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Stability of cellulose in water cluster—insight from density functional theory and infrared spectroscopy

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Cellulose is a main constituent of wood, and it provides excellent strength and stiffness to plant cell walls. Cellulose exists in crystalline, semi-crystalline, or amorphous phase and consists of linearly arranged glucose polymers that are strongly bound through hydrogen bonds and form highly crystalline fibrils. Wood has a strong tendency for absorbing or desorbing water due to changes in relative humidity of the surrounding air. This sorption process apparently undergoes a swelling process that highly affects the resulting mechanical, physical, and chemical properties of wood. In particular, the interphase of cellulose-hemicellulose is one of the predominant regions responsible for swelling of wood (Kulasinski et., 2015). Knowledge about the amount of moisture taken by cellulose is essential to understand weight percentage gain (WPG) of wood and the extent of alteration in its physical properties. In order to properly account WPG features, the number of water molecules required to stabilize the cellulose chain needs to be calculated.

The present work uses density functional theory (DFT) method to investigate the cellulose-water interaction at the atomic level. This method highlights the number of water molecules that can interact with cellulose, hydrogen bond strength, and cellulose-water signature in the NIR spectrum. A single cellobiose (dimer of glucose) unit is considered here as sufficient to represent the cellulose model, while still assuring reasonable computation time and cost. The DFT calculations are performed at dispersion-corrected wB97X-D/6-311g(d,p) level of theory, which is proven to be consistent for intermolecular interaction and reproducing hydrogen bonds. The hydrogen bond characteristics and fundamental infrared frequencies are evaluated and compared with experiments to provide a clear description of changes in O-H stretching frequencies. This study unravels the IR and, consequently, NIR spectra, contains vibrations of cellulose-water in combination bands and overtones regions as well as proposes the quantity of water molecules absorbed by cellulose to account WPG or moisture content in wood.

Keywords: cellulose, moisture, density functional theory, near infrared (NIR), hydrogen bonding

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