

# Study on benzoic acid by THz time-domain spectroscopy and density functional theory

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In this letter, we employ terahertz time-domain spectroscopy (THz-TDS) technology to measure the THz absorption spectrum and refractive index of benzoic acid at room temperature. Linearity combination of atomic orbital (LCAO) within the density functional theory (DFT) is also used to compute the vibrational absorption spectra of benzoic acid in monomer and dimer. In addition, based on the results obtained from density functional calculation, the origins of observed intra-molecular and inter-molecular vibrational modes under specific peaks are interpreted.

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Terahertz (THz) radiation, which lies in the frequency gap between infrared (IR) and microwaves, has not been well investigated due to the lack of high-efficient sources and detectors. With the great development of femto-second laser technology, THz-frequency research has received tremendous attention and numerous breakthroughs of THz technology have been presented to the public, specially the development of THz time-domain spectroscopy (THz-TDS).

THz-TDS technology based on femto-second laser technology has been considered as a competitive method for inspection and detection of biological macro-molecules. It has been widely used in the last decade owing firstly to its unique advantages over other spectroscopic techniques; and secondly to the fact that many biological molecules have distinctive absorption features in the THz region. The application of this technology in materials is extensive, ranging from solid crystals to cancer cells<sup>[1-3]</sup>. Moreover, vibrational modes found in the THz region of the spectrum are not only highly characteristic for the molecule, but also for its environment. For example, polymorphs consisting of the same elements present different THz absorption spectra because of the varied structure<sup>[4,5]</sup>.

Vibrational modes in the biological molecule can either be localized to intra-molecular modes or inter-molecular modes by comparing the material in crystalline solid and amorphous form. For example, non-covalent inter-molecular force, the dominant cause of low THz spectra in saccharides, has been studied by comparing the THz absorption spectra of glucose in polycrystalline with amorphous form<sup>[6]</sup>. Different absorption spectra of polycrystalline and amorphous glucose lead to the conclusion that distinct spectral features observed in the polycrystalline glucose are caused by concerted intermolecular vibrational modes of long-range order. Meanwhile, all sharp spectral features disappear in amorphous glucose due to the lack of long-range symmetry.

Some theories are also used to differentiate the intra- and inter-vibrational modes of biological molecules in THz spectra. For example, the theory of linearity combination of atomic orbital (LCAO) is inclined to compute the molecule in the monomeric form to predict intra-molecular modes mostly located in the mid-IR. Although the calculation of a molecule in the gaseous phase through the LCAO method always fails to predict lower THz vibrational modes (typically below 4 THz), some polymers calculated by this method obtained good results for interpreting the observed distinct absorption peaks<sup>[7,8]</sup>. Compared with the above method, the plane-wave pseudopotential (PWP) approach within the density functional formalism is used to calculate the periodic system by taking into account the periodic arrangement of atoms in the crystal<sup>[9]</sup>.

In this letter, we employ THz-TDS technology to measure the THz spectrum of benzoic acid at room temperature. The theory of LCAO within the density functional theory (DFT) is used to distinguish the intra- and inter-vibrational modes of benzoic acid by computing the spectra of benzoic acid in monomeric and dimeric form. Furthermore, the origins of the observed intra- and inter-molecular vibrations under specific peaks are analyzed based on the results from the density-functional calculation.

Standard transmission THz-TDS used in the experiment has been described previously<sup>[10]</sup>. The photoconductive emitter is used to generate THz radiation detected effectively by electro-optic sampling (EOS) with a bandwidth between 0.1 and 4.0 THz. Four off-axis parabolic mirrors are used to collect and collimate THz radiation. Output signals from the balanced photodiodes are monitored by a lock-in amplifier and a computer. The samples are measured at room temperature.

The THz pulse field transmitted through a sample is modified by dispersion and absorption of the sample. The ratio of the electric field strength transmitted through the empty aperture  $E_r$  and the sample aperture  $E_s$  can be given as follows<sup>[11]</sup>

$$\begin{aligned} E_s(\omega)/E_r(\omega) &= \frac{t_{01}p_s[\omega, d]t_{10}}{p_r[\omega, d]} \\ &= t_{01}t_{10} \exp\{-j[\tilde{n}_s(\omega) - 1]\omega d/c\} \end{aligned}$$

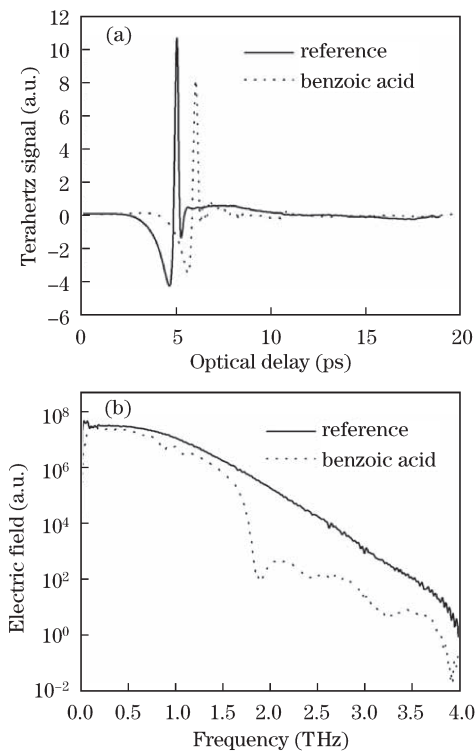


Fig. 1. (a) Signals and (b) spectra of reference and benzoic acid.

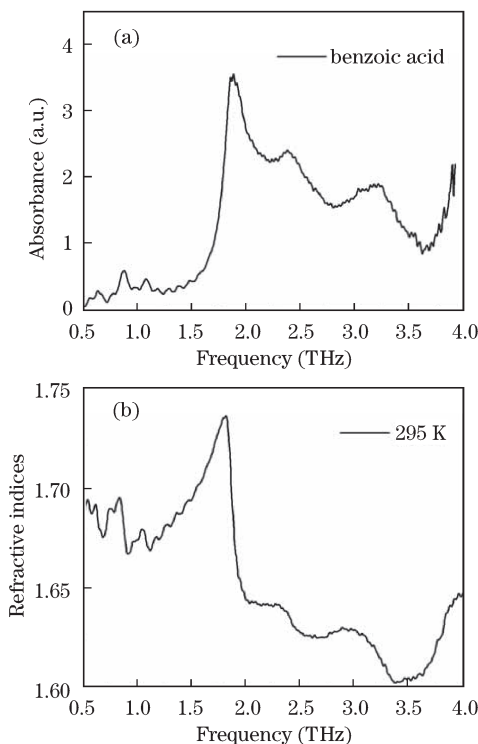


Fig. 2. (a) Experimental absorption spectra and (b) refractive index of benzoic acid.

$$= t_{01}t_{10} \exp(-\kappa\omega d/c) \exp\{j[n_s(\omega) - 1]\omega d/c\} \\ = \rho(\omega) e^{-j\varphi(\omega)}, \quad (1)$$

where  $p_s$  and  $p_r$  are the coefficients of propagation in the sample and air, respectively;  $d$  is the thickness of the

sample;  $\tilde{n}_s = n_s - jk$  is the complex refractive index of the sample;  $\omega$  is the angular frequency;  $t_{01}$  is the transmission coefficient from air to sample while  $t_{10}$  is the transmission coefficient from sample to air; and  $\rho(\omega)$  and  $\varphi(\omega)$  are the ratio of the amplitude and phase of the sample and reference signal, respectively. The refractive index can be obtained via Eq. (1):

$$n(\omega) = \frac{\varphi(\omega)c}{\omega d} + 1. \quad (2)$$

The sample was purchased from TianDa Chemical Reagent Factory in the purest form (>99%) and was used without further purification. It was prepared by using 151-mg benzoic acid crystal and pressing it into the 0.9-mm thick disk under a pressure of 1.8 tons.

Time-domain and frequency-domain spectra of the reference pulse and the benzoic acid are presented in Figs. 1(a) and (b). Figures 2(a) and (b) are the absorption spectrum and refractive index, respectively. The absorption spectrum was obtained in the frequency range of 0.5 to 4 THz because of the limitation of experimental equipment. In Fig. 2(a), several characteristic peaks, namely, strong peaks at 1.88, 2.39, 3.24, and 3.79 THz, and weak peaks at 0.63, 0.88, 1.07, and 3.55 THz, are clearly seen.

In Fig. 3, the calculated absorption spectra of benzoic acid in monomer and dimer using the hybrid exchange-correlation function of B3LYP of LCAO method within the DFT are shown. A single benzoic acid molecule possesses  $C_s$  symmetry while this is  $C_{2h}$  for the dimeric form. In the THz range below 4 THz, only one IR-active mode of gas-phase benzoic acid monomer exists. The absorption peak at 1.92 THz ( $63.36 \text{ cm}^{-1}$ ) arises from the rocking of carboxyl and phenyl out of the molecular plane, which belongs to intra-molecular vibration. However, due to the  $C_{2h}$  symmetry, four IR-active modes are presented in the gas-phase benzoic acid dimer, namely, 0.55 THz ( $18.10 \text{ cm}^{-1}$ ), 0.92 THz ( $30.35 \text{ cm}^{-1}$ ), 1.76 THz ( $58.18 \text{ cm}^{-1}$ ), and 2.55 THz ( $84.15 \text{ cm}^{-1}$ ). These modes show a slight difference compared to the data obtained in Ref. [12], which shows three spectral peaks at 0.54 THz ( $17.80 \text{ cm}^{-1}$ ), 1.76 THz ( $58.60 \text{ cm}^{-1}$ ), and 2.55 THz ( $84.30 \text{ cm}^{-1}$ ), using DFT calculation. Owing to the same symmetry and basis set, the discrepancy may be caused by the different requirements of calculational accuracy because the absorption intensity value at 0.92 THz is three orders of magnitude less than the others.

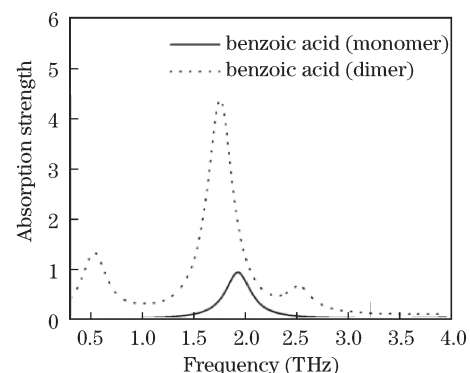


Fig. 3. DFT calculations of benzoic acid.

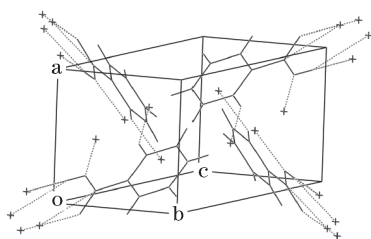


Fig. 4. The benzoic acid molecule in the crystalline unit cell, inter-molecular force and hydrogen bonds are shown in dashed lines.

The origin of the absorption peak at 1.76 THz is caused by the wagging vibration in the molecular plane while the rest are caused by the bending and rocking vibration out of the plane.

However, even if the calculations are performed on the benzoic acid molecule in monomer and dimer, a difference still exists between the absorption spectra of experimental data and the theoretical calculations. This difference is mainly due to the lack of taking the spatial arrangement of the crystal structure into full account. In Fig. 4, the benzoic acid in the crystalline phase is shown. There are four molecules in the crystalline unit cell. Dashed lines present the inter-molecular force and the hydrogen bonds. The calculation should become better in the range of 0.3–4 THz using the unit cell shown in Fig. 4 as the input to predict the THz spectrum of molecules. In other words, to obtain a realistic description of the low vibrational modes below 4 THz in crystal, the full crystal structure must be taken into account.

In conclusion, based on the results presented in this letter, benzoic acid has shown distinct absorption peaks in the THz range. Compared to the absorption spectra of benzoic acid between theoretical calculation and THz-TDS experiment. It can be seen clearly that the absorption peak at 1.88 THz is a strong coupling between the intra-and inter-molecular vibrational modes while the rest peaks in our dimer calculation are mainly caused by

the intermolecular force. For the time being, the absorption peaks of the THz-TDS experiment cannot be fully understood one by one due to the limitation of our calculation. However, the problem can be solved by considering and calculating the larger molecule complex in the crystalline unit cell.

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