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# Evaluation of hydrogen bond networks in cellulose Iβ and II crystals using density functional theory and Car–Parrinello molecular dynamics

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ABSTRACT

Crystal models of cellulose Iβ and II, which contain various hydrogen bonding (HB) networks, were analyzed using density functional theory and Car–Parrinello molecular dynamics (CPMD) simulations. From the CPMD trajectories, the power spectra of the velocity correlation functions of hydroxyl groups involved in hydrogen bonds were calculated. For the Iβ allomorph, HB network A, which is dominant according to the neutron diffraction data, was stable, and the power spectrum represented the essential features of the experimental IR spectra. In contrast, network B, which is a minor structure, was unstable because its hydroxymethyl groups reoriented during the CPMD simulation, yielding a different crystal structure to that determined by experiments. For the II allomorph, a HB network A is proposed based on diffraction data, whereas molecular modeling identifies an alternative network B. Our simulations showed that the interaction energies of the cellulose II (B) model are slightly more favorable than model II(A). However, the evaluation of the free energy should be waited for the accurate determination from the energy point of view. For the IR calculation, cellulose II (B) model reproduces the spectra better than model II (A).



## 1. Introduction

Cellulose has several crystalline allomorphs, of which cellulose Iβ and II are the most important [1–4]. Cellulose Iβ is the main component of higher plants and, as such, is the most abundant form of cellulose. In contrast, cellulose II is the allomorph corresponding to the regenerated cellulose obtained by mercerization or precipitation of cellulose from solution [3].

Crystalline cellulose form three-dimensional hydrogen-bonded networks with their many hydroxyl groups. These hydrogen bonds play an important role in the structural stability and dynamics of cellulose. However, it is difficult to determine the hydrogen bond structure of cellulose with high accuracy using classical techniques such as X-ray and neutron diffraction because the hydrogen atoms interact very weakly with X-rays and neutron data suffers from a relatively low signal/noise ratio.

Nishiyama et al. proposed, based on neutron fiber diffraction data, that two types of hydrogen bond networks coexist in cellulose Iβ, referred to as Iβ(A) and Iβ(B). The ratio of these hydrogen bond patterns was determined to be A:B = 85:15 [2]. Molecular dynamics simulations and quantum mechanical calculation suggest that Iβ(B) is less stable than Iβ(A), and that, even at low temperature, this ratio does not change [5,6].

The hydrogen bond structure of cellulose II was proposed by Langan et al. based on X-ray and neutron diffraction (referred to as II(A)) [3]. However, MD simulations of cellulose II crystal using the structure proposed by Langan et al. as the initial structure result in a hydrogen bonding structure with a tautomeric hydroxyl orientation (II(B)), unlike that of the refined structure. In addition, the density functional theory (DFT)-calculated total energy is lower for the II(B) pattern [7].

Infrared spectroscopy is another tool sensitive to hydrogen bonds and has been extensively applied for the investigation of cellulose crystals [8–14]. However, the vibrational spectra, including infrared spectra, do not directly provide a hydrogen-bonding scheme and their explicit interpretation is not obvious.

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In this work, the validities of the previously proposed hydrogen bond structural models were assessed from the point of view of the interaction energies and molecular vibration. Two hydrogen bond models, Iβ(A) and Iβ(B) in cellulose Iβ and II(A) and II(B) in cellulose II, were evaluated from the intermolecular interactions obtained from DFT calculations. In addition, the thermal motions of the hydroxyl groups in the cellulose crystals were investigated using Car–Parrinello molecular dynamics (CPMD) simulations. Power spectra were calculated from the velocity correlation functions of these hydroxyl groups. Each O-H stretch vibrational mode in the calculated power spectra was assigned by comparison with the experimental IR spectra.

## 2. Methods

### 2.1. Nomenclature of atoms and conformational parameters of cellulose

The unit cells of cellulose Iβ and cellulose II are shown in Fig. 1(a) and (b), respectively. Both Iβ and II belong to the monoclinic space group $P2_1$ [2,3]. The unit cells contain two cellobiose units. Cellulose chains are packed parallel in cellulose Iβ, whereas they are anti-parallel in cellulose II [2,3]. The nomenclature and the conformational parameters of the cellulose chains used in the present work are shown in Fig. 1(c). The torsion angles $\varphi$ and $\psi$ at the glycosidic linkage are defined as $\varphi$ (O5-C1-O1-C4′) and $\psi$ (C1-O1-C4′-C3′), respectively. Torsion angle $\omega$ at the C6 primary alcohol group is defined as $\omega$ (O5-C5-C6-O6). Torsion angle $\omega$ can adopt three stable conformations *gt* ($\omega = 60°$), *tg* ($\omega = 180°$), and *gg* ($\omega = 300°$). Cellulose Iβ is known to take the *tg* conformation, while cellulose II adopts the *gt* conformation. Torsion angles describing the orientation of the various hydroxyl groups attached to carbon atoms C2, C3 and C6 are defined by τ2 (C1-C2-O2-HO2), τ3 (C2-C3-O3-HO3), and τ6 (C5-C6-O6-HO6), respectively.

The starting models for cellulose Iβ and cellulose II(A) were based on X-ray and neutron fiber diffraction refinement [2,3]. In contrast, the initial II(B) model was constructed according to the results obtained in our MD simulations [7]. The torsion angles τ2 and τ6 of II(B) model were set at $\tau2_{ori} = \tau2_{cen} = 120°$ and $\tau6_{ori} = \tau6_{cen} = 300°$ for the origin and center chains, respectively. The hydrogen bonding network structure of these four models are shown in Figs. 3 and 4. DFT calculation is generally expensive to perform using large size of crystal model which consists of plural number of the unit cells. Therefore, in this work, we focused to investigate only the structure and dynamics of hydroxyl groups of cellulose in the crystal. Since the motion of hydroxyl groups is localized, we considered that the motion of hydroxyl groups of cellulose can be evaluated using a unit cell model.

### 2.2. Structural optimization and calculation of interaction energies

The four crystal models were optimized by DFT calculations using Quantum Espresso [15]. The Perdew-Burke-Ernzerhof (PBE) gradient–corrected functional was used to describe the exchange-correlation energy [16]. Ultrasoft pseudopotentials and plane wave basis sets with a kinetic energy cut off at $E_{cut} = 70$ Ry were used in these calculations. In addition, the PBE-D long-range dispersion correction proposed by Grimme was applied to account for London dispersion interactions [17]. 2 × 2 × 2 Monkhorst-Pack *k*-point grids were used to sample the Brillouin zone, and full optimization was performed on both cell parameters and internal geometries [18].

The interaction energies between the cellulose chains in the crystal models were evaluated using cluster models of isolated

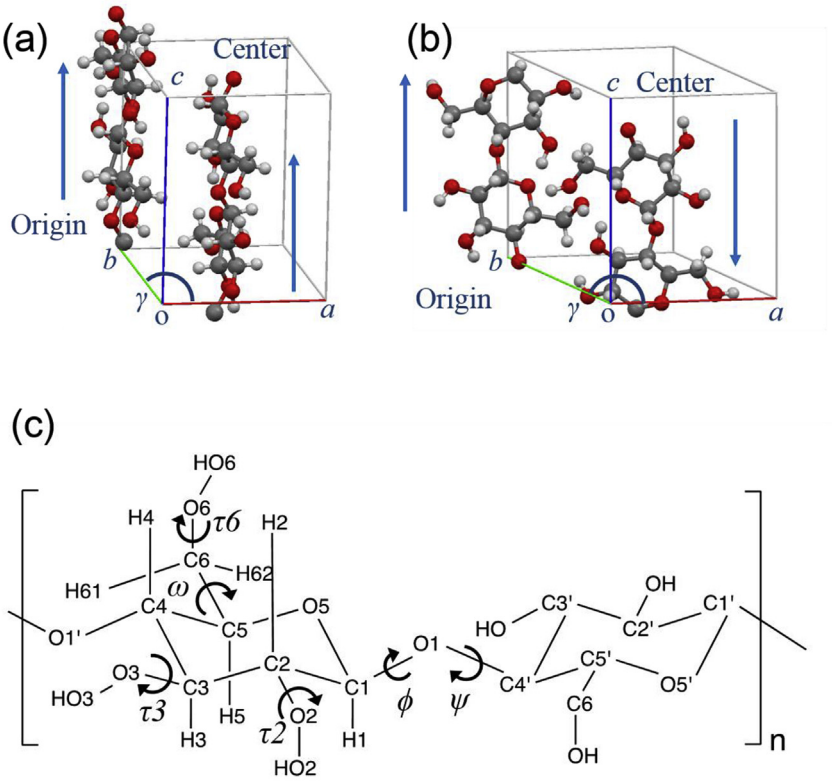


**Fig. 1.** The unit cells of cellulose Iβ (a) and cellulose II (b) crystals. The nomenclature of the atoms and some torsion angles in a cellulose chain are shown in (c).