



Terahertz absorption spectra of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol

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ABSTRACT

The terahertz spectra ($8\text{--}128\text{ cm}^{-1}$) of three structural isomers have been measured using terahertz time-domain spectroscopy at room temperature. Substantial differences among these THz spectra have been found and implied that THz-TDS is an excellent tool to identify isomers. Numerical calculation based on solid-state density functional theory has been carried out and assigned the observed THz features theoretically. Good agreement between the calculated and experimentally measured spectra for benzene-1,2-diol and benzene-1,3-diol has been achieved. According to the calculated results, it is found that the measured THz spectra of these two isomers mainly originate from intermolecular vibrations.

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1. Introduction

It is well known that, isomers can exhibit different physical and chemical properties. This fact indicates the applications of isomeric materials to the production of food and pharmaceuticals deserve special consideration. And also, a fast and effective tool for detecting them is of particular importance. Nowadays, terahertz time-domain spectroscopy (THz-TDS) has become a promising candidate for characterization of materials, since THz spectroscopy has high sensitivity to the conformation and structure of molecules as well as its adjacent environment [1–3]. Recent study has experimentally demonstrated that the isomers' identifications can be done by THz-TDS. However, the origins of the observed spectral features were not specifically discussed in these works due to lack of the appropriate theory and good simulation [4–8] to interpret the obtained spectral features.

As we know, THz spectra may come from various rotational, vibrational and translational modes of molecule, which makes the assignment of specific spectra difficult via the experimental data directly. The first attempt to theoretically interpret the origins of THz spectral features is the density functional theory (DFT) of single molecule, which is popularly used in mid-infrared calculation [9,10]. However, this theory has proven to be an incomplete description of the observed THz spectrum and made it appropriate only for computing intra-molecular modes [11,12] due to lack of the inter-molecular forces consideration. To achieve better understanding of the THz spectral features, new theoretical treatments for both inter- and intra-molecular modes should be developed. Recent researches have shown that solid-state DFT is a powerful

method for reproducing the experimental THz spectral features and assigning the calculated modes to their corresponding experimental features [11–15].

Benzene-1,2-diol (catechol or pyrocatechol), benzene-1,3-diol (resorcinol) and benzene-1,4-diol (hydroquinone), are all positional isomers as they have the same functional groups attached to different positions of benzene ring. Although the THz spectra of α -benzene-1,4-diol and β -benzene-1,4-diol clathrates have been investigated experimentally [16]. To the best of our knowledge, the experimental THz spectra of benzene-1,2-diol and benzene-1,3-diol have not been reported yet. In this Letter, we have experimentally measured the THz absorption spectra ($8\text{--}128\text{ cm}^{-1}$) of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol using THz-TDS. Substantial differences among these isomers in THz region have been found, where characteristic absorption features come primarily from inter- and intra-molecular modes. On the other hand, we use solid-state DFT to theoretically simulate and assign the observed THz spectra of benzene-1,2-diol and benzene-1,3-diol, respectively. Good agreement between the experimental and calculated spectra in terms of both peak positions and intensities has been achieved.

2. Experimental and theoretical methods

In our experiment, THz spectra ($8\text{--}128\text{ cm}^{-1}$) of three isomers, benzene-1,2-diol (catechol or pyrocatechol), benzene-1,3-diol (resorcinol) and benzene-1,4-diol (hydroquinone), were measured using TPS-3000 (TeraView Ltd.) with the spectral resolution of 1.2 cm^{-1} .

Benzene-1,2-diol (catechol, CAS-number 120-80-9) was obtained from Tianjin Kermel Co. Ltd.; benzene-1,3-diol (resorcinol, CAS-number 108-46-3) was purchased from ShangHai Shanpu

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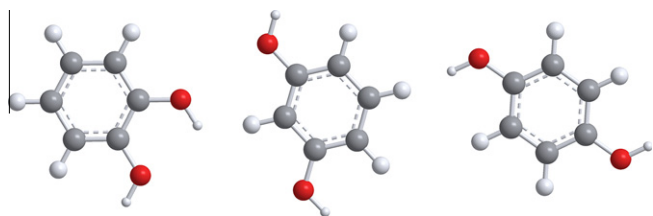


Figure 1. The molecular structures of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol.

Co. Ltd. and benzene-1,4-diol (hydroquinone, CAS-number 123-31-9) was acquired from Sinopharm Chemical Reagent Co. Ltd. All three samples are in analytical reagent (>99%) and used without further purification. The samples were first crushed into fine powder by using mortar and pestle to minimize the particle scattering. Then, three samples in the pure form were compressed into 1.18-mm-thick pellets with the pressure of 600 kg/cm², respectively. Theoretically, the calculation for periodic system was based on the plane-wave density functional methods within the generalized gradient approximation [17,18]. Norm conserving pseudopotentials in the Kleinman–Bylander form [19] were used and all calculations employed the Perdew–Burke–Ernzerhof (PBE) functional [20]. The total energy was converged to 10^{−8} eV/atom and the maximum forces between atoms were less than 10^{−5} eV/Å. A plane wave cutoff energy was used at 1200 eV. Brillouin zone integrations were performed with the Monkhorst–Pack method using the *k*-point mesh separated by 0.05 Å^{−1}. The Γ -point was used to calculate vibrational frequency. The IR intensity for normal mode was calculated from the oscillator strength to give the effective charges and the normal mode eigenvectors. It is worthy to note that atomic coordinates were optimized under the fixed unit cell taken from experimental measurements. Specifically, crystal cell parameters of benzene-1,2-diol were taken from Ref. [21]: space group P21/c (*Z* = 4), *a* = 10.082 Å, *b* = 5.518 Å, *c* = 10.943 Å, α , γ = 90.0°, β = 118.53°. Crystal cell parameters of benzene-1,3-diol were taken from Ref. [22]: space group Pna21 (*Z* = 4), *a* = 10.530 Å, *b* = 9.530 Å, *c* = 5.60 Å, α , β , γ = 90.0°. The molecular structures of these isomers are presented in Figure 1.

3. Results and discussion

Figure 2 shows the THz absorption spectra (8–128 cm^{−1}) of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol at room temperature. Distinct differences among these THz spectra can be seen, indicating that THz spectroscopy is an excellent tool for the isomers identification.

Table 1 lists spectral peaks of these isomers one by one in the range of 8–128 cm^{−1}. Specifically, three discernible THz spectral features of benzene-1,2-diol are shown at the following frequencies: 63.7, 81.5 and 112.0 cm^{−1}. These spectral peaks exhibit experimental intensities ranging from high to low. And also, a shoulder peak at 66.0 cm^{−1} can be observed. For benzene-1,3-diol, six features have been observed in the absorption spectrum at the following frequencies: 54.7, 57.8, 61.0, 80.0, 98.5 and 111.0 cm^{−1}. The most prominent spectral feature lies at 111.0 cm^{−1}, a low-intensity spectral feature is presented at 80.0 cm^{−1}, a shoulder feature can be observed at 54.7 cm^{−1}, and the remaining three features belong to the medium-intensity types. For benzene-1,4-diol, twelve obvious absorption features are observed in the spectrum at 28.3, 32.6, 38.7, 51.2, 54.9, 61.0, 69.2, 75.4, 83.6, 98.3, 103.8, and 114.0 cm^{−1}. The highest-intensity feature lies at 98.3 cm^{−1} and two low-intensity absorptions appear at 28.3 and 32.6 cm^{−1}. The two weak shoulders locate at 51.2 and 103.8 cm^{−1}, with the central peak at 54.9 and 98.3 cm^{−1}, respectively. The other seven features can be easily recognized due to their medium intensity.

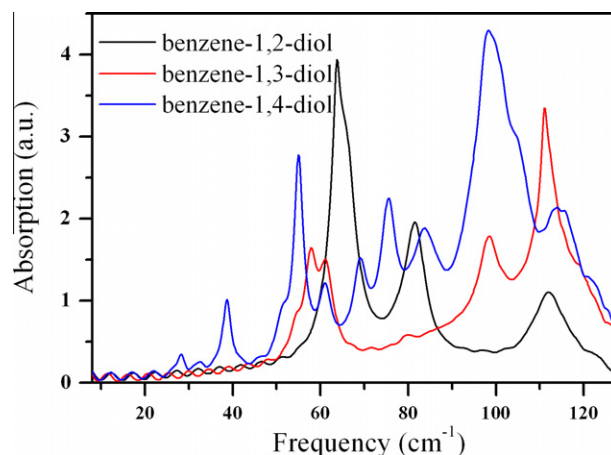


Figure 2. The measured absorption spectra of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol in the range of 8–128 cm^{−1}.

Table 1

The experimental frequencies (cm^{−1}) of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol.

Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol
63.7	54.7 ^a	28.3
66.0 ^a	57.8	32.6
81.5	61.0	38.7
112.0	80.0	51.2 ^a
	98.5	54.9
	111.0	61.0
		69.2
		75.4
		83.6
		98.3
		103.8 ^a
		114.0

^a Denoted as the shoulder peak.

As seen in Figure 1, there are 14 atoms in a single molecule of these isomers. According to X-ray crystallography, benzene-1,2-diol has C_s molecular symmetry while benzene-1,3-diol and benzene-1,4-diol have C_{2v} and C_{2h} molecular symmetries, respectively. Because the calculated lowest-frequency intra-molecular modes are higher than 128 cm^{−1}, we can infer that the isolated-molecule modes have no contributions in our interested region. On the other hand, it is known that hydrogen bonding and other inter-molecular interactions of molecules within the different solid structures may cause variable numbers of inter-molecular modes in the THz region. For our molecular system, there is strong evidence from X-ray crystallography that the crystal structures of these isomers are substantially different. Specifically, unit cell of benzene-1,2-diol is monoclinic with C_{2h} crystal symmetry (*Z* = 4) [21] while benzene-1,3-diol is orthorhombic with C_{2v} crystal symmetry (*Z* = 4) [22] and benzene-1,4-diol is hexagonal with S₆ crystal symmetry (*Z* = 54) [23], respectively. Additionally, the hydrogen bond networks of these isomers in unit cell are different from each other, as seen in Figure 3. It is found that THz spectrum of benzene-1,4-diol has the most absorption features among these isomers, which may partially be originated from that the most molecules and intermolecular hydrogen bonds in the unit cell of benzene-1,4-diol.

A crystal benzene-1,2-diol unit cell containing 4 molecules with 56 atoms leads to 165 optical modes: 40B_u + 41A_u + 42A_g + 42B_g. Of these modes, 144 belong to intra-molecular vibrations while the remaining 21 (4B_u + 5A_u + 6A_g + 6B_g) can be attributed to inter-molecular phonons. Since the point group of benzene-1,2-diol unit cell is in C_{2h} symmetry, vibrational modes with A_u and B_u symmetries are only infrared active.

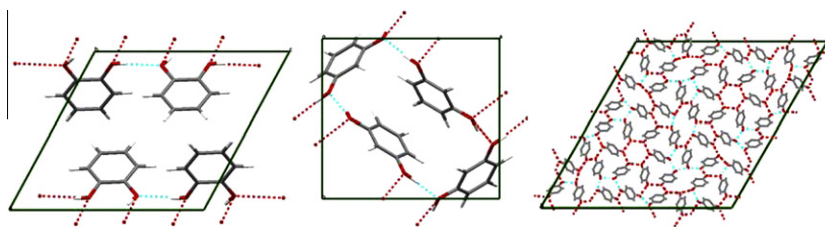


Figure 3. Molecular arrangement and crystal packing of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol. The left-hand panel is a view along the crystalline *b* axis, the mid- and the right-hand ones are the views along the crystalline *c* axis. The green and dashed lines show the hydrogen bonds between molecules in the unit cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Figure 4 shows the result of the THz experimental spectrum and compares with the theoretical data. It is evident that a very good reproduction of the observed THz spectral features has been achieved. On the basis of the simulated spectrum in Table 2, a total of eight vibrational modes are obtained in the range of 8–128 cm^{-1} . Specifically, the two calculated modes at 55.9 and 61.5 cm^{-1} are related to the feature observed at 63.7 cm^{-1} in the experimental spectrum. The calculated mode at 63.7 cm^{-1} corresponds to the experimental shoulder at 66.0 cm^{-1} . It is worthy noting that measurement in low temperature or with the higher frequency resolution may help to observe this shoulder peak obtained at room temperature easily [24,25]. The feature at 81.5 cm^{-1} in our experiment is primarily assigned to the calculated modes at 83.8 and 89.0 cm^{-1} . Two calculated modes at 113.7 and 117.2 cm^{-1} are likely responsible for the experimental features at 112.0 cm^{-1} . This good-to-excellent agreement between solid-state DFT and experiment in the case of benzene-1,2-diol suggests that non-covalent inter-molecular forces are the key to generate THz spectrum of solid-state material.

Even though, it is clear that there is a discrepancy between the experimental and calculated data. For example, the calculated mode at 101.7 cm^{-1} is located in a region where no absorption is observed. The conceivable explanation for this is that this mode may coincide with the vibrational modes contributing to the experimental peak at 112.0 cm^{-1} . Table 2 shows the descriptions for each vibrational mode. Descriptions of each mode were made by visual inspection

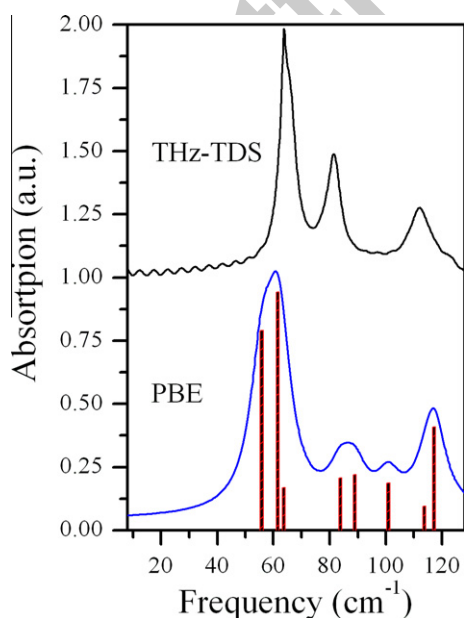


Figure 4. The experimental and calculated THz spectra of benzene-1,2-diol in the range of 8–128 cm^{-1} . An empirical full-width half-maximum of 9 cm^{-1} Lorentzian line shape has been convolved with the theoretical data for visual comparison.

Table 2

The experimental and calculated frequencies (cm^{-1}) of benzene-1,2-diol.

Experiment RT	Calculation	
	PBE	Description ^b
63.7	55.9 (3.59) ^a	ET along <i>a</i> axis
	61.5 (4.30)	ER along <i>b</i> axis
66.0	63.7 (0.77)	ER along <i>c</i> axis
81.5	83.8 (0.94)	ER along <i>b</i> axis
	89.0 (1.00)	ER along <i>b</i> axis
	101.7 (0.85)	ER along <i>c</i> axis
112.0	113.7 (0.43)	ER along <i>a</i> axis
	117.2 (2.41)	ER along <i>b</i> axis

^a Infrared intensities (km/mol) are shown in parentheses.

^b ET, external translation; ER, external rotation.

of the atomic displacements and are based on the most significant contributions to the vibrational mode character. Since the normal modes have been assigned to features seen in the experimental results, the nature of the origins of these measured spectral features can be attributed to the inter-molecular vibrations.

A crystal benzene-1,3-diol unit cell containing 4 molecules with 56 atoms leads to 165 optical modes: $41B_1 + 41B_2 + 41A_1 + 42A_2$. Of these modes, 144 belong to intra-molecular vibrations while the remaining 21 ($5B_1 + 5B_2 + 5A_1 + 6A_2$) can be attributed to inter-molecular phonons. Since the point group of benzene-1,3-diol is in C_{2v} symmetry, the modes of A_1 , B_1 and B_2 symmetries would be infrared active. The comparison between the experimental and solid-state calculated THz spectra of benzene-1,3-diol is shown in Figure 5. It can be seen that, the simulation provides a reasonable agreement to the experimental data.

Based on the calculated results in Table 3, five predicted modes were assigned to six experimental features. However, three calculated modes at 70.8, 104.8 and 124.9 cm^{-1} are too weak to be visible in Figure 5. Specifically, the experimental feature at 61.0 cm^{-1} corresponds directly to the calculated modes at 65.4 cm^{-1} and the weak absorption at 80.0 cm^{-1} corresponds to the calculated mode at 77.6 cm^{-1} . Besides, the absorptions at 98.5 and 111.0 cm^{-1} in the experimental spectrum can be primarily assigned to the calculated mode at 100.9 and 118.1 cm^{-1} , respectively. Although the PBE function obtains an overall high quality of spectral reproduction across the interested region, there is still disagreement in the number of observed absorptions versus calculated modes. For example, there is a question on the location or intensity of the calculated mode at 91.7 cm^{-1} , which is no absorption observed in our experimental spectrum. The conceivable explanation for this is that the mode may coincide with the vibrational modes contributing to the experimental peak at 98.5 cm^{-1} , or it is possible that the calculated intensity is overestimated by the DFT calculations. It is worthy to note that this phenomenon can be found in other solid-state calculations [26,27]. Additionally, there are three experimental spectral peaks shown in the range of 50–70 cm^{-1} , while the PBE function only presents one large peak at 65.4 cm^{-1} . The

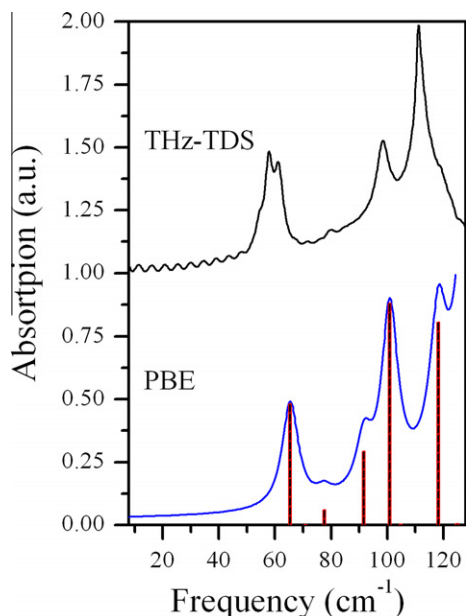


Figure 5. The experimental and calculated THz spectra of benzene-1,3-diol in the range of 8–128 cm^{-1} . An empirical full-width half-maximum 7 cm^{-1} of Lorentzian line shape has been convolved with the theoretical data for visual comparison.

Table 3

The experimental and calculated frequencies (cm^{-1}) of benzene-1,3-diol.

Experiment	Calculation	
RT	PBE	Description ^b
54.7		
57.8		
61.0	65.4 (3.49) ^a	ET along c axis
	70.8 (0.01)	ET along c axis
80.0	77.6 (0.36)	ET along a axis
	91.7 (1.76)	ET along b axis
98.5	100.9 (5.93)	ER along b axis
	104.8 (0.02)	ER along a axis
111.0	118.1 (4.47)	ER along b axis
	124.9 (0.03)	ER along c axis

^a Infrared intensities (km/mol) are shown in parentheses.

^b ET, external translation; ER, external rotation.

most possible explanation may be due to the inability of the theoretical modeling to accurately estimate the inter-molecular non-covalent interactions.

The comparison between the experimental result and simulated data is shown in Table 3, and the origins of these calculated features are listed one by one. Since the normal modes have been assigned to features seen in the experimental results, the nature of the origins of the measured four spectral features can be attributed to the inter-molecular vibration. Besides, we experientially predict that the two measured features at 54.7 and 57.8 cm^{-1} may come from intermolecular vibrations since the peak positions of the two spectral features are lower than that of the other four features in the range of 8–128 cm^{-1} . It is worthy noting that this prediction can be sustained by some THz spectral assignments [11,14].

A crystal benzene-1,4-diol unit cell contains 54 molecules [23]. Even converting to a primitive cell, it still has 18 molecules with 753 optical modes: $187\text{E}_u + 188\text{A}_u + 189\text{E}_g + 189\text{A}_g$. Among these modes, 648 modes belong to intra-molecular vibrations while the other 105 ($25\text{E}_u + 26\text{A}_u + 27\text{E}_g + 27\text{A}_g$) come from inter-molecular phonons. Since the point group of benzene-1,4-diol is in S_6 symmetry, only the modes of E_u and A_u symmetries will be infrared active.

However, there are 252 atoms in the unit cell of benzene-1,4-diol, which makes the simulation based on solid-state DFT very hard currently for us due to the huge computational requirement.

4. Conclusions

In conclusion, we have measured the THz spectra of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol by using THz-TDS at room temperature. These isomers can be clearly distinguished by their THz absorption spectra, implying that THz-TDS is a good tool for isomers identification. To understand the origins of these measured THz spectra, solid-state DFT was used to simulate and assign the observed THz features of benzene-1,2-diol and benzene-1,3-diol theoretically. Reasonable agreement between experimental and calculated spectra has been achieved. According to the calculated results, it is found that the observed THz spectra of these two isomers mainly originate from the intermolecular vibrations. As for benzene-1,4-diol, future work may be focused on exploiting the origin of THz spectrum by using solid-state calculation.

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