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Terahertz spectral investigation of anhydrous and monohydrated glucose using terahertz spectroscopy and solid-state theory

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ABSTRACT

The terahertz absorption spectra of anhydrous and monohydrated glucose have been investigated and compared by using THz spectroscopy and solid-sate density functional theory. The unrevealed mechanism of THz spectral differences of both materials measured has been analyzed based on the crystalline structure. Solid-state calculations of the THz characteristic spectra using Perdew–Burke–Ernzerhof functional have provided the satisfactory spectral reproduction for these two materials. It is found that the characterized features of monohydrated glucose mainly come from the intermolecular modes of water–glucose and glucose–glucose molecules, while those of anhydrous glucose origin from the interactions of glucose molecules.

1. Introduction

Terahertz (THz) radiation locates between the infrared and microwave region of the electromagnetic waves. The central part of this frequency range is usually defined as the region from 0.3 THz to 3 THz (10–100 cm^{-1}). In recent years, advancements in generation and detection of THz radiation using femtosecond pulsed laser systems have brought THz spectroscopy to a new level in material spectral investigations, such as surveillance of chemical reaction [1,2], identification of biological molecules [3,4], and standoff detection of explosives [5–7]. All these applications are based on the fact that THz spectra are highly sensitive to the molecules involved, and its adjacent environment. Now, THz spectral investigations can be used not only for material identification but also for molecular property interpretation [8–11].

Solid material may turn into hydrous form during processing, and the physical properties of polycrystalline hydrate are often quite different from its anhydrous form [12–14]. Today, many materials are popularly used with their hydrous and anhydrous forms in our daily life, for example, the anhydrous and monohydrated glucose. Anhydrous glucose can be popularly used in pharmacy and candy production, while monohydrated glucose containing both the glucose and water molecules is often used as the orally taken medicine for the quick supplement of human energy and body fluid. The popular application of these two materials in daily life makes the investigation of anhydrous and monohydrated glucose by using THz technique important and meaningful.

So far, lots of THz spectral investigations of anhydrous glucose have been reported [15–19], but the measured features are not interpreted by solid-state theory. For monohydrated glucose, the dehydration kinetics has been investigated using THz time-domain spectroscopy (THz-TDS) [18], three bands are observed in the range of 10–100 cm^{-1} [15,18]. In our investigation, two more spectral features are obtained experimentally in the same frequency region and the calculation has demonstrated the existence of these characteristic features. In this paper, the room-temperature THz absorption spectra of anhydrous and monohydrated glucose have been investigated by utilizing THz-TDS and solid-state density functional theory. Two new room-temperature characteristic THz spectral features of monohydrated glucose are observed in the region of 10–100 cm^{-1} at the first time, to the best of our knowledge. Specifically, monohydrated glucose has shown absolutely different THz absorption peaks compared to anhydrous glucose investigated in our previous work [17]. The unrevealed reason of these spectral differences has been explained based on the crystalline unit cell. Moreover, the experimental features of both materials are well interpreted by the calculations based on solid-state theory, and the well-understanding of these features is achieved.

2. Experimental and theoretical method

THz absorption spectra of monohydrated glucose were measured by using a commercial spectrometer of TPS-3000 (TeraView Ltd.). In this spectrometer, a femtosecond laser pulse is used to excite a semiconductor-based photoconductive antenna, which emits broadband radiation over 8–120 cm^{-1}. Another photoconductive antenna is used to detect the transmitted radiation. Finally, a signal

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that is proportional to the THz electric field is obtained. More details of the experimental set-up can be found in Ref. [4].

Monohydrated Glucose (CAS-number 14431-43-7) was purchased from Hangzhou Dayangchem Co. Ltd. Experiments were performed for monohydrated glucose in four pellets with different thickness. Two sample pellets A and B were made by pure monohydrated glucose, and the other two pellets C and D were made by the mixtures of monohydrated glucose and polytetrafluoroethene (PTFE) powder in the mass ratios of 1:2 and 1:3, respectively. The thicknesses of these four samples were 1.26 mm for A, 0.78 mm for B, 1.23 mm for C and 1.28 mm for D. All the sample pellets were compressed into pellets with a pressure of 600 kg/cm^2.

Calculations of both materials were performed using the plane-wave density functional theory (DFT) within the generalized gradient approximation [20,21]. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functionals [22] and the Norm-conserving Troullier–Martins pseudopotentials [23] were utilized in simulation, the total energy was converged to 10^{-8} eV/atom, the maximum forces between atoms were less than 10^{-4} eV/Å, and a plane wave cutoff energy was used as 1000 eV. More details of the calculated method can be found in Ref. [24]. The simulation was performed based on crystal cell parameters of anhydrous glucose taken from Ref. [25]: space group P212121 ($Z = 4$), $a = 10.366$ Å, $b = 14.851$ Å, $c = 4.975$ Å, α, β, $\gamma = 90.0°$. The crystal cell parameters of monohydrated glucose were taken from Ref. [26]: space group $P2_1/n$ ($Z = 2$), $a = 8.803$ Å, $b = 5.085$ Å, $c = 9.708$ Å, α, $\gamma = 90.0°$, $\beta = 97.67°$. Fig. 1 shows the crystal packing arrangement of anhydrous glucose and monohydrated glucose and Fig. 2 presents the atomic labeling scheme adopted for structural descriptions.

3. Results and discussion

The room-temperature THz spectra of monohydrated glucose from 10 cm^{-1} to 100 cm^{-1} are shown in Fig. 3. To detect these features clearly, experiments were performed in four different sample pellets. Specifically, samples A and B were prepared by pure monohydrated glucose in the weight of 170 mg and 100 mg, respectively. Three distinct absorption peaks at 50.8, 60.1, and 65.9 cm^{-1} were observed clearly, but the two spectral bands located in higher frequency region are too strong in absorption to identify their exact peak positions. Thus, samples C and D were prepared by mixing monohydrated glucose with PTFE powders to dilute absorption of pure monohydrated glucose. The mass ratios

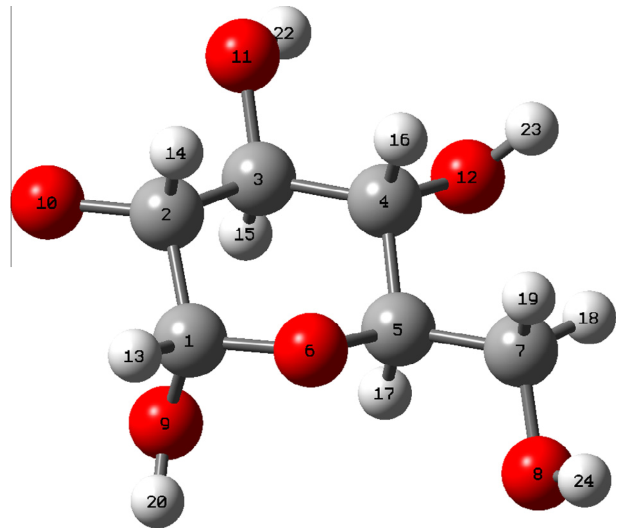

Fig. 2. The atomic labeling scheme for glucose molecule.

of mixed samples C and D were arranged at 1:2 and 1:3, respectively. Finally, two distinct spectral features located at 78.7 and 80.9 cm^{-1} were observed clearly from these mixed samples, and D presented all the spectral features of monohydrated glucose from 10 cm^{-1} to 100 cm^{-1}, although the first peak is slightly weak. Compared to three features observed in the previous work [15,18], five distinct absorption peaks were observed in our experiment. The later calculated result has demonstrated the existence of these characteristic peaks.

According to our previous work [17], seven spectral features of anhydrous glucose has been observed in the range of 10–100 cm^{-1}, distributed mainly as two weak peaks and five strong peaks in the region of 40–100 cm^{-1}. For monohydrated glucose, five spectral peaks are mainly located in the region of 50–85 cm^{-1}. Fig. 4 presents the measured characteristic features of both materials in the region of 10–100 cm^{-1}, and the spectral features measured in this paper are clearer than those of presented in previous work [15,18], indicating these spectral distributions used in identification of glucose and its hydrated compound more easily.

Fig. 4 indicates THz spectral differences between anhydrous and monohydrated glucose are obvious, the reason may have to be traced back to their different crystalline structures due to the

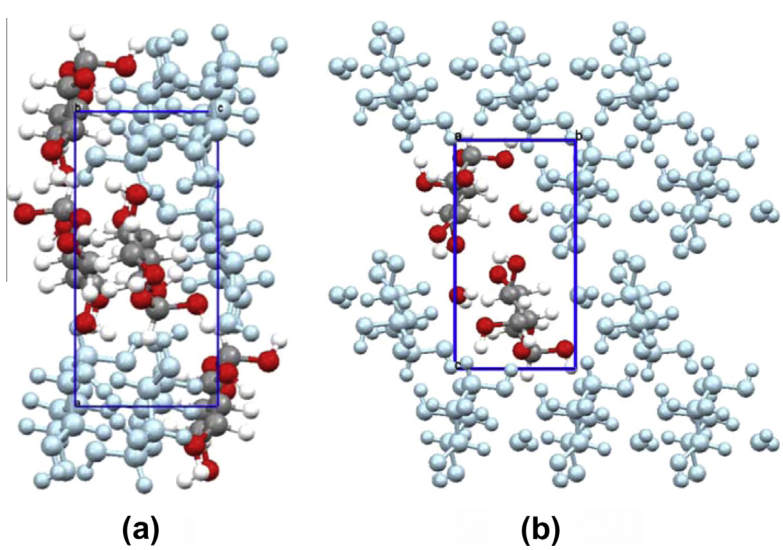

Fig. 1. The unit cells and molecular arrangements of anhydrous glucose (a) and monohydrated glucose (b).