Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Structural resolution of carbohydrate positional and structural isomers based on gas-phase ion mobility-mass spectrometry

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Abstract: This report describes the rapid characterization of positional and structural carbohydrate isomers based on structural separations provided by ion mobility-mass spectrometry (IM-MS). Many of the diseases associated with glycoprotein variation can be more effectively treated with earlier detection substantiating the need for high-throughput methodologies for glycan characterization. This remains particularly difficult due to heterogeneity, branching, and large size of carbohydrate moieties which creates the potential for numerous isobaric positional and structural isomers that are difficult to characterize using conventional MS methods. IM-MS provides rapid (μs to ms) structural separations by IM and subsequent identification by MS which presents a means for characterization of positional and structural carbohydrate isomers. To chart the structural variation observed in IM-MS, the ion-neutral collision cross sections for over 300 carbohydrates are reported. This diversity can also be varied through the utility of using different alkali metals to tune separation selectivity via alkali metal-carbohydrate coordination. Furthermore, the advantages of combining either pre- and/or post-IM fragmentation prior to MS analysis is demonstrated for enhanced confidence in carbohydrate identification.

Table S1. Carbohydrate collision cross sections reported in this work.

Name (parent name if a fragment species)[1]	species	*m/z* (Da)	Ω (Å^2)	σ (# of measurements)
B_1 (P1 tri)	$[M+Na]^+$	185.1	53.6	3.8(5)
$^{2,4}A_2$ (P1 tri)	$[M+Na]^+$	245.0	72.5	1.2(5)
$^{2,4}X_0$ (Le^ALe^x)	$[M+Na]^+$	253.0	35.9	2.0(5)
$^{2,4}X_0$ (Di-Le^A)	$[M+Na]^+$	253.0	94.0	0.8(7)
Y_1-N_2 (B tetra type 1)	$[M+Na]^+$	285.0	82.3	1.1(5)
Y_1-N_2 (P1 tri)	$[M+Na]^+$	285.3	85.3	2.8(5)
Z_1 (LacNAc)	$[M+Na]^+$	295.0	96.3	7.4(5)
Z_1 (B2-tri)	$[M+Na]^+$	295.3	89.7	2.1(5)
Z_1 (P1 tri)	$[M+Na]^+$	295.3	88.2	7.1(5)
$^{0,2}A_2$ (Pk)	$[M+Na]^+$	305.0	96.6	4.6(5)
$^{1,5}A_2$ (P1 tri)	$[M+Na]^+$	319.3	95.7	3.1(5)
$^{1,5}A_2$ (Galα3-type1)	$[M+Na]^+$	319.3	99.0	3.2(5)
$^{0,2}X_1$-N_2 (Galα3-type1)	$[M+Na]^+$	327.3	111.6	4.7(9)
B_2 (LNFP1)	$[M+Na]^+$	331.0	118.6	0.5(7)
B_2 (Lac)	$[M+Na]^+$	347.0	108.4	3.5(7)
B_2 (P1 tri)	$[M+Na]^+$	347.3	101.4	6.6(5)
$^{0,2}X_1$ (P1 tri)	$[M+Na]^+$	355.3	106.6	1.8(5)
$^{1,5}A_2$ (LNnT)	$[M+Na]^+$	360.0	106.9	2.1(5)
Y_2 (LNFP2)	$[M+Na]^+$	362.3	113.5	1.3(8)
Y_2 (LNFP1)	$[M+Na]^+$	365.0	112.8	1.3(12)
C_2 (P1 tri)	$[M+Na]^+$	365.3	102.0	3.1(5)
lactose	$[M+Na]^+$	365.3	121.1	6.4(16)
maltose	$[M+Na]^+$	365.3	124.6	2.0(8)
C_2 (Lac)	$[M+Na]^+$	365.4	107.5	1.4(7)
$^{2,4}X_1$ (Pk)	$[M+Na]^+$	374.0	127.3	2.8(8)
$^{2,4}X_1$-N_2 (P1 tri)	$[M+Na]^+$	387.4	117.6	3.2(8)
$^{2,4}X_1$-N_2 (B2-tri)	$[M+Na]^+$	387.4	105.7	1.4(5)
B_2 (Di-Le^c)	$[M+Na]^+$	388.0	111.1	1.1(7)
B_2 (LNnT)	$[M+Na]^+$	388.0	113.6	0.9(5)
B_2 (LNT)	$[M+Na]^+$	388.0	115.8	2.3(10)
B_2 (P1 penta)	$[M+Na]^+$	388.0	114.2	0.8(5)
B_2 (LacNAc)	$[M+Na]^+$	390.0	116.9	1.7(7)
$^{2,4}A_3$ (H-type2-LN-LN)	$[M+Na]^+$	391.0	122.3	0.5(5)
C_2 (Le^c)	$[M+Na]^+$	405.0	124.9	3.4(7)
LN	$[M+Na]^+$	405.0	129.2	2.1(23)
C_2 (LacNAc)	$[M+Na]^+$	405.0	130.6	3.0(5)
C_2 (P1 penta)	$[M+Na]^+$	406.0	118.3	2.1(9)
C_2 (Di-Le^c)	$[M+Na]^+$	406.0	125.3	5.6(5)
C_2 (GNLNLN)	$[M+Na]^+$	406.0	118.0	4.0(5)
M-N_2 (Lac)	$[M+Na]^+$	406.0	122.3	2.8(11)

C_2 (LNT)	$[M+Na]^+$	406.0	119.4	1.5(5)
$^{2,4}A_3$ (Pk)	$[M+Na]^+$	407.0	116.4	1.4(5)
$^{2,4}A_3$ (P1 antigen)	$[M+Na]^+$	407.0	123.0	3.4(10)
$^{2,4}A_3$ (P1 tri)	$[M+Na]^+$	407.3	119.5	2.1(5)
$^{2,4}A_3$ (Galα3-type1)	$[M+Na]^+$	407.3	118.5	0.6(8)
C_4/Y_3 (LNFP1)	$[M+Na]^+$	409.4	129.8	1.1(17)
$Y_{3\beta}/C_2$ (LNFP2)	$[M+Na]^+$	409.4	139.5	2.6(9)
$Z_{1\alpha}$-N_2 (Le^ALe^x)	$[M+Na]^+$	413.0	108.7	4.7(5)
Z_2 (LNnT)	$[M+Na]^+$	416.0	74.7	1.1(5)
$Y_{1\alpha}$-N_2 (2'F-B type 2)	$[M+Na]^+$	431.0	125.0	3.0(5)
Y_2 (P1 antigen)	$[M+Na]^+$	434.0	131.0	1.4(5)
Y_2 (LNnT)	$[M+Na]^+$	434.0	110.5	1.6(5)
Lac	$[M+Na]^+$	434.4	130.3	3.5(15)
$^{0,3}A_3$ (P1 tri)	$[M+Na]^+$	437.0	133.0	1.2(7)
$Z_{1\alpha}$ (Di-Le^A)	$[M+Na]^+$	441.4	132.1	2.7(13)
Y_2-N_2 (H-type2-LN-LN)	$[M+Na]^+$	447.0	133.4	1.1(5)
Y_2-N_2 (Di-Le^c)	$[M+Na]^+$	447.0	131.3	1.8(25)
Y_2-N_2 (LNT)	$[M+Na]^+$	447.0	127.9	8.1(26)
M-N_2 (LacNAc)	$[M+Na]^+$	447.0	137.2	0.9(17)
M-N_2 (Le^c)	$[M+Na]^+$	447.0	136.4	1.0(10)
Y_2-N_2 (P1 penta)	$[M+Na]^+$	447.0	134.1	0.3(8)
Y_2-N_2 (Galα3-type1)	$[M+Na]^+$	447.4	125.6	1.4(5)
Y_2-N_2 (B2-tri)	$[M+Na]^+$	447.4	137.7	0.8(9)
Y_2-N_2 (P1 tri)	$[M+Na]^+$	447.4	133.6	0.8(17)
$^{2,4}A_3$ (GNLNLN)	$[M+Na]^+$	448.0	115.1	0.5(8)
$^{0,2}X_2$-N_2 (Pk)	$[M+Na]^+$	448.0	137.8	1.6(8)
$^{2,4}A_3$ (LNnT)	$[M+Na]^+$	448.0	132.7	2.6(5)
$^{1,3}A_3$ (Galα3-type1)	$[M+Na]^+$	448.4	128.0	2.0(5)
$^{0,2}A_{2\alpha}$ (Di-Le^A)	$[M+Na]^+$	451.0	132.2	3.1(5)
$^{0,2}A_3$ (H-type2-LN-LN)	$[M+Na]^+$	451.0	130.6	0.6(5)
Z_2 (P1 tri)	$[M+Na]^+$	457.0	122.1	1.3(12)
Z_2 (Galα3-type1)	$[M+Na]^+$	457.0	122.3	1.0(7)
Z_2 (GNLNLN)	$[M+Na]^+$	457.0	108.3	1.3(5)
$Y_{1\alpha}$ (Le^ALe^x)	$[M+Na]^+$	459.0	107.5	1.4(5)
$Y_{1\alpha}$ (Di-Le^A)	$[M+Na]^+$	459.4	126.6	1.8(12)
$^{1,5}X_2$ (P1 antigen)	$[M+Na]^+$	462.0	121.2	0.7(9)
$^{0,2}A_3$ (Pk)	$[M+Na]^+$	467.0	127.0	2.8(5)
$^{0,2}A_3$ (Galα3-type1)	$[M+Na]^+$	467.4	131.8	1.1(6)
$^{0,2}A_3$ (P1 tri)	$[M+Na]^+$	467.4	125.4	2.4(5)
Y_2 (LNT)	$[M+Na]^+$	475.0	102.5	0.5(5)
Y_2 (Di-Le^c)	$[M+Na]^+$	475.0	138.0	1.3(5)
Y_2 (P1 penta)	$[M+Na]^+$	475.0	135.3	3.5(7)
Y_2 (P1 tri)	$[M+Na]^+$	475.4	130.0	0.5(11)

LacNAc	$[M+Na]^+$	475.4	146.9	2.2(17)
Y_2 (Galα3-type1)	$[M+Na]^+$	475.4	133.8	0.6(7)
Le^c	$[M+Na]^+$	475.4	138.9	2.0(14)
Y_2 (B2-tri)	$[M+Na]^+$	475.4	145.6	1.7(7)
$^{1,5}X_{1\alpha}$ (Di-Le^A)	$[M+Na]^+$	487.4	125.0	2.3(12)
$^{0,2}X_2$-N_2 (P1 antigen)	$[M+Na]^+$	489.0	150.6	3.4(5)
$^{0,2}X_2$-N_2 (P1 tri)	$[M+Na]^+$	489.5	139.1	3.3(5)
B_2 (B tetra type 1)	$[M+Na]^+$	493.0	132.3	1.9(8)
$^{1,5}X_{2\alpha}$ (B tetra type 1)	$[M+Na]^+$	503.0	93.0	1.4(5)
$^{1,5}X_2$ (Di-Le^c)	$[M+Na]^+$	503.0	152.0	3.4(5)
$^{1,5}X_2$ (GNLNLN)	$[M+Na]^+$	503.0	138.5	1.5(5)
$^{1,5}X_2$ (LNT)	$[M+Na]^+$	503.0	108.1	0.7(5)
$^{1,5}X_2$ (H-type2-LN-LN)	$[M+Na]^+$	503.0	139.3	2.4(8)
$^{1,5}X_2$ (Galα3-type1)	$[M+Na]^+$	503.4	144.8	3.5(8)
$^{1,5}A_{2\alpha}$ (Le^ALe^X)	$[M+Na]^+$	506.0	107.9	2.0(5)
$^{0,2}A_3$ (LNnT)	$[M+Na]^+$	508.0	107.8	2.2(5)
B_3 (Pk)	$[M+Na]^+$	509.0	132.1	1.3(5)
$^{1,5}A_3$ (P1 tri)	$[M+Na]^+$	522.5	136.0	0.7(4)
$^{1,5}A_3$ (Galα3-type1)	$[M+Na]^+$	522.5	143.9	2.5(9)
C_3 (Pk)	$[M+Na]^+$	527.0	139.4	1.8(12)
$^{0,2}X_2$-N_2 (Di-Le^c)	$[M+Na]^+$	531.0	109.1	1.5(5)
$^{0,2}X_2$-N_2 (LNT)	$[M+Na]^+$	531.0	115.3	1.6(6)
B_3 (LNFP1)	$[M+Na]^+$	533.0	151.5	0.7(9)
$^{2,4}X_{1\alpha}$-N_2 (B tetra type 1)	$[M+Na]^+$	534.0	108.6	1.1(5)
$B_{2\alpha}$ (Le^ALe^X)	$[M+Na]^+$	534.0	109.0	1.6(5)
B_3 (H-type2-LN-LN)	$[M+Na]^+$	534.0	143.6	1.7(8)
B_2 (LNFP2)	$[M+Na]^+$	534.0	152.2	0.6(5)
$B_{2\alpha}$ (Di-Le^A)	$[M+Na]^+$	534.5	143.2	2.4(22)
$^{3,5}X_1$-N_2 (Galα3-type1)	$[M+Na]^+$	535.0	145.5	1.8(5)
$Y_{3\beta}/Z_{3\alpha}$ (LNFP2)	$[M+Na]^+$	547.3	169.1	5.8(5)
$^{0,3}X_1$ (Galα3-type1)	$[M+Na]^+$	547.5	160.3	3.4(10)
$^{2,4}X_2$-N_2 (B2-tri)	$[M+Na]^+$	549.5	166.3	6.2(9)
B_3 (Di-Le^c)	$[M+Na]^+$	550.0	147.7	1.8(33)
B_3 (LNT)	$[M+Na]^+$	550.0	142.4	1.9(9)
B_3 (P1 penta)	$[M+Na]^+$	550.0	150.6	0.3(13)
B_3 (P1 antigen)	$[M+Na]^+$	550.0	145.2	4.0(10)
B_3 (LNnT)	$[M+Na]^+$	551.0	157.9	1.0(6)
C_3 (LNFP1)	$[M+Na]^+$	551.0	134.1	1.6(9)
C_3 (H-type2-LN-LN)	$[M+Na]^+$	552.0	129.8	3.2(8)
B_3 (Galα3-type1)	$[M+Na]^+$	552.5	144.0	2.0(9)
B_3 (B2-tri)	$[M+Na]^+$	552.5	144.3	1.2(5)
$C_{2\alpha}$ (Di-Le^A)	$[M+Na]^+$	552.5	146.0	1.7(25)
C_3 (LNFP2)	$[M+Na]^+$	552.5	151.3	0.9(5)

B_3 (P1 tri)	$[M+Na]^+$	552.5	130.7	2.1(13)
$C_{2\alpha}$ (Le^ALe^x)	$[M+Na]^+$	553.0	146.4	1.4(8)
$^{2,4}X_{1\alpha}$ (Di-Le^A)	$[M+Na]^+$	561.5	121.5	2.0(5)
$^{3,5}X_1$ (Galα3-type1)	$[M+Na]^+$	563.0	126.8	0.7(5)
C_3 (LNT)	$[M+Na]^+$	568.0	150.7	1.9(5)
C_3 (P1 antigen)	$[M+Na]^+$	568.0	148.6	1.2(6)
C_3 (Di-Le^c)	$[M+Na]^+$	568.0	152.8	2.3(31)
Y_3 (LNFP1)	$[M+Na]^+$	568.0	157.4	0.4(5)
C_3 (P1 penta)	$[M+Na]^+$	568.0	153.4	0.8(5)
C_3 (B2-tri)	$[M+Na]^+$	568.5	157.7	1.3(8)
C_3 (P1 tri)	$[M+Na]^+$	568.5	157.8	1.1(11)
M-N_2 (Pk)	$[M+Na]^+$	568.5	148.8	1.1(17)
C_3 (Galα3-type1)	$[M+Na]^+$	568.5	152.2	2.5(12)
$Z_{2\alpha}$-N_2 (Di-Le^A)	$[M+Na]^+$	575.5	150.2	3.2(5)
$^{2,4}X_2$ (P1 antigen)	$[M+Na]^+$	577.0	161.9	5.6(5)
$^{2,4}X_2$ (P1 penta)	$[M+Na]^+$	577.0	160.5	0.8(11)
$^{2,4}X_2$ (Galα3-type1)	$[M+Na]^+$	577.5	164.1	4.6(8)
$^{2,4}X_2$ (P1 tri)	$[M+Na]^+$	577.5	112.2	1.9(5)
$^{2,4}X_2$ (LNnT)	$[M+Na]^+$	578.0	108.8	1.2(5)
$^{2,4}X_2$-N_2 (LNT)	$[M+Na]^+$	591.0	153.7	1.8(7)
$^{2,4}X_2$-N_2 (Di-Le^c)	$[M+Na]^+$	591.0	157.2	1.7(5)
Z_3-N_2 (P1 penta)	$[M+Na]^+$	591.0	145.9	0.9(5)
B_3 (GNLNLN)	$[M+Na]^+$	591.5	155.8	0.4(5)
$Y_{2\alpha}$-N_2 (Di-Le^A)	$[M+Na]^+$	593.6	157.3	1.8(24)
$Y_{2\alpha}$-N_2 (Le^ALe^x)	$[M+Na]^+$	594.0	162.3	2.6(13)
$Y_{2\alpha}$-N_2 (B tetra type 1)	$[M+Na]^+$	594.0	159.7	2.0(18)
$^{2,4}A_4$ /$Y_{3\alpha}$ (LNFP2)	$[M+Na]^+$	594.6	174.5	2.2(5)
Pk	$[M+Na]^+$	596.5	160.3	1.6(16)
Y_3-N_2 (P1 penta)	$[M+Na]^+$	609.0	160.1	1.7(10)
$Y_{2\beta}$-N_2 (B tetra type 1)	$[M+Na]^+$	609.6	163.2	0.9(14)
M-N_2 (B2-tri)	$[M+Na]^+$	609.6	170.6	1.4(18)
M-N_2 (Galα3-type1)	$[M+Na]^+$	609.6	154.1	2.2(24)
M-N_2 (P1 tri)	$[M+Na]^+$	609.6	161.9	1.2(30)
Y_3-N_2 (LNnT)	$[M+Na]^+$	610.0	165.9	2.0(12)
C_3 (GNLNLN)	$[M+Na]^+$	610.0	161.7	0.2(5)
$^{2,4}A_4$ (Di-Le^c)	$[M+Na]^+$	611.0	160.4	1.5(6)
$^{2,4}A_4$ (LNT)	$[M+Na]^+$	611.0	163.4	1.3(7)
$^{2,4}A_4$ (P1 antigen)	$[M+Na]^+$	611.0	158.8	4.1(9)
$^{2,4}X_2$ (LNT)	$[M+Na]^+$	619.0	169.2	2.4(5)
$Y_{2\alpha}$ (B tetra type 1)	$[M+Na]^+$	622.0	160.4	3.3(5)
$^{3,5}A_4$ (LNT)	$[M+Na]^+$	624.0	123.6	0.7(5)
Z_3-N_2 (GNLNLN)	$[M+Na]^+$	633.0	169.9	1.9(5)
Z_3-N_2 (Di-Le^c)	$[M+Na]^+$	633.0	166.0	1.9(5)

Z_3-N_2 (LNT)	$[M+Na]^+$	633.0	132.9	2.8(5)
Y_3 (P1 penta)	$[M+Na]^+$	637.0	170.1	1.4(8)
B2-tri	$[M+Na]^+$	637.6	177.8	3.7(18)
Galα3-type1 (1)	**$[M+Na]^+$**	**637.6**	**162.9**	**3.2(63)**
P1 tri (2)	**$[M+Na]^+$**	**637.6**	**169.3**	**1.2(88)**
$Y_{2\beta}$ (B tetra type 1)	$[M+Na]^+$	637.6	172.6	1.7(8)
Y_3 (LNnT)	$[M+Na]^+$	638.0	168.4	3.4(5)
Y_3 (P1 antigen)	$[M+Na]^+$	638.0	168.2	1.4(7)
$^{1,5}X_{2\alpha}$ (Di-Le^A)	$[M+Na]^+$	649.6	168.1	2.6(5)
Y_3-N_2 (LNT)	$[M+Na]^+$	651.0	180.3	2.5(6)
Y_3-N_2 (GNLNLN)	$[M+Na]^+$	651.0	173.0	1.8(9)
Y_3-N_2 (Di-Le^c)	$[M+Na]^+$	651.0	172.7	1.9(28)
$^{0,2}X_{2\beta}$-N_2 (B tetra type 1)	$[M+Na]^+$	651.6	171.5	3.4(5)
Z_3 (GNLNLN)	$[M+Na]^+$	661.0	110.4	2.2(5)
$^{0,2}A_4$ (P1 penta)	$[M+Na]^+$	670.0	171.4	1.1(5)
$^{0,2}A_4$ (LNT)	$[M+Na]^+$	671.0	170.1	1.6(7)
$^{0,2}X_{2\alpha}$-N_2 (Di-Le^A)	$[M+Na]^+$	676.6	183.3	3.3(8)
$^{0,2}X_{2\alpha}$-N_2 (Le^ALe^x)	$[M+Na]^+$	677.0	175.6	2.5(5)
Y_3 (GNLNLN)	$[M+Na]^+$	679.0	177.2	5.5(5)
Y_3 (Di-Le^c)	$[M+Na]^+$	679.0	176.5	1.9(8)
$^{1,5}A_4$ (P1 penta)	$[M+Na]^+$	684.0	176.9	3.4(5)
$^{0,2}X_3$-N_2 (P1 penta)	$[M+Na]^+$	692.0	145.8	1.0(5)
$^{0,2}X_3$-N_2 (LNT)	$[M+Na]^+$	693.0	111.8	2.2(5)
$B_{3\alpha}$ (Di-Le^A)	$[M+Na]^+$	696.6	175.9	1.9(27)
$B_{3\alpha}$ (Le^ALe^x)	$[M+Na]^+$	697.0	172.0	2.7(11)
B_4 (LNFP1)	$[M+Na]^+$	697.0	180.4	0.5(10)
$B_{3\beta}$ (LNFP2)	$[M+Na]^+$	697.0	180.1	1.5(5)
B_4 (H-type2-LN-LN)	$[M+Na]^+$	697.0	178.5	1.7(12)
B_3 (B tetra type 1)	$[M+Na]^+$	697.6	170.8	1.4(10)
$^{1,5}X_3$ (Di-Le^c)	$[M+Na]^+$	707.0	144.0	5.6(5)
$^{1,5}X_3$ (LNT)	$[M+Na]^+$	707.0	148.1	0.5(5)
$^{1,5}X_3$ (GNLNLN)	$[M+Na]^+$	707.0	147.1	2.1(5)
B_4 (P1 penta)	$[M+Na]^+$	712.0	171.4	1.9(5)
B_4 (P1 antigen)	$[M+Na]^+$	713.0	167.2	3.0(5)
C_3 (B tetra type 1)	$[M+Na]^+$	714.6	179.6	1.3(14)
$C_{3\alpha}$ (Di-Le^A)	$[M+Na]^+$	715.0	176.0	1.6(18)
$C_{3\alpha}$ (Le^ALe^x)	$[M+Na]^+$	715.0	173.7	2.1(8)
C_4 (LNFP1)	$[M+Na]^+$	715.0	180.5	1.9(8)
$C_{3\beta}$ (LNFP2)	$[M+Na]^+$	715.0	183.8	1.2(5)
C_4 (P1 antigen)	$[M+Na]^+$	731.0	169.8	1.5(5)
C_4 (LNnT)	$[M+Na]^+$	731.0	173.3	1.8(11)
Y_4 (LNFP1)	$[M+Na]^+$	731.0	179.7	0.6(5)
$Y_{3\beta}$ (LNFP2)	$[M+Na]^+$	731.0	176.5	0.9(5)

$Z_{1\beta}$-N_2 (2'F-B type 2)	$[M+Na]^+$	737.7	180.7	2.9(14)
$^{1,5}X_{3\alpha}$ (LNFP2)	$[M+Na]^+$	742.0	191.3	1.1(5)
$^{2,4}X_3$-N_2 (P1 penta)	$[M+Na]^+$	752.0	174.1	3.1(5)
B_4 (GNLNLN)	$[M+Na]^+$	753.0	183.9	0.9(5)
$^{2,4}X_3$-N_2 (H-type2-LN-LN)	$[M+Na]^+$	753.0	179.3	1.6(8)
B_4 (LNT)	$[M+Na]^+$	754.0	180.0	2.9(16)
B_4 (Di-Le^c)	$[M+Na]^+$	754.0	182.7	3.2(30)
$Y_{1\beta}$-N_2 (2'F-B type 2)	$[M+Na]^+$	755.7	187.5	1.6(23)
M-N_2 (B tetra type 1)	$[M+Na]^+$	755.7	187.1	0.8(19)
$^{0,2}X_{3\alpha}$ (LNFP2)	$[M+Na]^+$	756.7	190.3	0.7(5)
$^{1,5}X_4$ (LNFP1)	$[M+Na]^+$	758.6	192.4	0.6(7)
$Y_{2\alpha'}$ (2'F-B type 2)	$[M+Na]^+$	768.0	183.8	3.3(8)
C_4 (LNT)	$[M+Na]^+$	772.0	180.5	1.6(27)
C_4 (Di-Le^c)	$[M+Na]^+$	772.0	180.2	2.1(32)
M-N_2 (LNnT)	$[M+Na]^+$	772.0	182.8	1.0(22)
$^{2,4}A_5$ (P1 penta)	$[M+Na]^+$	772.0	173.6	1.6(5)
$^{2,4}A_5$ (P1 antigen)	$[M+Na]^+$	773.0	177.5	1.6(5)
Z_4 (P1 antigen)	$[M+Na]^+$	782.0	149.1	2.1(4)
B tetra type 1	$[M+Na]^+$	783.7	195.6	1.9(27)
$Y_{1\beta}$ (2'F-B type 2)	$[M+Na]^+$	783.7	196.4	4.4(10)
LNnT	$[M+Na]^+$	799.7	188.0	1.3(28)
Y_4 (P1 antigen)	$[M+Na]^+$	800.0	146.7	3.3(8)
Y_4-N_2 (P1 penta)	$[M+Na]^+$	812.0	178.3	0.7(13)
M-N_2 (Di-Le^c)	$[M+Na]^+$	812.8	185.2	1.6(45)
M-N_2 (LNT)	$[M+Na]^+$	812.8	190.7	0.8(41)
Y_4-N_2 (GNLNLN)	$[M+Na]^+$	813.0	191.5	0.9(8)
Y_4-N_2 (H-type2-LN-LN)	$[M+Na]^+$	813.0	191.0	1.6(7)
$^{0,2}A_5$ (P1 penta)	$[M+Na]^+$	832.0	183.2	0.7(5)
$^{0,2}A_5$ (P1 antigen)	$[M+Na]^+$	833.0	185.0	3.1(5)
Y_4 (P1 penta)	$[M+Na]^+$	840.0	184.1	0.6(13)
3'SLN-Lec	$[M+Na]^+$	840.8	188.0	0.9(5)
Di-Le^c (3)	**$[M+Na]^+$**	**840.8**	**187.3**	**1.5(76)**
LNT (4)	**$[M+Na]^+$**	**840.8**	**196.4**	**1.4(67)**
Y_4 (GNLNLN)	$[M+Na]^+$	841.0	200.1	2.1(10)
Y_4 (H-type2-LN-LN)	$[M+Na]^+$	841.0	198.7	2.2(6)
B_3 (2'F-B type 2)	$[M+Na]^+$	844.0	198.0	4.1(9)
C_3 (2'F-B type 2)	$[M+Na]^+$	861.0	198.5	2.4(15)
$^{0,2}A_5$ (GNLNLN)	$[M+Na]^+$	874.0	172.6	2.0(8)
LNFP1 (5)	**$[M+Na]^+$**	**875.0**	**204.4**	**1.4(162)**
LNFP2 (6)	**$[M+Na]^+$**	**875.0**	**201.3**	**1.2(181)**
LNFP3	$[M+Na]^+$	875.0	199.2	1.0(17)
B_5 (P1 antigen)	$[M+Na]^+$	875.0	187.8	1.8(5)
LNFP5	$[M+Na]^+$	875.0	201.8	0.7(18)

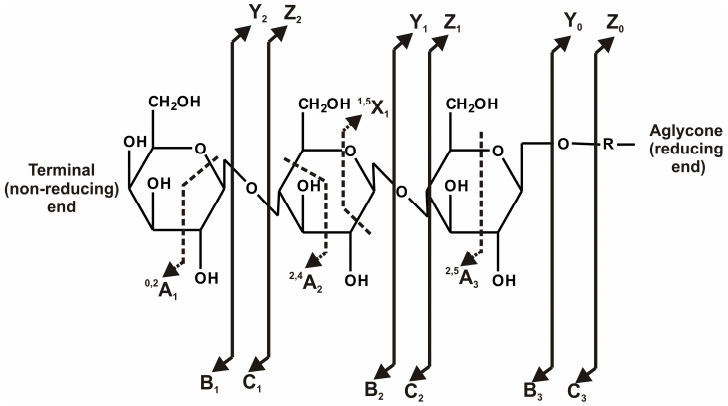
C_5 (P1 antigen)	$[M+Na]^+$	893.0	194.4	0.8(7)
$^{0,2}X_4$-N_2 (GNLNLN)	$[M+Na]^+$	896.0	147.4	0.6(5)
B_5 (H-type2-LN-LN)	$[M+Na]^+$	900.0	209.3	2.9(12)
M-N_2 (2'F-B type 2)	$[M+Na]^+$	902.0	207.3	1.7(24)
$^{2,4}A_4$ (Di-Le^A)	$[M+Na]^+$	903.0	198.7	5.2(5)
$^{2,4}A_4$ (Le^ALe^x)	$[M+Na]^+$	903.0	199.2	4.5(5)
B_5 (P1 penta)	$[M+Na]^+$	915.0	197.0	2.1(8)
C_5 (H-type2-LN-LN)	$[M+Na]^+$	918.0	206.6	2.5(12)
2'F-B type 2	$[M+Na]^+$	929.8	217.3	2.7(27)
C_5 (P1 penta)	$[M+Na]^+$	933.0	192.3	0.7(8)
M-N_2 (P1 antigen)	$[M+Na]^+$	933.8	195.8	1.3(15)
$Z_{3\alpha'}$-N_2 (Di-Le^A)	$[M+Na]^+$	941.0	219.6	2.7(5)
$Y_{3\alpha''}$-N_2 (Le^ALe^x)	$[M+Na]^+$	948.0	200.8	7.0(5)
$^{2,4}X_4$-N_2 (GNLNLN)	$[M+Na]^+$	956.0	213.3	2.6(5)
$Y_{1\beta \text{ or } 3\alpha''}$-$N_2$ (Le^ALe^x)	$[M+Na]^+$	959.0	211.0	1.6(20)
$Y_{3\alpha'}$-N_2 (Di-Le^A)	$[M+Na]^+$	959.0	211.0	1.8(30)
P1 antigen	$[M+Na]^+$	961.8	203.4	0.9(18)
$Y_{3\alpha''}$ (Di-Le^A)	$[M+Na]^+$	971.0	206.3	1.4(5)
$Y_{3\alpha'}$ (Le^ALe^x)	$[M+Na]^+$	971.0	206.9	1.6(13)
M-N_2 (P1 penta)	$[M+Na]^+$	974.4	202.9	0.7(15)
C_5 (GNLNLN)	$[M+Na]^+$	975.0	215.3	1.3(11)
$^{0,2}X_{3\alpha''}$-N_2 (Le^ALe^x)	$[M+Na]^+$	985.0	218.3	2.2(10)
$C_{3\beta}$ (Di-Le^A)	$[M+Na]^+$	987.0	214.7	2.3(33)
α-cyclodextrin	$[M+Na]^+$	995.6	200.7	0.5(4)
$^{0,2}X_{1\beta \text{ or } 3\alpha''}$-$N_2$ (Di-Le^A)	$[M+Na]^+$	1001.0	209.3	1.8(5)
$^{0,2}X_{2\alpha'' \text{ or } 1\beta}$-$N_2$ (Le^ALe^x)	$[M+Na]^+$	1001.0	217.7	2.1(9)
P1 penta	$[M+Na]^+$	1002.4	206.2	0.6(30)
M-N_2 (GNLNLN)	$[M+Na]^+$	1015.9	220.6	2.3(24)
Y_5-N_2 (H-type2-LN-LN)	$[M+Na]^+$	1016.0	220.2	2.2(4)
$^{1,5}A_4$ (Di-Le^A)	$[M+Na]^+$	1018.0	208.6	4.0(5)
LNDFH1	$[M+Na]^+$	1023.0	225.6	1.1(18)
LNDFH2	$[M+Na]^+$	1023.0	220.6	1.0(18)
GNLNLN	$[M+Na]^+$	1043.9	230.5	0.8(25)
B_4 (Di-Le^A)	$[M+Na]^+$	1046.0	228.0	2.4(13)
C_4 (Le^ALe^x)	$[M+Na]^+$	1064.0	225.2	2.8(17)
C_4 (Di-Le^A)	$[M+Na]^+$	1064.0	225.4	2.4(30)
$^{2,4}X_{3\alpha'}$ (Le^ALe^x)	$[M+Na]^+$	1073.0	227.3	1.4(5)
M-N_2 (Le^ALe^x)	$[M+Na]^+$	1105.0	232.4	1.5(23)
M-N_2 (Di-Le^A)	$[M+Na]^+$	1105.0	230.9	1.0(37)
Le^ALe^x	$[M+Na]^+$	1133.0	237.9	3.3(25)
Di-Le^A	$[M+Na]^+$	1133.0	238.9	3.1(49)
β-cyclodextrin	$[M+Na]^+$	1157.0	231.4	0.6(4)
Y_6-N_2 (H-type2-LN-LN)	$[M+Na]^+$	1178.0	232.0	1.4(7)

Tri-LacNAc	$[M+Na]^+$	1206.0	232.6	0.6(5)
Y_6 (H-type2-LN-LN)	$[M+Na]^+$	1206.0	238.7	4.2(8)
C_7 (H-type2-LN-LN)	$[M+Na]^+$	1283.0	243.2	4.0(8)
M-N_2 (H-type2-LN-LN)	$[M+Na]^+$	1324.2	245.5	0.4(7)
H-type2-LN-LN	$[M+Na]^+$	1352.2	252.1	0.6(7)

1. Carbohydrate nomenclature:

2'F-B type 2	Galα1-3[Fucα1-2]Galβ1-4[Fucα1-3]GlcNAcβ-Sp
3'SLN-Lec	Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-3GlcNAcβ-Sp
α-cyclodextrin	Cyclomaltohexaose
β-cyclodextrin	Cyclomaltoheptaose
B2-tri	Galα1-3Galβ1-4GlcNAcβ-Sp
B tetra type 1	Galα1-3[Fucα1-2]Galβ1-3GlcNAcβ-Sp
Di-Le^A	Galβ1-3[Fucα1-4]GlcNAcβ1-3Galβ1-3[Fucα1-4]GlcNAcβ-Sp
Di-Le^c	Galβ1-3GlcNAcβ1-3Galβ1-3GlcNAcβ-Sp
Galα3-type1	Galα1-3Galβ1-3GlcNAcβ-Sp
GNLNLN	GlcNAcβ1-3(Galβ1-4GlcNAcβ1-3)$_2$β-Sp
H-type2-LN-LN	Fucα1-2(Galβ1-4GlcNAcβ1-3)$_3$β -Sp
Lac	Galβ1-4Glcβ-Sp
Lactose	Galβ1-4Glc
LacNAc	Galβ1-4GlcNAcβ-Sp
Le^ALe^x	Galβ1-3[Fucα1-4]GalNAcβ1-3Galβ1-4[Fucα1-3]GlcNAcβ-Sp Le^c Galβ1-3GlcNAcβ-Sp
LN	Galβ1-4GlcNAc
LNDFH1	Fucα1-2Galβ1-3[Fucα1-4]GlcNAcβ1-3Galβ1-4Glc
LNDFH2	Galβ1-3[Fucα1-4]GlcNAcβ1-3Galβ1-4[Fucα1-3]Glc
LNFP1	Fucα1-2Galβ1-3GlcNAcβ1-3Galβ1-4Glc
LNFP2	Galβ1-3[Fucα1-4]GlcNAcβ1-3Galβ1-4Glc
LNFP3	Galβ1-4[Fucα1-3]GlcNAcβ1-3Galβ1-4Glc
LNFP5	Galβ1-3GlcNAcβ1-3Galβ1-4[Fucα1-3]Glc
LNnT	Galβ1-4GlcNAcβ1-3Galβ1-4Glcβ-Sp
LNT	Galβ1-3GlcNAcβ1-3Galβ1-4GlcNAcβ-Sp
Maltose	Glcα1-4Glc
P1 antigen	Galα1-4Galβ1-4GlcNAcβ1-3Galβ1-4Glcβ-Sp
P1 penta	Galb1-3GalNAcβ1-3Galα1-4Galβ1-4GlcNAcβ-Sp
P1 tri	Galα1-4Galβ1-4GlcNAcβ-Sp
Pk	Galα1-4Galβ1-4Glcβ-Sp
Tri-LacNAc	(Galβ1-4GlcNAcβ1-3)$_3$β-Sp

Fuc - Fucose
Gal - Galactose
Glc - Glucose
GlcNAc - N-acetylglucosamine
GalNAc – N-acetylgalactosamine
Neu5Ac - N-Acetylneuraminic Acid
Sp – azide spacer not utilized in these studies but which readily loses N_2 in the MS accounting for some carbohydrate fragment peaks



Scheme S1. Carbohydrate fragmentation is specified in Domon-Costello nomenclature (B. Domon and C. E. Costello, *Glycoconjugate Journal*, 1988, **5**, 397-409)

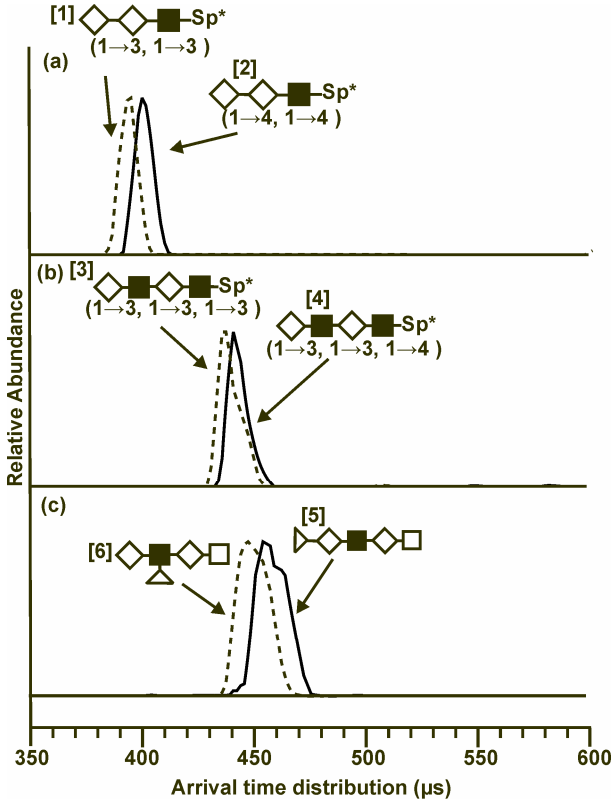


Figure S1. Drift time profiles at higher electrostatic field strengths (27 volts cm^{-1} Torr) used within the ion mobility drift cell that correlate with the lower field strength (20.6 volts cm^{-1} Torr) presented in Figure 2. Structures of the oligosaccharides are replaced with shape representations. Drift times are related to the ion structure in that larger, more elongated ions experience more collisions with the neutral buffer gas present in the drift cell causing a longer drift time than more compact structures. (a) In the comparison between glycans 1 (dotted line) and 2 (solid line), the 1→3 linkages of glycan 1 cause it to have a shorter drift time which indicates a more compact structure that glycan 2, which is more elongated. (b) Glycans 3 (dotted line) and 4 (solid line) have differing drift times due to the change in one glycosidic linkage. The 1→3 linkages allow glycan 3 to adopt a more compact conformation when compared to its positional isomer, which has one 1→4 linkage. (c) Drift time profiles for glycans 5 (solid line) and 6 (dotted line) are compared. LNFP2 has a shorter drift time than LNFP1 at both voltages. This is attributed to increased branching in LNFP2 that allows the glycan to adopt a more compact structure. Individual monosaccharide representations are as follows: ◊ - galactose; ■-N-acetylglucoseamine; Δ -fucose; with linkage information for the positional isomers provided in the parenthesis below each representation.

Table S2. Carbohydrate collision cross sections with various alkali metal coordination.

Carbohydrate Name	species	*m/z* (Da)	Ω (Å^2)	σ (# of measurements)
LNFP1	$[M+Li]^+$	859.0	203.1	1.2(20)
LNFP2	$[M+Li]^+$	859.0	198.7	1.3(20)
LNFP1	$[M+Na]^+$	875.0	204.4	1.4(162)
LNFP2	$[M+Na]^+$	875.0	201.3	1.2(181)
LNFP1	$[M+K]^+$	891.0	205.0	0.7(23)
LNFP2	$[M+K]^+$	891.0	202.6	1.6(20)
LNFP1	$[M+Rb]^+$	937.5	198.4	1.5(20)
LNFP2	$[M+Rb]^+$	937.5	197.5	1.7(20)
LNFP1	$[M+Cs]^+$	985.0	204.0	2.1(20)
LNFP2	$[M+Cs]^+$	985.0	199.7	1.7(20)