Low-frequency Vibrational Dynamics of Poly(lactic acid) Stereocomplex Studied by THz spectroscopy and Solid-state DFT Simulation

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***Abstract*—This work uses the poly(lactic acid) stereocomplex (scPLA) system as an example to illustrate a comprehensive study of the low-frequency vibrations of polymers through an interplay of THz spectroscopy, solid-state DFT simulation and a recently developed mode analysis method.**

I. INTRODUCTION

POLYMERS ranging from familiar synthetic plastics to natural biopolymers, play an essential and ubiquitous role in everyday life. At ambient temperature their major dynamic functions related to thermal, mechanical and various biological properties are mediated by the low-frequency vibrations. Understanding the low-frequency vibrations of polymers at the ab initio level is the key to understanding the mechanism of these functions. This task has been allowed by the great advances of terahertz (THz) spectroscopy and solid-state density functional theory (DFT). This work presents a comprehensive investigation of the low-frequency normal modes of crystalline polymer systems. To this end, we adopt the poly(lactic acid) stereocomplex (scPLA) as an example, because this material is relatively easy to be prepared with high crystallinity, and has sharp-peak feature in THz spectroscopy. Moreover, its THz bands show interesting temperature dependence such as anomalous frequency shift and very weak relaxation effect. By generalizing a recently developed mode-analysis method [1, 2] in the building-block molecule systems to the polymer system, we achieve a quantitative understanding of the nature of the simulated normal modes. This may suggest a solution to the question as to how the microscopic atomic normal mode structures and dynamics affect the macroscopic properties of scPLA, such as its sound mechanical properties compared with its homo-crystalline systems.

II. RESULTS

The scPLA sample was prepared by annealing a piece of casted film of 1:1 (molar ratio) mixture of ploy(L-lactide) and poly(D-lactide) at 200 ℃ for 3 h. Its high crystallinity has been confirmed by the sharp-peak feature of its x-ray diffraction spectrum (not shown here).

The THz spectrum was measured by a THz time domain spectrometer (Aispec, Japan) at 78 K.[3] The solid-state DFT calculations implemented with a periodic boundary condition were performed using the CRYSTAL14 software package.[4, 5] The Grimme dispersion correction term[6] D^* (whose parameters were re-optimized by Civalleri et al.[7] for the application in the solid molecular systems) was used to augment the B3LYP functional[8, 9] to construct a B3LYP-D^* model. Geometry optimization and frequency calculation were performed using the 6-311G(d,p) basis set.[10] The geometry was optimized by relaxing both the atomic coordinates and the unit cell parameters. The trigonal unit cell structure (Fig. 1) of scPLA, measured by the X-ray diffraction method at room temperature,[11] was used as the starting point (*P3c* space group symmetry; cell parameters: $a = b = 14.98$ Å, $c = 8.70$ Å; $\alpha=\beta=90^\circ$, $\gamma=120^\circ$).

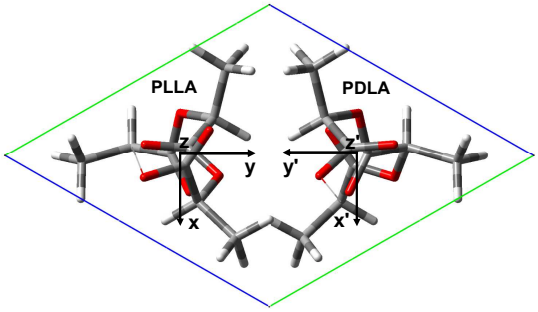

Fig. 1. Packing structure of scPLA in the unit cell. The three principal axes of the PLLA and PDLA units are shown respectively.

A global scaling factor s_6 was used to adjust the strength of the dispersion correction term such that the simulated unit cell volume was used as a scaling criterion. We consider that a balance between the dispersion correction term and the corresponding DFT functional was achieved once the simulation could produce a unit cell volume with a shrinking rate <0.1% smaller than the experimental value. The frequency calculations were performed by diagonalizing the mass-weighted Hessian matrix in Cartesian coordinates at the gamma point. The IR intensities were determined using the Berry phase approach.[12, 13]

Fig. 2 shows a comparison between the THz spectrum of scPLA and the normal mode simulation result. Three peaks, denoted by *a*, *c* and *d*, among the four strong resonant peaks have been satisfactorily reproduced. Both mode *a* and *d* belong to the A1 space group representation. It is worth noting that peak *c* is represented by a pair of degenerated modes belonging to the E representation, and they are denoted by *c1* and *c2*, respectively.

Fig. 3 shows the analysis results of the vibrational characteristics of the PLLA and PDLA units in the four simulated normal modes. Mode *a* features a primary intramolecular vibration and a secondary intermolecular libration; both mode *c1* and *c2* feature a primary intramolecular vibrations and secondary intermolecular translations and librations; Mode *d* features a primary intermolecular libration and a secondary intramolecular vibration.

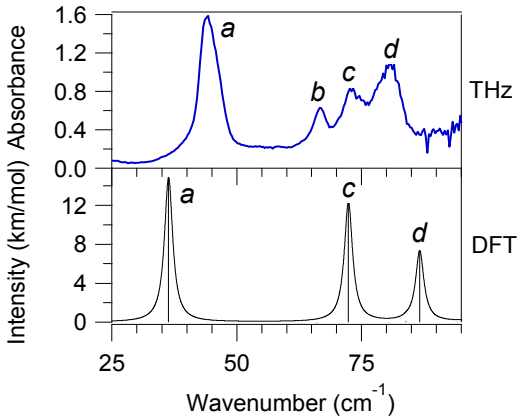

Fig. 2. Comparison between the THz spectrum of scPLA and the simulated normal modes. Lorentzian line shape functions having FWHM=1.0 cm^{-1} are convolved with all simulated modes to provide a visual guide.

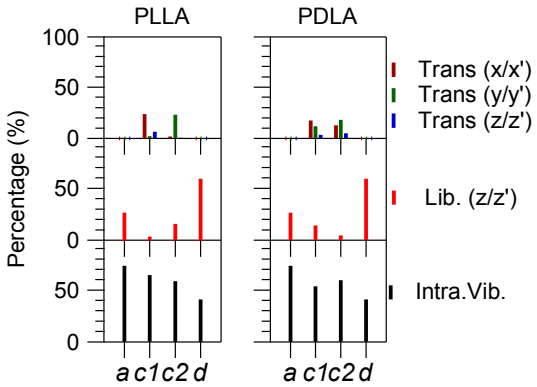

Fig. 3. Vibrational characteristics of the four THz modes. Vibrations of the PLLA and PDLA units in each mode are decomposed into three translations along the three principal axes, a libration around the *z* (*z'*) axis, and an intramolecular vibration, respectively.

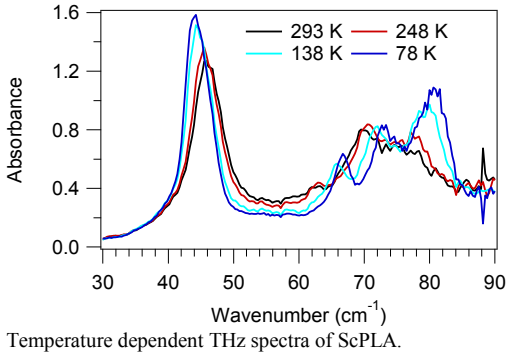

Fig. 4. Temperature dependent THz spectra of ScPLA.

It should be noted that peak *b* is not reproduced. Its origin may be due to the following three scenarios. First, it may originate from the amorphous zone in the scPLA sample that was not taken into account in simulation. Second, it may result from the different temperature dependency of the pair of degenerate normal modes *c1* and *c2*. Although the pair of modes degenerates in energy in the 0 K-simulation, they may have distinct temperature dependency (Fig. 4) due to different degrees of anharmonicity. As a result, they separate at the elevated temperature. Third, peak *b* may indicate the existence of an exciton or polaron state of the mode *c*. The experiment shows that the intensity of mode *c* has barely temperature dependency, implying its very weak energy relaxation. The intensity of peak b, on the other hand, decreases gradually with the decrease of temperature. Detailed theoretical treatment will be presented in this regard.

III. Summary

This work has explored the low-frequency normal modes of the scPLA system. THz modes of scPLA have been satisfactorily reproduced in theory and quantitatively assigned. The nature of one peak which does not match the simulation result has been qualitatively discussed.

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