FOUNDATIONS
ADVANCES

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Supporting information for article:

Multipole electron densities and structural parameters from synchrotron powder X-ray diffraction data obtained with a MYTHEN detector system (OHGI)

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S1. Diamond HC/Rietveld refinement fit

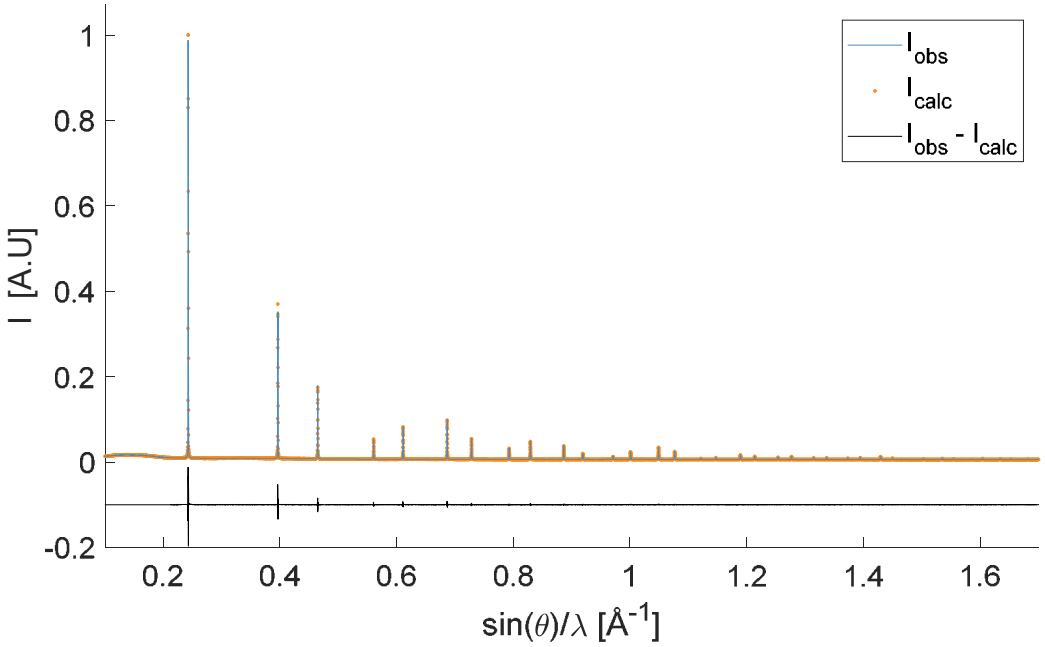

Figure S1 OHGI SPXRD data and the corresponding HC/Rietveld model fit. See text for details.

S2. Urea Rietveld refinement parameters.

The Rietveld model used in structure factor extraction for urea corresponds to the one in Svane *et al.*, 2019. It is repeated here for the reader's convenience. We used a pseudo-Voigt profile description with GU, GX, GW, LY-coefficients. The strain present in urea crystal required the inclusion of sample strain parameters in the [400], [202] and [220]-directions along with a mixing parameter, zeta (Stephens, 1999). A zero-shift parameter was included for the OHGI data but unnecessary for AVID due to the integration routine. The background was in both cases described by linear interpolation between points chosen automatically by JANA2006 and manually adjusted based on visual inspection. C, O and N coordinates and anisotropic ADPs were refined within crystallographic symmetry constraints. H atom positions were fixed at the neutron reference (Swaminathan *et al.*, 1984), with the ADPs of H being scaled to neutron using a 2-parameter linear correction factor calculated with the program UijXN based on C, O and N vibrational parameters (Blessing, 1995). An anomalous dispersion correction was implemented based on tabulated values from the program WinGX. The profile parameters are given in Table S1.

Table S1 Rietveld refinement parameters for OHGI and AVID data. ADPs are given as 10^{-4} Å^2.

	OHGI-IAM	**OHGI-MM**	**AVID-IAM**
R/wR(obs) (%)	8.78/2.32	4.85/1.16	5.68/4.12
R_P/wR_p	2.69/1.63	2.38/1.45	3.23/2.54
GOF	2.70	2.40	12.10
Scale	2.203(1)	2.143(1)	0.6634(4)
a [Å]	5.57957(4)	5.57952(4)	5.578071(9)
c [Å]	4.68434(3)	4.68433(2)	4.687410(6)
GU	47(2)	37(2)	-6.7(1)
GW	1.28(1)	1.370(8)	0.28(5)
LX	-0.10(2)	-0.30(2)	-0.153(3)
LY	3.6(4)	5.5(3)	5.02(5)
Zeta	0.389(9)	0.484(6)	0.448(2)
Shift	0.008(5)	0.011(3)	---------
S400	2.24(4)	2.69(3)	1.657(6)
S220	-0.66(1)	-0.835(4)	-0.5454(9)
S202	0.029(3)	0.023(7)	0.018(1)
***z*(C)**	0.3261(3)	0.3282(2)	0.3286(1)
***z*(O)**	0.5957(1)	0.5949(1)	0.59690(7)
***x*(N)**	0.14440(8)	0.14357(7)	0.14357(5)
***z*(N)**	0.1776(1)	0.1765(1)	0.17823(7)
U11(C)	162(6)	138(5)	128(2)
U33(C)	162(7)	39(6)	93(2)
U12(C)	64(9)	-28(7)	13(3)
U11(O)	169(4)	145(4)	167(1)
U33(O)	64(5)	58(4)	84(2)
U12(O)	32(5)	-4(5)	27(2)
U11(N)	278(4)	219(3)	253(1)
U33(N)	44(4)	102(4)	108(2)
U12(N)	-230(5)	-136(4)	-125(2)
U13(N)	15(3)	-16(3)	9(1)

As the exact profile description is heavily dependent on the experimental setup, a direct comparison of values between AVID and OHGI data is not meaningful. The narrow peaks of AVID data require an even more accurate profile description. A comparison between IAM and MM form factors on the OHGI data reveals a significant improvement in all fit quality descriptors on the introduction of aspherical

atomic form factors. The improvement with form factor model indicates, that an extraction of structure factors with iterative aspherical form factor optimization could be possible with data of this quality.

The ADPs are larger in the IAM modelling of OHGI data compared to the multipolar modelling. This is likely an effect of the displacement parameters absorbing the combined effect of vibration and aspherical form factors.

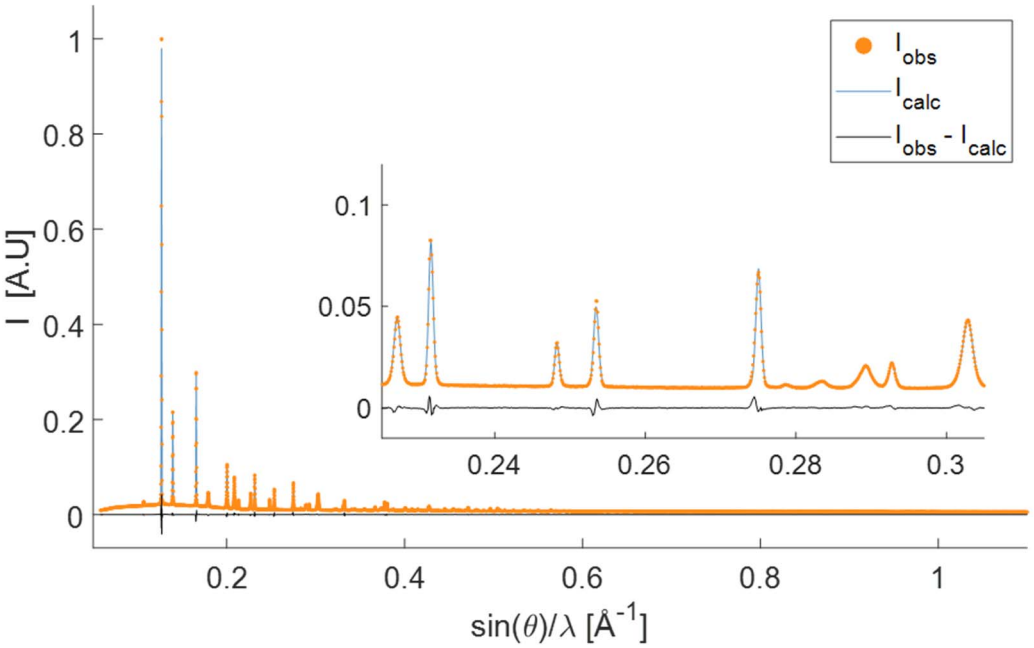

Figure S2 OHGI SPXRD data and the corresponding multipolar model fit. The quality of the fit is excellent at both low and high angles with no systematic undescribed features.

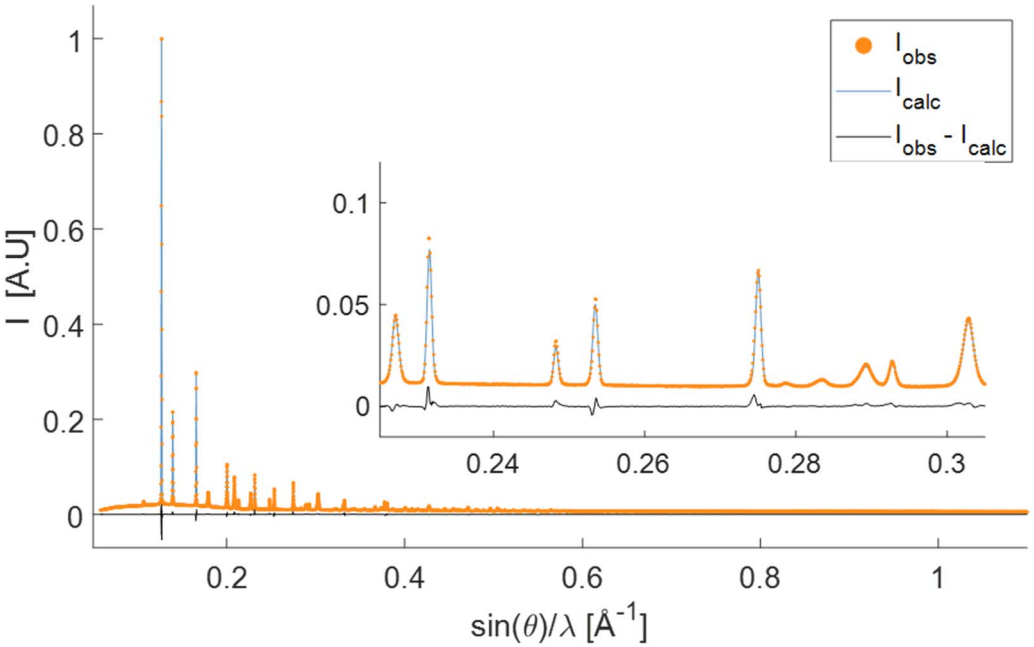

Figure S3 OHGI SPXRD data and corresponding IAM fit. The fit quality is slightly lower than with aspherical atomic scattering factors.

S3. Urea Multipolar refinement parameters

Table S2 Refined parameters for multipolar models against different structure factor lists. The naming scheme is given in the text. SC reference refers to structure factors from Birkedal *et al.* (2004) but refined with the MM model. Neutron refers to structure factors from Swaminathan *et al.* (1984) included for atomic position comparison. The population of individual multipolar functions are not listed. Neutron ADPs are calculated based on linear interpolation between the 123 K and 60 K data. Note that SC reference ADPs were collected at 123 K and not scaled. The unit of ADPs is 10^{-4} Å^2.

	OHGI-IAM	**OHGI-MM**	**AVID-IAM**	**SC reference**	**Neutron**
R/wR (%)	4.71/1.24	3.49/0.78	4.23/2.43	1.29/0.77	1.36/1.06
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.07	1.07	1.00	1.44	0.77
No. of ref. (I > 0)	729	714	566	1045	191
GOF	2.7	1.69	34.0	1.64	1.22
$\langle F_o/\sigma(F_o)\rangle$	362.1	383.3	2738	367.8	865.2
***z*(C)**	0.3269(3)	0.3278(1)	0.3284(4)	0.32820(4)	0.3284(4)
***z*(O)**	0.5965(2)	0.5951(1)	0.5966(5)	0.59636(4)	0.5971(5)
***x*(N)**	0.14452(7)	0.14363(5)	0.1442(2)	0.14491(3)	0.1448(2)
***z*(N)**	0.1775(2)	0.1768(1)	0.1780(4)	0.17819(4)	0.1786(2)
P_V(C)	3.5(2)	3.5(1)	3.4(2)	3.74(4)	------
P_V(O)	6.16(7)	6.41(4)	7.0(1)	6.51(2)	------
P_V(N)	5.5(1)	5.59(7)	5.0(2)	5.12(3)	------
P_V(H1)	0.76(5)	0.74(3)	0.80(8)	0.86(1)	------
P_V(H2)	0.85(4)	0.74(3)	0.96(7)	0.89(1)	------
κ(C)	1.06(2)	1.07(1)	1.22(4)	1.017(4)	------
κ(O)	1.021(5)	0.999(3)	1.04(1)	0.966(2)	------
κ(N)	0.979(1)	0.995(7)	1.09(3)	0.996(3)	------
U_{11}(C)	169(2)	145(1)	87(5)	149(1)	125(5)
U_{33}(C)	145(4)	38(2)	56(6)	66.6(5)	58(3)
U_{12}(C)	64(3)	-21(2)	0(6)	-2(1)	0(4)
U_{11}(O)	175(2)	149(1)	136(5)	194(1)	169(6)
U_{33}(O)	73(4)	71(3)	55(7)	65.4(4)	54(4)
U_{12}(O)	38(3)	-2(2)	29(9)	17(1)	11(5)
U_{11}(N)	283(2)	224(1)	227(5)	290(1)	243(4)
U_{33}(N)	44(3)	101(3)	66(5)	94.0(4)	86(2)
U_{12}(N)	-230(3)	-127(2)	-129(6)	-155(1)	-125(2)
U_{13}(N)	-16(1)	-16(1)	6(3)	0.0(3)	2(3)

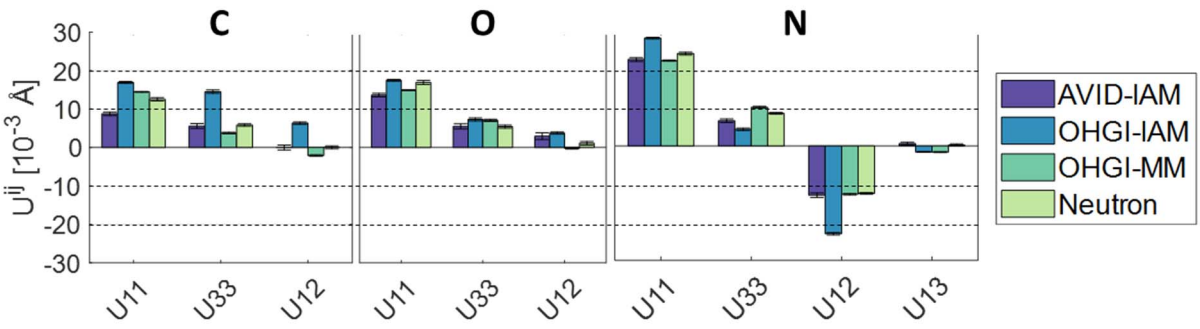

Figure S4 ADP comparison for powder-based multipolar models with scaled neutron values. The naming scheme is given in the text.

S4. Xylitol Rietveld profile parameters

The peak profile in the OHGI xylitol data was described using a Pseudo-Voigt profile description with GU, GW and LY-coefficients. The integration routine required the inclusion of a zero-shift parameter. Visual inspection of the diffractogram revealed significant peak asymmetry which was included in the profile description through a Simpson asymmetry parameter (Petrícek *et al.*, 2014). The background was described by linear interpolation between 59 points, which were initially automatically placed by the JANA software and subsequently manually adjusted as necessary based on visual inspection. An overall scale factor and a background scale factor was included in the Rietveld refinement. The OHGI data were collected up to 156°, but was cut at 58°, which was beyond the furthest observed peak. Within the used data region, four separate regions of 0.05° were excluded as a poor hot channel correction rendered them unusable.

Multiple approaches were attempted with the atomic positions, vibrations and atomic form factors. These approaches are described in the main text. An example powder pattern fit using atomic positions and vibrations fixed at neutron values and a multipolar description fitted to SC structure factors is shown in Figure S5. In Figure S6, a powder pattern fit to the same data with an IAM atomic form factor description, refined positions and vibrations for non-H atoms and without refinement of the background scale factor. These two models represent two extremes. Visually, the quality of the two models are indistinguishable, so the remaining powder pattern fits are not shown. All models provide a good fit to the data. Note that the powder pattern fit does not improve on introduction of aspherical atomic scattering factors though the extracted structure factors do. Fit quality indicators are shown in Table S3.

Table S3 Fit quality indicators for xylitol powder pattern fits used in the extraction of structure factors.

	IAM	**MM**	**MM-XYZU**
R/wR(obs)	5.85/6.37	6.05/6.11	4.30/4.48
$\boldsymbol{R_P/wR_p}$	1.84/2.91	1.79/2.84	1.88/3.30
GOF	5.71	5.59	6.47
$\langle \boldsymbol{F_o/\sigma(F_o)} \rangle$	69.3	74.6	76.2

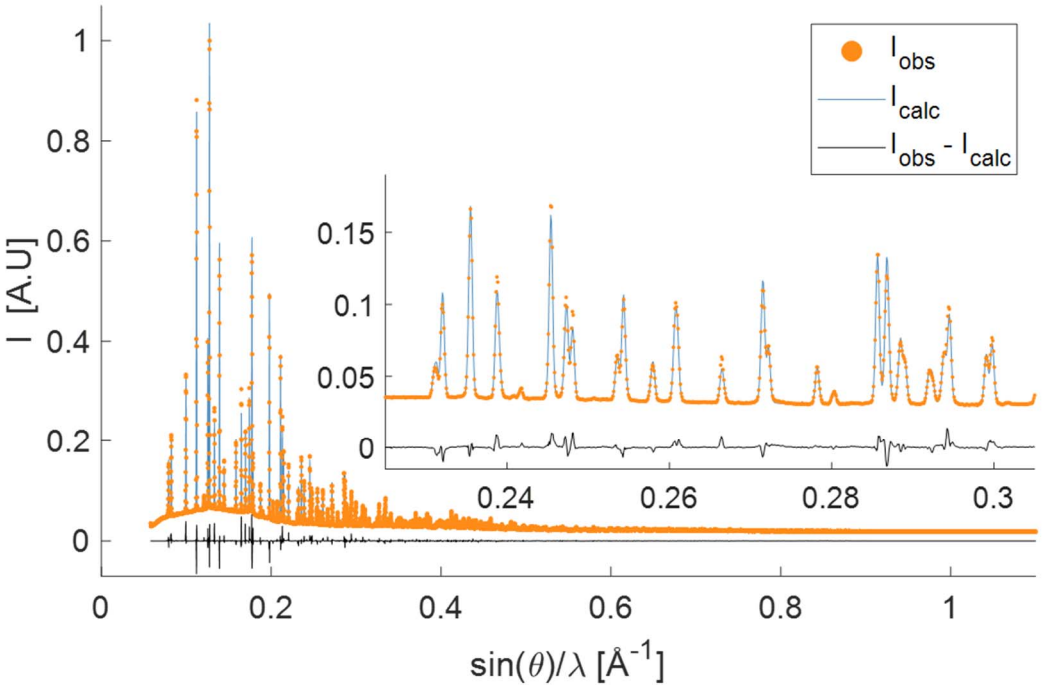

Figure S5 Xylitol OHGI data and corresponding Rietveld pattern. The difference line is plotted in black. The model shown here uses neutron positions and ADPs and a multipolar description fitted to SCXRD data (Madsen *et al.*, 2004).

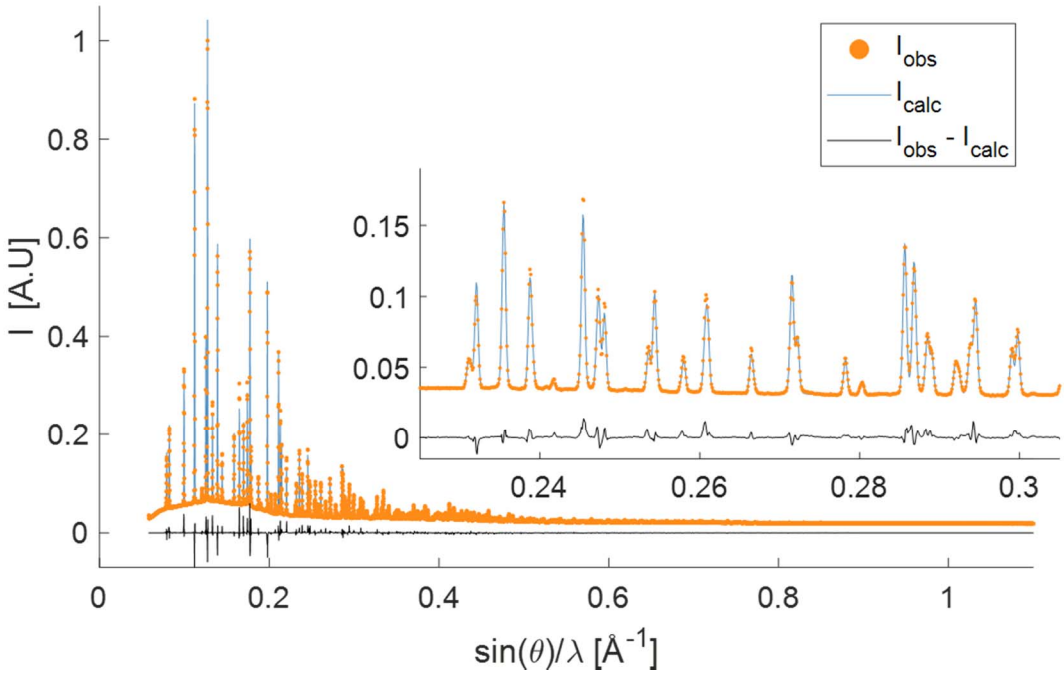

Figure S6 Xylitol OHGI data and corresponding Rietveld pattern. The difference line is plotted in black. The model shown uses refined positions and ADPs of non-H atoms, while H atoms are fixed at neutron values. The atomic form factors are based on IAM.

S5. Xylitol SPXRD(OHGI)-based deformation and residual density contour plots

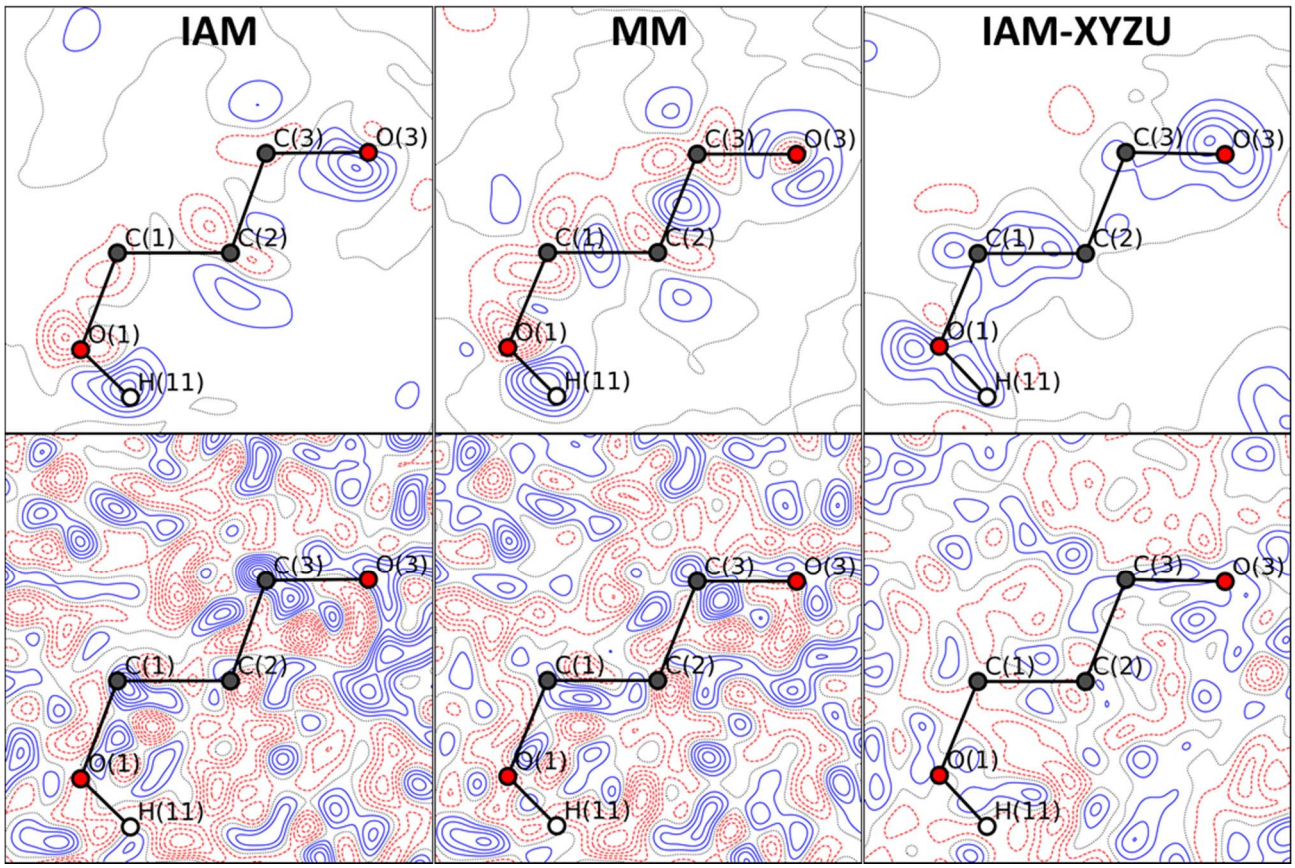

Figure S7 Xylitol static deformation density (top) and residual density (bottom) for structure factors extracted with the MM and IAM on the left and right, respectively. Contour levels are 0.1 e $Å^{-3}$, and 0.05 e $Å^{-3}$, respectively with negative contours shown in red and positive in blue.

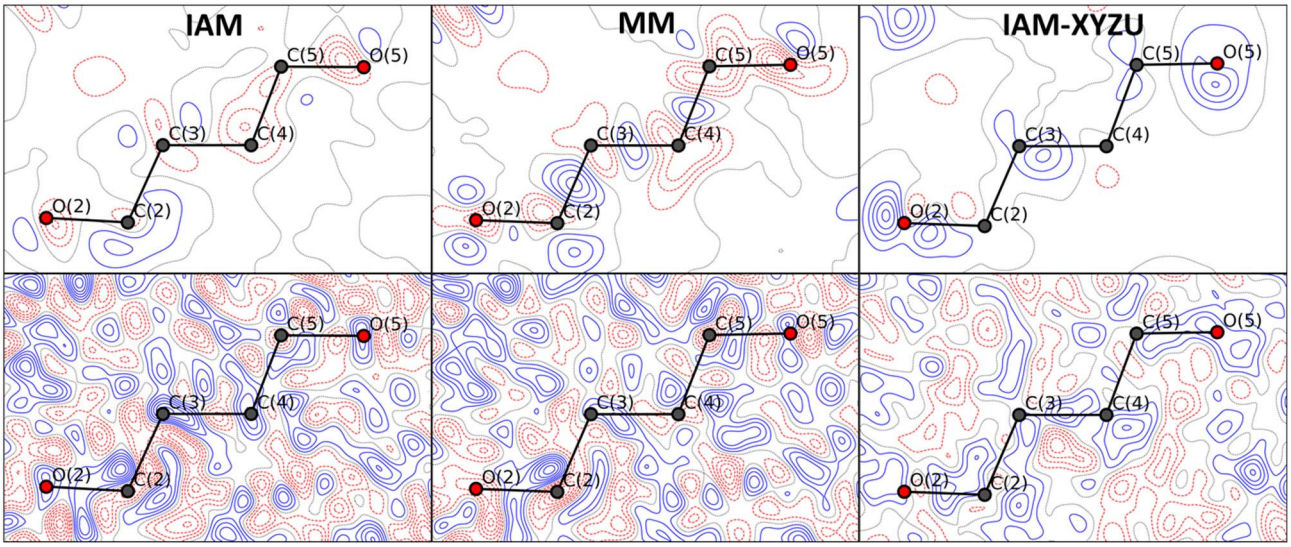

Figure S8 Xylitol static deformation density (top) and residual density (bottom) for structure factors extracted with the MM and IAM on the left and right, respectively. Contour levels are 0.1 e $Å^{-3}$, and 0.05 e $Å^{-3}$, respectively with negative contours shown in red and positive in blue.

Table S4 MM fit quality for SPXRD (OHGI) and SCXRD data

	IAM	**MM**	**MM-XYZU**	**Reference**
R/wR	5.85/6.37	4.91/4.85	3.06/3.21	1.64/1.43
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.9034	0.9034	0.9034	1.2173
No. of ref. (I > 0)	4042	4042	4042	9942
GOF	1.05	1.00	0.67	0.71
$\langle F_o/\sigma(F_o)\rangle$	69.3	74.6	76.2	174.8

S6. Xylitol bond lengths for SPXRD (OHGI), neutron and SCXRD data

	IAM	MM	MM-XYZU	SC reference	Neutron
C1-C2	1.5829	1.5506	1.5144	1.5164	1.5151
C2-C3	1.4891	1.4962	1.5342	1.5357	1.5332
C3-C4	1.5492	1.5386	1.5291	1.5310	1.5293
C4-C5	1.4758	1.4897	1.5207	1.5212	1.5206
C1-O1	1.4672	1.4558	1.4236	1.4247	1.4236
C2-O2	1.4413	1.4398	1.4260	1.4299	1.4276
C3-O3	1.4762	1.4373	1.4237	1.4259	1.4242
C4-O4	1.4631	1.4568	1.4324	1.4340	1.4323
C5-O5	1.4496	1.4277	1.4210	1.4217	1.4203
O1-H1	0.9988	1.0026	0.9996	0.9961	0.9984
O2-H2	0.9768	0.9801	0.9791	0.9774	0.9794
O3-H3	0.9580	0.9740	0.9865	0.9865	0.9865
O4-H4	0.9893	0.9843	0.9727	0.9697	0.9720
O5-H5	0.9695	0.9686	0.9867	0.9836	0.9872
C1-H1a	1.0662	1.0826	1.1112	1.1113	1.1110
C1-H1b	1.1038	1.1172	1.1008	1.0990	1.1007
C2-H2	1.0764	1.0836	1.1040	1.1042	1.1041
C3-H3	1.1140	1.1263	1.1105	1.1087	1.1109
C4-H4	1.0836	1.0989	1.1038	1.1006	1.1031
C5-H5a	1.0717	1.0846	1.0995	1.1008	1.0991
C5-H5b	1.1240	1.1528	1.1076	1.1069	1.1079