Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Gas Phase Dynamics, Conformational Transitions and Spectroscopy of Charged Saccharides: the Oxocarbenium Ion, Protonated Anhydrogalactose and Protonated Methyl Galactopyranoside

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Supplementary figures

Fig. S1 shows the rapid decay at ~350 K of a higher energy conformer of βMeGal-H$^+$ (~0.5 eV above the minimum energy conformer) in which the hydroxyl groups of the pyranose assume a clockwise orientation. The figure shows the changes in two key dihedral angles Φ_3 and Φ_4 which effect the clockwise to counterclockwise hydroxyl group transition.

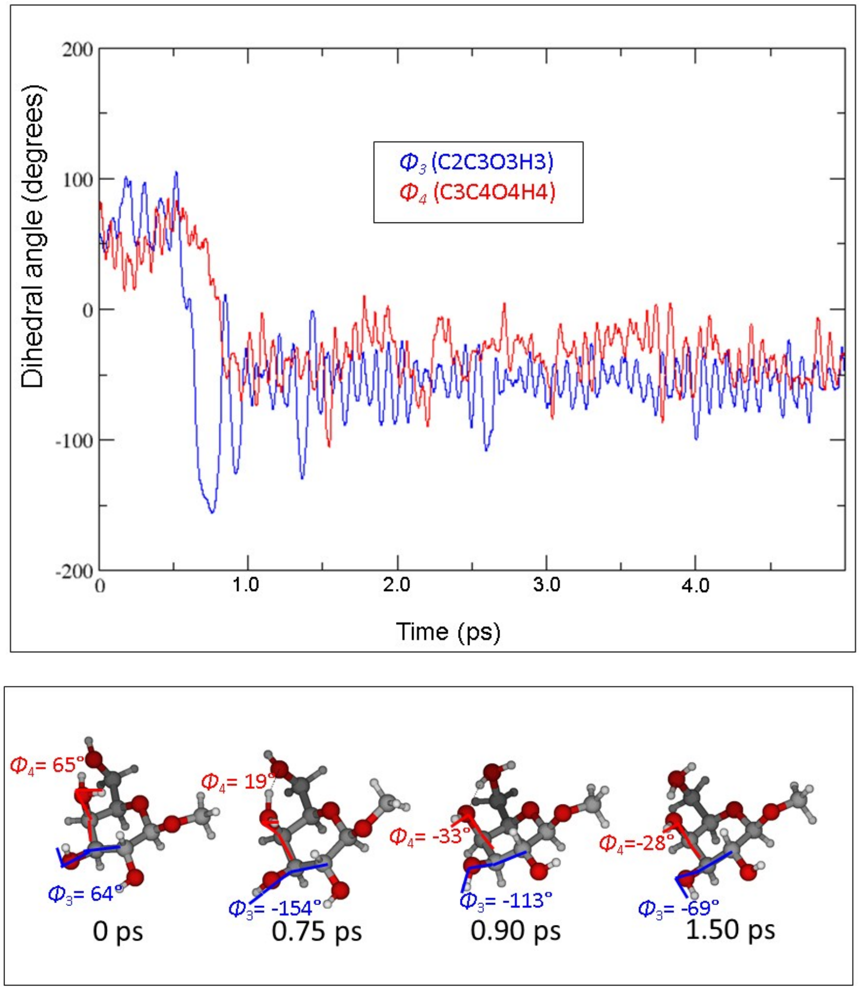

Fig. S1 (top panel) Evolution of two dihedral angles (distinguished by colour) of the~ 0.5 eV conformer of βMeGal-H$^+$ (starting structure). (bottom panel) Snapshots show clockwise to counterclockwise transition in the orientation of the hydroxyl groups along the trajectory.

Optimization of the minimized structures of protonated methyl D-galactopyranoside with the methanol moeity cleaved yielded two distict low energy conformers of g alactosyl oxocarbenium ion which are shown in Fig. S2. The conformers differ mainly in the orientation of the hydroxymethyl group. The lowest energy conformer displayed a *gtTT* hydroxymethyl group orientation , whereas the 0.470 eV conformer's hydroxylmethyl group is in a *tgMGG* orientation.

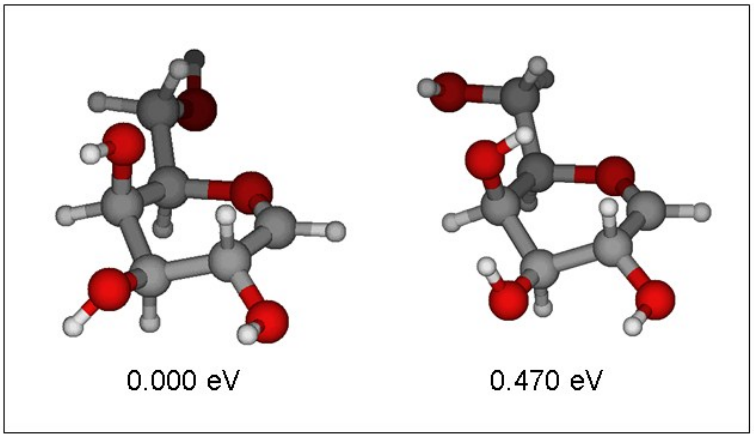

Fig. S2 Conformers of galactosyl oxocarbenium ion and their relative energies optimized at the B3LYP-D/6-311++G(d,p) level of theory.

Initiation of AIMD trajectories at ~350 K from the 0.470 eV conformer of galactosyl oxocarbenium ion resulted in a very rapid decay to a number of lower energy conformers. Fig. S3 shows the temporal changes in the relative potential energy over the course of a trajectory. The figure notes potential energy minima where stable conformers were identified.

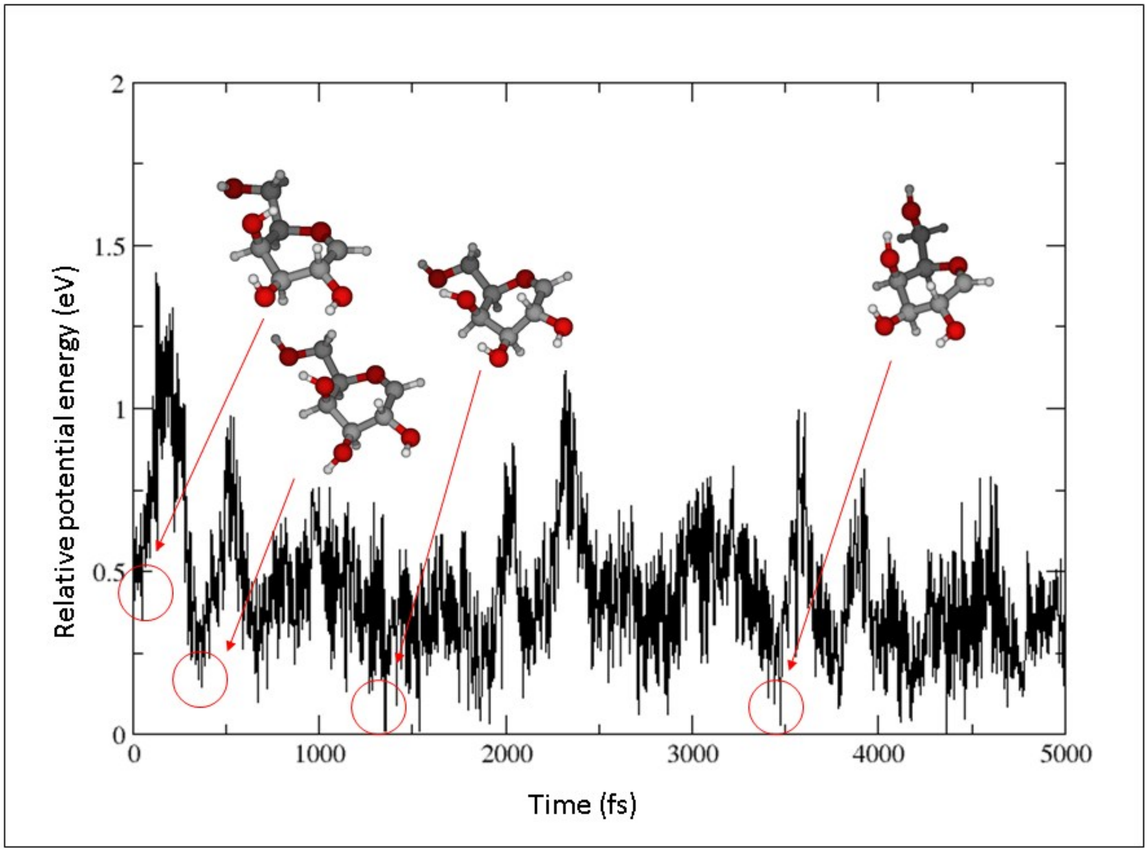

Fig. S3 Evolution of the relative potential energy along the trajectory beginning with the 0.470 eV conformer of galactosyl oxocarbenium ion. Circles at energy minima show the relative energies of the conformers that appear over the course of the simulation.

AIMD trajectories at ~350 K intiaited from the mimimium energy structure of a higher energy conformer of protonated levogalactosan (0.366 eV above the lowest energy conformer) resulted in decay to the lowest energy conformer within ~1 ps. Fig. S4 shows the temporal changes in relative potential energy and Φ_6 dihedral angle along the trajectory.

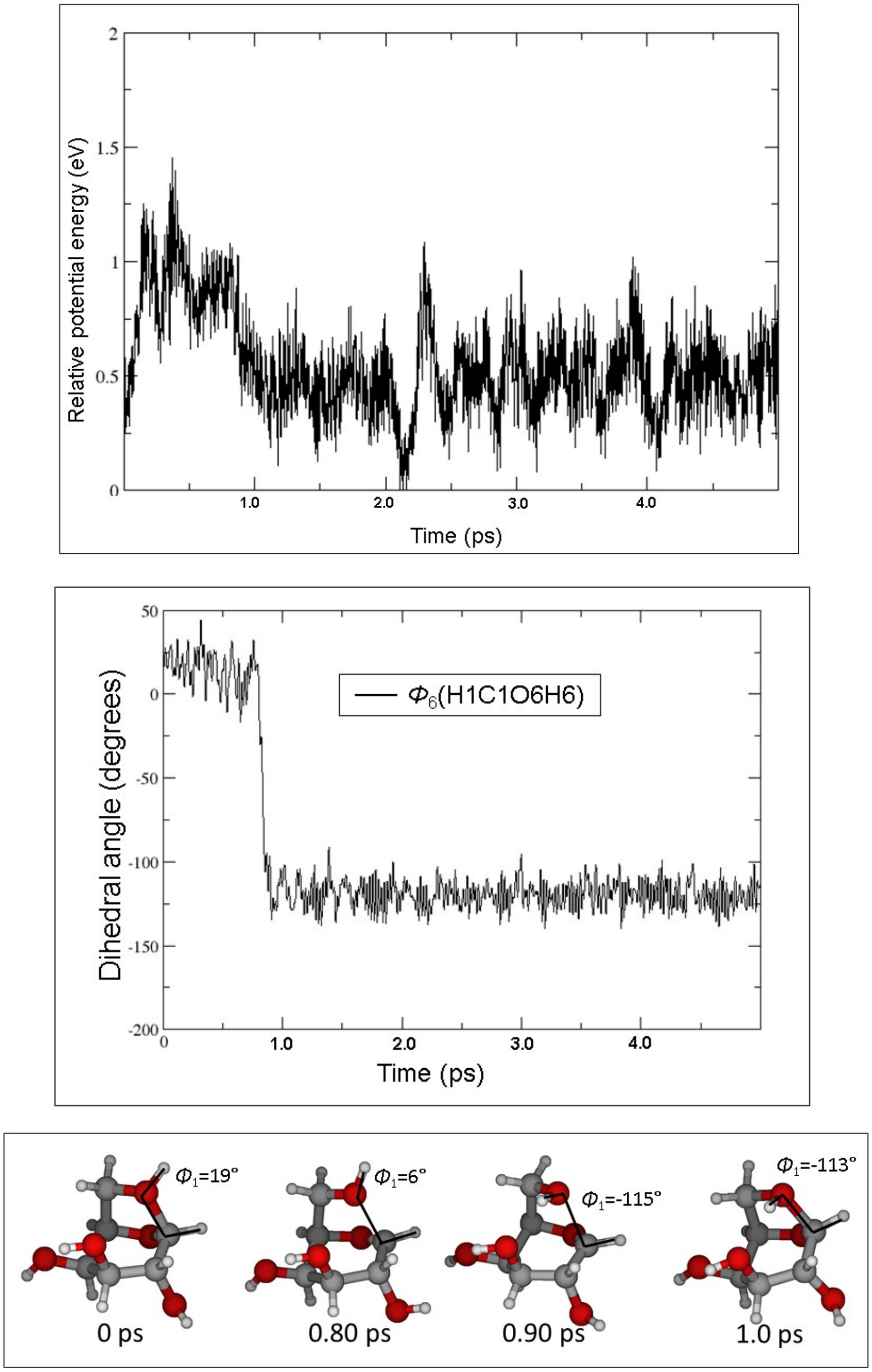

Fig. S4 (top panel) Evolution of relative potential energy along the trajectory initiated from a 0.366 eV conformer of protonated levogalactosan. (middle panel) Evolution of dihedral angle (H1C1O6H6) along the trajectory. (bottom panel) Snapshots along the trajectory.

The atom connectivity in protonated 1,6-Anhydro-α-D-galactofuranose is not directly comparable to that of the pyranose species. Fig. S5 compares the IRMPD spectrum of the m/z 163 species from methyl β-D-galactopyranoside with the VSCF spectrum of 1,6-Anhydro-α-D-galactofuranose. The OH stretches responsible for the VSCF calculated transitions are identified in the figure.

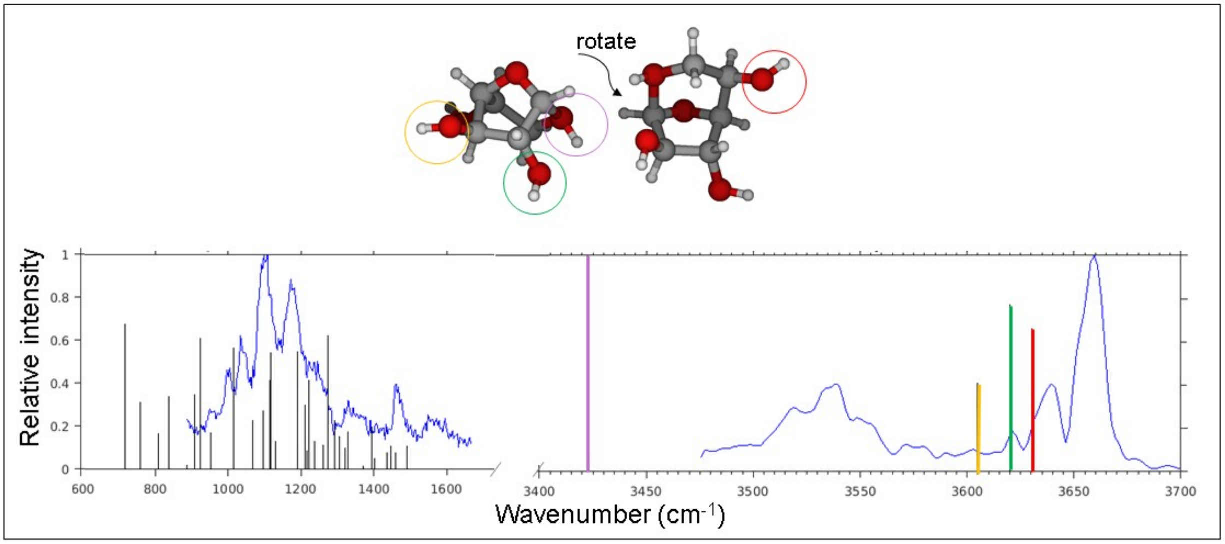

Fig. S5 Comparison of the IRMPD spectrum of the *m/z* 163 species from methyl β-D-galactopyranoside (in blue) with the calculated VSCF spectrum protonated 1,6-Anhydro-α-D-galactofuranose. Vibrational transitions are colour-coded.

Table S1 compares VSCF calculated OH stretches for conformers of galactosyl oxocarbenium ion and anhydrogalactose with both the harmonic and experimental OH-stretching transitions. The table notes where VSCF deviation from experiment is minimal, suggesting that these conformers that may be present under the experimental conditions.

Table S1. Vibrational transitions for low energy conformers of galactosyl oxocarbenium ion (I), the lowest energy conformer of protonated 1,6-Anhydro-α-D-galactofuranose (II), the lowest energy conformer of protonated levogalactosan (III) and the lowest energy conformer of protonated 1,4-Anhydro-β-D-galactopyranose (IV), cm^{-1}.

Conformer	Mode description	Harmonic	VSCF	Expt.[a]	Expt.[b]	VSCF deviation from expt.[b,c]
I (0.237 eV)	σ-6	3833	3618	3656	3659	41
	σ-2	3795	3583	3642	3640	57
	σ-3	3761	3545	-	3621	76
	σ-4	3693	3457	3538	3538	81
I (0.258 eV)	σ-6	3838	3624			35
	σ-2	3833	3620			20
	σ-4	3815	3605			16
	σ-3	3790	3578			40
I (0.276 eV)	σ-6	3939	3582			77
	σ-2	3789	3670			30
	σ-4	3781	3572			49
	σ-3	3754	3616			78
I (0.298 eV)	σ-6	3834	3621			38
	σ-2 + σ-3 sym	3829	3678			38
	σ-2 + σ-3 asym	3827	3661			40
	σ-4	3721	3491			47
I (0.340 eV)	σ-6	3838	3624			35
	σ-3	3830	3616			24
	σ-4	3807	3595			47
	σ-2	3804	3598			60
II (0.237 eV)	-	3843	3630			29
	-	3834	3620			20
	-	3820	3605			16
	-	3638	3423			115
III (0.000 eV)	σ-4	3846	3632			27
	σ-2	3837	3624			16
	σ-3	3758	3541			3
	σ-6	2741	2344			-
IV (0.319 eV)	σ-6	3848	3635			24
	σ-2	3838	3624			16
	σ-3	3826	3611			73
	σ-4	2903	2575			-

[a] From IRMPD spectrum of *m/z* 163 species derived from methyl α-D-galactopyranoside.

[b] From IRMPD spectrum of *m/z* 163 species derived from from methyl β-D-galactopyranoside.

[c] Highlight shows close (≤40 cm^{-1}) agreement between calculated and experimental transitions.