# Analysis of Raman spectra by quantum chemical calculations of modelized starch

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**[Introduction]** Starch is the most common carbohydrate widely found in general staple foods, such as rice, corn, wheat, and potatoes, as the primary energy source for the human body. Starch includes amylose and amylopectin based on the helical structure due to the curl of the intramolecular hydrogen bonds. Compared to amylose with a linear structure interconnected by α-1,4 glycosidic linkages of glucose units, amylopectin has not only a glucose backbone interconnected by α-1,4 glycosides but also a branching structure bridged by α-1,6 glycosides.[1] Raman spectroscopy can provide detailed information on the chemical structure and intermolecular interactions with its nondestructive, multidimensional, and feasible features. In this research, the structural features of linear glucose models with their calculated Raman spectra are investigated by quantum chemical calculations.

**[Calculation]** Amylose model with a linear eight-glucose: the structures were optimized by the B3LYP/3-21G method. Obtained cyclic and helix structures were examined by the calculated Raman spectra. Amylose model with a linear four-glucose: starting from the structure optimized by the semi-empirical method, PM6,[2] the ADDF calculation[3] under the PM6 method was used to find rational structures preferring lower energy. Raman spectra of stable structures were calculated by the CAM-B3LYP/3-21G method.[4]

**[Results and Discussion]** Calculated Raman spectra of the linear eight-glucose were shown in Fig. 1. The main characteristic peaks of the calculated Raman spectra are compared with that of the experimental spectrum.[6] It has been confirmed the orientation of $CH_2$-OH terminal groups can influence the conformation of formed structures. Helical structures can be produced with a variety of $CH_2$-OH orientations. However, there are subtle differences in the structure, which can be confirmed by Raman spectra. Compared with the cyclic structure ②, the helical structure ① has a strong peak at 1342 $cm^{-1}$ from the C-O-H bending and $CH_2$ twisting and a strong peak at 1085 $cm^{-1}$ from the C-O-H bending. This indicates that these peaks can be used to separate the helical structures from the respective of Raman spectra. In contrast, the peak at 1342 $cm^{-1}$ and 1085 $cm^{-1}$ of the helical structure ③ and ④ are more similar to that of the measured spectrum. All the helix results show a weak peak at 1462 $cm^{-1}$ from the $CH_2$ bending.

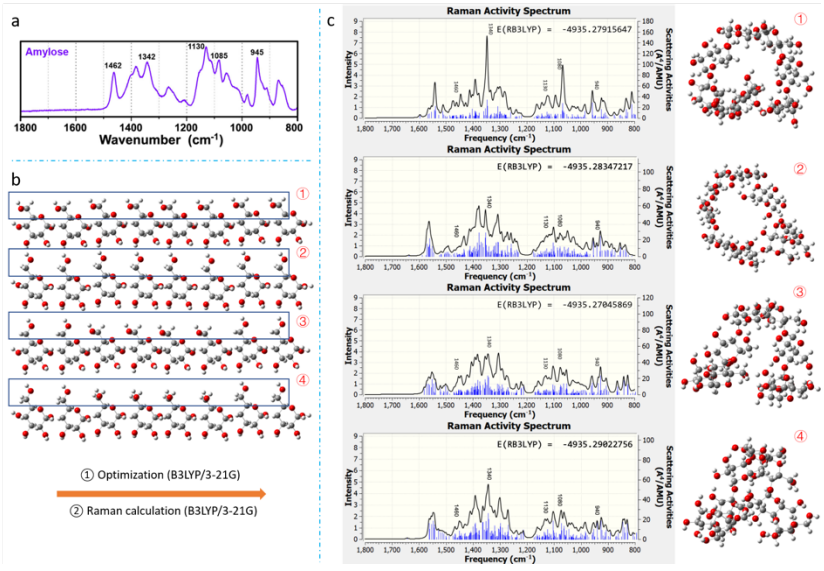


Fig 1. **a**, measured Raman spectra of amylose[1]; **b**, amylose models with a linear eight-glucose with different $CH_2$-OH orientations; **c**, calculated Raman results and their helical or cyclic structures. Details will show on the poster.

## References

[1] R. Kizil, *et al.*, *J. Agric. Food Chem.*, **2002**, 50, 3912-3918. [2] J. J. P. Stewart, *J. Mol. Model.*, 13, **2007**, 1173-213. [3] S. Maeda, *et al.*, *Bull. Chem. Soc. Jpn.*, **2014**, 87, 1315-1334. [4] T. Yanai, *et al.*, *Chem. Phys. Lett.*, **2004**, 393, 51-57. [5] Gaussian 16, Revision B.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2016. [6] M.Bağcıoğlu, et al., *PLoS One.*, **2015**, 10, 9.