1P-049

低波数ラマン分光と量子化学計算による高分子の振動解析

（関学理工 [1]，近大理工 [2]，理研 [3]）山本 茂樹 [1]，森澤 勇介 [2]，保科 宏道 [3]，
佐藤 春実 [1]，尾崎 幸洋 [1]

Low-frequency Raman spectroscopy and quantum chemical calculations of polymers

(Kwansei Gakuin Univ.[1], Kinki Univ.[2], RIKEN[3]) Shigeki Yamamoto[1],
Yusuke Morisawa[2], Hiromichi Hoshina[3], Harumi Sato[1], Yukihiro Ozaki[1]

Introduction. Vibrational spectra of molecules in low frequency region, typically below ~300 cm^{-1}, arise not only from the intramolecular interactions but also from the intermolecular interactions. Polymers are tempting target for low frequency vibrational spectroscopy because the spectra directly provide information about intermolecular interaction, which is a key to understand properties of polymers, and various samples have been measured since 1970's.[1] In our previous studies, THz spectra of poly(3-hydroxybutyrate) (PHB) were measured and the obtained spectra showed vibrational peaks due to weak hydrogen bonds among helices.[2,3] However, the assignment of the THz vibrational bands is not assured if only based on an experimental spectroscopic method. We attempt to assign the bands based on comparisons of Raman, THz absorption spectra and the polarizations of the bands, and quantum-mechanically calculated spectra. Such a methodology will enable the certain assignments of the bands, which have been desired in the field of the spectroscopies in the THz region.

Experiments and Spectral Calculations. Raman spectrum of the crystalline powder PHB (Aldrich, used as received) was collected at room temperature with a laser power of 16 mW at the sample (514.5 nm) by using a Raman microscope (HR800, Horiba). The Raman scattered light was collected by an objective lens (50x), passed through an edge-filter with a wavenumber-cut-off at ~50 cm^{-1}, diffracted by a grating of 1800 lines/mm, and then detected by a Peltier-cooled CCD. The total exposure time was 500 s.

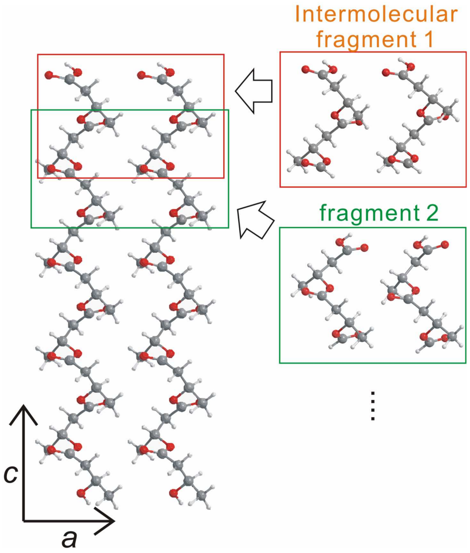

Figure 1. Schematic presentation of the CCT method for the transfer of tensors of the fragment for intermolecular interaction along the *a* axis.

Raman and IR absorption spectra in the THz region of the crystalline PHB were calculated by the density functional theory at the level of B97-1[4]/6-31++G** aided with the Cartesian coordinate tensor transfer (CCT) method.[5] From the X-ray crystal structure of the lamellar crystalline PHB,[6] molecular fragments were created along the polymer chain (basic fragment), as containing two polymer chains along the *a* axis (fragment A) and along the *b* axis (fragment B). For the vacuum calculation, the only tensors of the basic fragments were transferred back to the whole structure of PHB by using a CCT program.[5] In the calculation under the explicit correction of intermolecular interactions, the tensors of the fragment A and B were also transferred (Figure 1) and averaged with those of the vacuum calculation.

Results and Discussions. Figure 2 (A) and (B) compare the calculated (top and middle) and the experimental (bottom) Raman and FIR spectra of crystalline PHB. The calculations were carried out under vacuum (top) and with the explicit correction for the intermolecular interactions (middle). The explicit correction improves significantly the agreements between the experiments and the calculations in terms of the spectral shapes, relative intensities, relative frequencies, and polarization states in the whole THz spectral range, but the vacuo calculation cannot reproduce the experimentally-observed perpendicular component at ~82 cm^{-1}. This perpendicular component originates from the intermolecular interactions among the PHB chains, as its polarization direction is along the *a* axis of the PHB and assigned to the out-of-plane C=O+CH_3 vibration. Therefore, we know that the intermolecular interactions on the C=O and CH_3 groups are directional as working along the *a* axis of the PHB. The present low-frequency Raman and FIR results are consistent with the previous works on the intermolecular hydrogen bonds of PHB, [1, 3] and strongly support their suggestions.

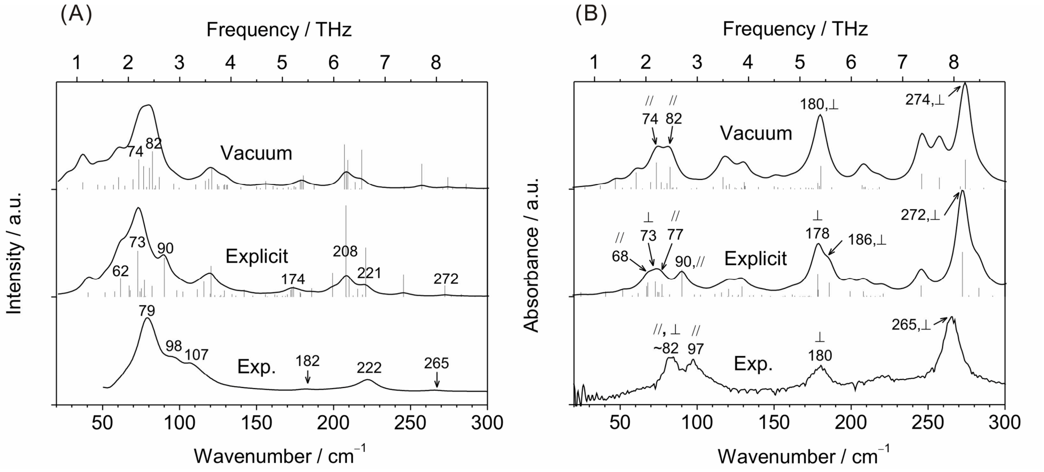

Figure 2. Comparison of the calculated (top and middle) and experimental (bottom) Raman (A) and FIR absorption (B) spectra of crystalline PHB. The calculations were carried out under vacuum (top) and with the explicit correction for the intermolecular interactions (middle). FIR spectrum is taken from ref. 2.

References [1] V. A. Bershtein *et.al.*, *Adv. Polym. Sci.*, 1994, **114**, 43-121. [2] H. Hoshina *et.al.*, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9173-9179. [3] H. Hoshina *et.al.*, *Appl. Phys. Lett.*, 2010, **100**, 101904. [4] F. A. Hamprecht *et.al.*, *J. Chem. Phys.*, 1998, **109**, 6264-6271. [5] P. Bouř *et.al.*, J , *J. Comput. Chem.*, 1997, **18**, 646-659. [6] M. Yokouchi *et.al.*, *Polymer*, 1973, **14**, 267-272.