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Tominaga, Keisuke

2020

Tominaga, K. (2020). THz molecular science in condensed phases. Proc. Of the 7th Asian Spectroscopy Conference (ASC 2020). doi:10.32655/ASC_8-10_Dec2020.25

<https://hdl.handle.net/10356/144252>

https://doi.org/10.32655/ASC_8-10_Dec2020.25

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THz Molecular Science in Condensed Phases

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Abstract

Terahertz (THz) frequency region is located between microwave and infrared regions, and molecular motions and intermolecular interactions in the THz region reflect unique properties of materials, which are important to understand structural stabilization, chemical reactions, and functionalities of molecular systems. We have been applying spectroscopic methods in the THz region to various problems in the research field of molecular science. By using THz time-domain spectroscopy (TDS), we can obtain both the absorption coefficient and refractive index of materials.

Molecular crystals in the solid state show vibrational structures even in the THz region at low temperatures, and mode assignment can be performed by using solid-state density functional theory and crystal structures obtained by X-ray diffraction measurement [1-4]. The agreement between the experiment and theoretical calculations depends on how we treat the intermolecular interactions in the calculations. Consideration of the London dispersion force is crucial to explain the vibrational spectra in the THz region. The normal modes are generally a mixture of intermolecular and intramolecular vibrational modes.

Hydrogen bonding liquids such as water interact with electromagnetic wave in a broad range from the MHz to mid-IR region. Liquid water has different types of molecular motion associated with hydrogen bond dynamics such as librations, intermolecular stretching mode, and collective reorientational relaxation, and these dynamics have specific time-scales and frequencies. In order to understand dynamics of water in the THz region, we perform broadband dielectric spectroscopy ranging from MHz to mid-IR region. The obtained complex dielectric spectra are analyzed in terms of a model function for time-correlation function of the total dipole moment of the system. This work is also extended to protein to investigate effects of thermal excitation and hydration on the protein dynamics [5-7].

Charge carriers in the condensed materials also interact with THz waves efficiently. The examples are conductive polymers and organic semiconductors. We investigated the charge carrier dynamics of benzoporphrin (BP) and BP-based bulk heterojunction thin films by using time-resolved THz spectroscopy [8, 9]. In both samples, we observed instantaneous appearance of transient THz signals, which are attributed to mobile charge carriers.

Keywords; terahertz spectroscopy, solid-state DFT calculation, molecular crystals, intermolecular vibration

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