Analysis of Intermolecular Vibrational Modes in Organic Compounds using Two-dimensional Terahertz Correlation Spectroscopy

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***Abstract*—In this study, the terahertz (THz) absorption spectra of tris(8-quinolinolato) aluminum were measured during 100–300 K. The temporal changes in the absorption spectra were analyzed using two-dimensional correlation spectroscopy (2DCOS). By comparing the cross peaks corresponding to the intermolecular vibrational modes, we concluded that the high-frequency band could be attributed to the vibration of the structure and the low-frequency band to the vibration between the structures. The exact frequencies of the overlapping vibrational bands and their assignments provide a new means to inspect the thermal behavior of the intermolecular vibrational modes.**

I. Introduction

BECAUSE of the great contribution and broad applications of terahertz (THz) time-domain spectroscopy (THz-TDS), rapid developments have been made in THz spectroscopy [1]. In the THz region, organic materials show characteristic spectra that originate from low-frequency intermolecular vibrational motion. Direct information about intermolecular interactions and intermolecular structures, such as crystal structure, cluster structure, and higher-order conformation of large molecules, can be obtained using THz spectroscopy. So, THz spectroscopy will be a powerful tool for research of organic compounds.

However, the low-frequency vibrational peaks at room temperature often have a broad line shape, and the peaks often overlap because of the rapid vibrational relaxation.

In this study, we performed two-dimensional correlation spectroscopy (2DCOS) to resolve the overlapping peaks in the THz spectrum [2]. 2DCOS is a recently developed spectral analysis method that has been used extensively for vibrational spectroscopy in the mid-IR and near-IR regions. Correlation of the intensity variations between frequencies can be observed in the 2D plots. By reading the 2D plots, we can get new insight into the relationship between low-frequency vibrational modes and higher-order conformations, which are directly reflective of the physical properties of organic compounds.

II. Experiments and Theory

The tris(8-quinolinolato) aluminum (Alq3), which is a typical organic emitting material, was selected for our study. By using a temperature-controlled heating cell placed on the THz-TDS apparatus, the THz spectra of Alq3 was measured by changing the temperature from 100 to 300 K. Absorption spectra of the sample were measured from 0.06 to 2 THz with a frequency resolution of 0.06 THz. The schematic diagram is shown in Fig.1.

The measured data in the time-domain were transformed into the frequency-domain first by using the fast Fourier transform (FFT) method. Then the complex two-dimensional (2D) correlation intensity is defined as[3]

$$\Phi(\nu_1,\nu_2)+i\Psi(\nu_1,\nu_2)=\frac{1}{\pi T}\int_0^\infty \tilde{Y}_1(\omega)\tilde{Y}_2^*(\omega)d\omega \qquad (1)$$

where the term $\tilde{Y}_1(\omega)$ is the Fourier form of the data measured at spectral variable ν_1. Likewise, $\tilde{Y}_2^*(\omega)$ is the conjugation of the Fourier form of the data measured at spectral variable ν_2. Φ is synchronous spectrum, and Ψ is asynchronous spectrum.

Eq. 1 is strictly in accordance with the mathematical derivation. However, the computation of the 2D correlation spectrum according to Eq. 1 for discrete data may become rather large. Fortunately, there are several computational shortcuts one can take to achieve an adequate numerical estimation of 2D correlation spectrum [4].

The synchronous 2D correlation spectrum and the asynchronous 2D correlation spectrum are given by two simple expressions

$$\Phi(\nu_1,\nu_2)=\frac{1}{m-1}\sum_{j=1}^{m}\tilde{y}_j(\nu_1)\tilde{y}_j(\nu_2) \qquad (2)$$

$$\Psi(\nu_1,\nu_2)=\frac{1}{m-1}\sum_{j=1}^{m}\tilde{y}_j(\nu_1)\sum_{k=1}^{m}N_{jk}\tilde{y}_k(\nu_2) \qquad (3)$$

where $\tilde{y}_j(\nu_i)$ is the spectrum intensity at a point of physical variable t_j. In this study, the physical variable is temperature. The term m is the number of the traces of dynamic spectrum collected. The term N_{jk} corresponds to the j th row and k th column element of the discrete Hilbert-Noda transformation matrix.

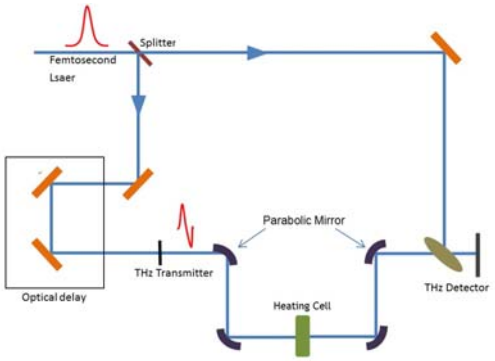

Fig. 1. The schematic diagram of terahertz variable temperature experiment.

III. RESULTS AND DISCUSSION

The 2DCOS method was applied to a series of spectra (the so-called dynamic spectra) that were measured at different temperatures. Fig. 2 shows the dynamic spectra and 2D correlation plots of the sample. In the synchronous plot, a positive correlation is observed between the bands at 1.11THz (37cm^{-1}) and 1.65THz (55cm^{-1}), which reflects a simultaneous increase in the intensities of the vibrational peaks. The asynchronous 2D plot shows correlation between the bands at 1.05THz (35cm^{-1}) and 1.2THz (40cm^{-1}), it is consistent with the pattern of intensity changes of two overlapped peaks.

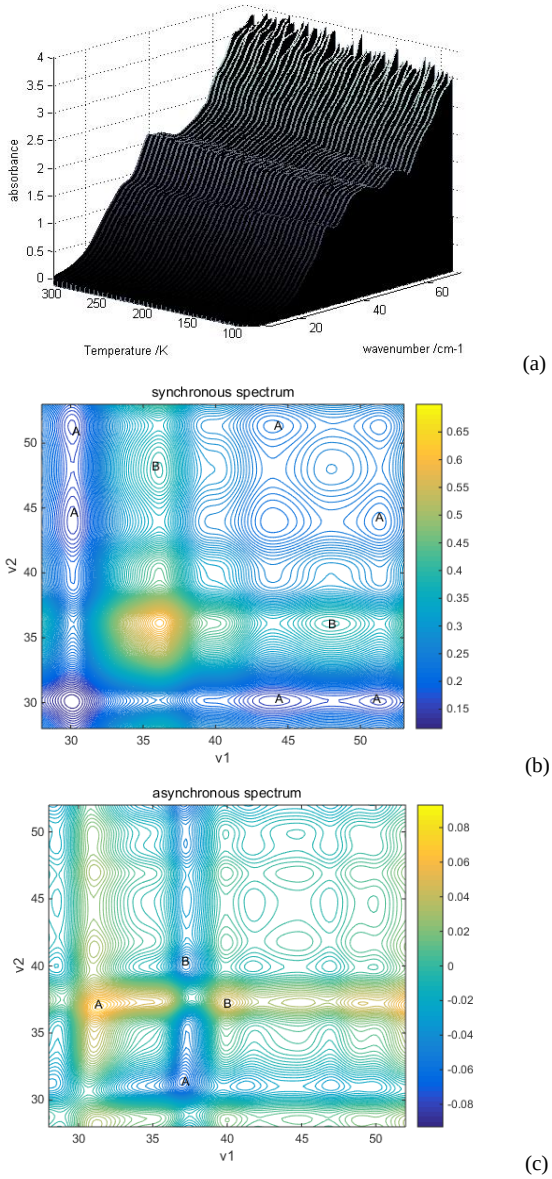

Fig. 2. (a) Dynamic spectra, (b) Synchronous and (c) asynchronous 2D correlation plots of tris(8-quinolinolato) aluminum during 100-300 K.

Fig. 2(a) shows the THz dynamic absorption spectra of Alq3 during temperature-rise period. Only the general trends of four absorption peaks varying with changing temperature can be observed. Then, there are abundant important information have to be obtained by the 2DCOS method.

In the synchronous spectrum shown in Fig. 2(b), there are five distinct autopeaks (on the diagonal line) located at 30.12, 36.12, 44.03, 47.83 and 51.23cm^{-1}, which reflects existing vibrations in the five frequencies are extremely sensitive to the temperature. There are eight cross peaks can be observed, and all the cross peaks are positive. The cross peaks can be divided to two group. The six peaks near the boundary are group A, the others are group B. The cross peaks of group A reveal that there is a highly positive correlation at 30.12, 44.03 and 51.23cm^{-1}. The other two cross peaks indicate that intensity at 36.12 cm^{-1} are increasing, while the intensity at 47.83 cm^{-1} is increasing. Highly positive correlation in the two groups may be assignable to the coupled intermolecular interactions or intermolecular structures. The spectral resolution of the 2D spectrum is higher than the resolution of dynamic spectrum, some overlapped peaks can be readily sorted out [4], and the coupling degrees between each absorption peaks are obtained.

Fig. 2(c) shows the asynchronous 2D correlation spectrum calculated by discrete Hilbert transformation method. The spectrum is filled with numerous cross peaks, and there are four cross peaks are distinct and typical. The peaks of group A are the two cross peaks at 31.42 cm^{-1} and 37.03 cm^{-1}. The one on the upper left corner is a positive peak, which indicates the vibration at 37.03 cm^{-1} changes in advance of the vibration at 31.42 cm^{-1}. On the other hand, the peaks of group B are the two cross peaks at 37.23 and 40.03 cm^{-1}, and the one on the upper left corner is a negative peak, which indicates that the vibration at 37.23 cm^{-1} changes in advance of the vibration at 40.03 cm^{-1}. According to the order of the changes related to the intensities of vibrations, the pattern of intensity changes may be predicted. Due to the previous study, the vibration due to hydrogen bonds between helical structures, which changes in advance of the skeletal vibration along the c-axis[2]. It is possible that the vibration at 37.23 cm^{-1} is a kind of the vibration due to the hydrogen bonds, rather than the skeletal vibration. This may bring much convenience to molecule simulation, especially for the multi-molecular simulation.

IV. SUMMARY

Because 2DCOS can easily visualize intensity changes in broad and overlapping peaks, spectral information from a blended system can be simplified into two dimensions. Therefore, 2DCOS is expected to be a new, powerful THz spectroscopy method that can be used when spectra contain vibrational bands that overlap and are difficult to resolve.

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