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Phonon Modes of Molecular Crystals Studied by Terahertz Spectroscopy and Solid-state Density Functional Theory; a Concept of Vibrational Coordinate Distribution

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[Introduction] Phonon, one of the fundamental vibration forms in the matter world, plays important role in various physical processes, e.g. thermal conduction, information conduction, biological functions, especially in the low-frequency region.[1] [2] Despite of the successful interpretation of phonons in the simple systems such as metal, semiconductor and inorganic solids, phonon modes in the more complicated molecular system have not been fully explored. This task has been enabled by recent advances of the terahertz (THz) spectroscopy and the solid-state density functional theory (DFT). In this work we will introduce a recent progress in understanding the low-frequency molecular phonons using the two methods.

[Methods] Two THz setups were used in this work. One is based on difference frequency mixing principle and was used to generate a broad THz radiation band from 20 to 200 cm^{-1}.[3] The other is a THZ-TDS system (Aispec, Japan) based on a photoconductive antenna system for generating and detecting THz radiation in a frequency region from 5-100 cm^{-1}. The solid-state DFT calculations implemented with a periodic boundary condition were performed in the CRYSTAL09 software package[4,5]. The Grimme's dispersion correction term D* was used to augment the DFT functionals. All calculations were carried out at the basis set level of 6-311G(d,p)[6]. The geometries were optimized under a full relaxation condition: both the atomic coordinates and unit cell parameters were allowed to relax. The frequency calculations were carried out by diagonalizing the mass-weighted Hessian matrix in Cartesian coordinates at the gamma point. The IR intensities were determined through the Berry phase approach.[7] In addition, accumulated DFT simulation evidence has indicated that the mixing of inter- and intra-molecular vibrations is an intrinsic property of molecular phonons in the low-frequency region. We have developed a quantitative mode-analysis method that allows for accurate characterization of a normal mode of interest into its elementary vibrational components such as intermolecular translation, libration and intramolecular vibrations.[8]

[Results and Discussion] A crucial issue in solid-state DFT is the accurate representations of intermolecular interactions such as electrostatic force, exchange-correlation interaction and dispersion force. The first two interactions have been thought much successfully described at the current functional level. However, the dispersion force remains a challenge to be surmounted. In the regards, the crystalline anthracene, a pure dispersion force system, serves as an ideal model to examine the accuracy of theoretical calculations. Consequently, the reliability of our simulations get proven against a rigorous criterion of the reproduction of a pair of modes B1 and B2 of crystalline anthracene (Fig. 1, left panel). The conventional viewpoint regards modes B1 and B2 as arising from the correlation field splitting of a butterfly motion, consequently they should have equivalent isotope shift (IS). In fact, the IS (4.7%) of B2 is slightly lower that that (5.5%) of B1. Our simulation results provide a satisfactory explanation as follows: firstly, the CFS has been accurately reproduced at an accuracy level of 5.1%. It is found that the splitting of B1 and B2 does not arise from one-component intramolecular vibration, but from a two-

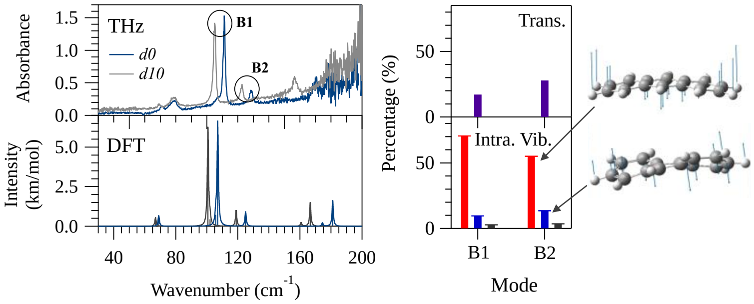

Fig. 1 Simulation result for crystalline anthracene. Left panel shows a comparison between the experimental and simulated THz modes for protonated and deuterated anthracene, respectively. Right panel shows the analysis results for mode B1 and B2.The upper and lower layers represent the percentage contributions of translation and intramolecular vibrations, respectively. The black column represents the residue motion.

component vibration involving a primary butterfly and a secondary out-of-plane torsion (Fig. 1, right panel); secondly, both modes have a relatively strong contribution from intermolecular translation, and the contribution in mode B2 is slightly larger than that in B1 (Fig. 1, right panel). Because the intermolecular translations normally possess smaller ISs than intramolecular vibrations, the IS of B2 consequently become small.

Gaining the confidence of the accuracy of the DFT simulations, we are able to apply a mode-analysis method recently developed[8] to shed light on the vibrational characteristics of low-frequency phonons in a series of typical molecular systems. The main results can be demonstrated by a comparison of three difference molecular systems: C60, adenine and L-alanine, which represent the readily increased intermolecular interactions from dispersion force, to the interplay of dispersion force and hydrogen bonds, to the interplay of Coulomb force, dispersion force and hydrogen bonds. As shown in Fig. 2, the mixing rate of inter- and intra-molecular vibrations exhibits a steady increase with the increased strength of intermolecular interactions, reflecting the intrinsic vibrational characteristics of different intermolecular force systems.[9]

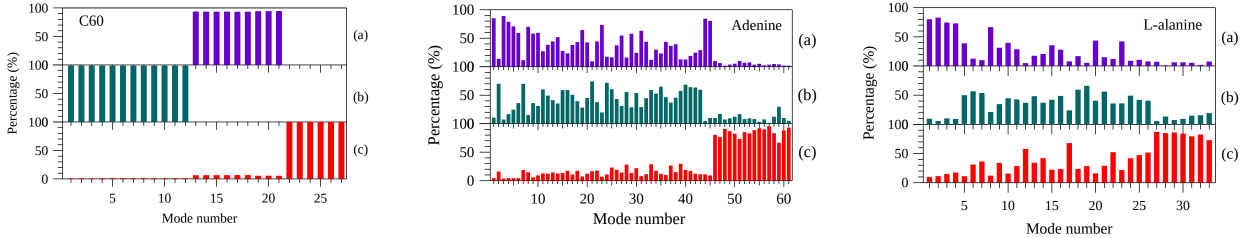

Fig. 2 Vibrational characteristics of molecular phonon modes below 300 cm^{-1} of crystalline C60, adenine and L-alanine systems, respectively. Panel (a), (b) and (c) represent the percentage contributions of intermolecular translation, libration and intramolecular vibrations, respectively.

Among the above three systems, L-alanine provides an old system of new interest, in which abundant information of intramolecular vibrations is hinder in the low-frequency phonons through the strong mixing with the intermolecular vibrations, and that was seldom explored in the past. To investigate the properties of such motions, we project the vibration vectors of the intramolecular components in the gamma-point phonon modes of L-alanine into a set of intramolecular vibrational coordinates properly introduced. As a result, a new phenomenon—vibrational coordinate distribution (VCD)—has been revealed. VCD describes a general distribution of important intramolecular vibrational coordinates, e.g. COO^- and $NH3^+$ torsions, in phonon modes of a broad frequency region (Fig. 3), which is totally contrary to the conventional point of view that intramolecular vibrations should be confined within a few modes resulting from the correlation field splitting. This finding may lead to a new recognition of the nature of molecular phonons in the biological systems and may imply solutions to several unsettled problems.

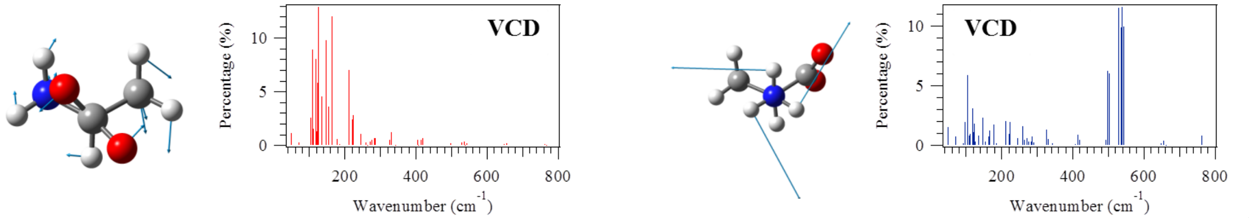

Fig. 3 VCDs of intramolecular vibrational coordinates in gamma-point optic phonons of crystalline L-alanine in a frequency region of 0- 800 cm^{-1}. The left and right panels show VCDs of two important intramolecular vibrations of COO^- torsion and $NH3^+$, respectively, for a demonstration.

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