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

Supporting Information:

Sodium-cationized Carbohydrate Gas-phase Fragmentation Chemistry: Influence of Glycosidic Linkage Position

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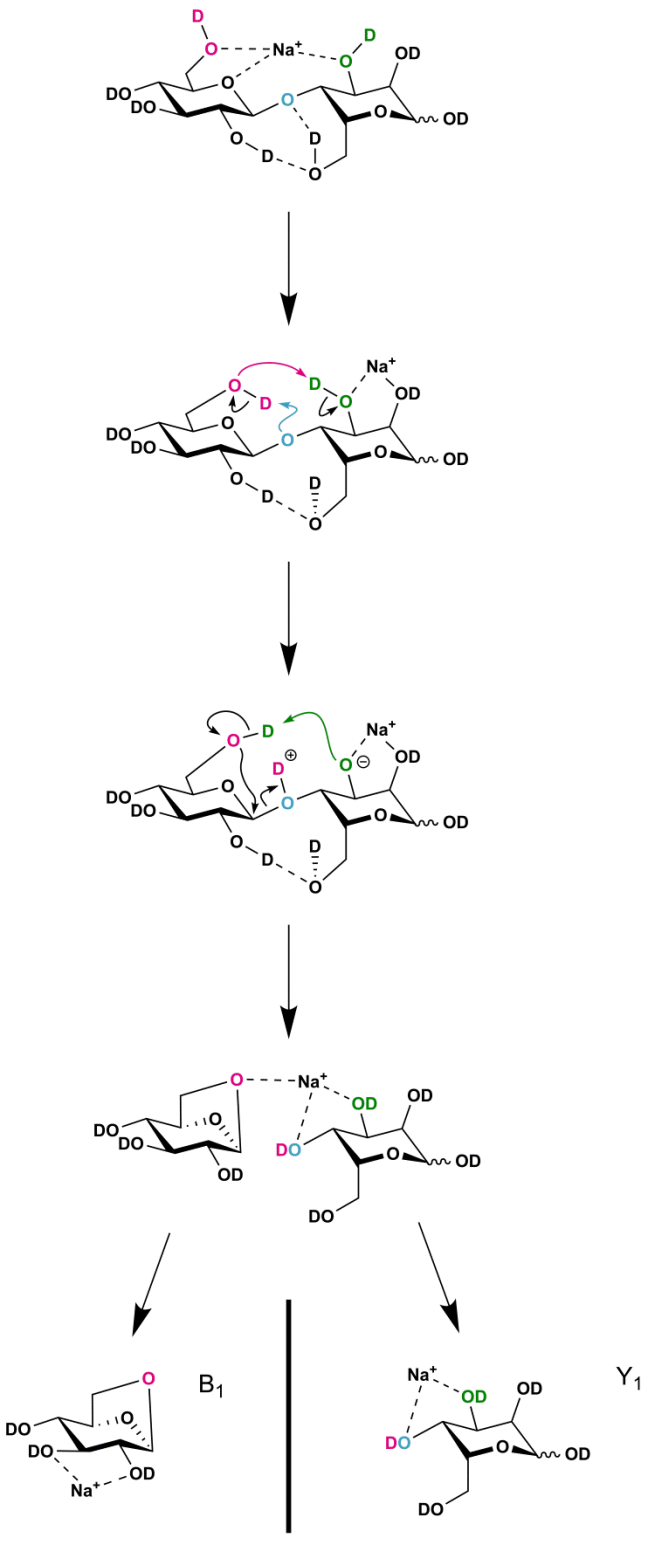
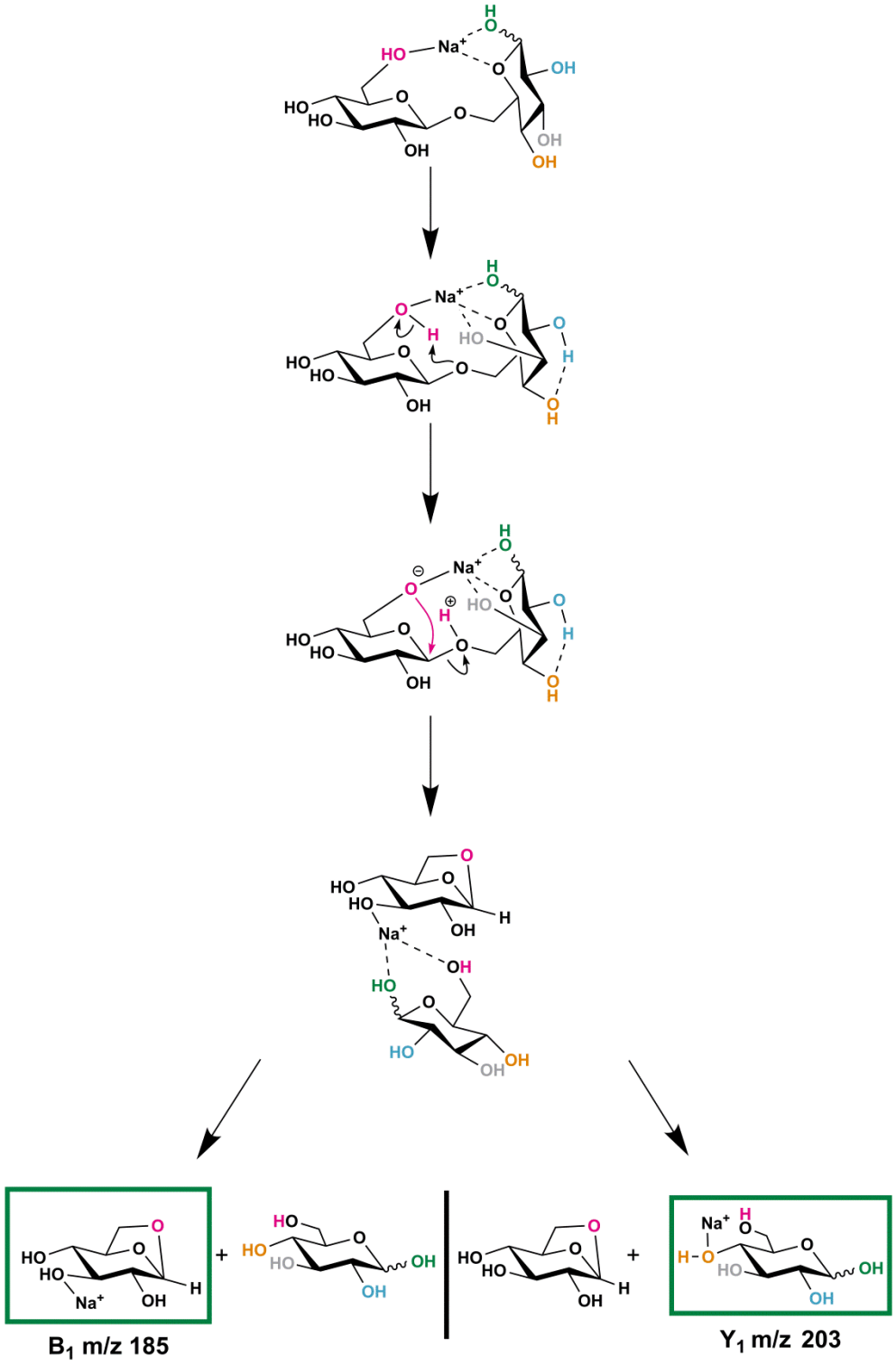
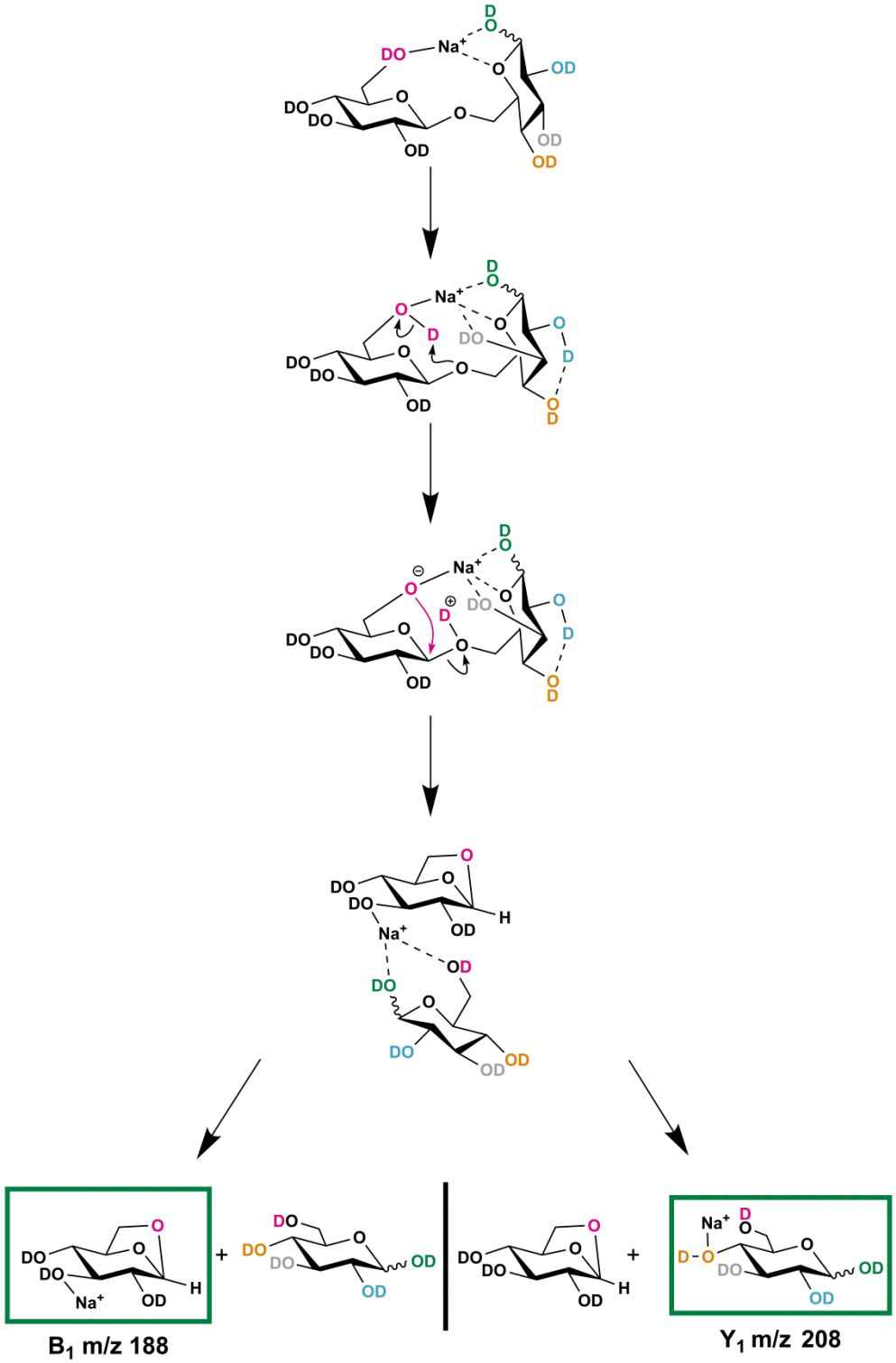
Key Words: Mass spectrometry, Collision-induced Dissociation, Ion Structure, Metal ions, Density functional theory, Glycans.



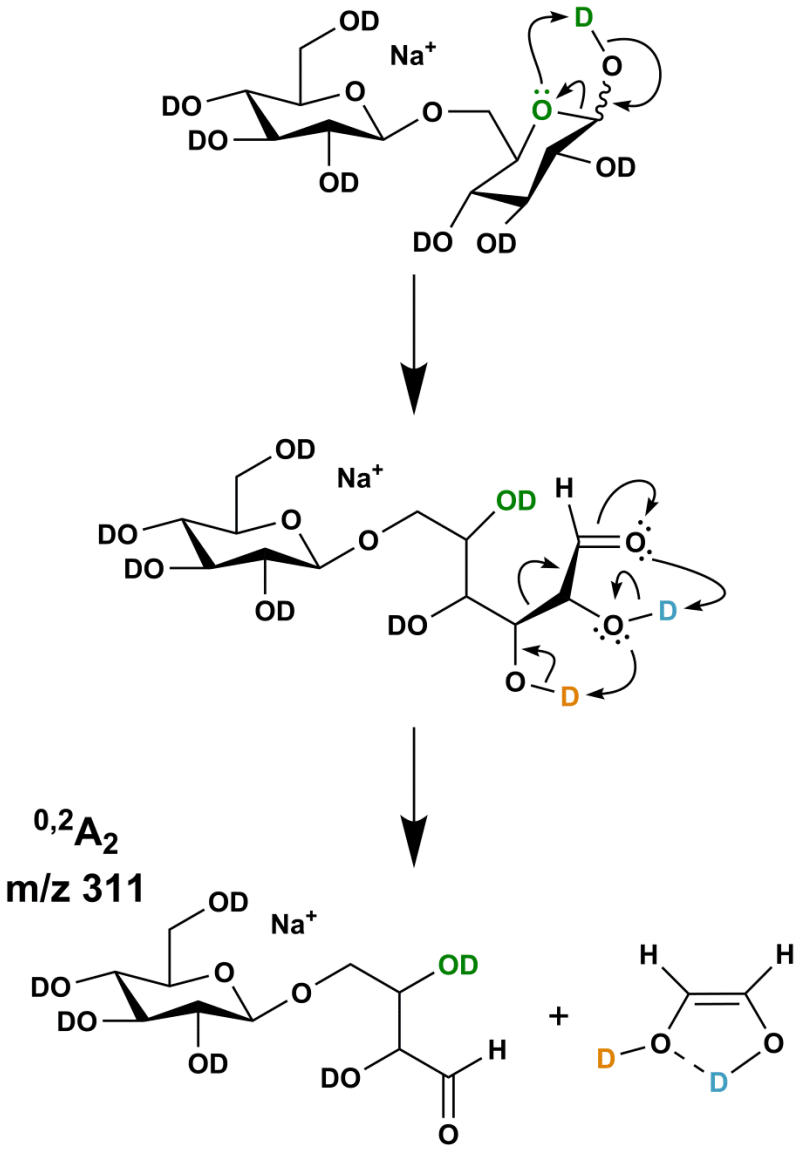
Scheme S1: The lowest energy B_1-Y_1 pathway for [Cellobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte.



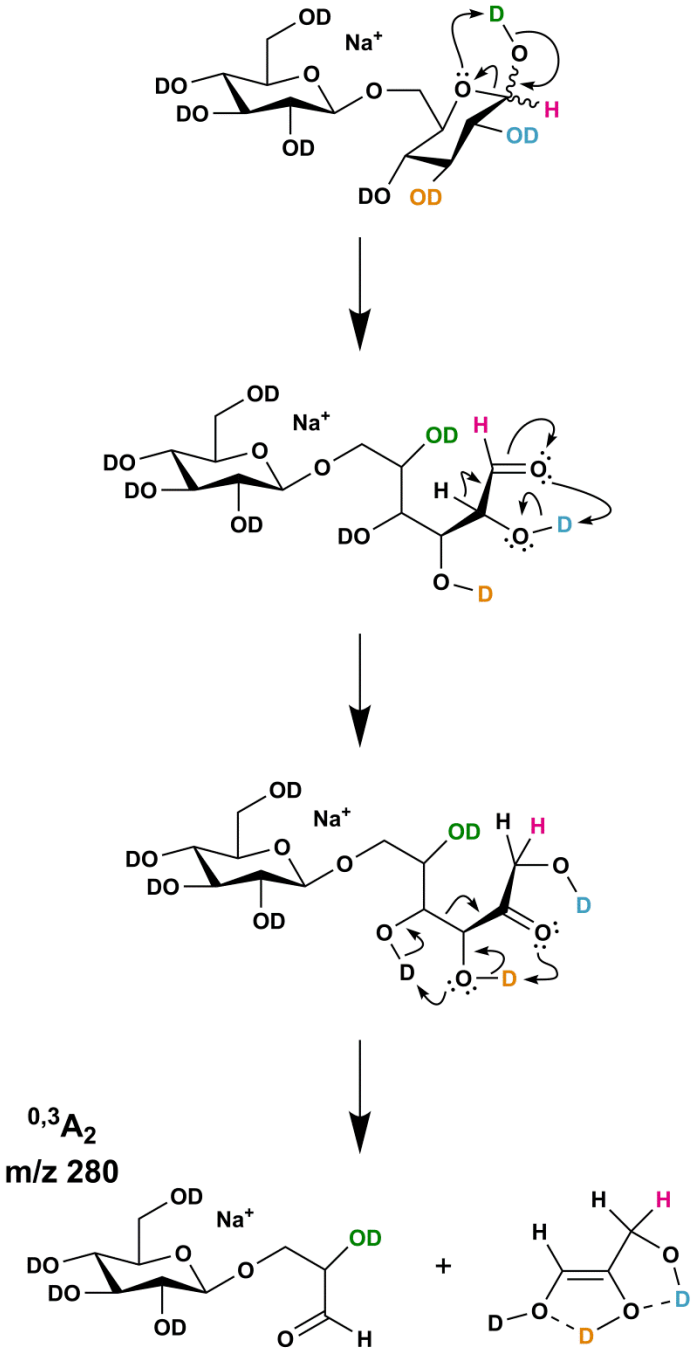
Scheme S2: The lowest energy B_1-Y_1 pathway for [Gentiobiose+Na]$^+$.



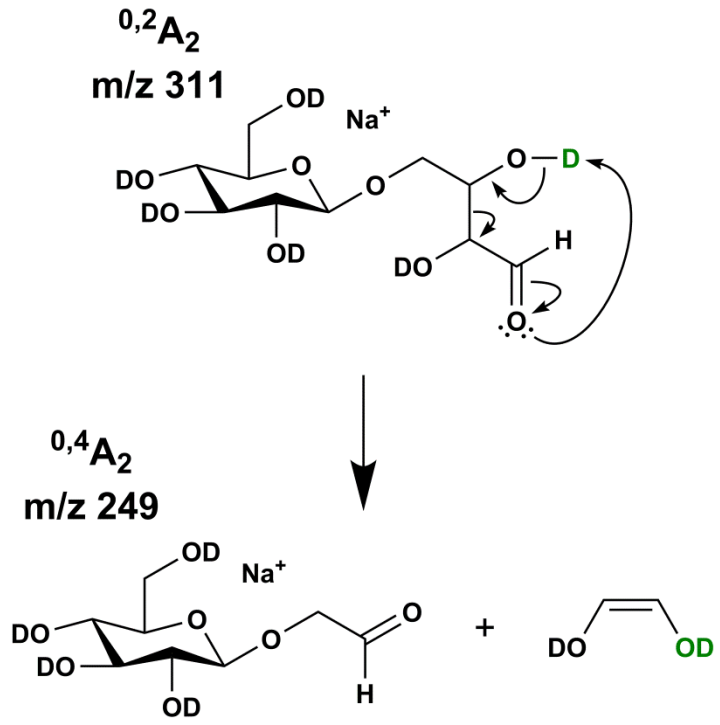
Scheme S3: The lowest energy B_1-Y_1 pathway for [Gentiobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte.



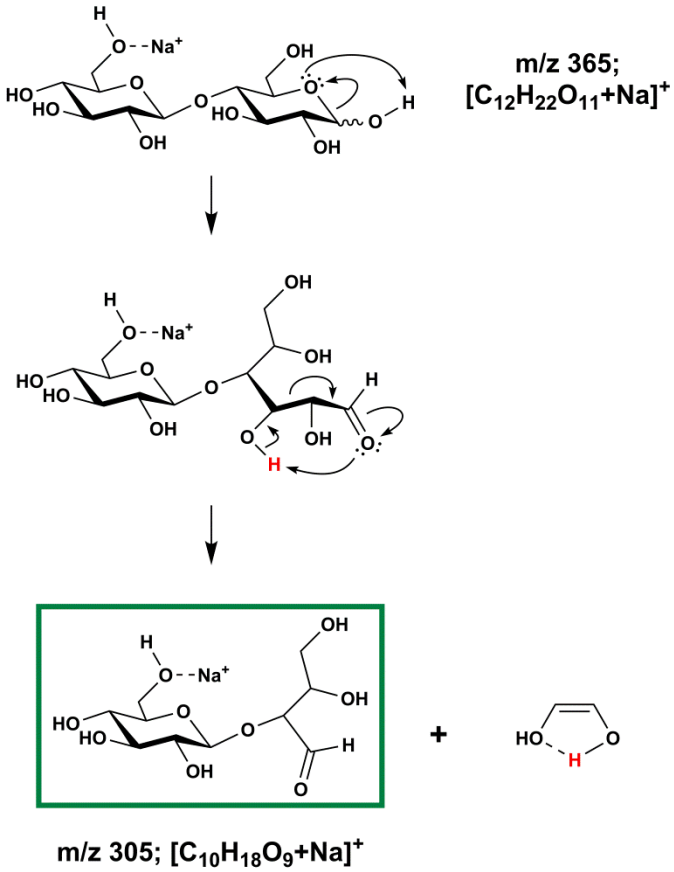
Scheme S4: The lowest energy $^{0,2}A_2$-X_0 pathway for [Gentiobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte.



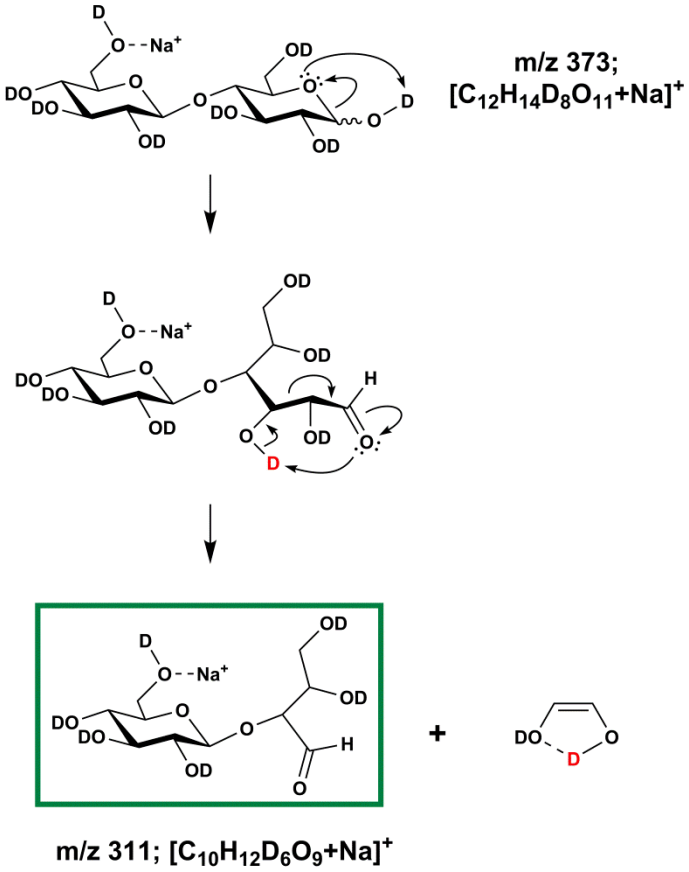
Scheme S5: The lowest energy $^{0,3}A_2$-X_0 pathway for [Gentiobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte.



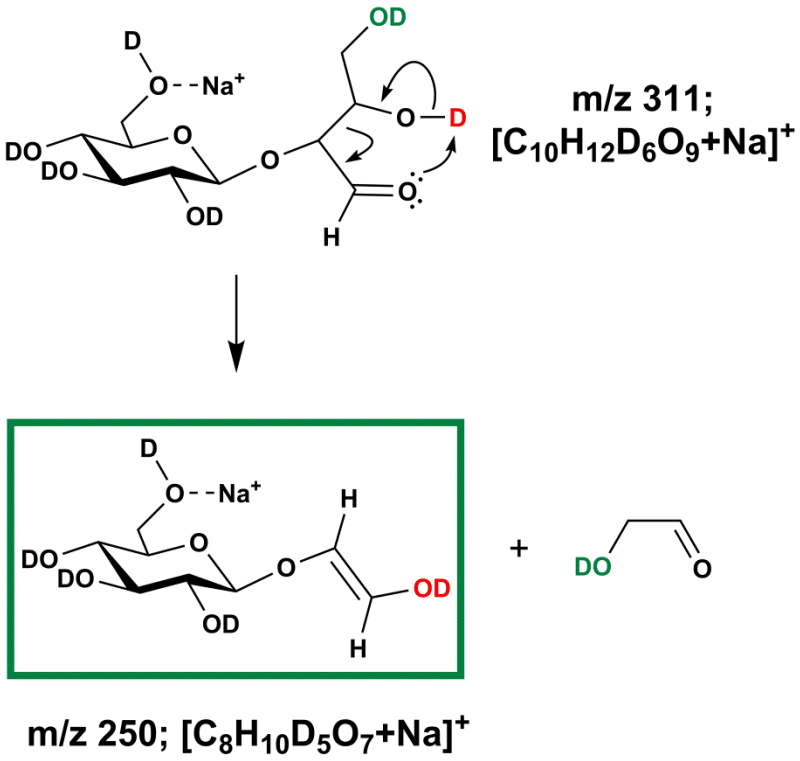
Scheme S6: The ${}^{0,2}A_2 \rightarrow {}^{0,4}A_2$-formation pathway for [Gentiobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte.



Scheme S7: The lowest energy $^{0,2}A_2$-forming pathway for [Cellobiose+Na]$^+$.



Scheme S8: The lowest energy $^{0,2}A_2$-forming pathway for [Cellobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte.



Scheme S9: The lowest energy $^{0,2}A_2 \rightarrow {}^{2,4}A_2$-formation for [Cellobiose+Na]$^+$ illustrated for the hydroxyl deuterated form of the analyte. Loss of glycolaldehyde includes a single deuteron corresponding to a loss of 61 u. This is in contrast with the deuterated Gentiobiose $^{0,2}A_2$ ion (Scheme 6, Table 1) which loses 62 u to form the $^{2,4}A_2$ ion (m/z 249) and *cis*-ethene-1,2-diol; HC(OD)=CH(OD).

Analyte	Transition Structure	E_{el}/H	$\Delta E_{el+ZPE,0K}$/ kJ mol^{-1}	ΔH_{298K}/ kJ mol^{-1}	ΔG_{298K}/ kJ mol^{-1}	ΔS_{298K}/ J mol^{-1}
Cellobiose	B_1-Y_1 *TS_A*	-1459.585487	229.3	228.4	227.9	1.4
Cellobiose	B_1-Y_1 *TS_B*	-1459.584806	229.5	227.7	231.9	-14.0
Cellobiose	Ring-opening	-1459.590974	214.9	215.7	211.7	13.6
Cellobiose	$^{0,2}A_2$	-1459.591155	204.1	204.7	203.4	4.4
Cellobiose	$^{0,2}A_2 =>^{2,4}A_2$	-1459.535660	341.3	344.9	283.9	204.8
Gentiobiose	B_1-Y_1	-1459.565898	267.4	267.3	263.3	13.3
Gentiobiose	Ring-opening	-1459.591961	196.4	195.9	195.7	0.8
Gentiobiose	$^{0,2}A_2$	-1459.596969	179.4	180.5	174.1	21.5
Gentiobiose	$^{0,3}A_2$	-1459.571078	245.8	248.1	236.3	39.6
Gentiobiose	$^{0,4}A_2$ (direct)	-1459.544823	302.9	309.0	291.6	58.4
Gentiobiose	$^{0,2}A_2 =>^{0,4}A_2$	-1459.545006	308.2	312.3	247.1	218.9

Table S1: Relative Energies of the Transition Structures of sodiated Cellobiose (β-D-glucopyranosyl-(1→4)-α-D-Glucose) & Gentiobiose (β-D-glucopyranosyl-(1→6)-α-D-Glucose) forms calculated at the M06-2X/6-31+G(d,p) level of theory.

Analyte	Transition Structure	E_{el}/H	$\Delta E_{el+ZPE,0K}$/ kJ mol^{-1}	ΔH_{298K}/ kJ mol^{-1}	ΔG_{298K}/ kJ mol^{-1}	ΔS_{298K}/ J mol^{-1}
Cellobiose	B_1-Y_1 *TS_A*	-1459.962526	225.4	222.9	229.0	-20.6
Cellobiose	B_1-Y_1 *TS_B*	-1459.962334	228.2	226.4	229.3	-9.7
Cellobiose	Ring-opening ${}^{0,2}A_2$	-1459.969094	211.8	208.2	218.8	-35.7
Cellobiose	${}^{0,2}A_2 => {}^{2,4}A_2$	-1459.919256	323.2	325.9	268.0	194.3
Gentiobiose	B_1-Y_1	-1459.951330	262.7	262.4	261.0	4.9
Gentiobiose	Ring-opening ${}^{0,2}A_2$	-1459.978358	193.5	190.8	198.3	-25.3
Gentiobiose	${}^{0,3}A_2$	-1459.953202	251.2	252.9	243.9	30.4
Gentiobiose	${}^{0,4}A_2$ (direct)	-1459.926336	310.3	315.5	300.8	49.2
Gentiobiose	${}^{0,2}A_2 => {}^{0,4}A_2$	-1459.92843	310.6	311.8	251.2	209.7

Table S2: Relative Energies of the Transition Structures of sodiated Cellobiose (β-D-glucopyranosyl-(1→4)-β-D-Glucose) & Gentiobiose (β-D-glucopyranosyl-(1→6)-β-D-Glucose) forms calculated at the M06-2X/6-311++G(2d,p)//M06-2X/6-31+G(d,p) level of theory.

Analyte	Transition Structure	E_{el}/H	$\Delta E_{el+ZPE,0K}$/ kJ mol^{-1}	ΔH_{298K}/ kJ mol^{-1}	ΔG_{298K}/ kJ mol^{-1}	ΔS_{298K}/ J mol^{-1}
Cellobiose	B_1-Y_1 *TS_A*	-1459.965384	226.5	225.6	225.1	1.4
Cellobiose	B_1-Y_1 *TS_B*	-1459.962334	233.6	232.4	232.5	-14.0
Cellobiose	Ring-opening ${}^{0,2}A_2$	-1459.969094	228.0	227.3	223.9	13.6
Cellobiose	${}^{0,2}A_2 => {}^{2,4}A_2$	-1459.919256	352.9	351.3	352.5	204.8
Gentiobiose	B_1-Y_1	-1459.947344	269.6	268.7	265.6	13.3
Gentiobiose	Ring-opening	-1459.970425	209.0	208.1	205.1	0.8
Gentiobiose	${}^{0,3}A_2$	-1459.953202	236.4	238.7	226.9	39.6
Gentiobiose	${}^{0,4}A_2$ (direct)	-1459.926336	295.1	301.2	283.8	58.4
Gentiobiose	${}^{0,2}A_2 => {}^{0,4}A_2$	-1459.92843	295.4	299.5	234.2	218.9

Table S3: Relative Energies of the Transition Structures of sodiated Cellobiose (β-D-glucopyranosyl-(1→4)-α-D-Glucose) and Gentiobiose (β-D-glucopyranosyl-(1→6)-α-D-Glucose) forms calculated at the M06-2X/6-311++G(2d,p)//M06-2X/6-31+G(d,p) level of theory.

Analyte	Transition Structure	E_{el}/H	$\Delta E_{el+ZPE,0K}$/ kJ mol^{-1}	ΔH_{298K}/ kJ mol^{-1}	ΔG_{298K}/ kJ mol^{-1}	ΔS_{298K}/ J mol^{-1}
Cellobiose	B_1-Y_1 *TS_A*	-1457.576976	227.4	224.9	231.1	-20.6
Cellobiose	B_1-Y_1 *TS_B*	-1457.576802	230.2	228.4	231.4	-9.7
Cellobiose	Ring-opening $^{0,2}A_2$	-1457.58682	205.2	201.6	212.3	-35.7
Cellobiose	$^{0,2}A_2 => ^{2,4}A_2$	-1457.528782	338.2	340.8	282.9	194.3
Gentiobiose	B_1-Y_1	-1457.565286	264.5	264.1	262.7	4.9
Gentiobiose	Ring-opening $^{0,2}A_2$	-1457.594017	190.8	188.1	195.6	-25.3
Gentiobiose	$^{0,3}A_2$	-1457.567628	252.1	253.4	244.4	30.4
Gentiobiose	$^{0,4}A_2$ (direct)	-1457.534519	327.1	332.4	317.7	49.2
Gentiobiose	$^{0,2}A_2 => ^{0,4}A_2$	-1457.537467	325.2	328.4	265.9	209.7

Table S4: Relative Energies of the Transition Structures of sodiated Cellobiose (β-D-glucopyranosyl-(1→4)-β-D-Glucose) & Gentiobiose (β-D-glucopyranosyl-(1→6)-β-D-Glucose) forms calculated at the MP2(Full)/6-311++G(2d,p)//M06-2X/6-31+G(d,p) level of theory.

Analyte	Transition Structure	E_{el}/H	$\Delta E_{el+ZPE,0K}$/ kJ mol^{-1}	ΔH_{298K}/ kJ mol^{-1}	ΔG_{298K}/ kJ mol^{-1}	ΔS_{298K}/ J mol^{-1}
Cellobiose	B_1-Y_1 *TS_A*	-1457.579963	227.6	226.7	226.2	1.4
Cellobiose	B_1-Y_1 *TS_B*	-1457.578078	236.0	2334.7	234.8	-14.0
Cellobiose	Ring-opening $^{0,2}A_2$	-1457.585463	219.6	218.9	215.5	13.6
Cellobiose	$^{0,2}A_2 => ^{2,4}A_2$	-1457.528782	367.3	365.7	366.8	204.8
Gentiobiose	B_1-Y_1	-1457.56123	269.3	268.3	265.3	13.3
Gentiobiose	Ring-opening $^{0,2}A_2$	-1457.588121	198.7	197.7	194.7	0.8
Gentiobiose	$^{0,3}A_2$	-1457.567628	234.6	236.9	225.1	39.6
Gentiobiose	$^{0,4}A_2$ (direct)	-1457.534519	309.7	315.8	298.4	58.4
Gentiobiose	$^{0,2}A_2 => ^{0,4}A_2$	-1457.537467	307.8	309.4	311.9	246.6

Table S5: Relative Energies of the Transition Structures of sodiated Cellobiose (β-D-glucopyranosyl-(1→4)-α-D-Glucose) & Gentiobiose (β-D-glucopyranosyl-(1→6)-α-D-Glucose) forms calculated at the MP2(Full)/6-311++G(2d,p)//M06-2X/6-31+G(d,p) level of theory.

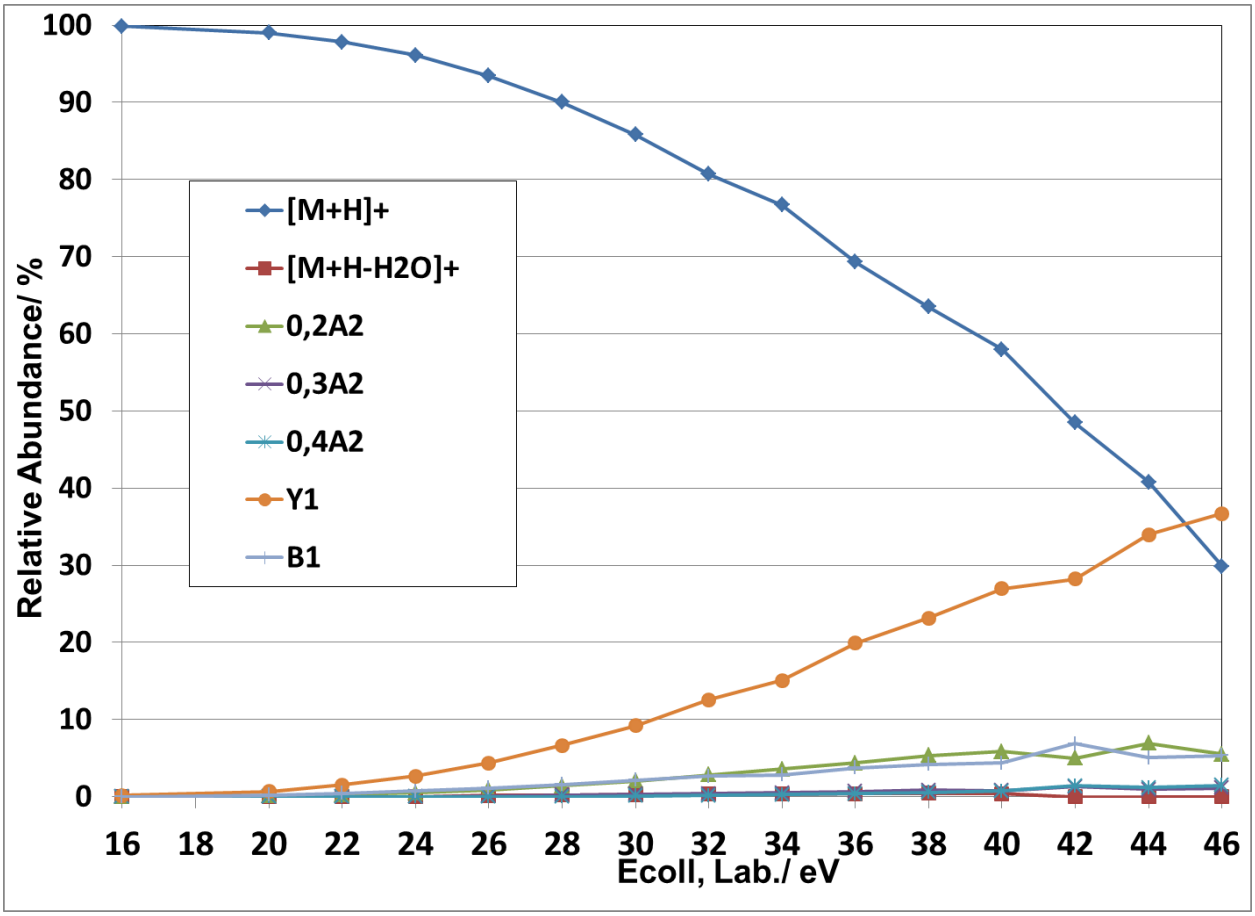


Figure S1: Relative proportions of peak current as a function of collision energy for [Cellobiose+Na]$^+$. Ion current reduction due to direct sodium loss (and/or scattering) beyond laboratory collision energies of 46 eV was too large to provide meaningful additional data points. See Chen et al., (*Phys.Chem.Chem.Phys.*, 2017, **19**, 15454) for specifics on the energetics of desodiation using [glucose+Na]$^+$.

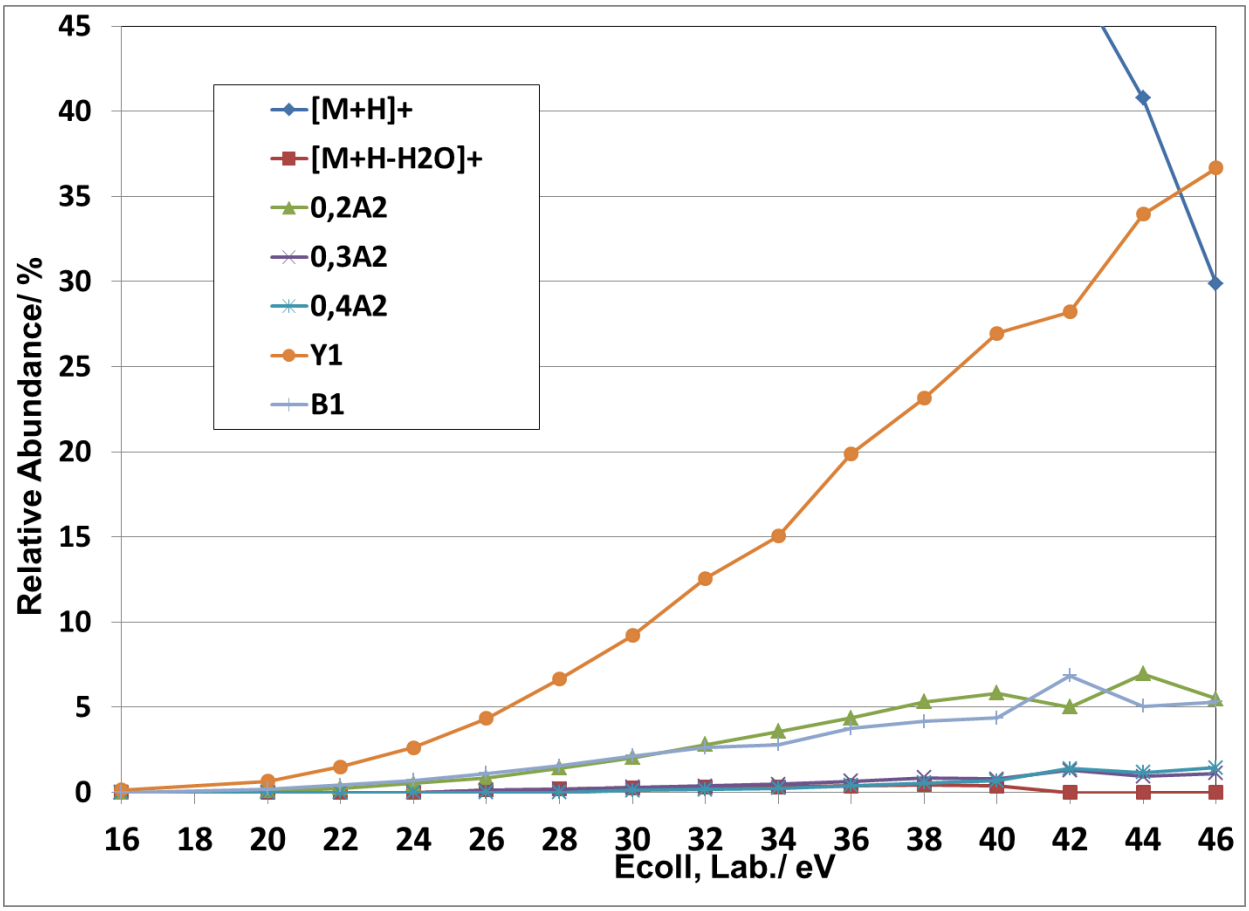


Figure S2: Relative proportions (with adjusted scale) of peak current as a function of collision energy for [Cellobiose+Na]$^+$. Ion current reduction due to direct sodium loss (and/or scattering) beyond laboratory collision energies of 46 eV was too large to provide meaningful additional data points. See Chen et al., (*Phys.Chem.Chem.Phys.*, 2017, **19**, 15454) for specifics on the energetics of desodiation using [glucose+Na]$^+$.

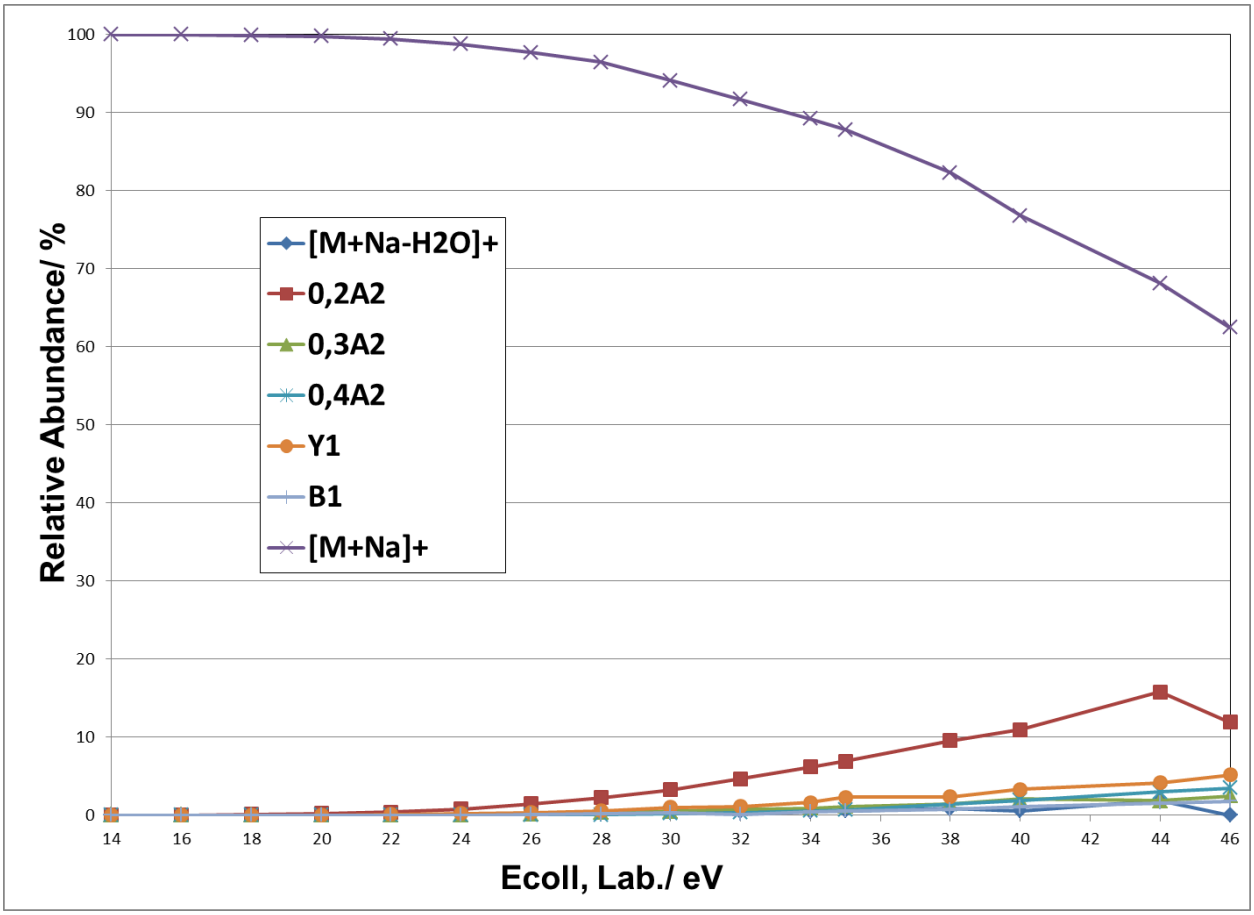


Figure S3: Relative proportions of peak current as a function of collision energy for [Gentiobiose+Na]$^+$. Ion current reduction due to direct sodium loss (and/or scattering) beyond laboratory collision energies of 46 eV was too large to provide meaningful additional data points. See Chen et al., (*Phys.Chem.Chem.Phys.*, 2017, **19**, 15454) for specifics on the energetics of desodiation using [glucose+Na]$^+$.

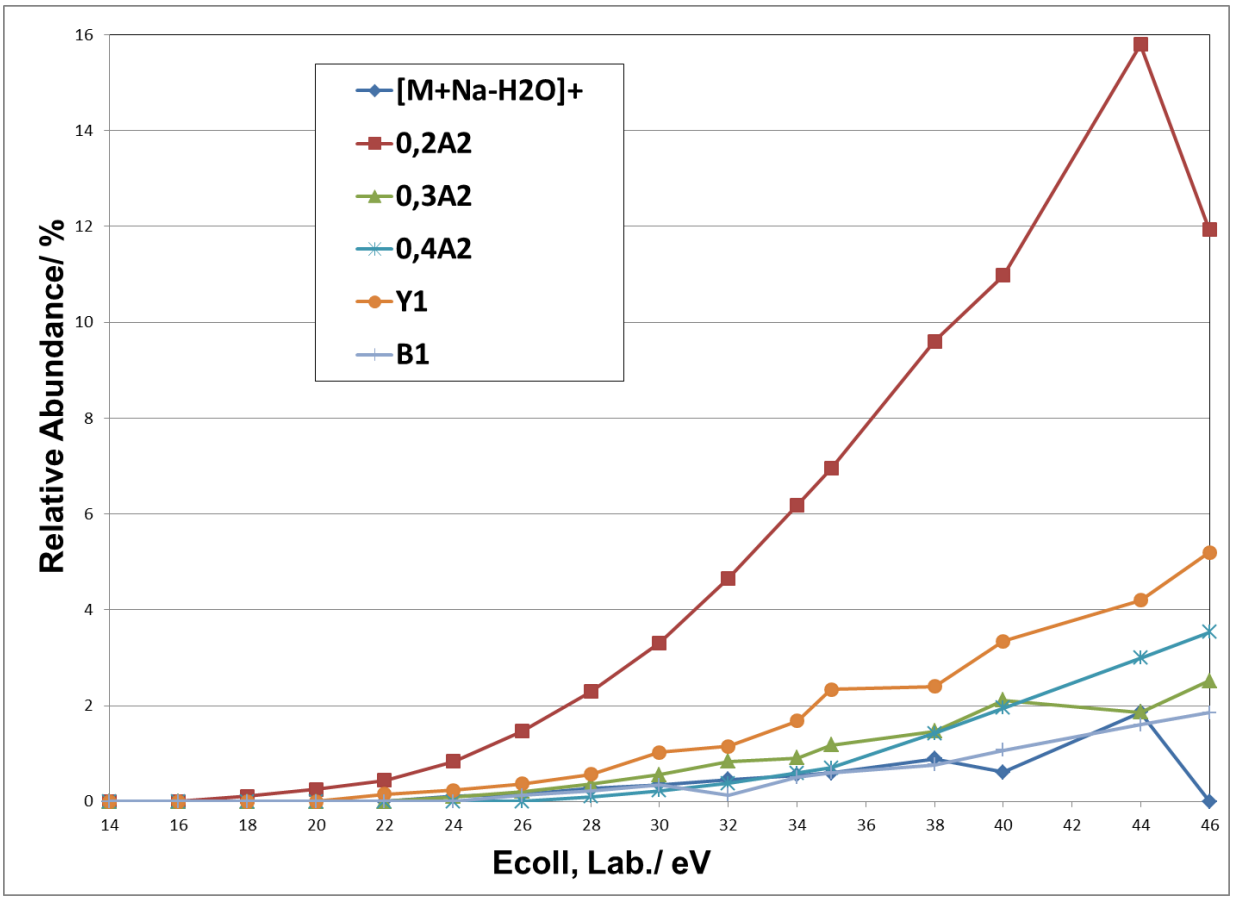


Figure S4: Relative proportions of peak current (excluding precursor, see Figure S3) as a function of collision energy for [Gentiobiose+Na]$^+$. Ion current reduction due to direct sodium loss (and/or scattering) beyond laboratory collision energies of 46 eV was too large to provide meaningful additional data points. See Chen et al., (*Phys.Chem.Chem.Phys.*, 2017, **19**, 15454) for specifics on the energetics of desodiation using [glucose+Na]$^+$.

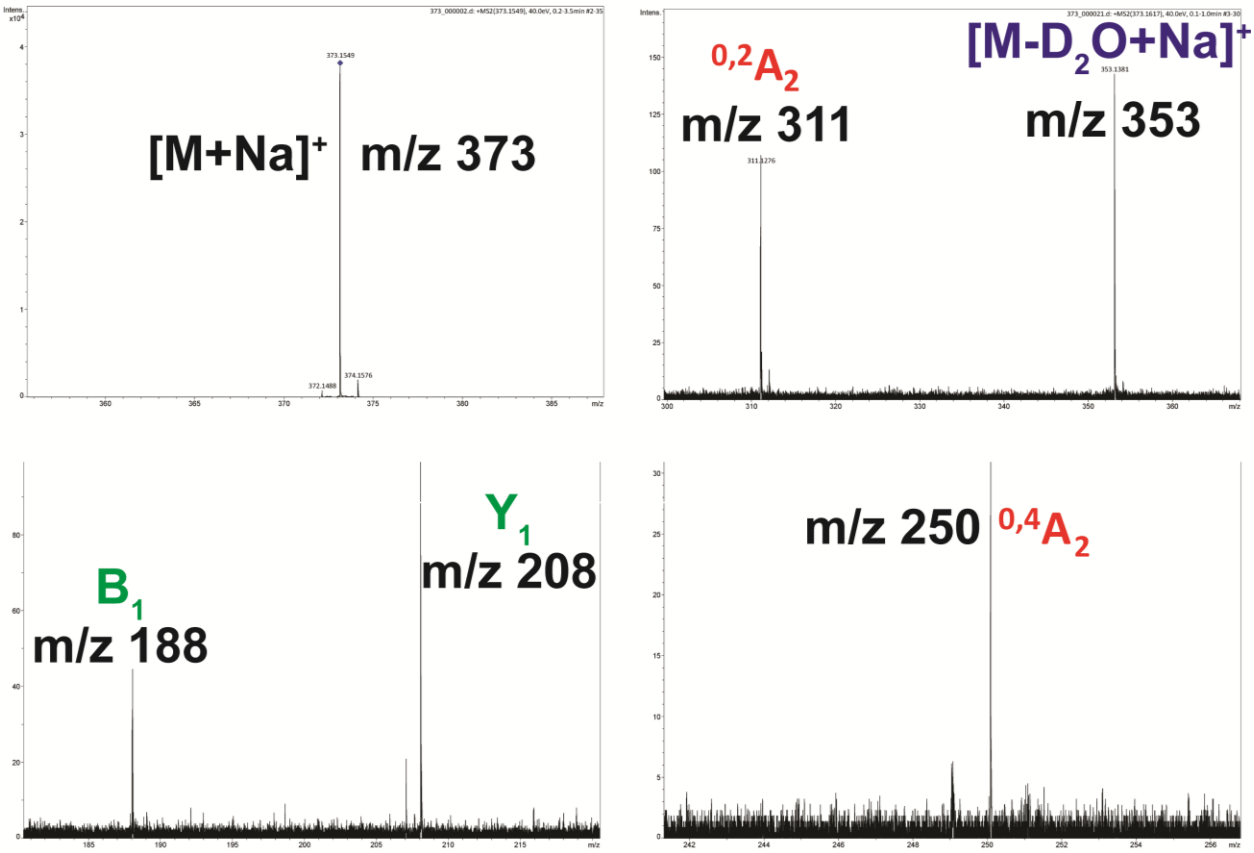


Figure S5: Example MS/MS spectra of sodiated deuterated hydroxyl Cellobiose, $[D_8\text{-Cellobiose+Na}]^+$.

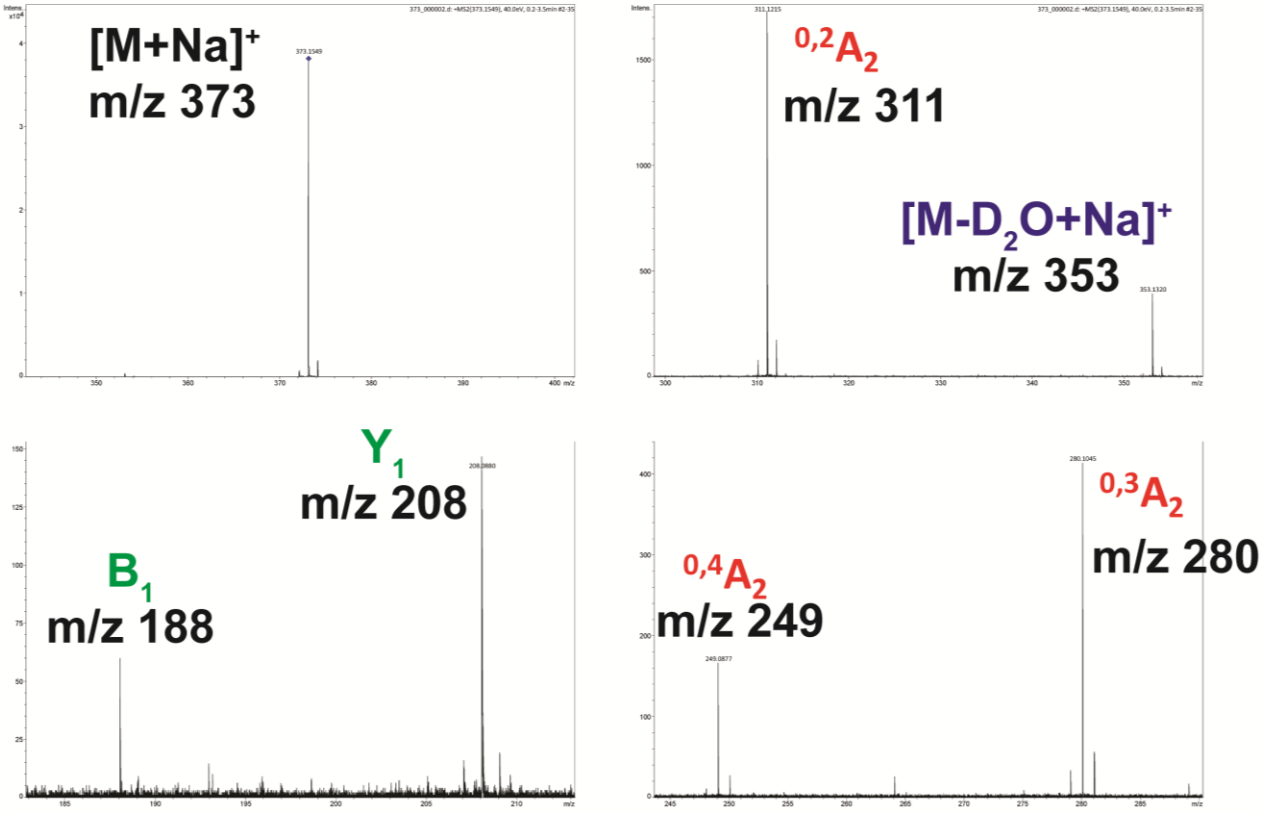


Figure S6: Example MS/MS spectra of hydroxyl deuterated, sodiated Gentiobiose, $[D_8\text{-Gentiobiose+Na}]^+$.

Additional Instrumentation specifics for sodiated Cellobiose and Gentiobiose MS collection:

Collision energy: 2-50eV in 2eV steps
Collision cell RF: 300 Vpp
Transfer Time 80 µs for both.
PrePulseStorage 5 µs.

Source: ESI.
Capillary: 3400 V
End Plate Offset: -500 V
Dry Gas (N2): 0.4 Bar, 4 L/min, 200 °C

Transfer:
Funnel/Multipole RF: 250 Vpp