in	$+(1)(2)(intra)H_2O+(2)$	$2)(3)(intra)H_2O+(1)$	6)(intra) $H_2O+(4)$ (
Structural	$(3)(intra)H_2O+(intra)$	$tra)H_2O+(intra)H_2O$	)(intra)H <sub>2</sub> O+(intra	$(3)(intra)H_2O+(intra)$	5)(6)(intra)H <sub>2</sub> O+(
Polymorphism	a)H <sub>2</sub> O+(intra)H <sub>2</sub> O	$+(1)(3)H_2O$	)H <sub>2</sub> O+(intra)H <sub>2</sub> O	)H <sub>2</sub> O+(intra)H <sub>2</sub> O	intra)H <sub>2</sub> O
ΔE (eV)	0.29	0.32	0.39	0.44	0.47
VDE (eV)	2.77	3.08	2.64	2.89	3.09
					Α
	<u> </u>	<b>P.</b> .			
	<u>"</u>			, <b>•</b> •••	
Optimized				4 <u>9</u> 9	
Optimized Anionic					
*					
Anionic		open chain (C)	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	β-pyranose ( <sup>2</sup> C <sub>5</sub> -	α- furanose (C <sub>4</sub> -
Anionic	open chain (A)	$+(1)(2)(intra)H_2O+($	chair)	chair)	endo)
Anionic	$+(1)(2)(intra)H_2O+($	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5)	chair) +(3)(4)H <sub>2</sub> O+(2)(3)	chair) +(1)(3)(intra)H <sub>2</sub> O+(	endo) +(3)(intra)H <sub>2</sub> O+
Anionic structure	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)(	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1)	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6)
Anionic	$+(1)(2)(intra)H_2O+($	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5)	chair) +(3)(4)H <sub>2</sub> O+(2)(3)	chair) +(1)(3)(intra)H <sub>2</sub> O+(	endo) +(3)(intra)H <sub>2</sub> O+
Anionic structure	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub>	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra
Anionic structure Structural Polymorphism	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O 0.48	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O 0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O 0.48	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O 0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism  ΔE (eV)  VDE (eV)	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O 0.48	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O 0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O 0.48	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O 0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized Anionic	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O 0.48	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O 0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O 0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized Anionic	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95  α- furanose (C <sub>4</sub> -	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O  0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized Anionic	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O  0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized Anionic	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95  α- furanose (C <sub>4</sub> - endo)	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O  0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Anionic structure  Structural Polymorphism ΔE (eV)  VDE (eV)  Optimized Anionic	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra) )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95  α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O  0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Structural Polymorphism ΔΕ (eV) VDE (eV)  Optimized Anionic structure  Structural Polymorphism	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95  α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+(6)(i ntra)H <sub>2</sub> O+(intra)H <sub>2</sub> O	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O  0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O
Structural Polymorphism  ΔE (eV)  VDE (eV)  Optimized Anionic structure	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(4)(5)(6)H <sub>2</sub> O +(intra)H <sub>2</sub> O  0.48  2.95  α- furanose (C <sub>4</sub> - endo) +(3)(intra)H <sub>2</sub> O+(6)(i ntra)H <sub>2</sub> O+(intra)H	+(1)(2)(intra)H <sub>2</sub> O+( 2)(intra)H <sub>2</sub> O+(3)(5) (intra)H <sub>2</sub> O+(6)(intr a)H <sub>2</sub> O+(1)(intra)H <sub>2</sub> O 0.64	chair) +(3)(4)H <sub>2</sub> O+(2)(3) (intra)H <sub>2</sub> O+(1)(3)( intra)H <sub>2</sub> O+(1)(intr a)H <sub>2</sub> O+(intra)H <sub>2</sub> O 0.83	chair) +(1)(3)(intra)H <sub>2</sub> O+( 2)(3)(intra)H <sub>2</sub> O+(1) (intra)H <sub>2</sub> O+(intra)H <sub>2</sub> O+(3)(intra)H <sub>2</sub> O  0.91	endo) +(3)(intra)H <sub>2</sub> O+ (4)(intra)H <sub>2</sub> O+(6) (intra)H <sub>2</sub> O+(intra )H <sub>2</sub> O+(intra)H <sub>2</sub> O

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  $\sim 8$  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  $\sim 2\times10^3$  g/L and  $\sim 100$ g/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.