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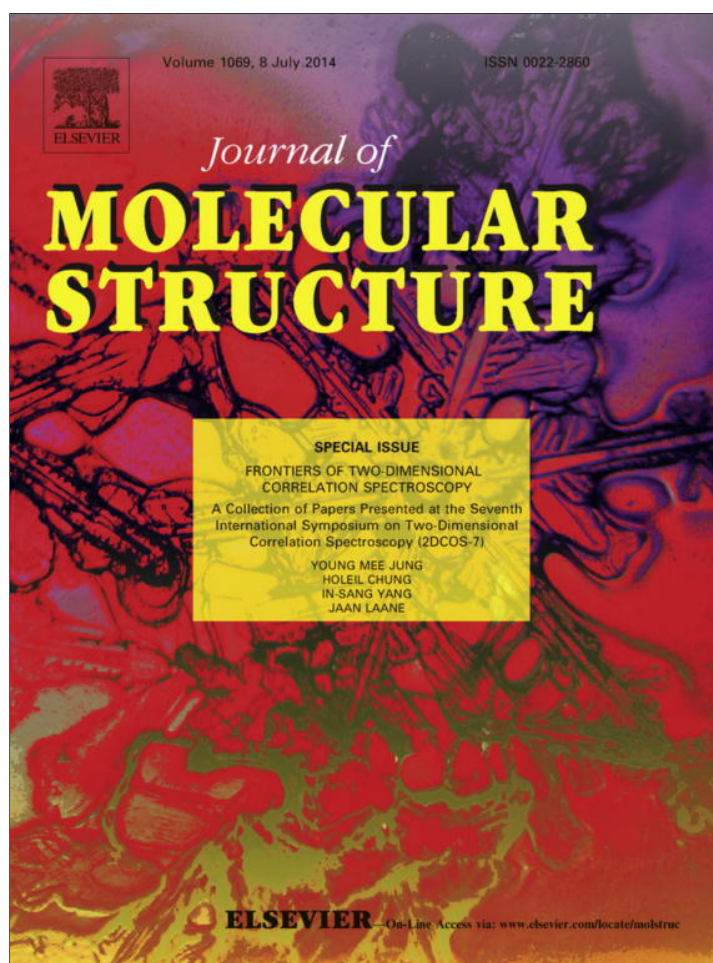


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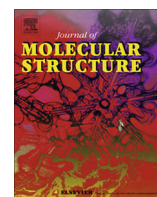
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# Separation of overlapping vibrational peaks in terahertz spectra using two-dimensional correlation spectroscopy



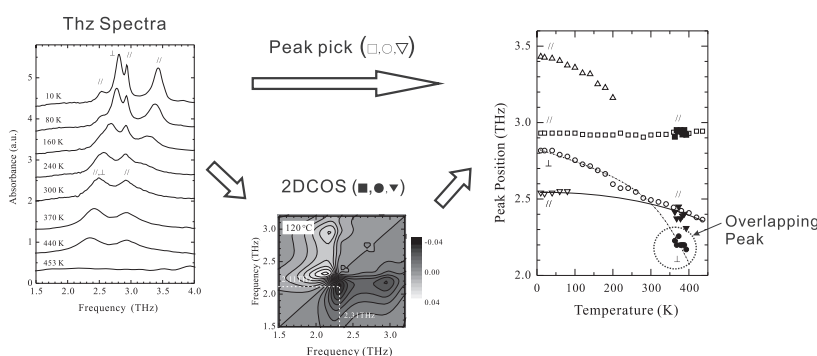
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## HIGHLIGHTS

- We have measured the terahertz absorption spectra of poly(3-hydroxybutyrate) during isothermal crystallization at 90–120 °C.
- The temporal changes in the absorption spectra were analyzed using two-dimensional correlation spectroscopy.
- The exact frequencies of the overlapping bands provide a new means to inspect the intermolecular vibrational modes.
- The large red-shift of the interhelix vibrational mode suggests a large anharmonicity in the vibrational potential.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 19 December 2013  
 Received in revised form 12 February 2014  
 Accepted 19 February 2014  
 Available online 11 March 2014

### Keywords:

Terahertz spectroscopy  
 Two-dimensional correlation spectroscopy  
 Low-frequency vibrational mode  
 Poly(3-hydroxybutyrate)

## ABSTRACT

In this study, the terahertz (THz) absorption spectra of poly(3-hydroxybutyrate) (PHB) were measured during isothermal crystallization at 90–120 °C. The temporal changes in the absorption spectra were analyzed using two-dimensional correlation spectroscopy (2DCOS). In the asynchronous plot, cross peaks were observed around 2.4 THz, suggesting that two vibrational modes overlap in the raw spectrum. By comparing this to the peak at 2.9 THz corresponding to the stretching mode of the helical structure of PHB and the assignment obtained using polarization spectroscopy, we concluded that the high-frequency band could be attributed to the vibration of the helical structure and the low-frequency band to the vibration between the helical structures. The exact frequencies of the overlapping vibrational bands and their assignments provide a new means to inspect the thermal behavior of the intermolecular vibrational modes. The large red-shift of the interhelix vibrational mode suggests a large anharmonicity in the vibrational potential.

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## 1. Introduction

In this decade, rapid developments have been made in the field of terahertz (THz) spectroscopy because of the contribution of

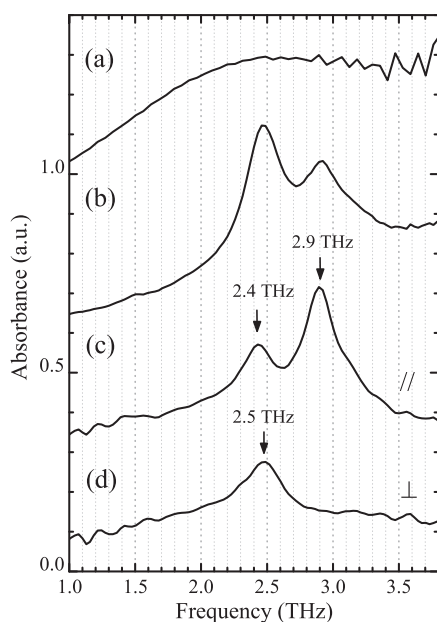
terahertz time-domain spectroscopy (THz-TDS) to quick and precise measurement of material properties [1,2]. Because THz-TDS can detect electromagnetic waves coherently, the obtained signal is free from thermal noise at room temperature [3]. As a result, a liquid-helium-cooled detector is not required for measurement, and quick and precise measurements are possible in the frequency region 0.1–3.0 THz. These advantages of THz-TDS allow for its

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application in the study of low-frequency vibrational spectroscopy. In the THz region, organic materials show characteristic spectra (the so-called fingerprint spectra) that originate from low-frequency intermolecular vibrational motion. Direct information about intermolecular interactions and intermolecular structures, such as crystal structure, cluster structure, and higher-order conformation of large molecules, can be obtained using THz spectroscopy. Because the intermolecular structure plays an important role in the physical and chemical properties of macromolecules, THz spectroscopy will be a powerful tool for research in polymer science [4–8].

In our previous studies, THz absorption spectra of poly (3-hydroxybutyrate) (PHB) were measured using THz-TDS and Fourier transform far-infrared spectroscopy (FT-FIR) [9–12]. PHB is a biodegradable polymer produced by natural bacteria [13], and its lamellar crystalline structure has been investigated by X-ray diffraction [14–17], differential scanning calorimetry [16], infrared spectroscopy [15,16,18,19], and Raman spectroscopy [18]. Recent X-ray diffraction studies by Sato et al. revealed that there are weak hydrogen bonds (around 5 kJ/mol) between the C=O and CH<sub>3</sub> groups, parallel to the *a*-axis [15–17].

Fig. 1 shows the THz absorption spectra for amorphous PHB (a) and crystalline PHB (b), and the polarized absorption spectra of the stretched PHB samples (c and d) measured by THz-TDS at room temperature [10]. Clear differences were observed between the spectra of amorphous and crystalline PHB, indicating that the absorption peaks due to crystalline PHB originated from the vibrational motions of the lamellar crystal. The direction of the vibrational transition moments was obtained from the polarization spectra of stretched PHB in which the crystal *c*-axis was aligned relative to the stretching direction [10,11]. When the polarization of the THz electric field was parallel to the *c*-axis (c), two peaks were observed at 2.4 and 2.9 THz. Since the vibrational dipole moment is parallel to the *c*-axis, these peaks were assigned to the skeletal motion of the polymer chains. On the other hand, the transition dipole moment of the peak observed at 2.5 THz was perpendicular to the *c*-axis (d), and hence, this peak was assigned to the vibrational motion of the hydrogen bonds between neighboring helices (*a*-axis).



**Fig. 1.** THz absorption spectra of (a) amorphous PHB and (b) crystalline PHB. (c) and (d) Polarized THz absorption spectra of stretched PHB samples, measured by THz-TDS. The angle between the direction of stretching and linear polarization of the THz electric field was set to (c) 0° and (d) 90°.

For complete assignment of these peaks, DFT-based spectral simulations (the Cartesian coordinate tensor transfer method) were performed. In this method, the original large molecular system is divided into smaller fragments, and their property tensors (force field, Raman polarizability, dipole derivative, etc.) are calculated using high-level theory and then transferred back to the original molecular system atom by atom. The details of this method are described elsewhere [20,21]. The peak at 2.4 THz was assigned as COO + CH<sub>2</sub> + CH<sub>3</sub>; the peak at 2.9 THz was assigned as CH<sub>2</sub> + CH<sub>3</sub>; and the peak at 2.5 THz was assigned as C=O (out of plane) + CH<sub>3</sub> [22]. The frequencies, intensities, and polarization of the calculated spectra were in good agreement with the experimental data.

THz spectroscopy can provide new insight into the relationship between low-frequency vibrational modes and higher-order conformations, which are directly reflective of the physical properties of PHB. However, the low-frequency vibrational peaks at room temperature often have a broad line shape, and the peaks often overlap because of the rapid vibrational relaxation. For example, there are three vibrational modes in the spectrum shown in Fig. 1(b), but two of them overlap at 2.5 THz. To reduce the line widths, the samples must be cooled to liquid-helium temperature (see Fig. 5). However, information on structural changes above the glass transition temperature is important to investigate polymer properties. Polarization spectroscopy may help in distinguishing between the direction of vibrational transition moments, but this technique requires stretched polymer samples, which are sometimes difficult to obtain.

In this study, we performed two-dimensional correlation spectroscopy (2DCOS) to resolve the overlapping peaks in the THz spectrum. 2DCOS is a recently developed spectral analysis method that has been used extensively for vibrational spectroscopy in the IR and near-IR regions [23–26]. Correlation of the intensity variations between frequencies can be observed in the two-dimensional plots. The 2DCOS method was applied to a series of spectra (dynamic spectra) that were measured by varying the external perturbation, *t*. Any suitable physical or chemical parameter can be selected for perturbation in the 2DCOS method, i.e. temperature, electric field, pH, or time. Because this method can easily visualize intensity changes in broad and overlapping peaks, spectral information from a blended system can be simplified into two dimensions. Therefore, 2DCOS is expected to be a new, powerful THz spectroscopy method that can be used when spectra contain vibrational bands that overlap and are difficult to resolve.

## 2. Experiments

In this study, the isothermal crystallization of PHB was measured by THz-TDS. Isotactic PHB homopolymer (Aldrich Corp.) was placed on a high-resistivity Si window, melted at 195 °C for 3 min, and then rapidly cooled (30 °C/min) to its crystallization temperature, *T<sub>c</sub>*. THz spectra during isothermal crystallization was measured by changing the crystallization temperature from 90 to 120 °C. The temperature of the samples was changed using a temperature-controlled heating cell (LINKAM: 19113L) placed horizontally on the THz-TDS apparatus. After the crystallization temperature was attained (*t* = 0), the THz absorption spectra were measured continuously as a function of time *t* (min). Absorption spectra of the sample were measured by THz-TDS (Aispec, BSD-1000) with a frequency resolution of 0.06 THz. The power spectra were obtained by Fourier transformation of the THz electric field waveforms. The spectrum of the blank Si window was used as a reference.

The temperature dependence absorption spectra of PHB from 10 to 300 K were measured by a Fourier transform far-infrared (FT-FIR) spectrometer (ABB Bomem Inc.: DA8) with a liquid-helium-cooled cryostat (Oxford Instruments: Cryojet).

### 3. Results and discussion

#### 3.1. 2DCOS analysis of THz spectra of PHB during isothermal crystallization

Fig. 2 shows the THz absorption spectra of PHB measured during isothermal crystallization at  $T_c = 90, 110$ , and  $120^\circ\text{C}$ , respectively. All the spectra show a broad structure at  $t = 0$ , indicating that most of the PHB in the samples is in the amorphous phase after rapid cooling to the crystallization temperature. Note that the small fringe in the spectra is due to the interference of THz waves within the  $100\text{-}\mu\text{m}$  thick sample. As the crystallization progresses, vibrational bands from the lamellar crystal arise at around 2.4 and 2.9 THz. The crystallization rate changes with temperature: The time taken for lamellar crystal growth at  $90$  and  $120^\circ\text{C}$  is 8 min and about 200 min, respectively. During the crystallization, the peak top of the vibrational band shifts to higher frequency. For example, at  $110^\circ\text{C}$ , the peak top was observed at around 2.2 THz at  $t = 20$  min, and it shifted to 2.4 THz as the crystallization progressed. However, it is difficult to decide whether this phenomenon is due to the change in the relative intensity of the overlapped bands or due to the frequency shift of one band by the raw spectra.

In this study, 2DCOS was applied to the THz time-dependent spectra during isothermal crystallization at different temperatures. For example, Fig. 3 shows the (a) synchronous and (b) asynchronous plots of the isothermal crystallization measured at  $110^\circ\text{C}$ . The raw spectra at  $t = 0\text{--}70$  min. are shown at the top of the plots. In the synchronous plot, a positive correlation is observed between the bands at 2.37 THz and 2.93 THz, which reflects a simultaneous increase in the intensities of the vibrational peaks due to the lamellar crystal. In contrast, these bands show a negative correlation with a broad frequency region from 0.8 to 2.0 THz, which arises from the absorption of amorphous PHB. Thus, the synchronous correlation plot clearly shows a change from the amorphous form of PHB to the lamellar crystal form.

The asynchronous 2D plot shows correlation between the bands at 2.20 THz and 2.39 THz. The pattern observed in Fig. 3 bears no

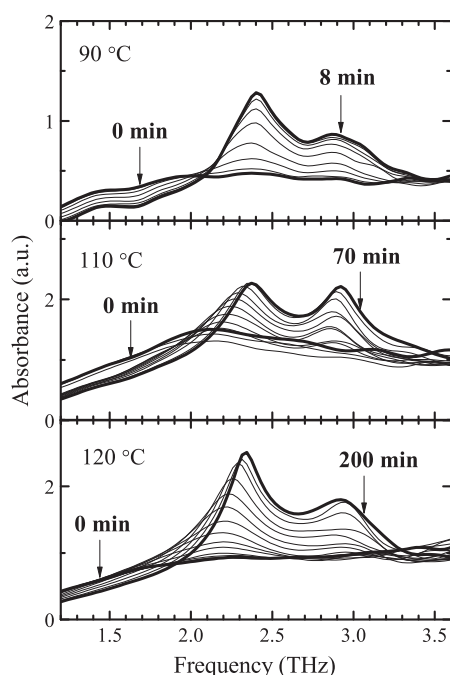


Fig. 2. THz absorption spectra of PHB measured during isothermal crystallization at  $90, 110$ , and  $120^\circ\text{C}$ .

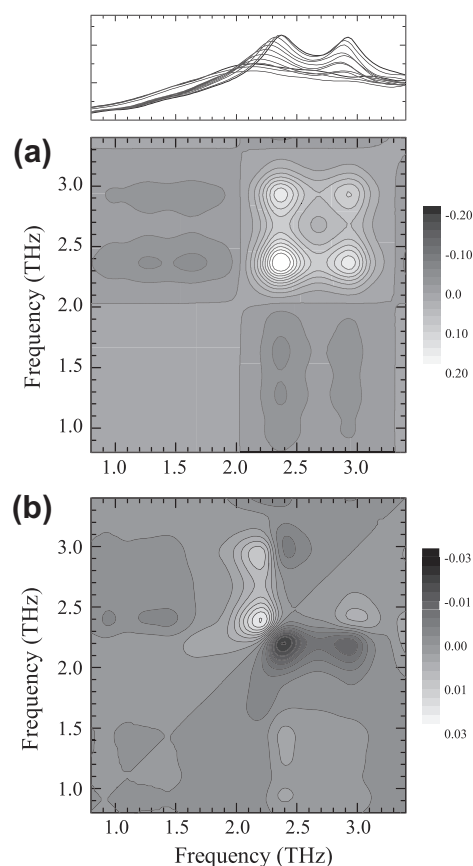


Fig. 3. (a) Synchronous and (b) asynchronous 2D correlation plots of PHB during isothermal crystallization at  $110^\circ\text{C}$ . The raw spectra at  $t = 0\text{--}70$  min. are also shown at the top of the plots.

similarity to the butterfly pattern, which arises from the frequency shift of a single peak; rather, it is consistent with the pattern of intensity changes of two overlapped peaks [26]. Therefore, we can conclude that there are two vibrational modes at 2.20 and 2.37 THz that undergo changes in intensity with time. The band at 2.20 THz shows negative cross peaks with those at 2.37 and 2.93 THz. By comparing the sign of the synchronous and asynchronous plots, it is shown that the band at 2.20 THz changes before the bands at 2.37 and 2.93 THz do. In our previous studies, we have assigned the peaks at 2.4 and 2.9 THz at  $25^\circ\text{C}$  to the skeletal vibration along the  $c$ -axis ( $\text{COO} + \text{CH}_2 + \text{CH}_3$  and  $\text{CH}_2 + \text{CH}_3$ ) on the basis of polarization spectra (Fig. 1 (c) and (d)) and DFT calculations [22]. On the other hand, another peak observed at 2.5 THz was assigned as the vibration of the  $\text{C=O} \cdots \text{H-C}$  hydrogen bond ( $\text{C=O}$  (out of plane) +  $\text{CH}_3$ ) [22]. This peak underwent a red-shift with increasing temperature, in contrast to the other two peaks (Fig. 5). These results facilitate interpretation of the patterns in the asynchronous plot at  $110^\circ\text{C}$ . The peak at 2.20 THz corresponds to the vibration due to hydrogen bonds between helical structures, which changes in advance of the skeletal vibration along the  $c$ -axis.

The results of 2DCOS analysis suggest the two-step crystallization of PHB at  $110^\circ\text{C}$ . During the isothermal crystallization,  $\text{C=O} \cdots \text{H-C}$  hydrogen bonds are initially formed, and subsequently, a well-defined skeletal structure of the lamellar crystal is established. A similar phenomenon was previously observed by Zhang et al. [27], in that study, the isothermal crystallization of PHB was followed at  $129^\circ\text{C}$  using IR spectra, and a peak originating from an intermediate state between the amorphous and lamellar crystalline forms of PHB was observed in the  $\text{C=O}$  stretching region.

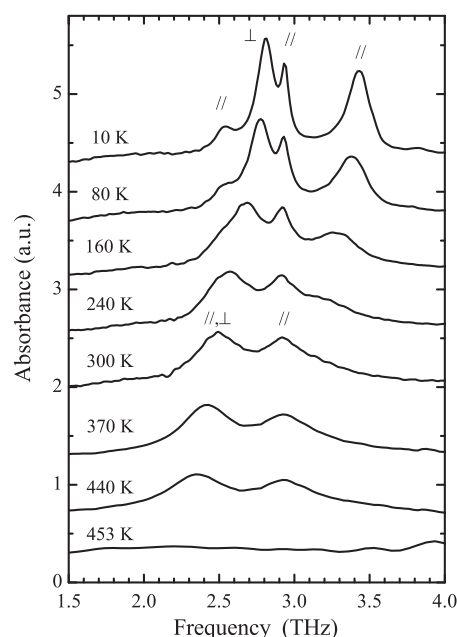


### 3.2. Temperature dependence of overlapped vibrational frequencies obtained by 2DCOS

From the asynchronous 2D plot, the frequencies of the overlapped bands are clearly resolved. Since the spectra were measured at the same temperature during the crystallization, we can obtain the exact frequencies of the vibrational modes of PHB in each crystallization temperature  $T_c$ . Fig. 4 shows the asynchronous 2D correlation plot of PHB for isothermal crystallization at  $T_c = 90, 100, 110$ , and  $120^\circ\text{C}$ . Cross peaks are observed between 2.41 and 2.26 THz at  $90^\circ\text{C}$ , 2.40 and 2.25 at  $100^\circ\text{C}$ , 2.39 and 2.20 THz at  $110^\circ\text{C}$ , and 2.31 and 2.12 THz at  $120^\circ\text{C}$ . As discussed in the previous section, the higher-frequency mode was assigned as the vibration of the skeletal motion  $\text{COO} + \text{CH}_2 + \text{CH}_3$  ( $//$   $c$ -axis) and the lower-frequency mode was assigned as  $\text{C}=\text{O}$  (out of plane) +  $\text{CH}_3$  ( $\perp$   $c$ -axis), which is the interhelix vibration due to the  $\text{C}=\text{O} \cdots \text{H}-\text{C}$  hydrogen bond. The obtained frequencies showed a slight shift with temperature.

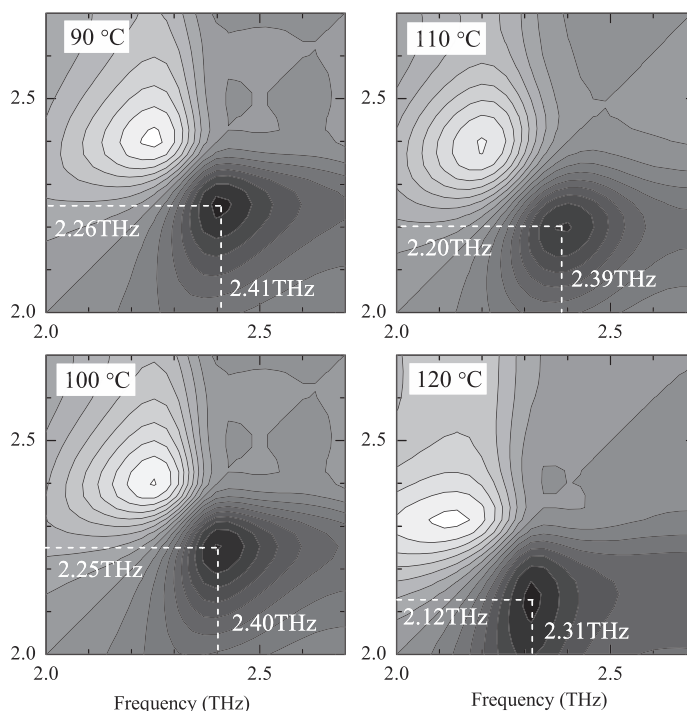
The resolved frequencies and assignments of the overlapping peaks provide new insight into the thermal behavior of the low-frequency vibrational modes of PHB. Fig. 5 shows the temperature dependence of the THz absorption spectra of PHB from 10 to 440 K. Four vibrational modes were observed at 2.55 ( $//$   $c$ -axis), 2.82 ( $\perp$   $c$ -axis), 2.93 ( $//$   $c$ -axis), and 3.43 ( $//$   $c$ -axis) THz at 10 K, but the peaks broadened and overlapped at higher temperatures. At temperatures exceeding 300 K, it was difficult to trace the peak position. Fig. 6 shows the peak positions of the vibrational modes obtained from the THz absorption spectra of PHB versus temperature. The open symbols show the frequencies of the peak selected from the absorption spectra. In our previous study [11], we concluded that the 2.55 THz peak measured at 10 K does not shift but disappears at higher temperatures, while the peak at 2.82 THz shifts continuously. However, 2DCOS gives a different assignment for the peak at higher temperatures.

We measured the isothermal crystallization at 90, 95, 100, 105, 110, 115, and  $120^\circ\text{C}$  and obtained the frequencies of the overlapped bands, which are marked by closed symbols in Fig. 6. Because the high-frequency modes ( $\blacktriangledown$ ) are assigned as  $\text{COO} + \text{CH}_2 + \text{CH}_3$  ( $//$   $c$ -axis), the band observed at 2.55 THz at 10 K was found to show a slight

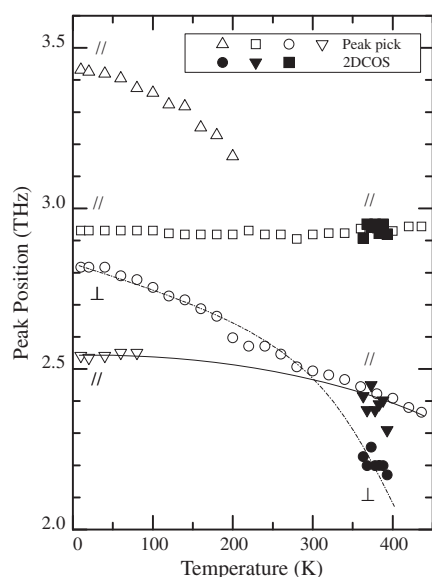


**Fig. 5.** THz absorption spectra of PHB measured from 10 to 440 K. The spectra from 10 to 300 K were measured by FT-FIR, and the spectra from 370 to 440 K were measured by THz-TDS. The polarization of the vibrational modes was measured at 10 K and 300 K.

red-shift at higher temperatures, as shown by the solid line in the figure. On the other hand, the low-frequency modes ( $\bullet$ ) are newly found at around 2.2 THz, which is assigned as the vibrational band of  $\text{C}=\text{O}$  (out of plane) +  $\text{CH}_3$  ( $\perp$   $c$ -axis) showing a large red-shift at higher temperatures, as indicated by the dashed line. The large frequency shift of the vibrational peak suggests a large anharmonicity of the vibrational potential because the energy separation between the vibrational levels is not equal to the anharmonic potential. The temperature dependence of the vibrational frequencies suggests huge



**Fig. 4.** Asynchronous two-dimensional correlation spectra of PHB during isothermal crystallization at 90, 100, 110, and  $120^\circ\text{C}$ .



**Fig. 6.** Peak positions of the THz absorption spectra of PHB in the range 2.0–3.6 THz versus temperature. The open symbols show the frequencies of the peak top in the absorption spectra. The closed symbols show the vibrational frequencies obtained by 2DCOS. Solid and dashed lines show the frequency shift of the vibrational modes.

anharmonicity of the interhelix vibrational potential of the C=O (out of plane) + CH<sub>3</sub> mode.

#### 4. Conclusion

In this study, 2DCOS was applied to the analysis of THz absorption spectra of PHB during isothermal crystallization, and overlapping vibrational peaks were resolved in asynchronous 2D plots. By changing the crystallization temperature from 90 to 120 °C, the exact frequencies and assignments of the overlapping vibrational bands were obtained, which provided a new perspective for the thermal behavior of the intermolecular vibrational modes. Thus, 2DCOS is a new, powerful tool for the analysis of THz spectra in which vibrational bands overlap and are difficult to resolve.

#### Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research in Japan (KAKENHI 20750067, 22360011) and Industry-

Academia Collaborative R&D from Japan Science and Technology Agency, JST. The authors are grateful to Prof. Yusuke Morisawa and Prof. Yukihiro Ozaki for helpful discussions.

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