

The optical properties of dinitrobenzoic acid isomers in the terahertz and infrared regions

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Abstract: The absorption spectra of four dinitrobenzoic acid isomers were acquired over the range of 0.3 ~ 2.2 THz using a terahertz time-domain spectroscopy (THz-TDS) system and over the range of 1 400 ~ 1 800 cm^{-1} using a Fourier transform infrared spectrometer (FTIR). These isomers generate very similar IR spectra but there are substantial differences in the THz region. Vibrational spectra were simulated using density functional theory and the results of these calculations explain the differences and similarities in both the THz and FTIR spectra. THz-TDS technique appears to be a powerful means of identifying isomers in the pharmaceutical and chemical industries.

Key words: isomers, absorption spectra, terahertz time-domain spectroscopy, infrared spectrometer, density functional theory

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二硝基苯甲酸同分异构体的太赫兹与红外光谱特性

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摘要: 利用太赫兹时域光谱系统(THz-TDS)和傅里叶变换红外光谱仪(FTIR)分别研究了2,4-,2,5-,3,4-,3,5-二硝基苯甲酸的吸收谱。实验结果表明,4种同分异构体的吸收光谱在红外波段(1 400 ~ 1 800 cm^{-1})表现出相似性,而在太赫兹波段(0.3 ~ 2.2 THz)却存在非常明显的区别。利用密度泛函理论(DFT)对4种物质的吸收频谱进行计算,并根据计算结果对吸收光谱的相似性和差异性进行解释。太赫兹时域光谱技术为鉴别物质的同分异构体提供了一种可行的手段。

关键词: 同分异构体;吸收谱;太赫兹时域光谱;红外光谱仪;密度泛函理论

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Introduction

Dinitrobenzoic acid is one of the most important organic synthesis intermediates, and is widely used in the pharmaceutical and chemical industries. Due to the possible variations in the relative positions of the carboxyl and nitro groups on the benzene ring, this compound has a series of isomers, each with different properties and applications. As an example, 2,4-dinitrobenzoic acid is an important pharmaceutical intermediate that is often employed in the synthesis of antibacterials, as well as in

clinical work and medical research. In contrast, 3,5-dinitrobenzoic acid is typically used to synthesize intermediates for dyes and liquid crystals, such as amidotrizoic acid and 3,5-diaminobenzoic acid. So far, there are various methods have been explored to identify materials, such as chromatography, near-infrared and Raman spectroscopy^[1-2]. However, it is difficult to realize fast and nondestructive detection. Therefore, rapidly and accurately identifying the different isomers of dinitrobenzoic acid prior to use is of great importance.

Terahertz time-domain spectroscopy (THz-TDS) is a novel spectral technique that has become increasingly

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popular since the 1990s. Over the past ten years in particular, due to collective nature modes of most bio-molecules are located in THz range, THz-TDS has been applied in such fields as pharmaceutical chemistry, biomedical engineering and security^[3-9]. THz-TDS has also become a promising candidate for the characterization of materials, since this technique is highly sensitive to the conformations and structures of molecules^[10-14], and significant research has been performed to assess the identification of isomers by THz-TDS^[15-16]. Zheng *et al.* successfully identified benzene-1, 2-diol, benzene-1, 3-diol and benzene-1, 4-diol using THz absorption spectra^[17], while Du *et al.* investigated the effects of positional isomerism in dihydroxybenzoic acids^[18]. Dash *et al.* demonstrated that the THz absorption spectra of cyanobenzaldehyde isomers exhibit several distinct resonance peaks in the range from 2 to 21 THz^[19]. However, the optical properties of the dinitrobenzoic acid isomers have never been systematically investigated in the THz and infrared (IR) regions, even though such analyses would improve our understanding of the variations in the optical spectra of isomers.

In the present work, the far-IR absorption spectra of dinitrobenzoic acid isomers were obtained using THz-TDS at room temperature. The experimental results show that these isomers generate different characteristic absorption peaks in 0.3 ~ 2.2 THz region, demonstrating that THz-TDS is an excellent tool for identifying the isomers of dinitrobenzoic acid. In addition, we investigated the absorption spectra of these isomers using an IR spectrometer over the 1 400 ~ 1 800 cm^{-1} range, which shows similar properties. At the same time, theoretical calculations based on density functional theory (DFT) were also carried out to assist in understanding the origins of the vibrational modes. The results of these calculations showed good agreement with the experimental data. This work has therefore provided an effective means of investigating and identifying the isomers of dinitrobenzoic acid.

1 Experiment and simulation details

1.1 Sample description

The chemical structures of the four dinitrobenzoic acid isomers investigated in this work are shown in Fig. 1. Quantities of 2,4-dinitrobenzoic acid (CAS-number 610-30-0), 2,5-dinitrobenzoic acid (610-28-6), 3,4-dinitrobenzoic acid (528-45-0) and 3,5-dinitrobenzoic acid (99-34-3), all analytical reagent purity ($\geq 98\%$), were purchased from J&K Scientific Ltd. and used without further purification. The reason of the missing 2,3-dinitrobenzoic acid (15147-64-5) and 2,6-dinitrobenzoic acid (603-12-3) is that they are synthesized abortively. Each isomer, as a powder, was mixed with polyethylene at a mass ratio of approximately 1:2 and then formed into smooth pellets, 0.84 ~ 0.90 mm thick and 13 mm in diameter, by applying a pressure of 3.8 MPa in a press unit for 3 min. The resulting discs were extracted and sealed in plastic while awaiting for analysis.

1.2 Experimental setups

The THz spectra of the dinitrobenzoic acid isomers were acquired using a standard transmission-type THz-TDS system over the range of 0.3 to 2.2 THz at room

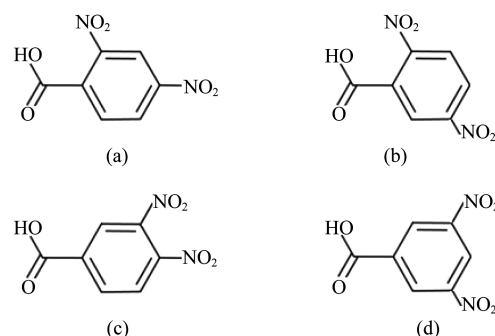


Fig. 1 Chemical structures of four different dinitrobenzoic acid isomers resulting from variations in the positions of the nitro groups in the benzoic acid structure: (a) 2,4-dinitrobenzoic acid, (b) 2,5-dinitrobenzoic acid, (c) 3,4-dinitrobenzoic acid, and (d) 3,5-dinitrobenzoic acid

图1 (a)2,4-二硝基苯甲酸, (b)2,5-二硝基苯甲酸, (c)3,4-二硝基苯甲酸和(d)3,5-二硝基苯甲酸的分子结构

temperature, as depicted in Fig. 2. The details of this instrumentation have been described previously^[20]. The entire apparatus was placed in a sealed chamber purged with dry nitrogen to eliminate any effects of atmospheric water vapor. During each experimental trial, the relative humidity in the chamber was maintained at less than 4.0%.

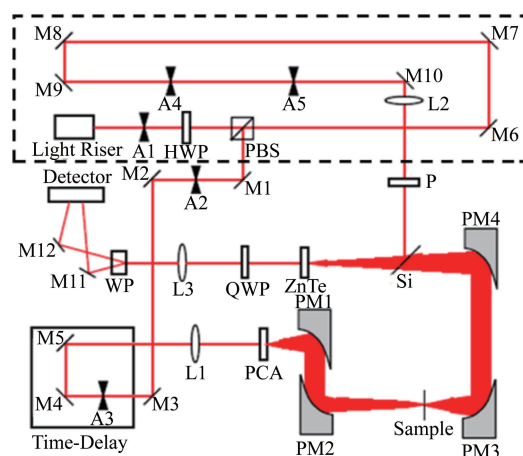


Fig. 2 Schematic of the standard transmission-type THz-TDS instrumentation

图2 透射式太赫兹时域光谱系统的光路示意图

In addition, a Fourier transform IR (FTIR) spectrometer was used to acquire the IR spectra of the isomers in the range from 400 cm^{-1} to 4 000 cm^{-1} . Combined with the following computational data, the properties of dinitrobenzoic acid isomers over the range of 1 400 ~ 1 800 cm^{-1} (42 ~ 54 THz) are the investigated focus of this work.

1.3 Theoretical calculations

Using the Gaussian 03 software package, in conjunction with the 6-31G basis set at the Becke-3-Lee-Yang-Parr (B3LYP) level, we employed DFT calcula-

tions to obtain the full geometric optimization of the spatial structures of the isomers. Fig. 3 shows the predicted molecular structures of these compounds following the geometric optimization. We also calculated the vibrational frequencies of each isomer on the same basis. The minimum energy structures were confirmed by the absence of imaginary frequencies when analyzing the vibrational spectra.

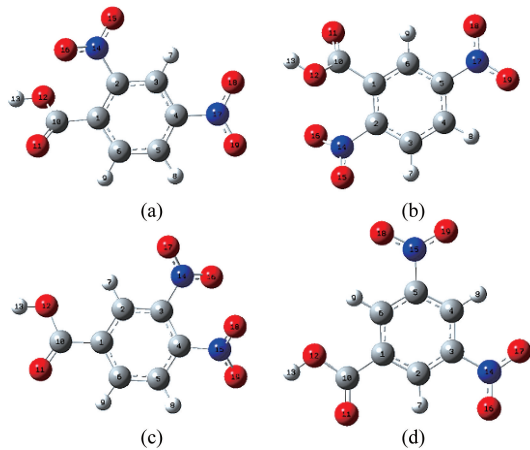


Fig. 3 Molecular structures of (a) 2,4-dinitrobenzoic acid, (b) 2,5-dinitrobenzoic acid, (c) 3,4-dinitrobenzoic acid, and (d) 3,5-dinitrobenzoic acid after geometric optimization

图3 (a)2,4-二硝基苯甲酸, (b)2,5-二硝基苯甲酸, (c)3,4-二硝基苯甲酸和(d)3,5-二硝基苯甲酸经几何优化之后的分子结构

2 Results and discussions

2.1 The terahertz absorption spectra of the isomers

The transmission spectra of the four isomers were obtained using THz-TDS over the frequency range of 0.3 to 2.2 THz at room temperature under nitrogen, and the corresponding absorption spectra are presented in Fig. 4. There are evidently significant differences among these spectra, both in the positions of the peaks and the general shape of the spectra, which may result from variations in the molecular structures of the isomers.

Table 1 The experimentally-obtained absorption peaks of the isomers of dinitrobenzoic acid

表1 二硝基苯甲酸4种同分异构体的吸收峰位置

Sample	2,4-	2,5-	3,4-	3,5-
Frequency/THz	0.776	1.055	1.025	0.542
	1.005	1.600	1.714	0.938
	1.421			1.392
	1.816			

Table 1 lists the spectral peaks as an aid to analyze the experimental results. Each isomer exhibits differences in the quantities and positions of the main peaks, as well as in the relative intensities of the peaks. The distinct differences among these THz spectra suggest that these isomers possess different optical properties and will have varying applications.

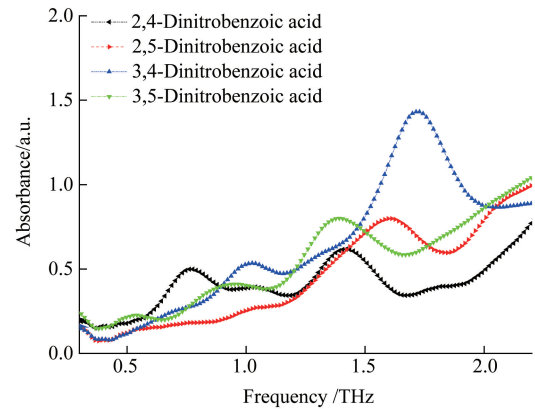


Fig. 4 The THz absorption spectra of 2,4-dinitrobenzoic acid (black line), 2,5-dinitrobenzoic acid (red line), 3,4-dinitrobenzoic acid (blue line) and 3,5-dinitrobenzoic acid (green line)

图4 二硝基苯甲酸4种同分异构体的THz吸收谱

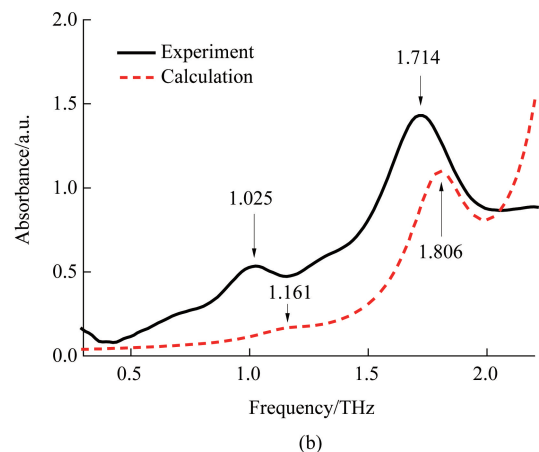
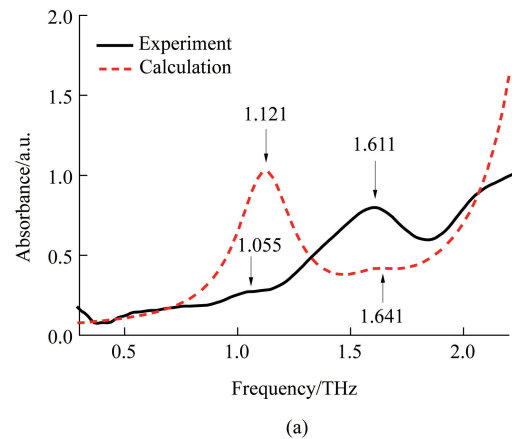


Fig. 5 Comparison of the experimental and theoretical spectra of (a) 2,5-dinitrobenzoic acid and (b) 3,4-dinitrobenzoic acid

图5 (a) 2,5-二硝基苯甲酸和(b)3,4-二硝基苯甲酸实验测得的吸收谱与计算所得吸收谱的比较

To better understand the origin of these THz resonances and the effects of variations in the nitro group positions, we calculated the vibrational frequencies of these isomers with the aid of the Gaussian View 3.09 software

package, using the optimized structures shown in Fig. 3, without applying a scaling factor. A comparison of the experimental and theoretical results is provided in Fig. 5. It can be seen that there is a close match at various frequencies in the case of the 2,5-dinitrobenzoic acid and 3,4-dinitrobenzoic acid. Taking the 2,5-dinitrobenzoic acid as an example, the calculated peak at 1.641 THz corresponds to an absorption peak at 1.611 THz in the experimental results. The matching frequency at 1.641 THz is caused by the relative out of plane wagging vibrations of the carboxylic group located at the first carbon atom and the nitro group located at the second, fifth carbon atom, with respect to the benzene ring. The calculation results also indicate that the absorption peaks in the THz region result from the collective vibrational modes accompanied by torsion of the entire molecule. The closely matching resonance frequencies of the dinitrobenzoic acid isomers and the possible origins of these resonances are summarized in Table 2. Here it is evident that minor changes in the chemical structures and bond characteristics result in variations in the resonance frequencies of the isomers.

2.2 The IR absorption spectra of the isomer

The above calculations also suggested that these isomers should generate highly similar spectra in the IR region (1 400 to 1 800 cm^{-1}), as shown in Fig. 6. We found that the isomers all produced three distinct absorption peaks located at approximately 1 490 (1 467-1 492), 1 540 (1 529-1 539) and 1 740 (1 734-1 740) cm^{-1} , primarily resulting from the stretching vibrations of N=O, C=C and C=O bonds. As an example, the calculated vibrational modes of 2,4-dinitrobenzoic acid at 1 492, 1 538 and 1 740 cm^{-1} are shown in Fig. 7.

To verify the accuracy of the calculated results, the IR spectra of the isomers were acquired using FTIR over the range of 1 400 to 1 800 cm^{-1} . As shown in Fig. 8, the isomers do produce three distinct absorption peaks located at approximately 1 490 (1 472-1 491), 1 540 (1 536-1 551) and 1 720 (1 705-1 722) cm^{-1} , respectively. Due to the similarity of the molecular structures, both the theoretical and experimental results therefore indicate that these isomers present highly similar optical properties or consistency of the spectrum in the IR region.

2.3 Discussions

From the experimental and simulated data, it can be seen that the various isomers of dinitrobenzoic acid ex-

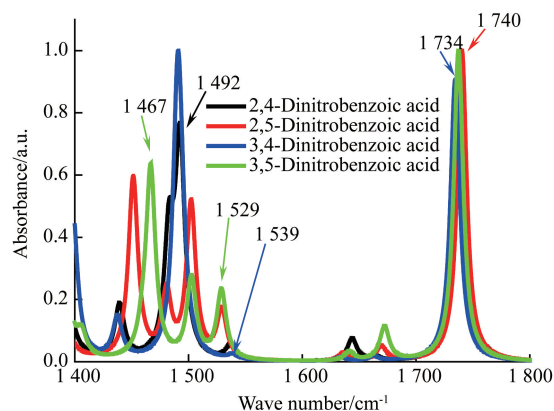


Fig. 6 The theoretical IR spectra of 2,4-, 2,5-, 3,4- and 3,5- dinitrobenzoic acid

图6 量化计算得到的2,4-, 2,5-, 3,4-和3,5-二硝基苯甲酸的红外谱

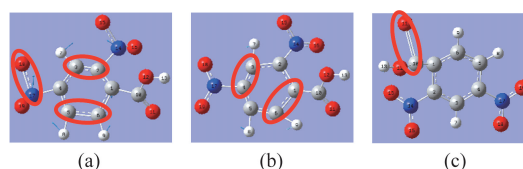


Fig. 7 Calculated vibrational modes of 2,4-dinitrobenzoic acid at (a) 1 492 cm^{-1} , (b) 1 538 cm^{-1} and (c) 1 740 cm^{-1}

图7 量化计算所得的2,4-二硝基苯甲酸在(a)1 492 cm^{-1} , (b)1 538 cm^{-1} 和(c)1 740 cm^{-1} 处的振动模式

hibit similar optical properties in the IR region but substantial differences in the THz range. The theoretical results confirm that variations in the collective vibrational modes, associated with relative wagging motions of the benzene ring and its substituent groups, lead to the differences in the THz region. Due to variations between isomers in the relative positions of the carboxyl and nitro groups, these collective vibrational modes change significantly. In the IR region, however, the absorption peaks of the isomers result from the stretching vibrations of N=O, C=C, and C=O bonds and so are all very similar to one another. Therefore, variations in the optical properties of the isomers resulting from relatively minor changes in structure between isomers can be studied more precisely using THz-TDS.

Table 2 Assignments of observed characteristic absorption frequencies of the isomers of dinitrobenzoic acid

表2 观察到的2,5-和3,4-二硝基苯甲酸的特征吸收频率所对应的分子振动模式分析

Sample	Experiment Frequency/THz	B3LYP/6-31G Frequency/THz	Assignment
2,5-	1.055	1.121	relative wagging of the carboxylic group (COOH-) located at the first carbon atom and the nitro group (NO ₂ -) located at the second carbon atom with respect to the benzene ring out of plane
2,5-	1.611	1.641	relative wagging of the carboxylic group (COOH-) located at the first carbon atom and the nitro group (NO ₂ -), respectively, located at the second, fifth carbon atom with respect to the benzene ring out of plane
3,4-	1.025	1.161	relative wagging of the nitro group (NO ₂ -) located at the third, fourth carbon atom with respect to the benzene ring out of plane
3,4-	1.714	1.806	relative wagging of the carboxylic group (COOH-) located at the first carbon atom and the nitro group (NO ₂ -), respectively, located at the third, fourth carbon atom with respect to the benzene ring out of plane

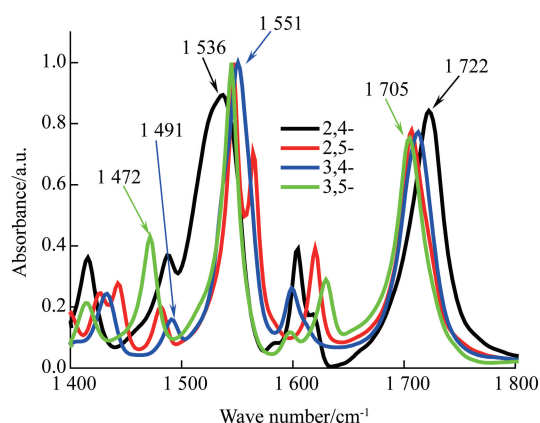


Fig. 8 The experimental IR spectra of 2,4-, 2,5-, 3,4- and 3,5-dinitrobenzoic acid

图8 实验测得的2,4-, 2,5-, 3,4-和3,5-二硝基苯甲酸的红外谱

It is clear that there is a discrepancy between the experimental and calculated results in the two different frequency regions. We have observed that most of the calculated absorption peaks appear slightly red shifted compared with the experimental counterparts. These discrepancies can possibly be attributed to several causes. Firstly, the lower temperature that were applied in the calculations would be expected to shift these peaks to higher frequencies^[21-23]. Secondly, the calculations involved several approximations, such as in the model potential and the assumed molecular geometry, as well as the rigid molecular approximation and the harmonic approximation in the lattice dynamics. These may have led to inaccuracies in the calculated results^[24].

3 Conclusions

We have acquired the THz and IR absorption spectra of four dinitrobenzoic acid isomers using THz-TDS over the range 0.3 to 2.2 THz and FTIR spectroscopy over the range 1 400 to 1 800 cm^{-1} , respectively. Theoretical calculations based on DFT were also carried out to simulate and assign the observed spectral features of the isomers, and reasonable agreement between the experimental and calculated spectra was observed. This investigation has demonstrated that the differences and similarities in the absorption spectra within these two frequency ranges result from the difference and similarity of the molecular structures of the isomers. THz-TDS was found to allow the effective differentiation of the isomers of dinitrobenzoic acid and so shows promise as an effective technique for the identification of these compounds.

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