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Intermolecular vibrational modes and H-bond interactions in crystalline urea investigated by terahertz spectroscopy and theoretical calculation

Yonghong Zhao [a,b], Zhi Li [a,c,*], Jianjun Liu [b,e], Cong Hu [b], Huo Zhang [a], Binyi Qin [a], Yifang Wu [d]

[a] School of Mechano-Electronic Engineering, Xidian University, Xi'an, Shanxi 710126,China
[b] Guangxi Key Laboratory of Automatic Detecting Technology and Instruments, School of Electronic Engineering and Automation, Guilin University of Electronic Technology, Guilin, Guangxi 541004, China
[c] Guilin University Of Aerospace Technology, Guilin, Guangxi 541004, China
[d] Department of Chemistry and Chemical Engineering, Heze University, Heze, Shandong 274015, China
[e] School of Electronic Information Engineering, Yangtze Nomal University, Chongqing 408100, China

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ABSTRACT

The characteristic absorption spectra of crystalline urea in 0.6–1.8 THz region have been measured by terahertz time-domain spectroscopy at room temperature experimentally. Five broad absorption peaks were observed at 0.69, 1.08, 1.27, 1.47 and 1.64 THz respectively. Moreover, density functional theory (DFT) calculation has been performed for the isolated urea molecule, and there is no infrared intensity in the region below 1.8 THz. This means that single molecule calculations are failure to predict the experimental spectra of urea crystals. To simulate these spectra, calculations on a cluster of seven urea molecules using M06-2X and B3LYP-D3 are performed, and we found that M06-2X perform better. The observed THz vibrational modes are assigned to bending and torsional modes related to the intermolecular H-bond interactions with the help of potential energy distribution (PED) method. Using the reduced-density-gradient (RDG) analysis, the positions and types of intermolecular H-bond interactions in urea crystals are visualized. Therefore, we can confirm that terahertz spectroscopy can be used as an effective means to detect intermolecular H-bond interactions in molecular crystals.

1. Introduction

Intermolecular interactions determine physical and chemical properties of a broad class of important systems such as liquids, solutions and molecular solids [1]. In particular, the hydrogen bond (H-bond),one of the most fundamental types of intermolecular interactions, has long attracted considerable attention due to their intriguing molecular architectures and practical applications in chemistry, biology material science, and so on [2–6]. The graphical analysis containing Hirshfeld surfaces analysis [7,8] and reduced density gradient (RDG) analysis [9] has been performed to reveal the nature of intermolecular interactions. Through these analysis methods, the positions and the strengths of intermolecular interactions were visualized.

Time-domain terahertz spectroscopy (THz-TDS) is a vibrational spectroscopic technique has been established as a powerful analytical tool for the detection of noncovalent interactions, such as H-bond interactions. Analytical applications of THz-TDS include discrimination of chiral solids [10], study of structurally similar cocrystals [11], probing noncovalent interactions in biomolecular crystals [12] and investigations into intermolecular and long-range intramolecular interactions within biological materials, such as proteins and DNA [13,14]. In this way, THz-TDS acts as an excellent method for probing intermolecular interactions, such as hydrogen bonds in solid state materials.

To better understand the molecular origins of observed spectral features, density functional theoretical (DFT) calculation is attractive as an effective tool to assign vibrational absorption peaks arising from intra- and intermolecular motions in the THz region. Though DFT calculation provides reliable predictions for many properties of various molecular solids and has an excellent agreement with experimental data, it is well known that pure DFT calculation does not describe a noncovalent interaction such as hydrogen bonding and van der Waals interaction [15]. M06-2X, a new hybrid meta-GGA exchange-correlation functional, developed by Zhao and coworkers [16] is recommended for the study of noncovalent interactions [17]. Moreover, when the empirical dispersion corrections evaluated with the scheme developed by Grimme and coworkers [18,19] are added to the energies calculated with popular functionals (such as B3LYP, BLYP, and so on), the performance of many popular functionals in describing the non-covalent interactions is substantially improved [20,21]. Thereby the peak-assignment of THz spectrum has been excellently improved.

In this study, we report the experimental THz absorption spectra of urea crystals from 0.6 to 1.8 THz at room temperature. Urea is an organic

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[*] Corresponding author at: School of Mechano-Electronic Engineering, Xidian University, Xi'an, Shanxi 710126, China.
E-mail address: guet.lizhi@yahoo.com (Z. Li).

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compound with the chemical formula NH_2CONH_2, and molecular graph is shown in Fig. 1(a), where two NH_2 groups are linked by one C═O functional group. Urea crystallizes in the $P - 42_1$ m space group with an tetragonal cell containing four molecules in the unit cell (as shown in Fig. 1(b)) [22]. Urea, as a small, planar, bifunctional molecule with four N—H hydrogen-bond donors and one oxygen fourfold hydrogen-bond acceptor, has been utilized in supramolecular chemistry [23], crystal engineering [24,25], and pharmaceutical industry [26,27]. Recently, THz absorption spectra of urea, uracil and their mixtures were studied by Jingqi Yang et al., and no obvious absorption peak of urea was observed in the range of 0.2–2 THz [28].As far as we know, there is no studies of the intermolecular interactions in urea crystals by the THZ-TDS. We also performed DFT calculation for the isolated urea molecule and calculations using M06-2X and B3LYP-D3 functionals for the cluster of seven urea molecules to predict the observed THz spectra. Our calculations clearly show there are intermolecular H-bond interactions in urea crystals, and all THz absorption peaks arising from these interactions. Based on the calculation of the potential energy distributions (PED) using Vibrational Energy Distribution Analysis Program (VEDA 4xx) [29], most observed vibrational modes were assigned accurately. To reveal the nature of the intermolecular H-bond interactions in urea crystals, we performed RDG analysis for the cluster of seven urea molecules. In this way, the positions and the types of intermolecular H-bond interactions in urea crystals were visualized.

2. Experimental and Theoretical Methods

2.1. Sample Preparation

Urea was purchased from Macklin Corporation (Shanghai, China) with purity of 99.0%, and was used without further purification. After dried at 50 °C for at least 1 h to remove water using a vacuum drying oven, urea was further grounded into fine powders using a mortar and pestle. Then the powders were pressed to the circular sheet approximately 1 mm thick by applying the pressure of approximate 6 tons. To reduce the influential error caused by thickness measuring, we adopt Absorbance, a dimensionless relative amount that indicates material's absorption levels, as the reference variable of the spectra [30].

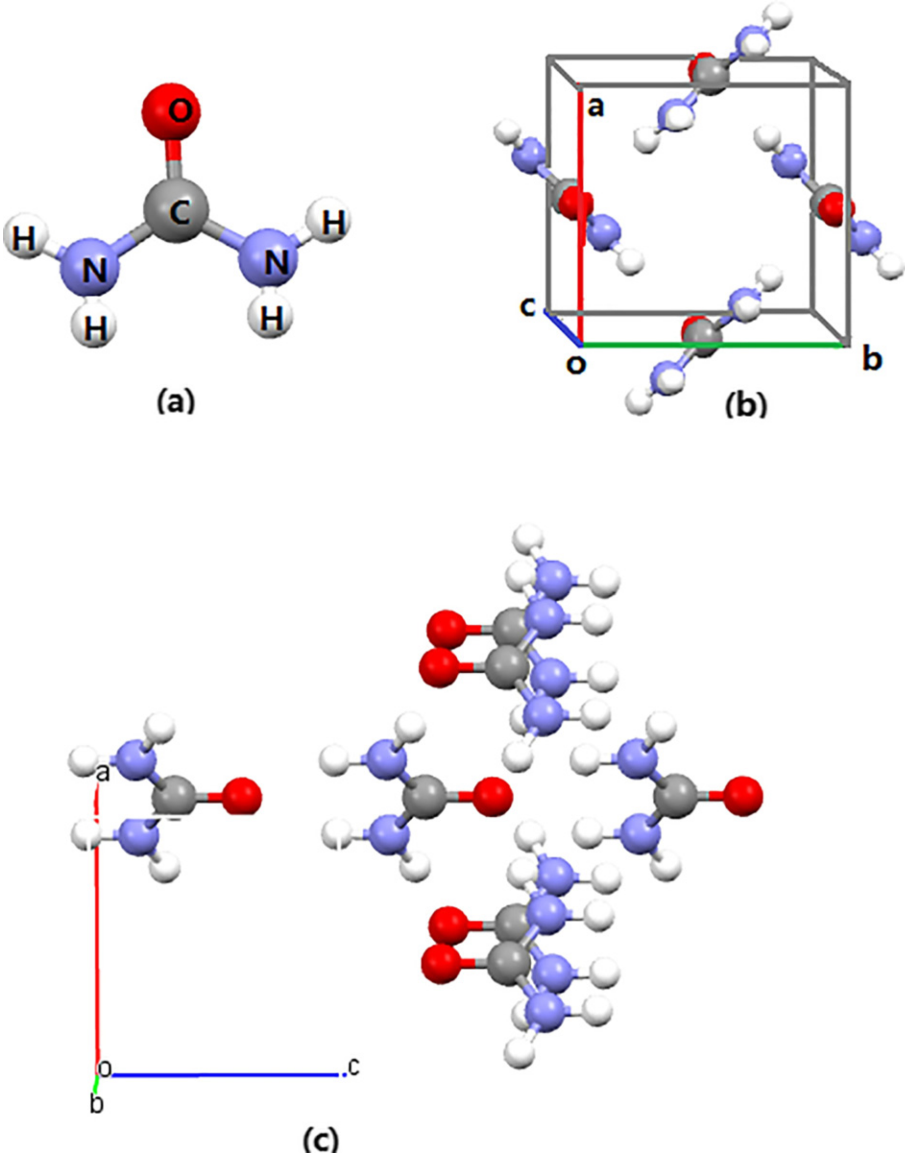

Fig. 1. (a) Labeled urea molecule. (b) Arrangement of molecules in the urea unit cell. (c) Urea crystalline environment modeled with a single urea surrounded by its six nearest neighbors with the geometry of the atoms taken from the known crystal structure of urea.