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Terahertz spectroscopy of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene

Jiaguang Han *, Hui Xu, Zhiyuan Zhu, Xiaohan Yu, Wenxin Li

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, P.O. Box 800-204, Shanghai 201800, PR China

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Abstract

The far-infrared THz spectra of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene have been measured using THz time-domain spectroscopy. The low-energy vibrational modes of measured molecules are discussed based on their characteristic and common features. The complex dielectric functions are obtained. Meanwhile, it is shown that the experimental results can be well fitted by a standard Lorentz model.

1. Introduction

Recently terahertz (THz) technology is becoming an extremely attractive research field and its applications have involved semiconductor, tomographic imaging, label free genetic analysis, cellular level imaging, biological sensing and so on [1,2]. Its applications in probing the low-energy vibrational spectroscopy of materials excite much interest because the vibrational spectroscopy plays a significant role in investigating the thermodynamic properties and structure of molecules [3,4]. Similarly, the low-energy modes is essential for many physical and chemical processes [5].

Generally, for crystalline, the internal motion, intermolecular modes and lattice vibrations contribute to far-infrared (FIR) THz absorption spectrum. The position and strength of low-frequency vibrational spectroscopy are highly sensitive to the conformation and structure of molecule and its environment. As a result, the high sensitivity of FIR THz spectroscopy provides us with a powerful and unique fingerprint to discriminate the conformation of molecules. And these observed fingerprint spectra are useful for medical diagnostics or materials discriminations such as distinction of isomeric conformation [6,7]. In this case, the characteristic absorption spectrum of the sample is an important and direct information. On the other hand, the problem whether the FIR THz spectra of molecules would exhibit some common features also should be considered and studied. Of course this needs to measure FIR THz spectra of many different samples. However, up to date, as we know there are lacking in the experimental data and theoretical studies about this thing. In this Letter, we have performed Terahertz time-domain spectroscopy (THz-TDS) on a series of similar molecules in crystalline form to explore some characteristic and common features of their THz spectra, which are related with their low-energy vibrational modes.

2. Experimental methods and materials

Fig. 1 shows the chemical structures of molecules of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene considered in this work. All molecules in the crystalline phase were purchased from Sigma–Aldrich and used without further purification. The samples were prepared by milling the crystals powder carefully and made into pellets with thickness between 1.1 and 3.0 mm by applying on approximate pressure

* Corresponding author. Fax: +862159553021.
E-mail address: han@sinr.ac.cn (J. Han).

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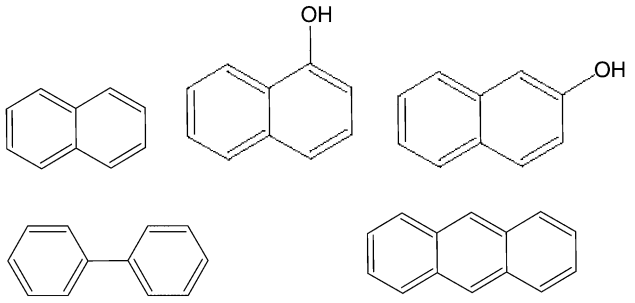

Fig. 1. Chemical structure of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene.

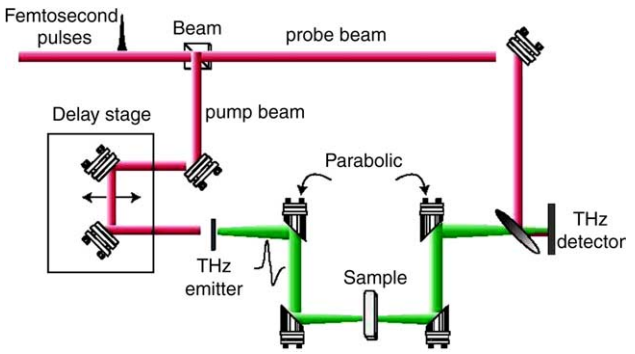

Fig. 2. Experimental setup for THz time-domain spectroscopy.

of 50 MPa with an oil press. All procedures were carried out well in the dark because of light sensitivity of naphthol.

A standard THz-TDS apparatus for FIR transmission measurements is illustrated in Fig. 2. The setup and corresponding experimental data analysis method have been discussed in detail in previous reports [3,6]. In brief, the laser was model-locked Ti: sapphire system that provided 100-fs pulses at a wavelength of 800 nm with average power of 700 mW and a repetition rate of 80 MHz. Pulsed THz radiation was produced by illuminating the GaAs photoconductor antenna and detected in a ZnTe crystal via electro-optical sampling. The used bandwidth of the spectrometer is 0.1–2.2 THz and the spectral resolution is better than 40 GHz. The THz beam path was purged with dry nitrogen in order to minimize the absorption of water vapor.

3. Results and discussion

The power absorption coefficient α and the index of refraction n of the different samples were obtained in the frequency range 0.1–2.2 THz. The collective data below 0.5 THz are not considered due to interference between reflections of the probe pulse inside the sample pellets. A gradual rise of the absorption baseline with increasing frequency results from scattering.

Fig. 3 shows the FIR power absorption coefficient α and the index of refraction n of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene recorded in the range 0.5–2.2 THz. The absorption coefficient is depicted by solid line and the index of refraction is by dash line. Distinct absorption peaks of every samples can be seen. The presence of the absorption features is confirmed by the observation of changes in the refractive index. Firstly, we can find some common information about the vibrational features of the measured molecules. As shown in Fig. 3a, d, e, for naphthalene, biphenyl and anthracene, there are no obvious resonance peaks below 60 cm^{-1} and the characteristic absorptions appear at the frequency above 60 cm^{-1}. For

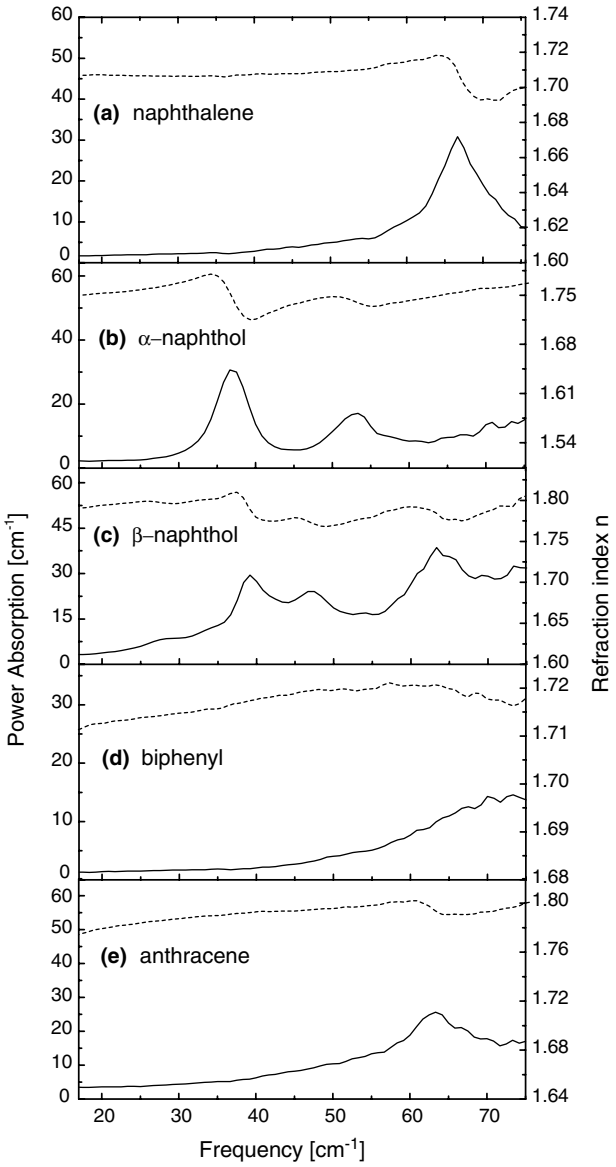

Fig. 3. The measured refractive index n (dash line) and the power absorption coefficient α (solid line) of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene.

these three samples there are no hydrogen bonds. In contrast, we can see from Fig. 3b, c, the marked absorption peaks of α-naphthol and β-naphthol are located between 30 and 60 cm^{-1}. For these two samples there are hydrogen bonds. Therefore the hydrogen bond may be a key factor.

Moreover, a strong and distinct absorption peak simultaneously appears in naphthalene, β-naphthol, and anthracene around 65 cm^{-1}. Why these three different molecules exhibit a so wonderful similar behavior around this frequency and why such a behavior can not be found for α-naphthol? Let us take these common and characteristic features into mind and proceed to the following discussion.

It is known that many factors contribute to the low-frequency spectrum and result in obvious absorption. Intermolecules vibrational modes or lattice vibration are considered as the main mechanisms in the THz frequency region. THz measurements of organic crystals allow us get the information on both molecular conformation and intermolecular environment. In the previous research about FIR THz spectra of DNA [6], retinal isomers [8], benzoic acid, glucose [7]and uric acid, polycrystalline saccharides [9], and biotin [10], the low-frequency discrete vibrational features have been demonstrated to be mainly associated with the collective vibrational modes of molecules held together by the hydrogen bonded networks. For these molecules, the hydrogen bond plays a significant role in the low-frequency vibrational modes. Based on this interpretation, in our present work, we attribute the distinct resonance peaks below 60 cm^{-1} to the collective motion of molecules linked by hydrogen bonds and that above 60 cm^{-1} to the lattice vibrations.

As discussed above, we have identified the distinct absorption peaks of α-naphthol and β-naphthol exhibiting between 30 and 60 cm^{-1} are associated with the collective motion of molecules linked by hydrogen bonds [11]. More precisely, from Fig. 3b, c, we also can find some pronounced distinctions between the spectra of α-naphthol and β-naphthol in spite of the very similar molecular structures . This indicates FIR absorption provides excellent probe of the isomeric structures with characteristic FIR fingerprints and this can be used in materials diagnostics [7,9,12].

For another three molecules without hydrogen bonds, naphthalene, biphenyl and anthracene do not show obvious characteristic absorption between 30 and 60 cm^{-1}. Their obvious resonances are located in the frequency range above 60 cm^{-1} and these features can be attributed to the lattice vibrations. However the distinction between them is easily seen. For naphthalene and anthracene the strong absorption is around 65 cm^{-1}, but for biphenyl it is around 70 cm^{-1}. Although we attribute all their absorptions to the lattice vibration qualitatively, the exact mechanism is not well understood and the detailed quantum chemical calculations are necessary in order to get more quantitative information on the lattice vibrations.

Till now, there is still one puzzling question. As shown in Fig. 3a, b, c, naphthalene and its derivative β-naphthol exhibit remarkable resonance around 65 cm^{-1}, but another derivative α-naphthol do not display the same feature at this frequency. We do no know how OH causes a so great influence on the lattice vibration that α-naphthol and β-naphthol exhibit a large difference.

Fig. 4 shows the real part ε_1 and imaginary part ε_2 of the dielectric function of all our studied samples, in which the frequency dependance of complex dielectric

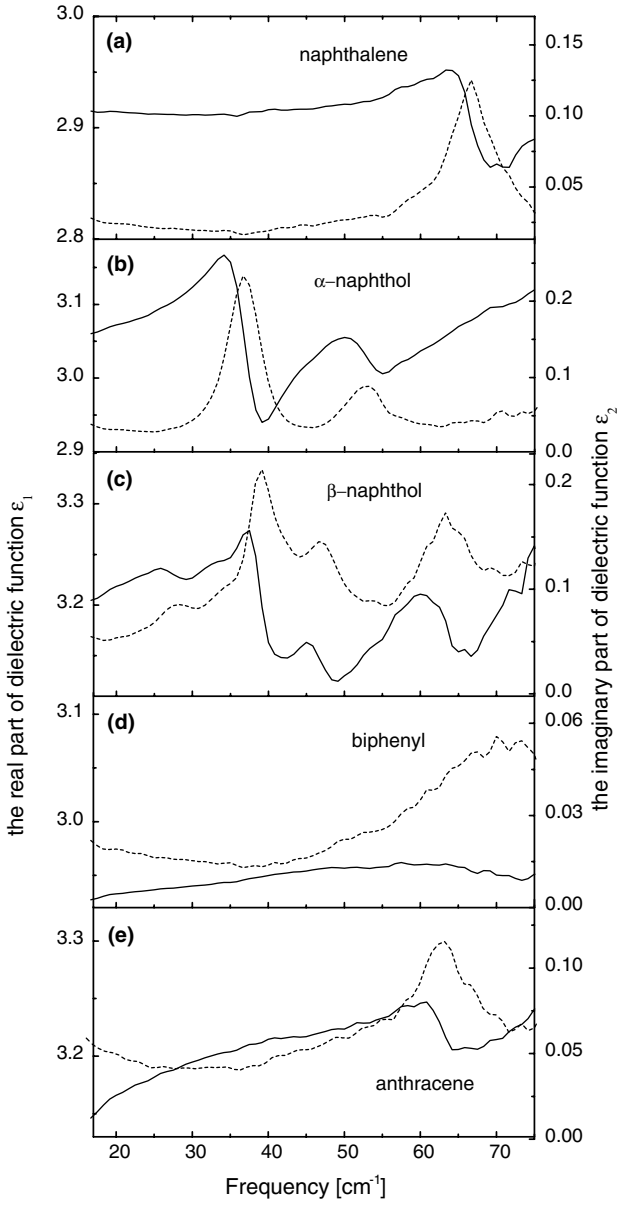

Fig. 4. The real part of dielectric function ε_1 (solid line) and the imaginary part of the dielectric function ε_2 (dash line) are experimentally obtained for all measured samples.

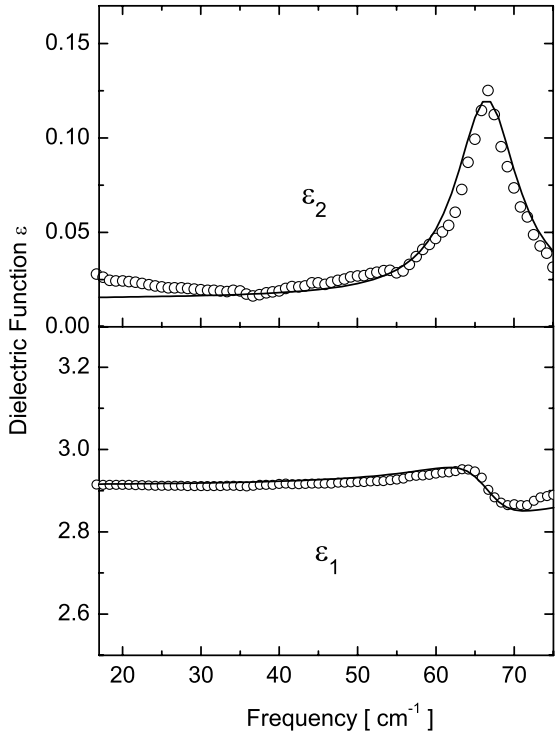

Fig. 5. Comparison of measured complex dielectric function(open circles) with calculated results(solid line) by Lorentz model. ε_1 and ε_2 are respectively the real part and imaginary part of the dielectric function of naphthalene.

function $\varepsilon(\omega)$ is obtained through the formula: $\varepsilon = (n + \mathrm{i}\kappa)^2$. The real part of the dielectric function indicates the resonance process related with similar mechanism as optical absorption, and the imaginary part describes the dielectric loss of this resonance process.

In addition it should be noted that the measured spectra can be fitted theoretically using a standard Lorentz model [6,8,13,14], which is described as following:

$$\varepsilon = \varepsilon_\infty + \sum_j \frac{S_j v_j^2}{v_j^2 - v^2 - \imath v \Gamma_j} = (n + \mathrm{i}\kappa)^2, \qquad (1)$$

where the sum is taken over the different oscillators with the center frequency v_j, the oscillator strength S_j and the line width Γ_j. ε_∞ denotes the high-frequency contribution to the dielectric function. This model offers a simple description of the complex dielectric function. Using this expression, the refractive index n, the real part and imaginary part of the dielectric function are easily obtained and then through the formula: $\alpha = 4\pi v\kappa/c$, the absorption coefficient can be calculated.

In Fig. 5, as an example, we present a theoretical fit to the real part and imaginary part of dielectric function of naphthalene using one oscillator. As one can see the fit is good. The center frequency, line width and oscillator strength can be extracted from the fit as: $v_j = 66.67$ cm^{-1}, $\Gamma_j = 9.5$ cm^{-1}, $S_j = 0.015$ cm^{-1}. The similar fittings are available for other measured samples if we take appropriate oscillator modes into account. A more accurate theoretical description will be taken into account in the later work including a complete fit to all experimental results.

4. Conclusion

In summary, we have performed an investigation into the low-energy vibrational modes of naphthalene, α-naphthol, β-naphthol, biphenyl and anthracene in crystalline form. Using TDS-THz spectroscopy, we have recorded the completed FIR THz spectra, represented as power absorption coefficient and index of refraction in frequency region between 0.1 and 2.2 THz. The complex dielectric function of all samples are also obtained at the same time. Many distinct characteristic and common features of their THz spectra could be identified as the signatures of intermolecules vibration linked by hydrogen bonds or lattice vibrations. The FIR spectroscopy not only provides a fingerprint of molecular conformation, which may be useful for isomer discrimination, but also allows us to get some visible common features between similar molecular structures although these common features are not yet understood clearly. We have further shown that the Lorentz model is available to give a good fit to the measured spectra.

References

[1] Bradley Ferguson, Xi-Cheng Zhang, Nat. Mater. 1 (2002) 26.
[2] Q. Chen et al., J. Opt. Soc. Am. B 18 (2001) 823.
[3] M.B. Johnston, L.M. Herz, et al., Chem. Phys. Lett. 377 (2003) 256.
[4] R. Pething, D.B. Kell, Phys. Med. Biol. 32 (1987) 933.
[5] E.J.W. List, C. Creely, et al., Chem. Phys. Lett. 325 (2000) 132.
[6] B. Fischer, M. Walther, P. Uhd Jepsen, Phys. Med. Biol. 47 (2002) 3807.
[7] M. Walther, P. Plochocka, B. Fischer, H. Helm, P. Uhd Jepsen, Biopolymers 67 (2002) 310.
[8] M. Walther, B. Fischer, M. Schall, H. Helm, P. Uhd Jepsen, Chem. Phys. Lett. 332 (2000) 389.
[9] P.C. Upadhya, Y.S. Shen, A.G. Davies, E.H. Linfield, Vibrat. Spectrosc. 35 (2004) 139.
[10] T.M. Korter, D.F. Plusquellic, Chem. Phys. Lett. 385 (2004) 45.
[11] P. Piaggio, M. RuiR, R. Tubino, G. Dellepiane, Spectrochim. Acta Part A 38 (1982) 913.
[12] M.R. Kutteruf, A.M. Brown, et al., Chem. Phys. Lett. 375 (2003) 337.
[13] J.G. Han, Z.Y. Zhu, et al., Phys. Lett. A 310 (2003) 457.
[14] D. Drogoman, M. Dragroman, Optical Characterization of Solid, Springer, Berlin, 2002.