

Temperature Dependence of Terahertz Spectra of Chlorophyll a and b

Ling Jiang¹, JiangPing Yu¹, Chun Li², YuTian Xu¹, BiaoBin Jin², and Yunfei Liu¹

¹College of Information Science and Technology, Nanjing Forestry University, Nanjing, Jiangsu210037, China

²School of Electronic Science and Engineering, Nanjing University, Nanjing, Jiangsu210093, China

Abstract— In this paper, we employ terahertz Time Domain Spectroscopy (THz-TDS) combined with temperature-tuned system to measure the temperature dependence of terahertz spectroscopic features of chlorophyll a and b samples. We investigated the absorbance of individual chlorophyll a and b respectively. The measured spectra showed two shoulders at 2.17 and 2.95 THz for the chlorophyll a sample, and 2.83 and 3.40 THz for the chlorophyll b sample. The measured absorption spectra were compared with the results simulated by Density Function Theory (DFT) using hybrid functional B3LYP with basis set of 6-31 G (d). The simulated results show more absorption peaks than measurement results. The discrepancy between simulation and experiment results originates from that the molecular structure used in the simulation is gas phase molecular model, which is different from crystal structure.

I. INTRODUCTION

To date, the terahertz (THz) spectroscopy has been widely applied in various fields of research to understand the THz frequency dynamics of biological molecular systems related to intermolecular vibrations and large-amplitude intramolecular modes [1]. Extensive spectroscopic studies in this region have been carried out, and THz spectroscopy has demonstrated that this method is complementary to other spectroscopic techniques. THz time-domain spectroscopy (THz-TDS) and Fourier transform infrared spectroscopy (FTIR) are two useful methods for evaluating the optical properties of materials and biological molecules in infrared range. THz-TDS focus on the spectral analysis in the low-frequency range between 0.1 and 4 THz, which obtains the simultaneous information of both the amplitude and phase of the THz electric field, making it an ideal tool in analyzing the sub-picosecond and picosecond dynamics of various molecular species. THz-TDS have been applied in many fields, such as medical diagnosis, pharmaceutical and biomolecular analysis, and security enhancement [2-5]. In this paper, we study the absorption characteristics of the chlorophyll a and b purchased from commercial company in order to investigate the temperature dependence of THz spectra for chlorophyll.

Furthermore, spectral calculations based on density functional theory (DFT) using Gaussian 09 were done for the chlorophyll. The density functional theory (DFT) calculation has proven to be a reliable theoretical method to predict accurate vibrational frequencies for typical small-size and medium-size molecules and interpret the measured infrared spectra in physical origin of these signatures [6-7].

II. RESULTS

The chlorophyll a and b samples measured in our experiment were purchased from Shanghai Baoman Co. and used without

further purification. Samples were prepared by weighing 50-100 mg of each solid and homogenizing the material in a mortar and pestle. This procedure ensured particle sizes sufficiently smaller than THz wavelengths to reduce baseline offsets at higher frequencies arising from non-resonant light scattering. The samples were pressed as a pellet in a 13 mm diameter vacuum die at the lowest possible pressures to minimize decomposition from transient heating. The pellets have thickness between 0.5 and 1 mm which is suitable for the measurement of the THz-TDS and FTIR spectroscopy. The samples were diluted with polyethylene powder.

The absorption spectra in the 0.1-4 THz range were obtained with the THz-TDS system working in transmission mode. The THz-TDS system provides a temperature-tuned sample chamber in order to observe the temperature dependence of THz spectra of chlorophyll samples. Figure 1 shows the measurement system.

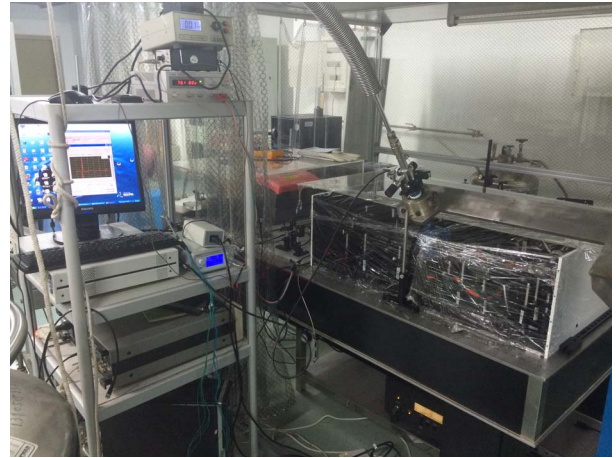


Fig. 1 Measurement system of THz-TDS.

We investigated the absorption spectra of the chlorophyll a and b at different temperatures. The measured spectra showed two shoulders at 2.17 and 2.95 THz for the chlorophyll a sample, as shown in Fig. 2. The measured spectra showed two shoulders at 2.83 and 3.40 THz for the chlorophyll b sample, as shown in Fig. 3. The slight ripple in Fig. 3 originates from the electromagnetic reflection between the sample and vacuum window. The absorption frequencies of the chlorophyll a and b are consistent at different temperatures, which indicate the intramolecular and intermolecular interaction does not change with the temperature for the chlorophyll molecules. The measured absorption spectra were compared with the results simulated by Density Function Theory (DFT) using hybrid functional B3LYP with basis set of 6-31 G (d). The simulated absorption frequency of chlorophyll a show a slight red shifts

around 0.25 THz for the two largest absorption peaks, and chlorophyll b doesn't appear shift. Those other absorption peaks in simulation do not appear in the measured results. The discrepancy between simulation and experiment results originates from that the molecular structure used in the simulation is gas phase molecular model, which is different from crystal structure. The simulation result omits the intermolecular interaction.

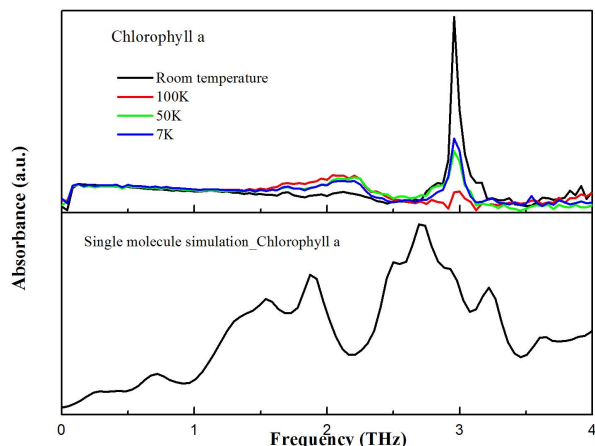


Fig. 2 Measured and simulated absorbance for chlorophyll a.

□ SUMMARY

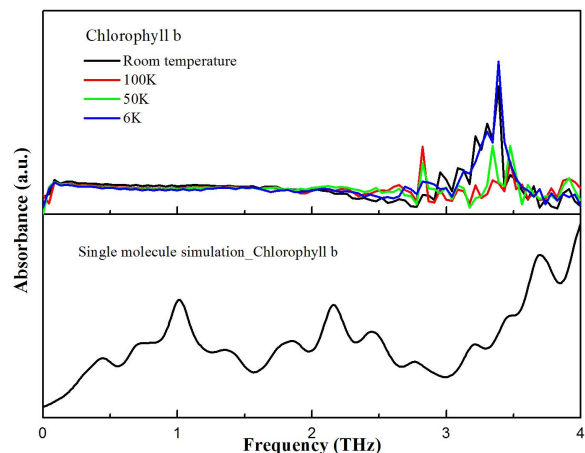


Fig. 3 Measured and simulated absorbance for chlorophyll b.

We employed THz-TDS spectroscopy to investigate the broad-band terahertz spectrum in the frequency range of 0.1-4 THz for chlorophyll a and b at different temperatures. The absorption frequencies of the chlorophyll a and b do not change with temperature. And there is no new absorption peak while the temperature was cooled down to helium temperature. Since the simulated results for single molecule do not consider the intermolecular interactions, the simulated and measured absorption spectra are not consistent.

ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China under Contracts 31170668 and 31200541, by the Natural Science Foundation of Jiangsu province under contract BK2012417, by the returned personnel foundation of ministry of education, and by the Priority Academic Program

REFERENCES

- [1]. K. Sakai (ed.), Terahertz Optoelectronics (Topics in Applied Physics vol. 97) (Springer-Verlag, Berlin, (2005).
- [2]. M. Nagel, F. Richter, P. Haring-Bolivar, and H. Kurtz, Phys. Med. Biol. 48, 3625 (2003).
- [3]. R. M. Woodward, V. P. Wallace, R. J. Pye, B. E. Cole, D. D. Amone, E. H. Linfield, and M. Pepper, J. Invest. Dermatol. 120, 72-78 (2003).
- [4]. K. Yamamoto, M. Yamaguchi, F. Miyamaru, M. Tani, M. Hangyo, T. Ikeda, A. Matsushita, K. Koide, M. Tatsuno, and Y. Miyami, Jpn. J. Appl. Phys., Part 2 43, L414-L417 (2004).
- [5]. K. Kawase, Y. Ogawa, and Y. Watanabe, Opt. Express 11, 2549-2554 (2003).
- [6]. M. Frisch et al, GAUSSIAN 09 (Revision D. 01), Gaussian, Inc., Pittsburgh PA, 2013.
- [7]. Matthew D. King and Timothy M. Korter, J. Phys. Chem. A 115, 14391-14396 (2011).