Supplementary Information (SI) for Physical Chemistry Chemical Physics.


# Raman optical activity study of deuterated sugars: deuterium labelling as a tool for structural analysis

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## Supporting Information

## Supporting Figures

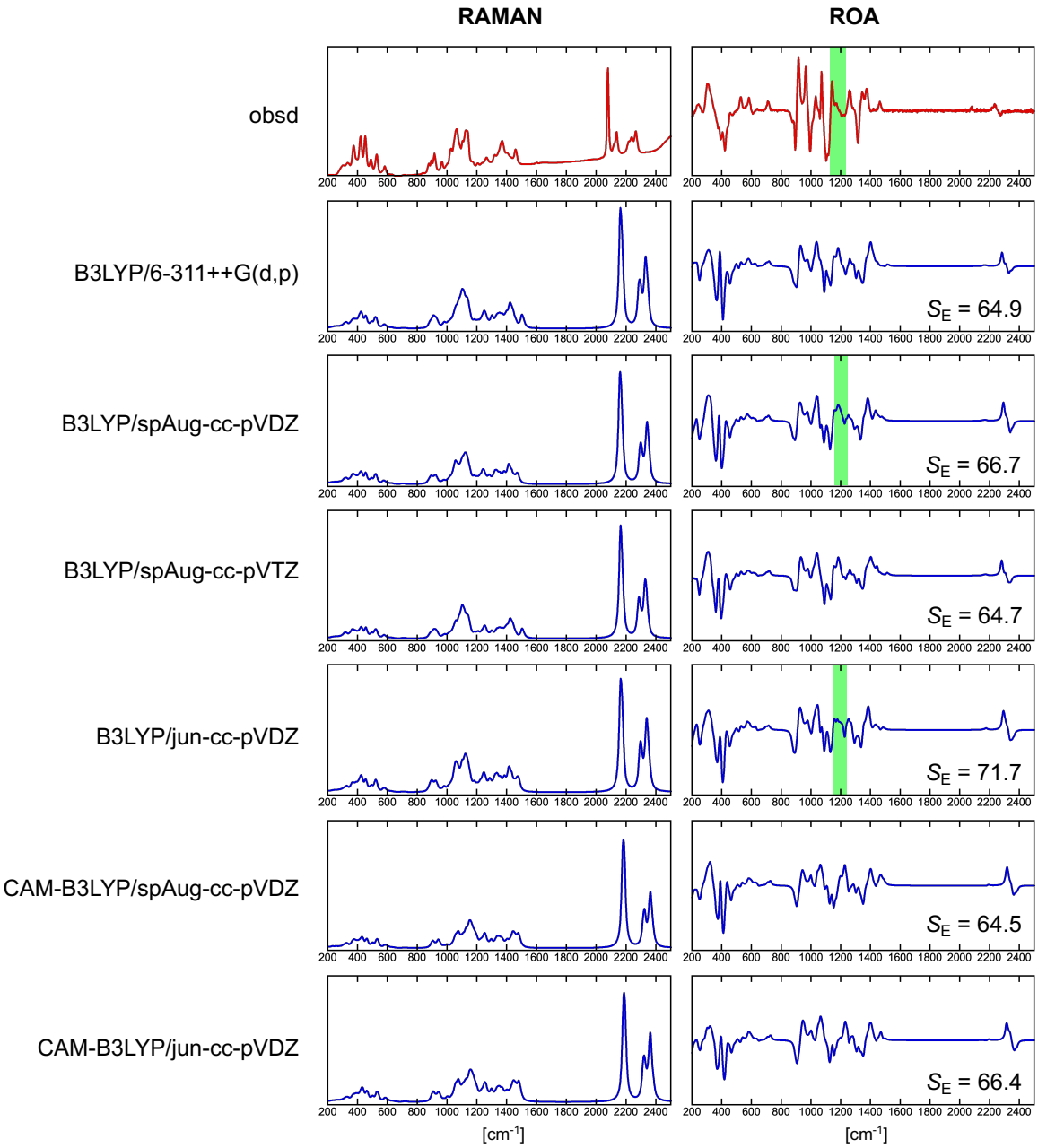


**Fig. S1** Test for several QM conditions for calculating Raman and ROA spectra of **$CD_3$-β-Glc** by a QM/MM method considering 20 snapshots. ROA spectral similarity ($S_E$) was obtained using CompareVOA software using the spectral region below 1500 cm$^{-1}$. B3LYP/spAug-cc-pVDZ and B3LYP/jun-cc-pVDZ conditions showed higher values than the others. With using qualitative comparisons, B3LYP/spAug-cc-pVDZ was selected for spectral calculations in this study. For example, in the highlighted region around 1200 cm$^{-1}$, positive signals predicted by B3LYP/jun-cc-pVDZ were weak, whereas the other conditions showed moderately strong positive signals.

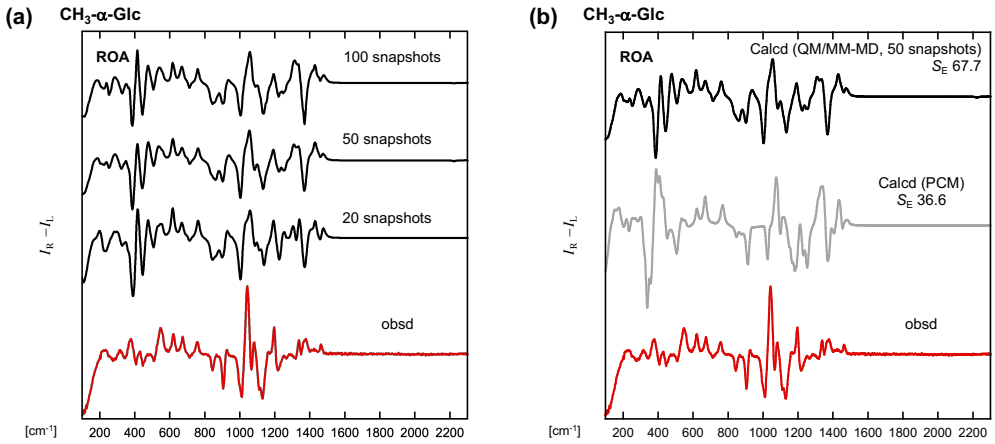


**Fig. S2** Comparison of observed and calculated ROA spectra of **$CD_3$-α-Glc**. (a) Comparison of the QM/MM spectra obtained by averaging 100, 50, and 20 snapshots. The ROA spectrum simulated by 50 snapshots was almost superimposable to that obtained by 100 snapshots, with differences in the intensity of several peaks. This observation led us to consider that 50 snapshots is satisfactory for this study. (b) Comparison of results calculated by QM/MM-MD and PCM. (b) PCM calculation was performed for a single molecule of **$CD_3$-α-Glc** at the B3LYP/spAug-cc-pVDZ with PCM for water (see computational details). ROA spectral similarity ($S_E$) was obtained using CompareVOA software using the spectral region below 1500 $cm^{-1}$.

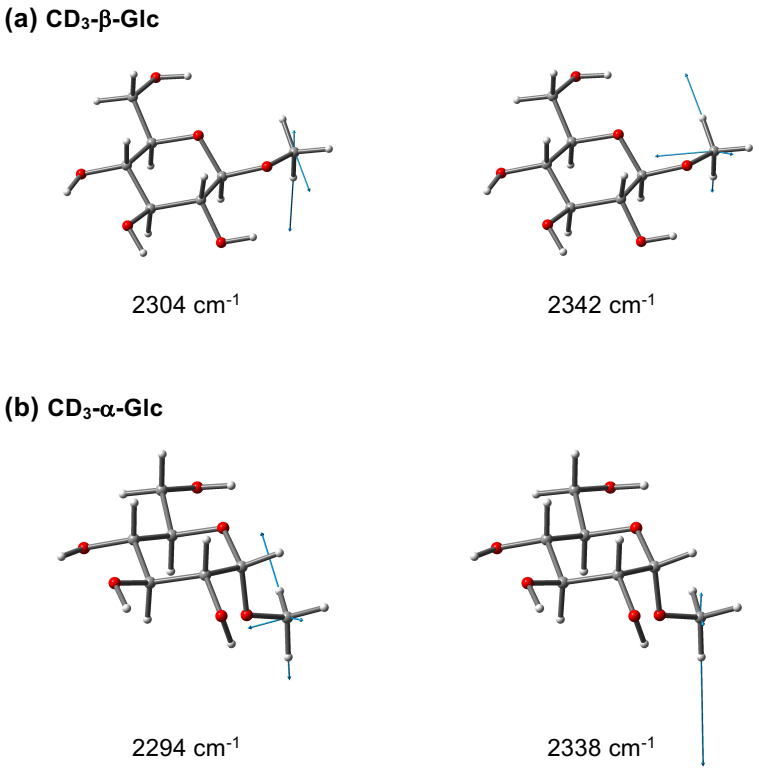


**Fig. S3** Vibrational modes of (a) **$CD_3$-β-Glc** and (b) **$CD_3$-α-Glc** exhibiting a pair of positive and negative signals in the C-D stretching region. Displacement vectors (arbitrary length) of each atom are shown as arrows.

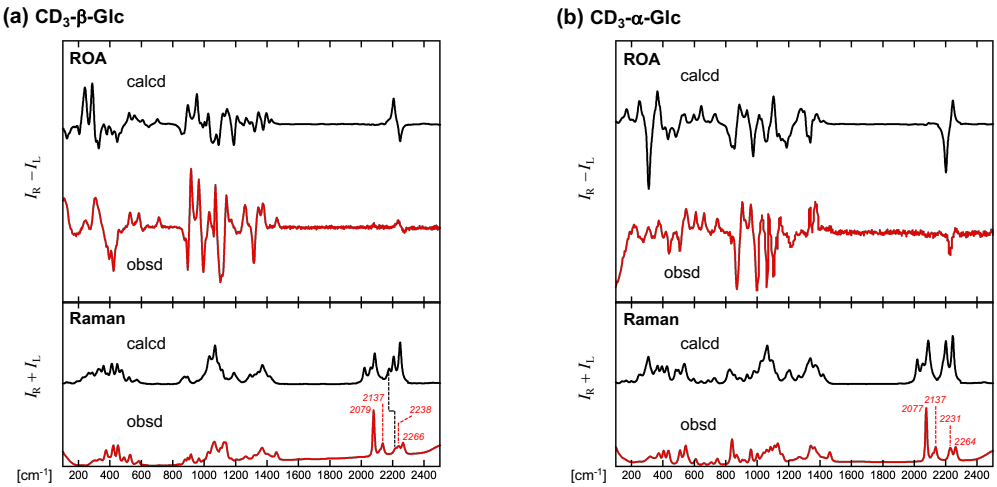


**Fig. S4** Comparison of observed (red) and anharmonically calculated PCM (black) ROA and Raman spectra of (a) **$CD_3$-β-Glc** and (b) **$CD_3$-α-Glc**. Calculated spectra were obtained by Boltzmann-averaging of the spectra of three conformers. In the Raman spectra in the C-D stretching region, anharmonic calculations predicted several signals. For example, a shoulder (indicated by a dotted line) appearing at the lower frequency side of the peak at 2238 $cm^{-1}$ of **$CD_3$-β-Glc** was reproduced in the anharmonic theoretical spectra. Anharmonic Raman spectra of both sugars also exhibited additional signals that may correspond to the experimental peak at 2137 $cm^{-1}$; however, relative intensity of the signals appearing at 2079/2077 $cm^{-1}$ and 2137 $cm^{-1}$ was not reproduced. In addition to the discrepancy in the C-D stretching region, the overall agreement between their Raman and ROA spectra remains to be improved in future studies.

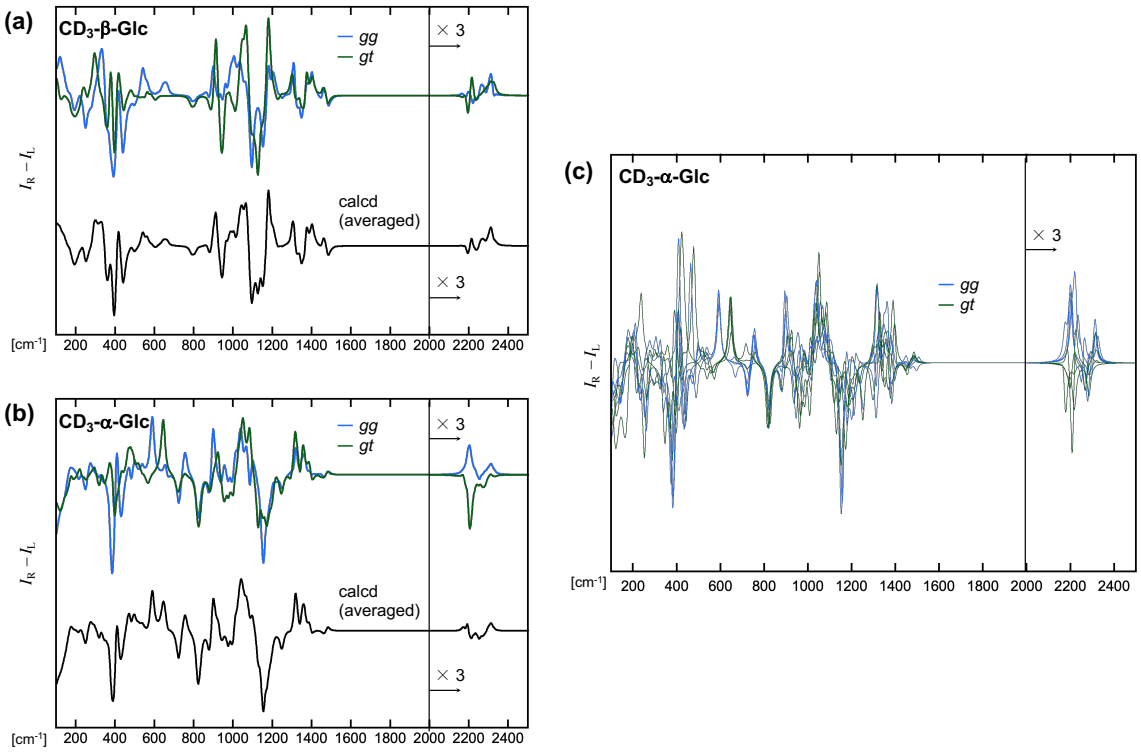


**Fig. S5** Comparison of calculated QM/MM ROA spectra of conformers of (a) **CD$_3$-β-Glc** and (b) **CD$_3$-α-Glc** differing in their C-6 hydroxymethyl orientation. Fifty snapshots were considered for obtaining the final calculated QM/MM ROA spectra (black) as described in Computational details on QM/MM-MD calculations. These 50 snapshots were classified into those with *gg* and *gt* conformers, and their ROA spectra were averaged to simulate the ROA spectra for *gg* conformers (blue) and *gt* conformers (green). (c) Calculated QM/MM ROA spectra of **CD$_3$-α-Glc** of each of randomly selected snapshots with *gg* (blue) and *gt* conformers (green). In the region around 2200 cm$^{-1}$, *gg* conformers of **CD$_3$-α-Glc** showed a positive signal whereas its *gt* conformers tend to show a negative one. The intensity of ROA spectra above 2000 cm$^{-1}$ is multiplied by a factor of 3 for clarity.

**Table S1** Assignment of the vibrational bands for (a) **$CH_3$-α-Glc**, (b) **$CD_3$-β-Glc**, (c) **$CD_3$-α-Glc**, (d) **$CH_3$-β-Glc-$d_5$**, and (e) **$CH_3$-α-Glc-$d_5$**. For the assignment for **$CH_3$-β-Glc**, see J. R. Cheeseman, M. S. Shaik, P. L. A. Popelier, E. W. Blanch, *J. Am. Chem. Soc.* 2011, **133**, 4991.

(a) **$CH_3$-α-Glc** (*gt* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 204 | 1 | -6 | OH twist |
| 251 | 2 | 18 | OH4 twist, OH2 twist |
| 316 | 5 | 3 | OH twist |
| 325 | 12 | 20 | OH twist |
| 340 | 2 | -69 | OH4 twist |
| 359 | 7 | -102 | OH6 twist, OH3 twist |
| 387 | 21 | 85 | OH6 twist |
| 407 | 14 | 45 | ring def, OH2 twist |
| 418 | 6 | -18 | OH2 twist |
| 429 | 4 | 19 | ring def, OH2 twist |
| 452 | 7 | -24 | ring def, OH2 twist, OH6 twist |
| 553 | 28 | 15 | ring breathing, C4-C5-O5 bend |
| 568 | 5 | -16 | ring def, C3-C4-C5 bend |
| 606 | 3 | -5 | ring def, O3-C3-C4 bend, C5-C6-O6 bend |
| 672 | 6 | 94 | ring def, C1-C2-O2 bend |
| 769 | 9 | 48 | ring def, O5-C1-C2 bend |
| 848 | 28 | -65 | ring def, $CH_2$ bend, νC5-O5 |
| 913 | 29 | -107 | ring def |
| 1020 | 1 | -35 | νC3-C4, C3-OH3 bend |
| 1030 | 13 | -137 | $CH_2$ bend, C6-OH6 bend, νC1-O1, ring def |
| 1049 | 10 | -37 | νC6-O6, $\nu_s$C5-O5-C1, ring def, C6-OH6 bend |
| 1072 | 7 | 195 | νC3-O3, νO1-C, νC1-C2, νC4-C5 |
| 1084 | 15 | 77 | νC6-O6, νC5-C1 |
| 1103 | 23 | 50 | νO1-C, C4-OH4 bend, νC4-C5 |
| 1107 | 41 | -58 | νO5-C1, νC2-O2, νC6-O6, C3-OH3 bend, ring def |
| 1119 | 19 | -13 | ring def, C4-OH4 bend, νC4-O4, νO1-C |
| 1131 | 34 | 7 | ring def, νC3-O3, C3-OH3 bend, C6-OH6 bend, νC4-O4 |
| 1155 | 11 | 57 | ring def, νC2-O2, νC4-O4, $CH_3$ def, C3-OH3 bend |
| 1165 | 10 | -6 | $CH_3$ def |
| 1166 | 24 | -134 | $CH_3$ def, $\nu_{as}$C5-O5-C1, $\nu_{as}$C2-C3-O3 |

| | | | |
|---|---|---|---|
| 1181 | 10 | -190 | νC2-C3, $CH_3$ def |
| 1210 | 8 | 58 | ring H torsions, $CH_2$ bend, C3-OH3 bend |
| 1211 | 13 | 65 | ring H torsions, $CH_3$ def |
| 1230 | 13 | -335 | ring H torsions, $CH_2$ bend, C6-OH6 bend |
| 1250 | 7 | 44 | ring H torsions, C4-OH4 bend, C2-OH2 bend |
| 1254 | 22 | -215 | ring H torsions, C3-OH3 bend, C2-OH2 bend |
| 1309 | 15 | 8 | ring H torsions, νC1-C2, C2-OH2 bend, C3-OH3 bend |
| 1314 | 4 | 185 | ring H torsions, $CH_2$ bend, C3-OH3 bend, C4-OH4 bend |
| 1345 | 11 | 169 | ring H torsions, C4-OH4 bend |
| 1353 | 10 | 56 | ring H torsions, $CH_2$ bend, C3-OH3 bend, C4-OH4 bend |
| 1369 | 22 | -142 | C1-H torsion, C2-H torsion |
| 1377 | 43 | -318 | C1-H torsion, C5-H torsion, $CH_2$ bend, C6-OH6 bend |
| 1386 | 8 | 236 | C1-H torsion, C5-H torsion, C6-OH6 bend |
| 1405 | 10 | -55 | νC2-C3, $CH_2$ bend, C3-H torsion, C2-H torsion, C2-OH2 bend |
| 1423 | 19 | 51 | $CH_2$ bend, C6-OH6 bend, C4-OH4 bend |
| 1431 | 8 | 69 | ring H torsions, C2-OH2 bend, ring def |
| 1440 | 14 | 194 | ring def, ring H torsions, νC3-C4 |
| 1450 | 19 | -15 | $CH_3$ def |
| 1458 | 20 | -52 | $CH_3$ def |
| 1464 | 20 | -12 | $\nu_{as}$C4-C5-C6, ring def, C4-OH4 bend, $CH_2$ bend |
| 1470 | 26 | 1 | $CH_2$ bend |
| 1473 | 20 | 33 | $CH_3$ def |

**$CH_3$-α-Glc** (*gg* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 221 | >0 | 6 | OH twist, C1-O1-C twist |
| 233 | 3 | -23 | OH twist, C1-O1-C twist |
| 253 | >0 | -7 | OH twist, $CH_2$ bend |
| 272 | 2 | 10 | OH twist, $CH_2$ bend |
| 306 | 2 | 33 | ring def, OH3 twist, OH4 twist |
| 319 | 10 | -32 | ring def, C1-O1-C bend, OH4 twist, OH6 twist |
| 337 | 1 | -6 | OH twist |
| 357 | 3 | -12 | ring def, OH twist |
| 361 | 8 | -62 | OH6 twist |
| 409 | 8 | 54 | ring def, OH2 twist |
| 415 | 5 | 33 | OH2 twist |
| 450 | 17 | -37 | ring def, OH2 twist, C1-O1-C bend |
| 510 | 22 | -46 | C3-C4-C5 bend, $CH_2$ bend |
| 534 | 4 | 38 | O2-C2-C3 bend, C3-C4-O4 bend, C5-C6-O6 bend |
| 558 | 15 | 6 | ring breathing, O2-C2-C3 bend |
| 621 | 13 | 76 | O1-C1-C2 bend |
| 713 | 10 | 5 | C5-C6-O6 bend, C1-C2-O2 bend |
| 773 | 6 | 57 | O5-C1-C2 bend |
| 876 | 34 | -36 | ring def, $CH_2$ bend |
| 915 | 34 | -146 | ring def, $CH_2$ bend |
| 932 | 21 | 42 | ring def, νC5-C6, $CH_2$ bend |
| 1026 | 9 | -183 | ring def, νC5-O5, C3-OH3 bend, νC2-O2, C2-OH2 bend, νC6-O6, C6-OH6 bend |
| 1035 | 6 | 167 | ring def, νC4-O4, C3-OH3 bend, C4-OH4 bend, νC6-O6 |
| 1056 | 18 | 15 | ring def, C2-OH2 bend, C3-OH3 bend, νC1-O1 |
| 1082 | 10 | 171 | νC1-C2, νC3-O3, νC4-C5, νC6-O6 |
| 1099 | 9 | -192 | $\nu_{as}$C5-O5-C1, $\nu_{as}$C1-O1-C, νC2-O3, C4-OH4 bend |
| 1108 | 37 | 148 | ring def, νO1-$CH_3$, νC2-O2, C2-OH2 bend, C3-OH3 bend |
| 1123 | 10 | 90 | ring def, νC4-O4, C4-OH4 bend, $\nu_{as}$C4-C5-C6, $CH_2$ bend, C6-OH6 bend |
| 1129 | 24 | -36 | νC3-O3, C3-OH3 bend, νC2-O2, C1-C2-C3 bend |
| 1149 | 26 | -174 | νC4-O4, C3-OH3 bend, $\nu_{as}$C5-C6-O6, νC2-O2, C2-OH2 bend |
| 1162 | 18 | -159 | $CH_3$ def, $\nu_{as}$C1-O5-C5, $\nu_{as}$O2-C2-C3, νC3-O3 |
| 1166 | 3 | 14 | $CH_3$ def |
| 1181 | 14 | 11 | νC2-C3, $CH_3$ def |

| | | | |
|---|---|---|---|
| | | | ring H bend, C3-OH3 bend, C4-OH4 bend, C2-OH2 bend, $CH_2$ bend, C6- |
| 1206 | 7 | -35 | OH6 bend |
| 1213 | 11 | 43 | $CH_3$ def, νC1-O1, C3-OH3 bend, ring H torsions |
| 1237 | 14 | 41 | ring H torsions, $CH_2$ bend, C2-OH2 bend, C4-OH4 bend, C6-OH6 bend |
| 1247 | 21 | -55 | C4-H torsion, C4-OH4 bend, C3-OH3 bend |
| 1256 | 18 | -87 | ring H torsions, C2-OH2 bend, C3-OH3 bend |
| 1309 | 13 | -9 | ring H torsions, C2-OH2 bend, C3-OH3 bend |
| 1329 | 17 | 276 | ring H torsions, C4-OH4 bend, C3-OH3 bend |
| 1339 | 7 | 77 | C5-H torsion, C4-H torsion |
| 1360 | 9 | -155 | C3-OH3 bend, $CH_2$ torsion, C6-OH6 bend |
| 1368 | 44 | -211 | C1-H torsion, C2-H torsion, C2-OH2 bend, C6-OH6 bend |
| 1373 | 6 | 193 | ring H torsions, $CH_2$ bend, C6-OH6 bend, C4-OH4 bend |
| 1385 | 15 | -73 | C1-H torsion |
| 1407 | 11 | -38 | ring H torsions, νC2-C3, $CH_2$ bend, C2-OH2 bend |
| 1419 | 29 | -31 | $CH_2$ bend, ring H torsions |
| 1432 | 10 | 68 | ring H torsions, ring def, C2-OH2 bend |
| 1443 | 12 | 64 | ring def, νC3-C4, C3-OH3 bend, C2-OH2 bend |
| 1452 | 17 | -16 | $CH_3$ def |
| 1456 | 23 | -114 | $CH_3$ def |
| 1461 | 17 | 200 | $\nu_{as}$C4-C5-C6, C4-OH4 bend, $CH_2$ bend |
| 1464 | 30 | -73 | $CH_2$ bend |
| 1475 | 18 | 34 | $CH_3$ def |

(b) **$CD_3$-β-Glc** (*gt* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 214 | 1 | -24 | OH2 twist, OH4 twist, C1-O1-C bending, ring def |
| 247 | 1 | 14 | OH4 twist, ring def |
| 276 | 3 | 50 | OH3 twist, OH6 twist, ring def |
| 317 | 8 | 50 | OH twist, ring def |
| 322 | 7 | 50 | OH twist, ring def |
| 337 | 2 | -28 | OH2 twist, OH3 twist, ring def |
| 357 | 8 | -137 | OH3 twist, OH6 twist, ring def |
| 384 | 22 | 43 | OH4 twist, OH6 twist, ring def |
| 399 | 10 | -26 | ring def, OH twist |
| 428 | 14 | 10 | OH twist, ring def |
| 456 | 15 | 20 | OH twist, ring def |
| 495 | 20 | -10 | OH twist, ring def |
| 588 | 11 | 3 | OH twist, ring def |
| 624 | >0 | 10 | OH twist, ring def |
| 644 | 1 | -9 | OH twist, ring def |
| 884 | 8 | -92 | ring def, $CH_2$ bend, $CD_3$ torsion |
| 900 | 8 | -18 | $CD_3$ def |
| 921 | 9 | 79 | ring def, $CH_2$ bend, $CD_3$ torsion |
| 988 | 6 | 96 | νC1-O1, $CD_3$ bend, νC3-O3, ring def |
| 1018 | 5 | -53 | C3-OH3 bend, νC3-C4, C2-OH2 bend, νC5-C6, $CD_3$ torsion, C4-OH4 bend |
| 1045 | 4 | 65 | νC1-O5, C3-OH3 bend, C4-OH4 bend, νC3-C4, νC2-O2, νC4-C5 |
| 1047 | 12 | -21 | $CD_3$ def |
| 1059 | 8 | 61 | $CD_3$ def |
| 1067 | 3 | -157 | $CH_3$ def, νC1-O5, C2-OH2 bend, νC2-C3, νC5-C6, ring def |
| 1070 | 10 | -154 | $CH_3$ def, C2-OH2 bend, νC4-C5, νC5-C6, νC6-O6, ring def |
| 1085 | 40 | 244 | C2-OH2 bend, C4-OH4 bend, νC6-O6, ring def, νC1-O5, νC2-O2, C2-OH2 bend, νC2-C3 |
| 1109 | 12 | 10 | C1-O1 stretch, νC2-O2, C3-OH3 bend, C4-OH4 bend, νC4-C5, C6-OH6 bend, ring def |
| 1112 | 25 | -6 | νC5-O5, νC6-O6, νO1-C, C3-OH3 bend, C4-OH4 bend |

| | | | |
|---|---|---|---|
| 1122 | 28 | 20 | νC3-O3, C3-OH3 bend, C2-OH2 bend, νC5-C6, νC4-O4, νC5-O5 |
| 1133 | 18 | -16 | νO1-$CH_3$, $CD_3$ def, ring def, νC2-O2 |
| 1137 | 53 | -48 | ring breathing, νC3-O3, νC2-O2, νC4-O4 |
| 1159 | 34 | -191 | νC5-C6, C1-O5-C5 bend, C3-C4-C5 bend |
| 1179 | 27 | 161 | νC1-C2, νC2-O2, C2-C1-H bend, νC4-O4 |
| 1199 | 2 | 123 | ring H torsion, C5-C6-H bend, $CH_2$ bend |
| 1217 | 4 | 99 | ring H torsion, νC1-O1, ring def |
| 1225 | 21 | -183 | ring H torsion, $CH_2$ bend, OH bend |
| 1238 | 24 | -364 | ring H torsion, $CH_2$ bending, OH bend, νC1-O1 |
| 1251 | 6 | 111 | ring H torsion, $CH_2$ bending, C4-OH4 bend, νC1-O1 |
| 1295 | 2 | -41 | ring H torsion, C2-OH2 bend, OH bend |
| 1310 | 9 | 153 | $CH_2$ bend, ring H torsions, C3-OH3 bend, C4-OH4 bend |
| 1336 | 14 | 78 | ring H torsions, $CH_2$ bend, C2-OH2 bend, C3-OH3 bend |
| 1339 | 12 | -17 | ring H torsions, $CH_2$ bend, C2-OH2 bend, C3-OH3 bend, νC5-O5 |
| 1362 | 12 | -77 | ring H torsions, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend, C6-OH6 bend |
| 1368 | 22 | -209 | ring H torsions, C5-C6-H bend, C6-OH6 bend |
| 1397 | 11 | 249 | ring H torsions, C5-C6-H bend, C6-OH6 bend, ring def |
| 1420 | 18 | 68 | ring H torsions, $CH_2$ bend, C2-OH2 bend, νC4-C5, C6-OH6 bend, C4-OH4 bend |
| 1433 | 10 | -96 | ring H torsions, νC1-C2, νC3-O3, $CH_2$ bend |
| 1435 | 27 | 58 | ring H torsions, $\nu_{as}$C2-C3-C4, ring def, C3-OH3 bend |
| 1440 | 11 | -26 | ring H torsions, $CH_2$ bend, C2-OH2 bend, ring def |
| 1463 | 23 | 47 | ring H torsions, $\nu_{as}$C4-C5-C6, C4-OH4 bend, C6-OH6 bend, C2-OH2 bend, νC1-C2 |
| 1470 | 28 | 81 | $CH_2$ bend |
| 2179 | 428 | -38 | $\nu_s CD_3$ |
| 2320 | 135 | 271 | $\nu_{as} CD_3$ |
| 2358 | 218 | -189 | $\nu_{as} CD_3$ |

**$CD_3$-β-Glc** (*gg* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 232 | 4 | -20 | OH twist |
| 259 | >0 | 10 | $CH_2$ bend, OH6 twist |
| 267 | 1 | -8 | OH twist, C1-O1-C bending, C5-O5-C1 bending |
| 293 | 3 | -14 | OH2 twist, OH4 twist |
| 301 | 9 | 41 | OH3 twist |
| 321 | 7 | 29 | OH4 twist, OH2 twist |
| 338 | 1 | -61 | OH twist |
| 348 | 5 | -65 | OH3 twist, OH4 twist |
| 359 | 6 | 47 | OH6 twist |
| 421 | 13 | 2 | ring def, OH6 twist |
| 425 | 11 | -14 | ring def, OH6 twist |
| 453 | 25 | -70 | ring def, ring H torsions |
| 533 | 30 | 58 | ring def |
| 571 | 7 | 38 | ring def, $CH_2$ bend, OH6 twist |
| 611 | 2 | 9 | ring def, C1-O1-C bend |
| 720 | 2 | 48 | ring def, C5-C6-O bend |
| 894 | 10 | 36 | ring def, O1-C bend, $CH_2$ bend |
| 900 | 5 | -134 | $CD_3$ def, $CH_2$ bend |
| 925 | 10 | 47 | $CH_2$ bend, ring def |
| 933 | 22 | 32 | νC5-C6, $CD_3$ def, H-C5-C6 bend, νC3-O3 |
| 988 | 7 | 119 | νO1-C, $CD_3$ def, ring def, νC2-C3 |
| 1038 | 9 | 48 | νC3-C4, νC4-O4, νC3-O3, νC3-O2, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend, νC6-O6 |
| 1047 | 12 | 45 | $CD_3$ def |
| 1052 | 6 | 138 | νC2-C3, C3-OH3 bend, νC3-O3, νC6-O6, $CD_3$ def, νC2-O2 |
| 1059 | 7 | -19 | $CD_3$ def |
| 1072 | 34 | 197 | νC5-O5, νC6-O6, νC1-C2, C2-OH2 bend, ring H torsions |
| 1077 | 22 | -271 | νC1-O5, νC6-O6 |
| 1099 | 4 | -63 | $\nu_{as}$C1-O5-C5, ring H torsions |
| 1114 | 18 | -24 | νC2-O2, νC3-O3, $\nu_{as}$C3-C4-C5, C3-OH3 bend, $CH_2$ bend, C6-OH6 bend |
| 1126 | 17 | 83 | νC4-O4, νC3-O3, $\nu_{as}$C5-C6-O6, C2-OH2 bend, C4-OH4 bend |

| | | | |
|---|---|---|---|
| 1131 | 22 | -53 | νO1-C, $CD_3$ def, $\nu_{as}$C1-C2-O2 |
| 1137 | 36 | -35 | $\nu_{as}$C2-C3-O3, C2-OH2 bend, νC2-O2, ring breathing |
| 1153 | 37 | -311 | νC5-O5, νC4-O4, C3-OH3 bend, νC1-O1, ring def |
| 1177 | 26 | 61 | $\nu_{as}$C1-C2-O2, ring H torsions, C3-OH3 bend |
| 1200 | 13 | 105 | ring H torsions, OH bend, $\nu_{as}$C1-O1-C |
| 1209 | 2 | 67 | ring H torsions, OH-bend, $\nu_{as}$C1-O1-C, $CH_2$ bend |
| 1232 | 16 | -49 | ring H torsions, C2-OH2 bend, C3-OH3 bend, $\nu_{as}$C1-O1-C |
| 1241 | 11 | 252 | ring H torsions, C3-OH3 bend, C4-OH4 bend, $CH_2$ bend, C6-OH6 bend |
| 1248 | 25 | -8 | ring H torsions, C4-OH4 bend, $CH_2$ bend, C6-OH6 bend |
| 1294 | 2 | -57 | ring H torsions, C2-OH2 bend |
| 1325 | 18 | 196 | ring H torsions, C3-OH3 bend, C4-OH4 bend |
| 1336 | 14 | -250 | ring H torsions |
| 1339 | 16 | -4 | ring H torsions, C2-OH2 bend, C3-OH3 bend |
| 1373 | 17 | 75 | ring H torsions, C4-OH4 bend, $CH_2$ bend, C6-OH6 bend |
| 1391 | 18 | 53 | ring H torsions, C5-C6-H bend |
| 1416 | 17 | -73 | $CH_2$ bend, C6-OH6 bend, νC5-C6 |
| 1430 | 12 | -69 | ring H torsions, νC1-C2 |
| 1438 | 35 | 12 | ring H torsions, νC2-C3, C2-OH2 bend, C3-OH3 bend |
| 1441 | 8 | -73 | ring H torsions, $\nu_{as}$C3-C4-C5, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend |
| 1460 | 25 | 274 | ring H torsions, νC4-C5, νC1-C2, C2-OH2 bend, C4-OH4 bend, $\nu_{as}$C1-C2-C3 |
| 1465 | 29 | -83 | $CH_2$ bend |
| 2179 | 422 | -23 | $\nu_s CD_3$ |
| 2320 | 134 | 307 | $\nu_{as} CD_3$ |
| 2358 | 218 | -143 | $\nu_{as} CD_3$ |

(c) **$CD_3$-α-Glc** (*gt* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 239 | 2 | 15 | OH4 twist, OH2 twist |
| 269 | 2 | 10 | OH3 twist, OH4 twist, ring def |
| 292 | 6 | 4 | OH twist, C1-O1-C bend |
| 301 | 6 | 39 | OH twist |
| 318 | 5 | -107 | OH twist |
| 338 | 5 | -80 | OH6 twist, OH3 twist |
| 374 | 24 | 74 | OH6 twist, OH2 twist, ring def |
| 388 | 6 | 144 | OH2 twist, OH6 twist |
| 401 | 14 | -97 | ring def, OH2 twist, OH6 twist |
| 422 | 6 | 8 | ring def |
| 440 | 8 | -38 | ring def, C1-O1-C bend, $CH_2$ bend, OH6 twist, OH2 twist |
| 547 | 27 | 14 | ring breathing, $CH_2$ bend |
| 557 | 10 | -14 | ring def, C2-OH2 bend |
| 656 | 6 | 106 | ring def, C1-O1-H bend, C2-OH2 bend, $CH_2$ bend |
| 751 | 12 | 39 | O5-C1-C2 bend |
| 834 | 31 | -53 | $CH_2$ bend, $CH_3$ def |
| 861 | 15 | -134 | $CD_3$ def, $CH_2$ bend, ring def, C6-OH6 bend |
| 902 | 5 | 76 | $CD_3$ def, C1-O1-C bend |
| 961 | 16 | 60 | C2-OH2 bend, CD3 def, C1-O1-C bend |
| 1008 | 9 | -111 | $CD_3$ def, νC3-C4, νC2-O2, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend, νC6-O6, ring def |
| 1014 | 7 | -85 | νC3-C4, $CD_3$ def, νO1-C, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend |
| 1030 | 12 | 21 | νC5-O5, C6-OH6 bend, $CH_2$ bend, C4-OH4 bend |
| 1042 | 12 | -66 | $CD_3$ def |
| 1054 | 5 | -185 | $\nu_{as}$O1-C1-C2, $CD_3$ def, νC1-O1 |
| 1054 | 13 | 242 | $CD_3$ def, νC4-O4 |
| 1068 | 12 | -41 | ring def, νC1-O5, νC6-O6, νO1-C, νC2-O2, C4-OH4 bend |
| 1085 | 11 | 76 | $\nu_{as}$C5-O5-C1, νC4-C5, C4-OH4 bend, $\nu_{as}$C1-O1-CD |
| 1092 | 36 | -38 | $\nu_{as}$C5-O5-C1, νC6-O6, νC2-O2, C3-OH3 bend, νC4-O4 |
| 1103 | 27 | -67 | νC3-O3, C4-OH4 bend, νC4-C5, νC5-C6 |
| 1116 | 40 | -58 | ring def, νO1-C, νC3-O3, C3-OH3 bend, νC4-O4, C6-OH6 bend |
| 1125 | 19 | 110 | $CD_3$ def, νO1-C, C3-OH3 bend, νC4-O4 |
| 1149 | 18 | -108 | ring def, νC5-C6, νC4-O4, C3-OH3 bend |

| | | | |
|---|---|---|---|
| 1155 | 18 | 135 | $\nu_{as}$C3-C2-O2, ring def, νC3-O3 |
| 1176 | 17 | -103 | $\nu_{as}$C1-C2-C3, νC1-O1 |
| 1202 | 6 | -26 | ring H torsion, C2-OH2 bend, $CH_2$ bend |
| 1222 | 15 | -350 | ring H torsions, $CH_2$ bend, C6-OH6 bend, C2-OH2 bend, C3-OH3 bend |
| 1243 | 10 | -15 | ring H torsion, C6-OH6 bend, C2-OH2 bend, C4-OH4 bend |
| 1247 | 24 | -182 | ring H torsion, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend |
| 1297 | 15 | 54 | ring-H torsions, νC1-C2, C2-OH2 bend, C3-OH3 bend |
| 1307 | 5 | 178 | ring-H torsions, $CH_2$ bend, C4-OH4 bend, C3-OH3 bend |
| 1337 | 14 | 149 | ring H torsions, $CH_2$ bend, C6-OH6 bend, C4-OH4 bend |
| 1344 | 9 | 68 | ring H torsions, $CH_2$ bend, C3-OH3 bend |
| 1358 | 30 | -224 | ring H torsions, νC1-C2, C2-OH2 bend |
| 1371 | 42 | -250 | ring H torsions, $CH_2$ bend, C6-OH6 bend |
| 1379 | 11 | 171 | ring H torsions, $CH_2$ bend, C6-OH6 bend, C2-OH2 bend |
| 1393 | 9 | -9 | ring H torsions, νC2-C3, $CH_2$ bend, C6-OH6 bend, C2-OH2 bend |
| 1412 | 18 | 115 | ring H torsions, νC5-C6, $CH_2$ bend, C6-OH6 bend, C2-OH2 bend, C4-OH4 bend |
| 1419 | 10 | 14 | ring H torsions, νC3-C4, $CH_2$ bend, C2-OH2 bend, C3-OH3 bend |
| 1426 | 17 | 225 | ring H torsions, $CH_2$ bend, νC1-C2, νC3-C4, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend |
| 1445 | 18 | -62 | νC4-C5, C4-OH4 bend, νC5-C6, $CH_2$ bend |
| 1462 | 29 | 51 | $CH_2$ bend |
| 2165 | 466 | 40 | $\nu_s CD_3$ |
| 2301 | 163 | -613 | $\nu_{as} CD_3$ |
| 2342 | 204 | 355 | $\nu_{as} CD_3$ |

**$CD_3$-α-Glc** (*gg* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 221 | 3 | -22 | OH twist |
| 240 | >0 | -11 | OH6 twist, OH4 twist, $CH_2$ bend |
| 259 | 2 | 11 | OH twist, $CH_2$ bend |
| 282 | 3 | 30 | OH twist |
| 293 | 9 | -27 | OH6 twist, OH4 twist |
| 333 | 4 | -32 | OH6 twist, OH2 twist |
| 345 | 6 | -54 | OH twist, ring def |
| 386 | 4 | 77 | OH2 twist |
| 404 | 10 | 9 | ring def, OH2 twist, OH6 twist |
| 440 | 18 | -37 | ring def, OH2 twist |
| 503 | 22 | -48 | ring def, C5-CH6 bend |
| 526 | 5 | 40 | ring def, C3-C4-O4 bend, C5-C6-O6 bend |
| 551 | 15 | 0 | ring breathing |
| 607 | 16 | 72 | ring breathing, C1-O1-C bend, C5-C6-O6 bend |
| 702 | 11 | 32 | ring def, C2-OH2 bend, C5-C6-O6 bend |
| 757 | 7 | 73 | ring def, O5-C5-C4 bend |
| 844 | 33 | -60 | ring def, $CD_3$ def |
| 880 | 21 | -153 | $CH_2$ bend, ring H torsions, $CD_3$ def |
| 903 | 4 | 83 | $CD_3$ def |
| 924 | 19 | 52 | $\nu_s$C4-C5-C6, νC3-O3 |
| 963 | 23 | -32 | $CD_3$ def, C1-O1-C bend, ring def |
| 1011 | 15 | -186 | νO1-C, $CD_3$ def, ring def |
| 1020 | 10 | 172 | νC5-O5, νC6-O6, C6-O6-O bend, ring def |
| 1031 | 7 | 57 | νC3-C4, C3-OH3 bend, ring def |
| 1042 | 13 | -55 | $CD_3$ def |
| 1054 | 8 | -40 | $CD_3$ def |
| 1069 | 12 | -15 | ring def, O5-C1 stretch, $CH_2$ bend |
| 1080 | 6 | -116 | $\nu_{as}$O5-C1-O1, νC2-O2, νO1-C, νC5-O5, C4-O1-H bend |
| 1090 | 25 | 136 | νC2-O2, νC1-O1, C3-OH3 bend, ring def |
| 1109 | 15 | -7 | $\nu_{as}$C4-C5-C6, $\nu_{as}$C3-O3, $\nu_{as}$C4-O4, C4-OH4 bend, $\nu_{as}$C6-O6, C6-OH6 bend |
| 1113 | 34 | -44 | $\nu_{as}$C4-C3-O3, $CD_3$ def |
| 1125 | 16 | 44 | νO1-C, $CD_3$ def, C3-OH3 bend, ring def |
| 1138 | 23 | -236 | ring def, νC4-O4, νC6-O6 |

| | | | |
|---|---|---|---|
| 1156 | 19 | 175 | $\nu_{as}$O2-C2-C3, νC5-O5, ring def |
| 1175 | 16 | 54 | $\nu_{as}$O1-C1-C2, νC2-C3, ring def |
| 1200 | 7 | -192 | ring H torsions, C2-OH2 bend, C3-OH3 bend, $CH_2$ bend |
| 1229 | 15 | 59 | $CH_2$ bend, ring H torsions, C4-OH4 bend, C2-OH2 bend |
| 1240 | 20 | -17 | ring H torsions, C3-OH3 bend, $CH_2$ bend, C4-OH4 bend |
| 1247 | 23 | -126 | ring H torsions, C2-OH2 bend, C3-OH3 bend, C4-OH4 bend |
| 1297 | 14 | 42 | ring H torsions, νC1-C2, C2-OH2 bend, C3-OH3 bend |
| 1320 | 17 | 239 | ring H torsions, C3-OH3 bend, C4-OH4 bend |
| 1330 | 11 | 56 | ring H torsions |
| 1350 | 8 | -96 | ring H torsions, νC5-C6, C3-OH3 bend |
| 1357 | 43 | -253 | ring H torsions, C2-OH2 bend, C6-OH6 bend, νC5-O5 |
| 1364 | 10 | 141 | ring H torsions, C4-OH4 bend, $CH_2$ bend, C6-OH6 bend |
| 1378 | 21 | -76 | ring H torsion |
| 1395 | 11 | 54 | ring H torsions, C2-OH2 bend, νC2-C3 |
| 1408 | 29 | -33 | ring H torsions, $CH_2$ bend, C6-OH6 bend |
| 1428 | 16 | 137 | ring H torsions, C2-OH2 bend, C3-OH3 bend, νC3-C4 |
| 1443 | 17 | 99 | νC4-C5, ring H torsions, C4-OH4 bend |
| 1456 | 29 | -66 | $CH_2$ bend |
| 2165 | 469 | 14 | $\nu_s CD_3$ |
| 2301 | 167 | -591 | $\nu_{as} CD_3$ |
| 2342 | 205 | 364 | $\nu_{as} CD_3$ |

(d) **$CH_3$-β-Glc-$d_5$** (*gt* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 237 | 2 | 26 | OH4 twist |
| 263 | 1 | 45 | OH2 twist, OH3 twist |
| 270 | 3 | 7 | OH2 twist |
| 292 | 6 | 52 | OH twist |
| 303 | 8 | 74 | OH twist |
| 310 | 2 | -38 | OH twist |
| 335 | 7 | -121 | OH6 twist |
| 371 | 24 | 57 | ring def, C1-O1-C bend |
| 384 | 15 | -60 | ring def, C5-C6-O6 bend |
| 417 | 16 | -5 | C2-C3-C4 bend, C5-O5-C1 bend |
| 434 | 9 | -12 | C1-O1-C bend, C1-C2-C3 bend |
| 463 | 18 | -5 | ring def, C5-C6-O6 bend |
| 555 | 8 | -2 | C3-C4-O bend, O2-C2-C3 bend |
| 558 | 8 | 16 | C1-O1-C bend, C2-C3-O3 bend |
| 606 | 3 | -6 | O5-C5-C4 bend, O5-C1-C2 bend |
| 787 | 6 | -24 | $CD_2$ bend, O5-C5-C6 bend, |
| 880 | 9 | -82 | $CD_2$ bend, ring D torsion |
| 885 | 8 | -63 | ring D torsions, $CD_2$ bend |
| 916 | 6 | 267 | ring D torsions, $CD_2$ bend |
| 937 | 7 | 6 | ring D torsions, C2-OH2 bend |
| 950 | 17 | -134 | ring D torsions |
| 956 | 23 | -31 | ring D torsions, νO1-C |
| 965 | 7 | -4 | ring D torsions |
| 979 | 19 | 57 | $CD_2$ bend, νC6-O6, ring D torsions, C3-OH3 bend |
| 988 | 2 | -54 | $CD_2$ bend, νC6-O6, ring D torsions, C3-OH3 bend, νC3-C4 |
| 1016 | 12 | -47 | ring def, νC6-O6, νO1-C, νC2-O2, $CD_2$ bend |
| 1038 | 6 | 40 | νC1-O5, $CD_2$ bend, νC4-C5 |
| 1049 | 4 | 213 | ring breathing, νC4-C5, C4-OH4 bend, $CD_2$ bend |
| 1068 | 36 | 198 | $CH_3$ def, νC1-C2, $CD_2$ bend |
| 1075 | 5 | 53 | νO5-C1, ring def, $CD_2$ bend, νC2-O2, |
| 1099 | 21 | -206 | νO5-C5, νO1-C, νC1-C2, νC3-O3, νC4-O4 |
| 1114 | 47 | -318 | $CD_2$ bend, ring def, νC6-O6, νO1-C |
| 1126 | 20 | -161 | $\nu_{as}$C4-C5-O5, C4-OH4 bend, ring def |

| | | | |
|---|---|---|---|
| 1155 | 11 | -69 | νC2-O2, C1-C2-C3 bend, $CH_3$ def, νO1-C |
| 1157 | 4 | -85 | $CH_3$ def |
| 1174 | 23 | -8 | $\nu_{as}$C5-C6-O6, $CD_2$ bend, νC4-O4, C3-OH3 bend |
| 1184 | 26 | 327 | ring breathing, $\nu_{as}$O2-C2-C3, νC3-O3, C2-OH2 bend |
| 1189 | 25 | 113 | $CH_3$ def, ring H torsions, νC5-C6, C3-OH3 bend |
| 1198 | 37 | -66 | ring H torsions, νC1-C2, C2-C3-C4 bend, νC3-O3, νC4-O4 |
| 1232 | 10 | -46 | $CH_3$ def, νC1-O1, ring H torsions |
| 1310 | 15 | 254 | ring H torsions, C4-OH4 bend, C6-OH6 bend |
| 1311 | 21 | -101 | ring H torsions, C6-OH6 bend |
| 1330 | 14 | -39 | ring H torsions, C6-OH6 bend, C3-OH3 bend, C5-O5-H bend |
| 1347 | 17 | -76 | ring H torsions, νC2-C3, C2-OH2 bend, C3-OH3 bend |
| 1363 | 21 | -103 | ring H torsions, $\nu_{as}$C2-C3-C4, C3-OH3 bend |
| 1380 | 21 | 161 | ring H torsions |
| 1394 | 8 | -91 | ring H torsions, $CH_3$ def, νC1-C2, νC4-C5, C4-OH4 bend |
| | | | ring H torsions, $\nu_{as}$C4-C5-C6, νC1-C2, C2-OH2 bend, νC5-C6, C4-OH4 |
| 1409 | 16 | 228 | bend |
| 1446 | 26 | 12 | $CH_3$ def |
| 1452 | 13 | 72 | $CH_3$ def, ring H torsion |
| 1468 | 20 | -134 | $CH_3$ def |
| 2199 | 222 | 210 | νCD |
| 2210 | 560 | -832 | νCD |
| 2216 | 20 | 649 | νCD |
| 2232 | 218 | -71 | νCD |
| 2318 | 206 | 87 | νCD |

**$CH_3$-β-Glc-$d_5$** (*gg* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 212 | 2 | 13 | OH twist, $CD_2$ bend |
| 224 | 3 | -17 | $CD_2$ bend, OH4 twist |
| 256 | 2 | -12 | OH4 twist, OH6 twist |
| 268 | 2 | -14 | OH2 twist |
| 280 | 4 | 60 | OH3 twist |
| 297 | 6 | 3 | OH4 twist |
| 314 | 3 | -79 | OH6 twist, OH4 twist |
| 331 | 5 | 47 | OH6 twist |
| 338 | 11 | -20 | OH3 twist, C1-O1-C bend |
| 408 | 13 | -23 | ring def |
| 418 | 10 | 2 | ring def, C1-O1-C bend |
| 432 | 25 | -63 | ring def |
| 500 | 20 | -21 | ring def |
| 536 | 16 | 73 | ring def |
| 558 | 6 | 32 | C1-O1-C bend, ring D torsions |
| 660 | 2 | 34 | C5-C6-O6 bend |
| 792 | 6 | -12 | $CD_2$ bend, C6-OH6 bend |
| 866 | 7 | 8 | $CD_2$ bend, νC5-C6 |
| 882 | 11 | -74 | ring D torsions, $CD_2$ bend |
| 893 | 8 | 151 | $CD_2$ bend, ring D torsions |
| 936 | 7 | 123 | ring D torsions, C2-OH2 bend |
| 953 | 20 | -93 | ring D torsions |
| 955 | 9 | 134 | ring D torsions |
| 956 | 23 | -55 | ring D torsions |
| 972 | 4 | -72 | ring D torsions |
| 983 | 17 | 49 | $CD_2$ bend, νC6-O6 |
| 1006 | 7 | 181 | νC3-O3, νO1-C |
| 1039 | 22 | 151 | $CD_2$ bend, νC4-O4, νO1-C, νC2-O2, ring def |
| 1050 | 17 | -34 | νC1-O5, ring def, $CD_2$ bend, C4-OH4 bend |
| 1061 | 21 | -21 | $CH_3$ def, ring def, C4-OH4 bend |
| 1079 | 17 | 1 | νC5-O5, ring def |
| 1083 | 24 | -24 | $CD_2$ bend |
| 1099 | 20 | -317 | ring def, νC5-O5, νC4-O4, νC3-O3, νO1-C |

| | | | |
|---|---|---|---|
| 1122 | 17 | 5 | $\nu_{as}$C4-C5-O5, C4-OH4 bend, ring def |
| 1154 | 15 | -151 | $CH_3$ def, νO1-C, νC2-O2, C3-OH3 bend, ring def |
| 1156 | 6 | -55 | $CH_3$ def |
| 1176 | 33 | -156 | C3-OH3 bend, νC4-O4, ring def |
| 1184 | 27 | 301 | ring breathing, $\nu_{as}$C2-C3-O3, C2-OH2 bend, νC2-O2 |
| 1196 | 35 | 94 | νC1-C2, $CH_3$ def, νC3-O3, C4-OH4 bend |
| 1214 | 9 | -68 | $\nu_{as}$C5-C6-O6, $CH_3$ def, νC1-O1, νC4-O4, C3-OH3 bend |
| 1231 | 10 | 3 | νC1-O1, $CH_3$ def, ring H torsion |
| 1296 | 13 | 139 | ring H torsions, C6-OH6 bend |
| 1308 | 16 | 172 | ring H torsions, C4-OH4 bend |
| 1332 | 25 | -203 | ring H torsions, C4-OH4 bend, C2-OH2 bend |
| | | | ring H torsions, C2-OH2 bend, νC3-O3, C3-OH3 bend, C4-OH4 bend, |
| 1349 | 21 | -115 | $\nu_s$C2-C3-C4 |
| 1363 | 21 | 112 | ring def, $\nu_{as}$C2-C3-C4, C3-OH3 bend, C4-OH4 bend |
| 1366 | 23 | -55 | ring H torsions |
| 1393 | 10 | -37 | ring H torsions, νC1-C2, νC4-C5, C4-OH4 bend |
| 1408 | 17 | 245 | ring H torsions, νC4-C5, C4-OH4 bend, $CH_3$ def, νC1-C2 |
| 1445 | 30 | 38 | $CH_3$ def |
| 1450 | 9 | 42 | $CH_3$ def |
| 1467 | 21 | -97 | $CH_3$ def |
| 2210 | 403 | 201 | νCD |
| 2210 | 383 | -89 | νCD |
| 2228 | 5 | -94 | νCD |
| 2234 | 313 | 185 | νCD |
| 2318 | 218 | 137 | νCD |

(e) **$CH_3$-α-Glc-$d_5$** (*gt* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 204 | >0 | 8 | OH2 twist, OH3 twist, C1-O1-C twist |
| 238 | 2 | 15 | OH4 twist, OH2 twist |
| 297 | 5 | 51 | OH twist |
| 306 | 7 | -54 | OH4 twist |
| 313 | 4 | -31 | OH6 twist, OH4 twist |
| 334 | 7 | -107 | OH6 twist, OH3 twist |
| 363 | 21 | 97 | OH6 twist |
| 386 | 7 | 118 | OH2 twist |
| 396 | 8 | -106 | ring def, OH6 twist |
| 402 | 10 | -25 | ring def |
| 429 | 12 | 15 | ring def, OH2 twist |
| 516 | 8 | 4 | ring def |
| 539 | 17 | -19 | ring def |
| 565 | 5 | -6 | ring def, ring D torsions |
| 641 | 9 | 111 | ring def, O5-C1-O1 bend, $CD_2$ bend |
| 721 | 21 | 17 | $CD_2$ bend, ring def |
| 750 | 10 | 36 | $CD_2$ bend, ring def |
| 823 | 19 | -173 | ring D torsions, ring def |
| 882 | 7 | -109 | $CD_2$ bend, C6-OH6 bend |
| 894 | 11 | 32 | ring D torsions |
| 926 | 6 | 131 | ring D torsions, $CD_2$ bend |
| 936 | 12 | 0 | ring D torsion, C2-OH2 bend |
| 952 | 14 | -166 | ring D torsions |
| 964 | 15 | -54 | ring D torsions |
| 980 | 14 | 43 | $CD_2$ bend, νC6-O6, ring D torsions |
| 996 | 11 | -28 | ring def, ring D torsions |
| 1012 | 13 | -196 | ring def, ring D torsions, νC4-O4 |
| 1017 | 6 | 208 | ring def, $CD_2$ bend |
| 1035 | 19 | -30 | $\nu_s$C1-O1-C, νC1-O5, ring def, $CD_2$ bend |
| 1055 | 13 | 243 | $CD_2$ bend, ring def |
| 1076 | 2 | 14 | νC1-O5, ring def, $CD_2$ bend, C4-OH4 bend |
| 1093 | 16 | 225 | $\nu_{as}$C1-O5-C5, νO1-C, $CD_2$ bend |
| 1115 | 12 | -45 | O1-C bend, νC4-O4, C4-OH4 bend, ring def |
| 1129 | 43 | -248 | νC6-O6, $CD_2$ bend, νC3-O3, $CH_3$ def |

| | | | |
|---|---|---|---|
| 1151 | 18 | -7 | ring def, νC2-O2, νC3-O3, C4-OH4 bend |
| 1158 | 4 | 15 | $CH_3$ def |
| 1174 | 33 | -323 | C3-OH3 bend, $\nu_{as}$C3-C4-O4, $\nu_{as}$C5-C6-O6, ring def |
| 1186 | 27 | 20 | ring def, C3-OH3 bend, νC5-C6 |
| 1196 | 24 | -124 | ring breathing, νC2-O2, νC4-O4 |
| 1201 | 4 | -95 | $CH_3$ def |
| 1255 | 33 | -207 | $\nu_{as}$C1-C2-C3, C2-OH2 bend, ring def |
| 1311 | 26 | 106 | C6-OH6 bend |
| 1317 | 13 | 193 | ring H torsions, C2-OH2 bend, C4-OH4 bend |
| 1326 | 13 | 137 | ring H torsions, C2-OH2 bend, C4-OH4 bend |
| 1342 | 16 | -147 | ring H torsions, νC3-C4, C3-OH3 bend |
| 1356 | 20 | 107 | ring H torsions, C3-OH3 bend |
| 1372 | 15 | 26 | ring H torsion |
| 1383 | 10 | 194 | ring H torsion |
| 1408 | 20 | -142 | ring H torsions, νC4-C5, C4-C5-H bend |
| 1442 | 17 | -56 | $CH_3$ def |
| 1450 | 25 | -11 | $CH_3$ def |
| 1467 | 20 | 17 | $CH_3$ def |
| 2199 | 201 | 206 | νCD |
| 2208 | 507 | -464 | νCD |
| 2223 | 126 | 222 | νCD |
| 2274 | 207 | -100 | νCD |
| 2318 | 199 | -24 | νCD |

**$CH_3$-α-Glc-$d_5$** (*gg* conformer)

| wavenumber | intensity (arb. units) | | |
|---|---|---|---|
| [$cm^{-1}$] | Raman | ROA | Modes |
| 204 | >0 | 10 | OH twist |
| 225 | 2 | -20 | OH6 twist, OH4 twist |
| 251 | 3 | -11 | OH twist |
| 281 | 2 | 33 | OH3 twist, OH4 twist |
| 303 | 4 | -61 | OH twist |
| 311 | 6 | 30 | OH4 twist, C1-O1-C bend, OH twist |
| 330 | 4 | -9 | OH6 twist |
| 338 | 7 | -75 | ring def, OH3 twist, OH6 twist |
| 384 | 4 | 73 | OH2 twist |
| 398 | 11 | 15 | ring def, OH twist |
| 430 | 17 | -25 | ring def, OH2 twist |
| 476 | 18 | -55 | ring def, O3-C3-C4 bend, $CD_2$ bend |
| 493 | 4 | 34 | C3-D torsion, ring def |
| 539 | 15 | -16 | ring breathing, O1-C1-O5 bend |
| 588 | 15 | 100 | ring breathing, C4-D torsion |
| 664 | 11 | 27 | ring D torsion, ring def |
| 731 | 10 | -40 | ring def, $CD_2$ bend, νC1-O1 |
| 757 | 12 | 85 | $CD_2$ bend, ring def |
| 820 | 27 | -154 | ring def, C2-D torsion |
| 876 | 11 | -109 | $CD_2$ bend, ring def, C6-OH6 bend |
| 887 | 4 | 17 | ring D torsions, $CD_2$ bend |
| 897 | 15 | 176 | ring D torsions, $CD_2$ bend |
| 936 | 13 | -18 | C4-D torsion, C4-OH4 bend, νC4-O4 |
| 954 | 14 | -33 | C3-D torsion, C4-D torsions, C3-OH3 bend |
| 957 | 18 | 12 | C3-D torsion, C4-D torsions |
| 977 | 5 | -52 | C3-D torsion, C4-D torsions, C3-OH3 bend, νC2-O2 |
| 983 | 18 | 79 | νC6-O6, $CD_2$ bend |
| 1005 | 23 | -102 | ring D torsions, ring def, νO1-C |
| 1016 | 5 | 56 | $\nu_{as}$C1-O5-C5, C4-OH4 bend, $CD_2$ bend, ring def |
| 1038 | 15 | -44 | $\nu_s$C1-O1-$CH_3$, ring def, νC4-O4, C4-OH4 bend |
| 1041 | 11 | 247 | ring def, $CD_2$ bend, $\nu_{as}$O5-C1-O1 |
| 1081 | 16 | -7 | $CD_2$ bend |
| 1085 | 13 | -75 | $\nu_{as}$C5-O5-C1, $\nu_{as}$C1-O1-C, $CD_2$ bend |
| 1102 | 15 | 140 | $\nu_{as}$C4-C5-O5, C4-OH4 bend |

| | | | |
|---|---|---|---|
| 1120 | 23 | -12 | $CH_3$ def, νO1-C, ring def, C4-OH4 bend |
| 1149 | 18 | -38 | ring def, C4-OH4 bend, νC2-O2, νC3-O3, νO1-C |
| 1159 | 3 | 49 | $CH_3$ def |
| 1174 | 38 | -400 | C3-OH3 bend, $\nu_{as}$C3-C4-O4 |
| 1194 | 39 | 75 | $\nu_{as}$C1-C2-O2 |
| 1199 | 5 | -106 | $CH_3$ def |
| 1218 | 9 | -89 | $CD_2$ bend, $\nu_{as}$C5-C6-O6 |
| 1256 | 31 | -246 | $\nu_{as}$C1-C2-C3, C2-OH2 bend, C4-OH4 bend |
| 1297 | 12 | 7 | C6-OH6 bend, C5-H torsion |
| 1318 | 19 | 340 | ring H torsion, C2-OH2 bend |
| 1327 | 16 | 36 | ring H torsion, C2-OH2 bend, C4-OH4 bend |
| 1337 | 36 | -249 | C4-OH4 bend, C5-H torsion, C6-OH6 bend |
| 1353 | 13 | 98 | C3-OH3 bend, C4-OH4 bend, ring H torsions, νC2-C3 |
| 1373 | 15 | 72 | C1-H torsion |
| 1384 | 11 | 160 | C1-H torsion, C3-OH3 bend, νC1-C2 |
| 1409 | 17 | -44 | νC4-C5, C4-OH4 bend, ring H torsion |
| 1444 | 14 | -56 | $CH_3$ def |
| 1449 | 27 | -12 | $CH_3$ def |
| 1468 | 21 | 42 | $CH_3$ def |
| 2209 | 411 | 271 | νCD |
| 2218 | 449 | -145 | νCD |
| 2227 | 22 | 254 | νCD |
| 2274 | 201 | -92 | νCD |
| 2317 | 210 | 56 | νCD |

## Optimized Cartesian Coordinates

**$CD_3$-β-Glc** conformer 1 calculated at B3LYP/spAug-cc-pVDZ

$\Delta E$ 0.000 kcal/mol, $P$ 44.2%

| | | | | |
|---|---|---|---|---|
| 1 | C | 1.428409 | -0.738454 | -0.206203 |
| 2 | C | -1.042562 | -1.15571 | -0.268371 |
| 3 | O | -0.152604 | 1.076704 | -0.316756 |
| 4 | C | -1.228679 | 0.290569 | 0.175336 |
| 5 | C | 1.111272 | 0.691337 | 0.22429 |
| 6 | C | 0.302576 | -1.669396 | 0.216834 |
| 7 | H | -1.071081 | -1.179217 | -1.371333 |
| 8 | H | 1.068843 | 0.740129 | 1.328162 |
| 9 | H | 0.28375 | -1.714356 | 1.320896 |
| 10 | H | 1.514322 | -0.767282 | -1.307588 |
| 11 | C | 2.119718 | 1.701346 | -0.284089 |
| 12 | H | 3.113536 | 1.463383 | 0.112658 |
| 13 | H | 2.162871 | 1.647561 | -1.385849 |
| 14 | O | -2.039136 | -2.002259 | 0.276137 |
| 15 | H | -2.897667 | -1.721073 | -0.073835 |
| 16 | O | 0.603521 | -2.954561 | -0.306008 |
| 17 | H | -0.06679 | -3.576573 | 0.013882 |
| 18 | O | 2.656193 | -1.122242 | 0.389437 |
| 19 | H | 2.779805 | -2.067949 | 0.215082 |
| 20 | O | 1.799378 | 3.015429 | 0.143905 |
| 21 | H | 0.881788 | 3.184638 | -0.119496 |
| 22 | H | -1.250153 | 0.360283 | 1.281897 |
| 23 | O | -2.413495 | 0.757311 | -0.364385 |
| 24 | C | -2.877402 | 1.979635 | 0.20472 |
| 25 | D | -3.000022 | 1.875325 | 1.29441 |
| 26 | D | -3.848272 | 2.192616 | -0.253998 |
| 27 | D | -2.181777 | 2.803495 | -0.008635 |

**$CD_3$-β-Glc** conformer 2 calculated at B3LYP/spAug-cc-pVDZ

$\Delta E$ 0.207 kcal/mol, $P$ 31.2%

| | | | | |
|---|---|---|---|---|
| 1 | C | 1.45685 | 0.494706 | 0.001905 |
| 2 | C | -0.93611 | 1.125092 | 0.365319 |
| 3 | O | -0.291086 | -1.168716 | 0.017847 |
| 4 | C | -1.3133 | -0.218838 | -0.245411 |
| 5 | C | 0.965179 | -0.833541 | -0.572066 |
| 6 | C | 0.404048 | 1.573668 | -0.189776 |
| 7 | H | -0.858513 | 0.993609 | 1.458286 |
| 8 | H | 0.854127 | -0.732139 | -1.667536 |
| 9 | H | 0.289904 | 1.766608 | -1.27218 |
| 10 | H | 1.64068 | 0.366732 | 1.082182 |
| 11 | C | 1.894321 | -1.999622 | -0.28859 |
| 12 | H | 1.506563 | -2.893587 | -0.803638 |
| 13 | H | 2.892551 | -1.776316 | -0.683692 |
| 14 | O | -1.884524 | 2.128252 | 0.047683 |
| 15 | H | -2.730757 | 1.881787 | 0.449934 |
| 16 | O | 0.882045 | 2.746329 | 0.453166 |
| 17 | H | 0.247072 | 3.459892 | 0.291343 |
| 18 | O | 2.662513 | 0.839489 | -0.661195 |
| 19 | H | 2.902975 | 1.734615 | -0.377251 |
| 20 | O | 2.042874 | -2.24685 | 1.101295 |
| 21 | H | 1.154674 | -2.376385 | 1.467439 |
| 22 | H | -1.443195 | -0.125159 | -1.342911 |
| 23 | O | -2.48799 | -0.646962 | 0.346648 |
| 24 | C | -3.127051 | -1.726593 | -0.330847 |
| 25 | D | -2.502395 | -2.630669 | -0.309095 |
| 26 | D | -3.340872 | -1.452868 | -1.376261 |
| 27 | D | -4.067085 | -1.917687 | 0.196623 |

**$CD_3$-β-Glc** conformer 3 calculated at B3LYP/spAug-cc-pVDZ

$\Delta E$ 0.349 kcal/mol, $P$ 24.6%

| | | | | |
|---|---|---|---|---|
| 1 | C | -1.266921 | 0.618593 | -0.258288 |
| 2 | C | 1.191556 | 1.032526 | -0.242406 |
| 3 | O | 0.291348 | -1.203695 | -0.341544 |
| 4 | C | 1.357968 | -0.422948 | 0.180989 |
| 5 | C | -0.975204 | -0.81777 | 0.178657 |
| 6 | C | -0.163531 | 1.549909 | 0.211344 |
| 7 | H | 1.249864 | 1.074571 | -1.343644 |
| 8 | H | -0.961987 | -0.865964 | 1.283487 |
| 9 | H | -0.177909 | 1.587135 | 1.315538 |
| 10 | H | -1.308954 | 0.645309 | -1.36159 |
| 11 | C | -2.001843 | -1.814808 | -0.343161 |
| 12 | H | -2.094466 | -1.706887 | -1.438264 |
| 13 | H | -1.647225 | -2.831845 | -0.131932 |
| 14 | O | 2.179219 | 1.861986 | 0.342616 |
| 15 | H | 3.044554 | 1.58115 | 0.009495 |
| 16 | O | -0.446678 | 2.837686 | -0.313757 |
| 17 | H | 0.215303 | 3.457078 | 0.02772 |
| 18 | O | -2.52771 | 0.998672 | 0.281129 |
| 19 | H | -2.697059 | 1.920656 | 0.033752 |
| 20 | O | -3.260858 | -1.666969 | 0.293583 |
| 21 | H | -3.476721 | -0.718046 | 0.278807 |
| 22 | H | 1.357486 | -0.508789 | 1.2868 |
| 23 | O | 2.551899 | -0.885663 | -0.341745 |
| 24 | C | 2.996049 | -2.122365 | 0.211972 |
| 25 | D | 3.091152 | -2.04234 | 1.306494 |
| 26 | D | 3.977552 | -2.329501 | -0.226412 |
| 27 | D | 2.302224 | -2.93749 | -0.037147 |

**$CD_3$-α-Glc** conformer 1 calculated at B3LYP/spAug-cc-pVDZ

$\Delta E$ 0.000 kcal/mol, $P$ 39.0%

| | | | | |
|---|---|---|---|---|
| 1 | C | 0.147233 | -1.533148 | -0.041596 |
| 2 | C | -1.568123 | 0.193651 | -0.675826 |
| 3 | O | 0.815465 | 0.685093 | -0.791945 |
| 4 | C | -0.462109 | 1.256259 | -0.587811 |
| 5 | C | 1.168742 | -0.400898 | 0.097825 |
| 6 | C | -1.252644 | -0.994294 | 0.238298 |
| 7 | H | -1.617094 | -0.165113 | -1.715114 |
| 8 | H | 1.170699 | -0.033663 | 1.138207 |
| 9 | H | -1.292853 | -0.66228 | 1.29282 |
| 10 | H | 0.1747 | -1.915719 | -1.081078 |
| 11 | H | -0.565582 | 2.004161 | -1.393114 |
| 12 | C | 2.580768 | -0.816667 | -0.292901 |
| 13 | H | 2.914265 | -1.628109 | 0.366326 |
| 14 | H | 2.574231 | -1.195817 | -1.332319 |
| 15 | O | -0.598682 | 1.88214 | 0.670741 |
| 16 | O | -2.851069 | 0.7396 | -0.385455 |
| 17 | H | -2.734832 | 1.315517 | 0.389701 |
| 18 | O | -2.171487 | -2.067125 | 0.034629 |
| 19 | H | -3.067833 | -1.707842 | 0.129819 |
| 20 | O | 0.503082 | -2.566212 | 0.870256 |
| 21 | H | -0.233514 | -3.197639 | 0.887244 |
| 22 | O | 3.511423 | 0.248458 | -0.145538 |
| 23 | H | 3.192853 | 0.978767 | -0.697759 |
| 24 | C | 0.173393 | 3.074586 | 0.823121 |
| 25 | D | 1.25178 | 2.860586 | 0.766942 |
| 26 | D | -0.066717 | 3.480931 | 1.812787 |
| 27 | D | -0.093511 | 3.813649 | 0.047376 |

**$CD_3$-α-Glc** conformer 2 calculated at B3LYP/spAug-cc-pVDZ

$\Delta E$ 0.052 kcal/mol, $P$ 35.7%

| | | | | |
|---|---|---|---|---|
| 1 | C | -1.069887 | 0.953115 | 0.175831 |
| 2 | C | 1.245537 | 0.705451 | -0.769373 |
| 3 | O | -0.233648 | -1.223784 | -0.561565 |
| 4 | C | 1.118518 | -0.811322 | -0.568162 |
| 5 | C | -1.099613 | -0.56406 | 0.391943 |
| 6 | C | 0.368308 | 1.45819 | 0.234138 |
| 7 | H | 0.904921 | 0.946995 | -1.787613 |
| 8 | H | -0.757453 | -0.782586 | 1.418853 |
| 9 | H | 0.757187 | 1.287477 | 1.255914 |
| 10 | H | -1.491912 | 1.182881 | -0.81951 |
| 11 | H | 1.575032 | -1.362506 | -1.408557 |
| 12 | C | -2.478793 | -1.185565 | 0.191572 |
| 13 | H | -2.433193 | -2.251607 | 0.480329 |
| 14 | H | -3.19893 | -0.678415 | 0.846982 |
| 15 | O | 1.794115 | -1.123669 | 0.632985 |
| 16 | O | 2.601981 | 1.134745 | -0.695125 |
| 17 | H | 2.992841 | 0.677033 | 0.068828 |
| 18 | O | 0.343433 | 2.8577 | -0.044081 |
| 19 | H | 1.263221 | 3.161577 | -0.10003 |
| 20 | O | -1.868154 | 1.542693 | 1.197748 |
| 21 | H | -1.767785 | 2.504245 | 1.119542 |
| 22 | O | -2.960268 | -1.042722 | -1.138362 |
| 23 | H | -2.297882 | -1.441127 | -1.724077 |
| 24 | C | 2.035034 | -2.518918 | 0.822318 |
| 25 | D | 1.090783 | -3.083627 | 0.863149 |
| 26 | D | 2.565944 | -2.621276 | 1.7763 |
| 27 | D | 2.662924 | -2.92011 | 0.007478 |

**$CD_3$-α-Glc** conformer 3 calculated at B3LYP/spAug-cc-pVDZ

$\Delta E$ 0.257 kcal/mol, $P$ 25.3%

| | | | | |
|---|---|---|---|---|
| 1 | C | 0.995921 | 0.935314 | 0.168343 |
| 2 | C | -1.462495 | 0.75953 | 0.592941 |
| 3 | O | 0.028077 | -1.149666 | 0.927342 |
| 4 | C | -1.294061 | -0.768616 | 0.602196 |
| 5 | C | 1.057686 | -0.594389 | 0.084609 |
| 6 | C | -0.380265 | 1.421964 | -0.266046 |
| 7 | H | -1.357667 | 1.121792 | 1.626947 |
| 8 | H | 0.900128 | -0.909607 | -0.961305 |
| 9 | H | -0.534158 | 1.147145 | -1.326366 |
| 10 | H | 1.162682 | 1.236794 | 1.220627 |
| 11 | H | -1.917193 | -1.228863 | 1.388302 |
| 12 | C | 2.388007 | -1.173279 | 0.574401 |
| 13 | H | 2.63459 | -0.747366 | 1.566044 |
| 14 | H | 2.274145 | -2.259343 | 0.699043 |
| 15 | O | -1.705658 | -1.228458 | -0.669034 |
| 16 | O | -2.765172 | 1.146126 | 0.168319 |
| 17 | H | -2.983423 | 0.581495 | -0.593117 |
| 18 | O | -0.39646 | 2.842074 | -0.127169 |
| 19 | H | -1.298243 | 3.146135 | -0.316513 |
| 20 | O | 2.031688 | 1.474938 | -0.656041 |
| 21 | H | 1.900512 | 2.43556 | -0.697695 |
| 22 | O | 3.440149 | -0.971991 | -0.356152 |
| 23 | H | 3.443613 | -0.027797 | -0.588712 |
| 24 | C | -1.88397 | -2.644119 | -0.750229 |
| 25 | D | -0.940126 | -3.175353 | -0.553725 |
| 26 | D | -2.222548 | -2.861121 | -1.770293 |
| 27 | D | -2.648241 | -2.982089 | -0.028648 |