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Simulation study on terahertz vibrational absorption in liquid crystal compounds

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The terahertz (THz) spectrum absorptions of nematic liquid crystal (LC) material, i.e. N-(p-methoxybenzylidene)-p-butylaniline (MBBA), and its relevant compounds are simulated in this paper by using the density functional theory (DFT) method. A strong absorptive frequency is located at 3.65 THz for the MBBA, which is in agreement with experimental data found in the literature. The result suggests that the DFT method is effective for dealing with the anisotropic nematic LC compounds.

Keywords: terahertz spectroscopy, N-(p-methoxybenzylidene)-p-butylaniline (MBBA), liquid crystal, density functional theory

PACC: 4270D, 9580G

1. Introduction

THz time-domain spectroscopy for studying liquid crystals (LCs) is a newly developed technique, which enables us to simultaneously acquire much molecular information, such as spectra, vibration, rotation and refractive indices. The frequency region between light wave and electric wave corresponds to those of some molecular rotational modes, hydrogen bond and intermolecular interaction. Hence the THz time-domain spectroscopy provides us with a powerful tool and technology for discussing molecular dynamics of materials involving LC compounds.[1−5] Some pioneering experiments on THz spectroscopy of liquid crystalline compounds, such as 4,4'-azoxydianisole (PAA) and N-(p-methoxybenzylidene)-p-butylaniline (MBBA), were carried out twenty years ago.[6] In recent years, similar experimental studies on LC phases in far-infrared spectrum region have been published frequently.[7−9] However, little study of the LC compounds has been carried out theoretically by using computer simulation, although the study is necessary and convenient for predicting spectrum properties. Because of the effective development of computational method, the density functional theory (DFT) method has proven to be a reliable theoretical method in predicting accurate vibrational frequencies for medium size molecules.[10,11] For a well-known detonator molecule 2,4-Dinitrotoluene (2,4-DNT),[12,13] encouraging simulation results have been obtained in the far-infrared spectrum region by using the DFT. To date, we have not found the numerical simulations of THz spectra for MBBA and its relevant compounds in the literature. Therefore, the present paper reports on the THz spectrum numerical results of MBBA and a series of compounds, N-(p-methoxybenzylidene)-p-octylaniline (MBOA), and N-(p-butoxybenzylidene)-p-butylaniline (BBBA) in a 0–6 THz region. The computational results are compared with some experimental data found from the literature. The results maybe are important for conducting an experimental and theoretical investigation on the relevant LC absorption spectrum in the THz band. Therefore, we except that the computational simulation method will be useful for predicting the THz spectrum information on the anisotropic LCs.

2. Computational methodology

Numerical calculations of molecular structures, vibrational frequencies and infrared intensities of MBBA, MBOA and BBBA are executed by using the Gaussian 03 package[14] with the Becke–3–Lee–Yang–Parr (B3LYP) functional[15,16] and 6-311+G** basis set[17,18] at a default temperature of 298.15 Kelvin (25°C). The molecular structures and phase sequence to be studied are shown in Fig.1. In our calculation

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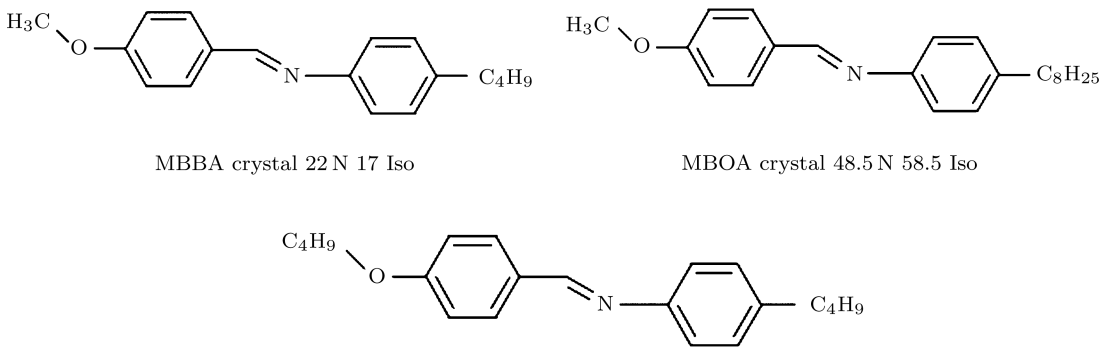


Fig.1. Chemical structures and phase transition temperatures (in °C) of MBBA, MBOA, and BBBA.

process using the Gaussian 03, the molecular minimum energy structures are found and confirmed by vibrational analysis. The required CPU time of our algorithm is less than 24 h per molecule. No negative frequency is found. The simulation work includes a preliminary study of molecule, 2,4-DNT,[12,13] to check the reliability of our calculation method. In order to obtain the infrared absorption spectra, the infrared intensity calculated by using the Gaussian package is treated by using the Swizard program.[19] This program can offer vibrational frequencies and intensities from the Gaussian 03 output files covering an IR absorption spectrum. The absorption profiles are calculated by using a model in which the half-bandwidth of each transition is taken as an empirical parameter. For electronic transitions, the half-bandwidth values depend on the nature of donor and acceptor orbitals. Therefore, an absorption profile can be calculated as a sum of Gaussian equations.[19]

3. Results and discussion

The preliminary calculations on the far-infrared spectrum for 2,4-DNT in a frequency range between 2 and 21 THz at 25°C are shown in Fig.2. For comparison, the numerical calculations and the experimental results reported in Ref.[12] are plotted in the figure. In a low frequency range (between 2 and 12 THz), three strong absorption peaks are observed to be centred at 4.95, 9.17 and 10.80 THz separately, which are in good accordance with those reported in Ref.[12]. In a range between 12 and 21 THz, although smaller errors exist in our calculations, the observed absorption peaks are comparable with those obtained experimentally. The results indicate that our calculation process is reliable and accurate.

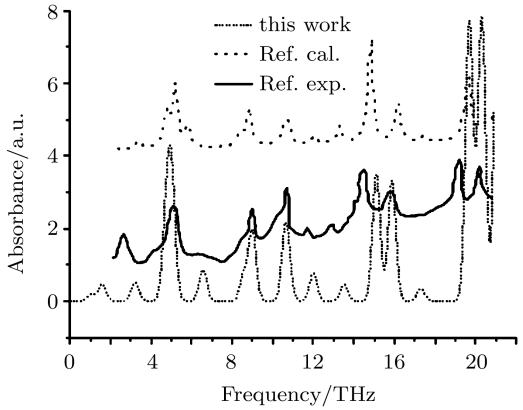


Fig.2. Comparison between absorption spectra for 2,4-DNT obtained from Ref.[7] and our calculations.

In order to compare the computed MBBA absorption bands with the observed results reported in Ref.[7], we have treated the experimental values and illustrated them in Fig.3. In Fig.3 of Ref.[7], the peaks of the transmissive spectra of MBBA do not show any pronounced difference between the parallel- and the perpendicular-polarized THz light; therefore, we have chosen only the parallel direction parts for different temperatures. Furthermore, the light transmittance reported in the literature is converted into light absorption for comparison with our calculations. It is obvious that their experimental absorptions are located at 2.94 and 3.94 (0°C), 3.76 (28°C) and 3.91 (60°C) THz bands, respectively. In Ref.[6], it was also reported that the MBBA indicated a strong absorption in the nematic phase, with a main peak at 4.05 THz ($135\,cm^{-1}$). Therefore, their measurements are both reliable.

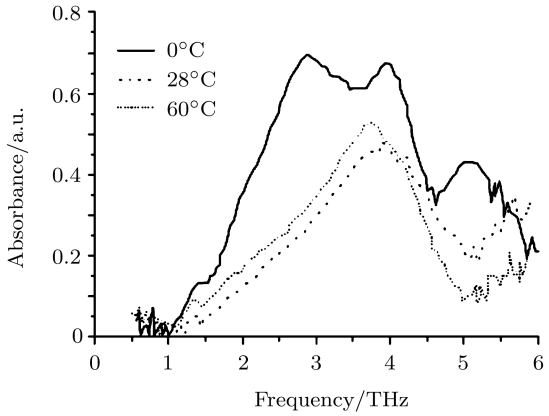


Fig.3. Treated experimental value of absorption band, cited from Ref.[2] for MBBA. Here, only parallel direction transmittance is given and converted into absorption.

Another IR spectrum experimental work on materials that involving the compounds MBBA, MBOA and BBBA[9] is also cited and shown in Fig.4. One can notice that the absorption peaks occur at 1.50 (BBBA), 2.10, 3.33, 3.47 (MBBA) and 4.03 (MBOA) THz bands. By comparing the measurements cited from Refs.[6,7] and those from Ref.[9], one can find that their strong absorption frequencies are different markedly for the compound MBBA.

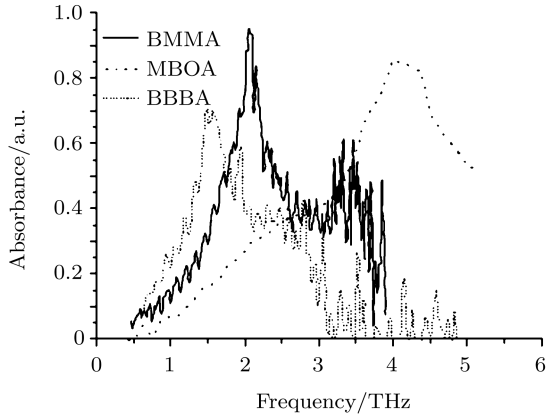


Fig.4. Treated experimental value of absorption band cited from Ref.[4] for compounds MBBA, MBOA and BBBA.

Figure 5 shows our results of compounds MBBA, MBOA and BBBA, obtained by using the Gaussian 03 with B3LYP functional and 6-311+G** basis set at a default temperature of 25°C. The frequency calculation is performed in a range from 0 to 120 THz. In order to compare our calculations with the experimental results cited from the literature in the same frequency range, the data for the IR spectrum absorption versus frequency in a range from 1 to 6 THz are collected and illustrated in Fig.5. It is clearly shown that the strong absorptions are located at 3.66 (MBBA), 3.84 (MBOA) and 4.41 (BBBA) THz bands. In addition, two weak absorptions are found to occur at 1.02 and 4.44 THz band for MBBA. Because of their similar molecular core structures, the strong absorption peaks are shifted in a narrow frequency region between 3.66 to 4.41 THz. The result indicates that there exists a larger error between our calculations and the measurements reported in Ref.[9]. Therefore, it is necessary to analyse the actual condition of the measurement.[9]

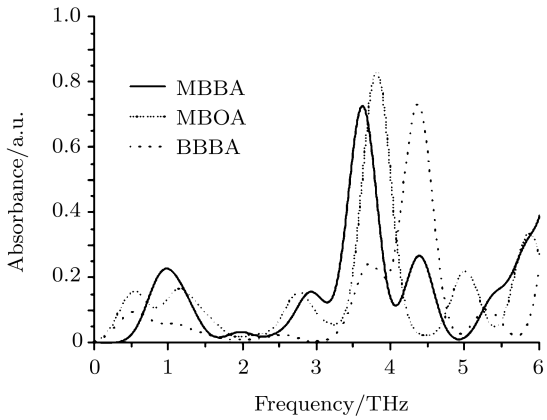


Fig.5. Our calculated results for MBBA, MBOA and BBBA by using the B3LYP functional and 6-311+G** basis set at 25°C.

Figure 6 shows the absorption spectra of the experiments[7,9] and our calculations for the compound MBBA. In a narrow region between 3.33 and 3.94 THz, although the material shows different absorption peaks corresponding to the crystal, nematic and isotropic phases, the peaks are convergent relatively. Particularly in the nematic phase, our calculated result (where the peak is located at 3.66 THz under 25°C) is in good agreement with the measured result in Ref.[7] (where the peak is located at 3.76 THz

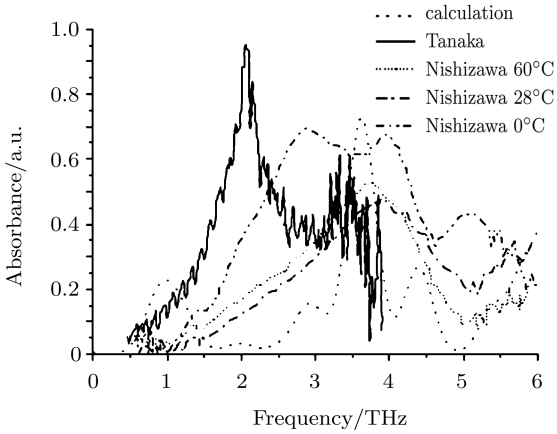


Fig.6. Comparison between measurements and our calculations for compound MBBA.

under 28°C). Compared with another experimental result (4.05 THz) in Ref.[6], our calculated result (25°C, 4.44 THz) is also in good agreement with the result. Therefore, the results indicate that our calculations are reliable and accurate. For the measurements in Ref.[9], although in the measured spectrum of MBBA there appear two stronger absorption peaks at 3.33 and 3.47 THz, they are obscure. Furthermore, the absorption peak at 2.10 THz is not found in our calculations, and neither is it in the measured results reported from other literature. Hence, we judge that the measurement reported in Ref.[9] maybe is in large error.

In summary, we carry out the terahertz time-domain spectrum study on nematic LC compounds MBBA, MBOA and BBBA numerically. The obtained results indicate that the nematic LCs show a strong absorption in a terahertz region. The theoretical method is simple and timesaving in calculation. We expect that this numerical method will be applied to more terahertz time-domain spectrum studies of an LC system.

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