SUPPORTING INFORMATION

Separation and Identification of Glycan Anomers

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KEYWORDS: glycans, carbohydrates, ion mobility spectrometry, ion spectroscopy, mass spectrometry

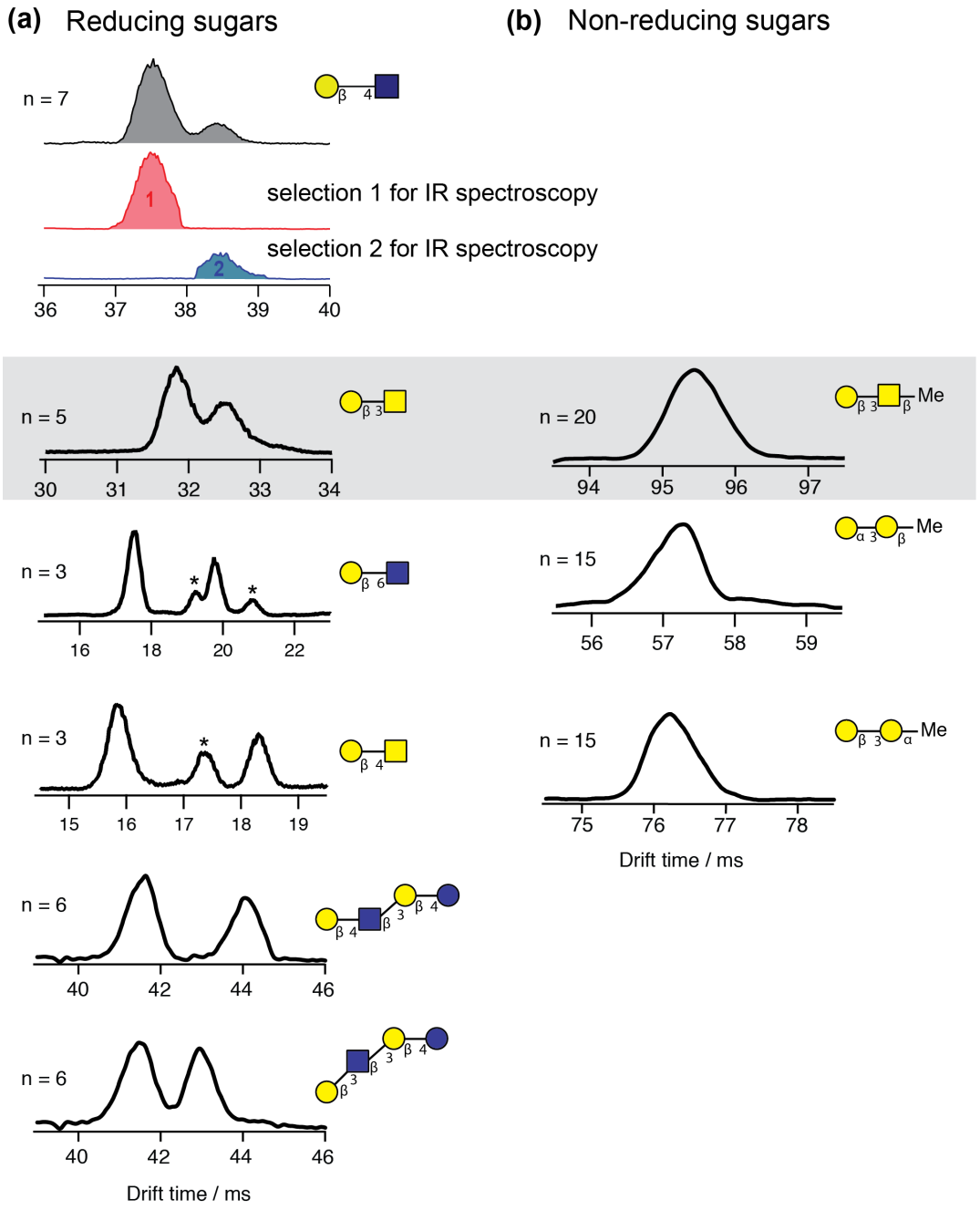

Figure S1: (a) ATDs of glycans with a free reducing-end OH group that are able to form α and β anomers at different number *n* of IMS cycles on the SLIM board. The type of sugar is annotated in Oxford nomenclature. The top three panels show exemplarily how two different drift peaks are selected into two portions that can then be investigated separately. **(b)** ATDs of glycans with a methylated reducing-end. As a consequence, the C_1 carbon on the reducing-end of these glycans are locked in their α and β anomeric configuration. An asterisk marks signals that are due to ions of slightly different *m/z*, which could not sufficiently filtered with the quadrupole MS used.

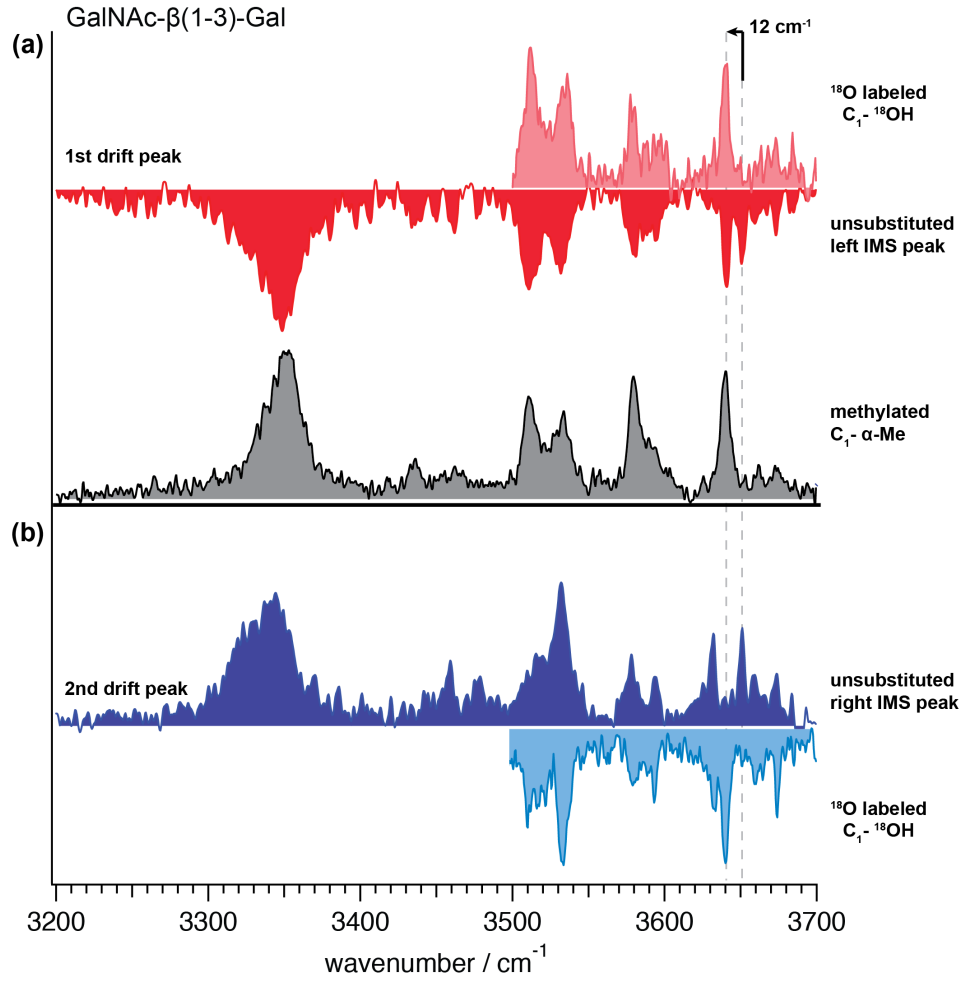

Figure S2: Infrared spectra of the mobility-selected left (**(a)**, dark red) and right (**(b)**, dark blue) drift peak of the disaccharide GalNAc-β(1-3)-Gal and the equivalent species with ^{18}O-substituted C_1-OH group (light colors), which exhibit a 12 cm^{-1} redshift in one absorption band. The spectrum of the methylated species GalNAc-β(1-3)-Gal-α-Me (grey) matches the spectrum of the left drift peak in position and intensities of absorption bands, with the exception of the absent C_1-OH oscillator for the methylated species. The left drift peak is thereby identified as the α anomeric form of GalNAc-β(1-3)-Gal and the right peak (by exclusion) as the β anomeric form.

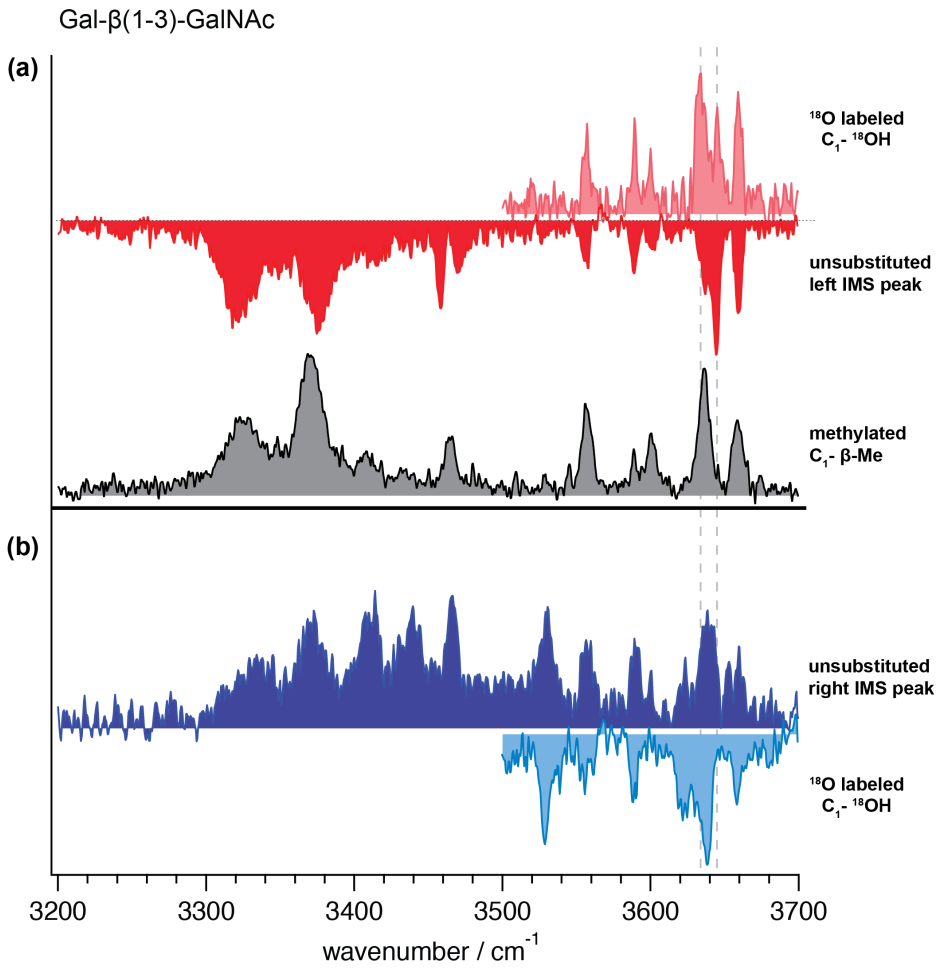

Figure S3: Infrared spectra of the mobility-selected left (**(a)**, dark red) and right (**(b)**, dark blue) drift peak of the disaccharide Gal-β(1-3)-GalNAc and the equivalent species with ^{18}O-substituted C_1-OH group (light colors), which exhibit a 12 cm^{-1} redshift in one absorption band. The spectrum of the methylated species Gal-β(1-3)-GalNAc-β-Me (grey) matches the spectrum of the left drift peak in position and intensities of absorption bands, with the exception of the absent C_1-OH oscillator for the methylated species. The left drift peak is thereby identified as the β-anomeric form of Gal-β(1-3)-GalNAc and the right peak (by exclusion) as the α anomer.

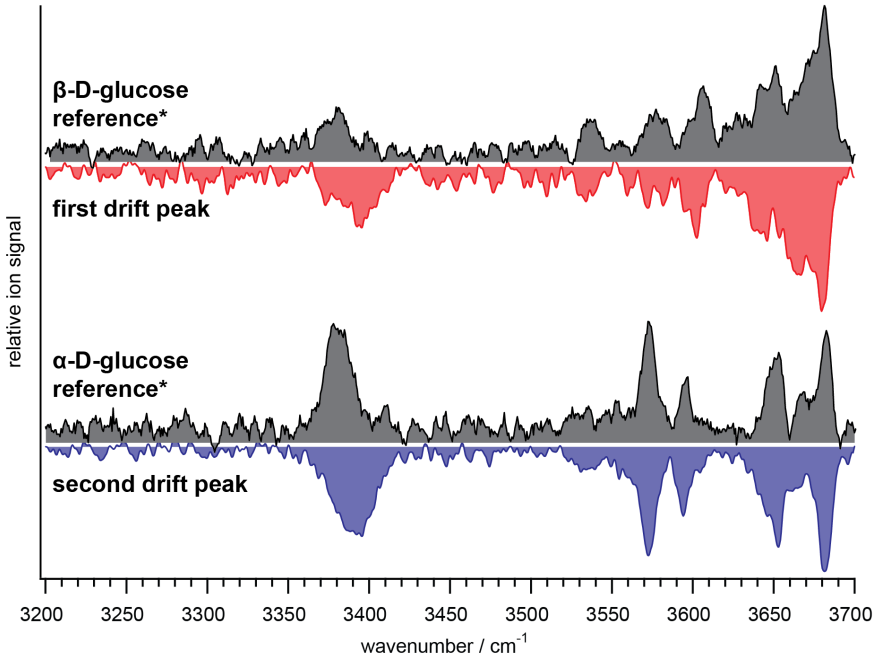

Figure S4: Infrared spectra of the mobility-separated first (red) and second (blue) drift peak of electrosprayed α-D-glucose and previously published reference spectra of the α and β anomers of glucose from a cryogenic, messenger-tagging, double-resonance spectroscopic experiment [1]. The good agreement with the reference spectra leads to the assignment of the α and β anomers to the first and second IMS drift peak, respectively.

GLUCOSE MUTAROTATION

The conversion reaction α-D-glucose $\rightleftharpoons_{k_\beta}^{k_\alpha}$ β-D-glucose can be treated as a first order reaction [2, 3] and the rate equation follows as

$$-\frac{dc_\alpha(t)}{dt} = \frac{dc_\beta(t)}{dt} = k_\alpha c_\alpha(t) - k_\beta c_\beta(t). \tag{S1}$$

Using the substitution for the observable rate $k = k_\alpha + k_\beta$ and the total concentration c_0, this can be written as

$$\frac{dc_\alpha(t)}{dt} + kc_\alpha(t) = k_\beta c_0. \tag{S2}$$

Under consideration of the boundary conditions for c_α and c_β

$$\begin{aligned} c_\alpha(t_0) &= c_0 \\ c_\beta(t_0) &= 0 \\ c_i(t \longrightarrow \infty) &= c_i^{eq} \end{aligned} \tag{S3}$$

the rate differential equation can be solved for $c_\alpha(t)$ and $c_\beta(t)$, respectively, with

$$c_\alpha(t) = c_\alpha^{eq} + (c_0 - c_\alpha^{eq})e^{-kt} \qquad (S4)$$
$$c_\beta(t) = c_\beta^{eq} - c_\beta^{eq}e^{-kt}.$$

The parameters c_α^{eq}, c_β^{eq}, and k can be obtained from fitting the experimental data describing the abundance of the α and β anomeric forms with these functions. This was done for the data shown in Fig. 5b in the main manuscript by using $c_\beta^{eq} = A$ and k as free fit parameters in the fit function $f(t) = A - Ae^{-kt}$. To obtain the specific rate constants we find the relationships

$$k_\beta = \frac{c_\alpha^{eq}}{c_0}k \qquad (S5)$$
$$\text{and} \qquad k_\alpha = k - k_\beta = \left(1 - \frac{c_\alpha^{eq}}{c_0}\right)k.$$

REFERENCES

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2. Kendrew, J.C. and Moelwyn-Hughes, E.A.; The Kinetics of Mutarotation in Solution. Proc R Soc Lond A Math Phys Sci. **176**, 352-367 (1940).
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