A first principle study of THz vibrational spectroscopy of molecular crystals

Feng Zhang[1] , Houng-Wei Wang[2] , Keisuke Tominaga[1] , and Michitoshi Hayashi[2]

[1]Mlecular Photoscience Research Center, Kobe University, Kobe, Japan
[2]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

Terahertz (THz) vibrational spectroscopy provides direct access to molecular phonons in the optical branch in the vicinity of the center of the Brillouin zone. Typical observable frequency region is 0.1 THz ~ 10 THz (3 cm^{-1} ~ 300 cm^{-1}) in which the intermolecular interaction plays an important role. The phonons at Gamma point, of course, provide valuable information on the characteristics of the crystal structures and dynamics. Moreover, vibrational spectroscopy techniques can easily be performed in the laboratory.

A great deal of progress has been made by several groups at identifying and characterizing the mixing of the intra-molecular vibrational motions with inter-molecular vibrations in the THz frequency region. However, a success of these attempts relies heavily on the accurate assignment of the vibrational modes. In particular, for the case in which non-trivial mixing of the intra- and inter-molecular vibrations exists, the mode assignment becomes formidable.

In this report, we will discuss the origin of the difficulty in mode assignment of THz-vibrational modes of molecular crystals and recent development of mode analysis methods in our groups. We will provide perspective of its application of THz vibrational spectroscopy to crystalline polymers by addressing the relationship between the packing and staking configurations of polymers and the characteristics of the THz vibrational spectroscopy.

References

[1] R. Dovesi, B. Civaller, R. Orland, C. Roetti, and V. R. Saunders, Rev. Comp. Chem., 21, 1 (2005).

[2] F. Zhang, M. Hayashi, H.-W. Wang, K. Tominaga, O. Kambara, J.-i. Nishizawa, et al., J Chem. Phys., 140, 174509 (2014).

[3] F. Zhang, H.-W. Wang, K. Tominaga, and M. Hayashi, J Phys. Chem. A, 119, 3008-3022 (2015).