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A New Approach for Non-destructive Detection of Dye Molecules by Combination of Terahertz Time-domain Spectra and Raman Spectra

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Abstract: Choosing dye molecules as probe molecules, a new approach was introduced by employing transient terahertz (THz) time-domain spectroscopy and Raman spectroscopy, much more information were obtained for molecular fine structures and molecular energy level. Combined with remarkable Raman modes, for the first time, it also provides a new general way for non-destructive detect and identification for dye molecules, as well as comprehensive information of molecular structures and energy levels. It was also reported that the methyl red, crystal violet and Rhodamine B also have strong absorption in THz wave band, especially notable that the Rhodamine B molecules present remarkable absorption behavior below the frequency of 1 THz which may bring forth potential applications in relative fields.

Key words: Non-destructive detect, dye molecules, terahertz, Raman

INTRODUCTION

In the frame of molecular energy level, the vibrational and rotational energy levels are usually represented by the Infrared and Raman spectroscopy. Actually for each molecule, the infrared and Raman spectroscopy have almost formed a series of dactylogram. However, they still cannot always reflect all the energy information of molecules with fine structure. Just as some Raman active modes representing non-active in infrared region and some infrared active modes vanished in Raman spectra, the rotational energy levels based on some vibrational energy level varied with the quantum number J increasing may not detected by infrared and Raman spectroscopy (Wang Shaohong *et al.*, 2003; Cao *et al.*, 2000; Cao, 2003; Cao and Lei, 2003).

The terahertz (THz) probe pulses consist of a single cycle of the electromagnetic field with a duration of less than 1 ps, covering the spectral range 0.1-2.7 THz (0.4-11 meV), exhibiting properties for both sides of the electromagnetic spectra. Actually, matters have special absorption for THz wave, especially for some macromolecules, including peotein and some other biologic molecules etc. Their vibrational and rotational spectra present many specific absorption peaks. It has become a new research direction, which study the spectral properties in this wave band and detects its structure character (Shen *et al.*, 2004; Dorney *et al.*, 2001; Taday *et al.*, 2003; Miyamaru *et al.*, 2003; Yu and Zeng, 2004). Like radio waves, THz can be transmitted through a wide variety of substances such as paper, cloth, ceramics, plastics, wood, bone, fat, various powders, dried food and so on. In addition, like light waves, they can easily be propagated through space, reflected, focused and refracted using THz optics. The range of potential application is probably to expand even further with the increased availability of many absorption spectra peculiar to specific chemicals (Mickan and Zhang, 2003; Bing *et al.*, 2001).

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As far as we know, THz spectroscopy and imaging has provided a powerful tool for the characterization of a broad range of materials, including semiconductors and biomolecules. At the same time, THz wave is also suitable for chemical component detection, being able to screen the measurement results having proven the existence of fingerprint spectra in the THz region. Owing to the wide range frequency band of THz pulse, much information besides what Raman and Infrared can represented may be detected. It means wide application foreground, as well as a new technique field of interdisciplinary collaborating investigation. Actually no other emission spectrum technique can reflect and confirm the absorption in THz region. Nevertheless, because of the different mechanism of THz with Raman, once an organic relationship between them for all kinds of molecules is set up, more comprehensive information may be obtained such as molecular structure and movement, including its vibrational and rotational energy levels. Series of the finger spectra of THz combined with Raman is expected to form useful databank.

Dye molecules is a kind of single structured general molecules with abundant vibrational energy levels and even acted as important token molecules on spectroscopy. In this study, time-domain and absorption spectra of methyl red, crystal violet and Rhodamine B were obtained, as well as their Raman scattering spectra respectively. It is especially notable that the Rhodamine B molecules present remarkable absorption behavior below the frequency of 1 THz. The mechanism and their spectrum structure from the three molecules are analyzed. It is concluded that not only Raman but also the THz wave can be applied in the research for dye molecules. The combination of the two methods provides a new general way for non-destructive inspection, which will give more comprehensive information on the photo-electronic and spectroscopic properties of materials.

MATERIALS AND METHODS

The samples, dye molecules, in the form of powders, were carefully mixed with polyethylene (PE) powder with varying weight ratios about 1:2, depending on the absorption strength of the sample material and pressed into 1 mm thick pellets. PE has low absorption ($<5 \text{ cm}^{-1}$ below 4 THz) and constant index of refraction in the range between 0.1 and 4 THz) (Markelz and Roitberg, 2000), slightly depending on the pressure applied during sample preparation.

A THz time-domain spectrometer setup (Rui and Chunming, 2004) with an optical layout was used in the experiments. The photoconductive antennas are driven by pulses of 30 fs duration from a Ti: sapphire oscillator. One of the antennas is used as a THz pulse emitter and the other one as a field-sensitive THz detector, gated by a second portion of the fs beam. The emitter consists of 10 μm wide metallic electrodes lithographically deposited on a semi-insulating InAs wafer. Charge carriers excited to the conduction band of the InAs substrate by the laser pulse are accelerated by the strong bias field, thereby emitting a short burst of electromagnetic radiation. The power of fs laser pulse used in present experiment is 400 mW and the available frequency range is 0.2-2.5 THz. Detect method adopt the electrical optical sampling technique with the ZnTe wafer as field-sensitive detector ($<110>$ ZnTe) (Markelz and Roitberg, 2000; Dorney *et al.*, 2001; Miyamaru *et al.*, 2003). The Reference pulse and sample pulse spectra are all obtained in nitrogen environment with the environment temperature at 26°C and relative humidity at 39%.

Raman spectra were recorded by an RFS 100/s FT-IR spectrophotometer (excited at 1064 nm). The exciting laser power was 50 mW for all samples.

RESULTS AND DISCUSSION

Figure 1 presents the THz Frequency spectra of Rhodamine B. it is notable that there are abundant absorption peaks from 0.2 to 2.5 T. Each of the peaks is clearly shown with great intensity. For example, the peaks at 1.76, 1.99, 2.05, 2.14, 2.25, 2.34 and 2.46 THz are dramatically assembled. It is remarkable that there are two peaks at 0.527 and 0.937 T, based on so small frequency; we guess

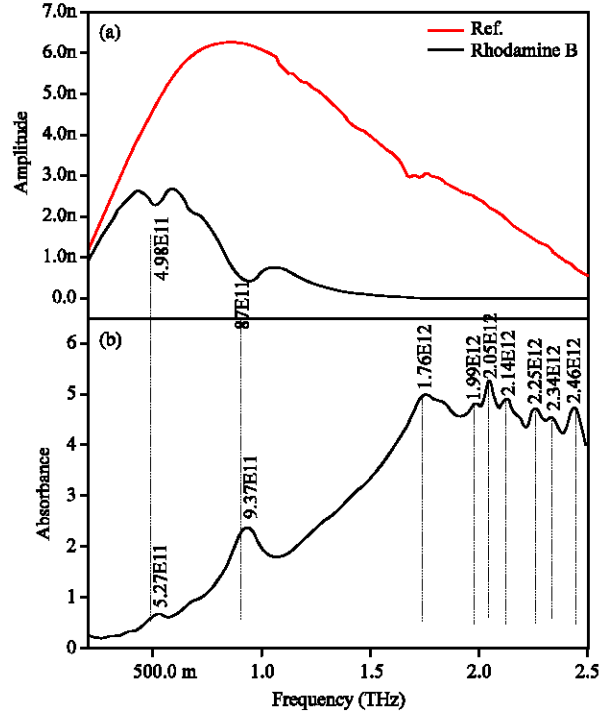


Fig. 1: (a) Fourier spectra of the sample pulse propagated through a 1 mm thick Rhodamine B pill (b) Absorption coefficient from 0.2 to 2.5 THz at temperatures about 295 K

these two modes are represent of molecular rotational energy level. In fact, according to the general calculation of DFT arithmetic, this absorption mainly results from the molecular rotation and twisting. The different peaks actually reflect the structure variety.

It is notable that most of the peaks such as the 1.2, 1.35, 1.52 and 2.31 THz, are remarkably sharp which means strong absorption for the relatively right frequency. It aims at absorption coefficient of Lecithin at different frequency and reflects the different vibrational or rotational energy level.

According to the physical model for THz optics parameter by Dorney and Duvillaret (Yu and Zeng, 2004), after simple deducing, we can obtain the refraction index n_s , extinction coefficient k_s and absorption coefficient α_s :

$$n_s(\omega) = \phi(\omega) \cdot \frac{c}{\omega d} + 1, \quad (1)$$

$$k_s(\omega) = \ln\left(\frac{4n_s(\omega)}{\rho(\omega) \cdot (n_s(\omega) + 1)^2}\right) \cdot \frac{c}{\omega d} \quad (2)$$

$$\alpha_s(\omega) = \frac{2k_s(\omega) \cdot \omega}{c} \quad (3)$$

In fact, the response of molecules to THz radiation mainly comes from the collective vibrational mode of molecular fabrication and conformation. This collective vibrational mode mostly reflects molecular integral frame information, but neither the relative localization electron structure that generally measured by optical method, nor the vibrational mode relative to single chemical bond.

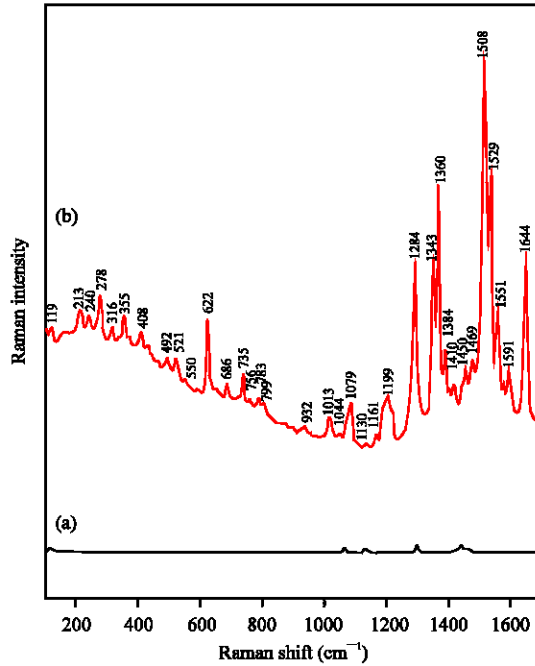


Fig. 2: Raman spectroscopy of polyethylene pill (a) and Rhodamin B pill intermingled with polyethylene (b)

Owing to the sensitivity of macromolecular structure to environment, the distributing and intensity of collective vibrational mode actually includes the influence of environment. Based on this, THz spectrum takes good advantages of studying the macromolecular structure, intermolecular action and the interaction between molecules and environment. The high relativities of spectrum at THz wave band and their overall structures are the important microcosmic foundation for fresh THz technology applied in dye molecules, as well as biology and biomedicine systems.

Figure 2b shows the Raman of Rhodamine B/polyethylene and similarly Fig. 2a aims at the Raman of pure solid polyethylene. As one knows, the Raman modes of Rhodamine B are extremely fruitful and strong, especially in the region from 1200 to 1600 cm^{-1} . There are abundant peaks whose relative Raman Intensity is ten times of that for polyethylene. Further more, there are some shoulders and brother peaks appeared, for example, 1343 and 1360 cm^{-1} are so close; and the mode at 1508 cm^{-1} produces two shoulder peaks, 1529 and 1551 cm^{-1} . The appearance of these peaks, as laid out and assigned in Table 1, reflects the activeness of Rhodamine B molecule structure for Raman scattering. While these shoulders, we guess it may result from the disturbance of rotational energy levels that based on some vibrational energy level.

Considering the total energy of molecular inside as $E = E_e + E_v + E_r$, where E_e is for the energy of electron movement, while E_v and E_r refer to vibrational and rotational energy of molecules. Since every kind of movement energy is quantized, when the molecular phase jumps from E'' to E' ($<E''$), it will emit electron-magnetic radiation of which frequency is determined by:

$$\begin{aligned}
 \nu &= \frac{E'' - E'}{h} = \frac{1}{h} [(E''_e + E''_v + E''_r) - (E'_e + E'_v + E'_r)] \\
 &= \frac{\Delta E_e}{h} + \frac{\Delta E_v}{h} + \frac{\Delta E_r}{h} = \nu_e + \nu_v + \nu_r
 \end{aligned}
 \tag{4}$$

Table 1: The intensities and band assignments of main Raman bands of Rhodamine B (Rh B)

Raman of Rh B (cm^{-1})	Assignment
1644 (s)	Arom C-C stretch
1591 (w)	C-H stretch
1551 (s)	Arom C-C stretch
1528 (w)	C-H stretch
1508 (s)	Arom C-C stretch
1426 (w)	C-H stretch
1360 (s)	Arom C-C stretch
1284 (vs)	Arom C-C stretch
1199 (m)	C-H inplane bend
1130 (w)	C-H stretch
932 (w)	C-H stretch
773 (m)	C-H stretch
622 (s)	C-C-C stretch
355 (w)	
278 (w)	
240 (w)	Ag-N stretch
213 (w)	

vs: very strong; s: strong; m: medium; w: weak

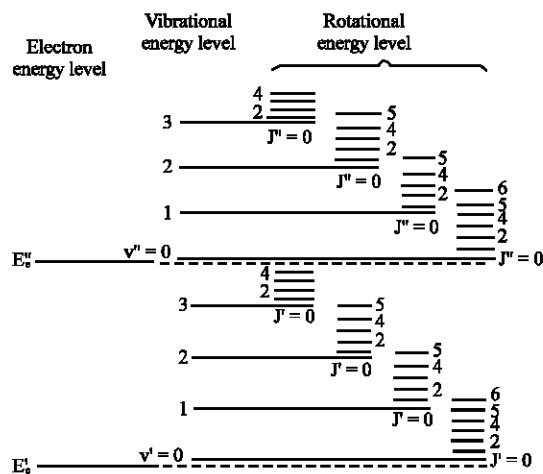


Fig. 3: Sketch map of energy levels, including electron energy, vibration energy and rotational energy level

Proved by theories and experiments, the energy difference of electron movement ΔE_e is the largest, while ΔE_r is the smallest and even usually $v_e > v_v > v_r$. This means there may be vibrational energy levels at every electron energy level, while rotational energy levels with smaller energy differences based on the vibrational energy level as well, as shown in Fig. 3.

According to Formula 4, the molecular spectra seem are composed of some discrete lines. However, it is not difficult to image, when the electron transition occur from one orbit to another, it will lead to the emission or absorption of radiation, as well as the changes of molecular electron cloud distribution and the inter-nuclear electrostatic forces. This may result in influence to the molecular binding force and inter-nuclear distance, which force the molecule to establish a new balance. So the molecular electron transition, changes of E_e , must lead to the changes of inter-atomic vibrational phase, shown in changes of E_v . Similarly, the vibrational phase changes may bring the increasing or decreasing of general molecular moment of inertia. So do the rotational phase changes. In brief, the molecular transition must bring along the transition between vibrational and rotational energy levels.

Because the energy difference ΔE_e is usually about 1-20 eV, the electron spectra result from transitions among electron energy levels, besides a few in near-infrared region, mainly locate in UV or visual field. While the transition between vibrational energy level or rotational energy level may be in infrared or far-infrared region.

On the one hand, if the electron energy and vibrational energy, except the rotational energy, of molecules show no changes ($\Delta E_e = \Delta E_v = 0$; $\Delta E_r \neq 0$), then, $\nu = \frac{\Delta E_r}{h} = \nu_r$ which presents the pure

rotational spectra. Regarding to the rotational energy interval ΔE_r is usually less than 0.05 eV, even below 10^{-4} , so the pure rotational spectra usually lies in the far-infrared or microwave region about 25-1000 μm . As we know, the metal bond vibration of some metallorganics, including many bond vibrations and even crystal lattice vibrations of crystal may also occurring far-infrared spectra.

On the another hand, if the vibrational and rotational energy levels both changed but the electron energy, (as $\Delta E_e = 0$, $\Delta E_v \neq 0$, $\Delta E_r \neq 0$), then the radiation frequency:

$$\nu = \frac{\Delta E_v + \Delta E_r}{h} = \nu_v + \nu_r \quad (5)$$

Here, it means the molecular vibration-rotational spectra. Owing to the vibrational energy difference is usually 0.05-1 eV, the basic frequency vibration-rotation spectra aim at 2.5-25 μm as known as middle-infrared region, but the extensive frequency band of molecular vibration, as well as combination frequency band, refers to near-infrared region of 0.75-2.5 μm . Since the vibrational phase changes cannot but bringing the varying of general molecular moment of inertia and rotational energy, it is obvious that the pure vibrational spectra couldn't be observed.

Though not all molecules has sound adsorption in THz region, as an all-pervading method, THz technique combined with Raman still fits ordinary molecules. For other evidence, Fig. 4 presents the THz frequency spectra of methyl red sample. Where (a) reflects to the relationship of swing and frequency and (b) refers to the Fourier spectra. As, there is a big absorption band at the whole. In addition, a number of peaks in the spectrum are presented, especially in the high frequency region, such as 1.49 and 1.61 THz.

Simultaneity, Fig. 5b shows the Raman scattering spectrum of the methyl red sample pill mixed with polyethylene. In order to exclude the interference Raman peaks, Fig. 5a presents the Raman of polyethylene pill without methyl red intermingled. Because the main Raman peaks of polyethylene are at the high frequency beyond 2000 cm^{-1} , there is relatively few interference Raman peaks appeared in the Raman spectra of methyl red sample pill. On the contrary, Fig. 5b presents very good signal-to-noise and abundant strong Raman peaks appear which refers to the vibrational modes of the fine structure of methyl red molecule. These modes are mainly focused on between $1000\text{-}1600\text{ cm}^{-1}$. The main three modes, 1146 , 1312 and 1396 cm^{-1} are rather sharp and strong, but not broadened or split for the intermingle of polyethylene. This means the macrocosmic intermingling of polyethylene at the general pressure doesn't affect the molecular structure of methyl red, so no difference plays role in the Raman scattering spectra.

Another example molecule was based on crystal violet. Figure 6 shows the absorption frequency spectrum of crystal violet propagated by THz wave. Similarly, a big absorption band together with several absorption peaks, such as 2.11, 2.28 and 2.43 THz, turn out to be harmoniously assembled. Similarly, Fig. 7 presents the Raman of crystal violet sample. It is noticeable that, as we can see, there is a very big package in the Raman spectrum at $300\text{-}1000\text{ cm}^{-1}$. And even the signal-to-noise at low frequency is not as good as high frequency. It seems not sound because that we usually think the

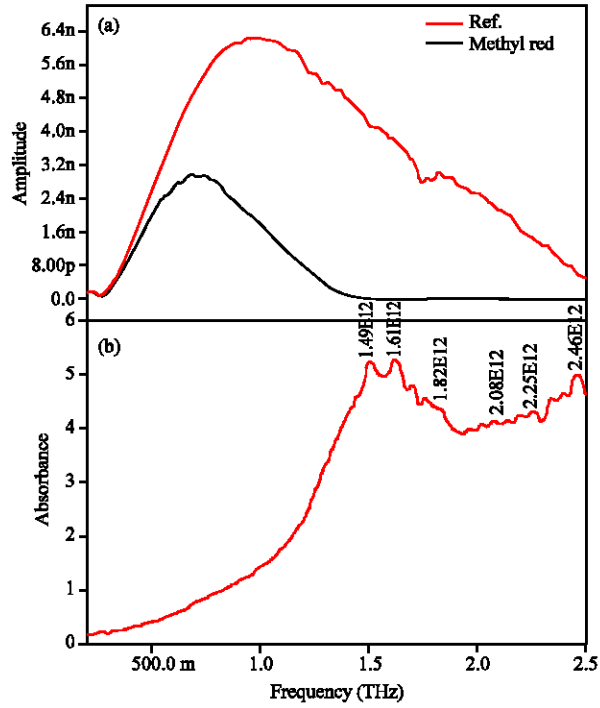


Fig. 4: (a) Fourier spectra of the sample pulse propagated through a 1 mm thick methyl red pill (b) Absorption coefficient of methyl red from 0.2 to 2.5 THz at temperatures about 295 K

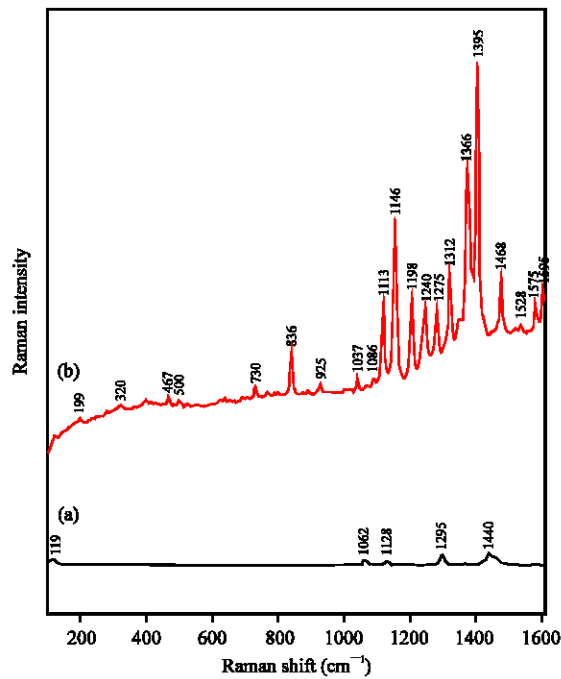


Fig. 5: Raman spectroscopy of polyethylene pill (a) and methyl red pill intermingled with polyethylene (b)

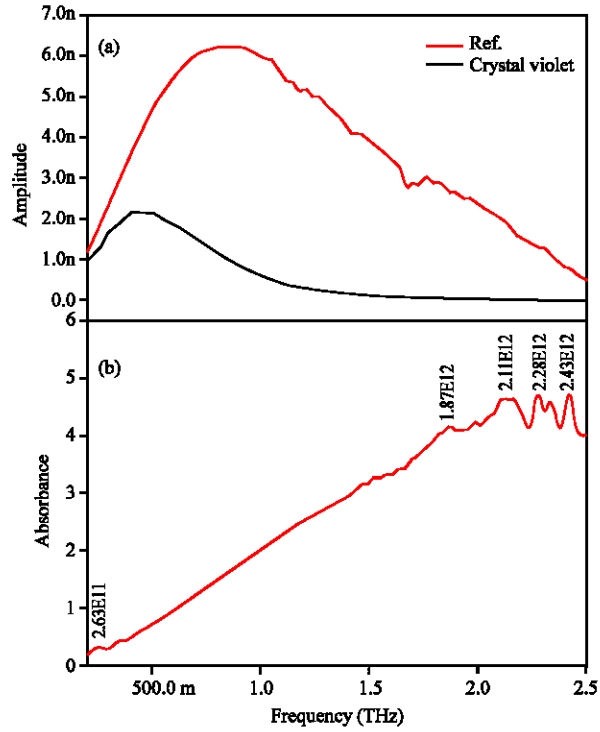


Fig. 6: (a) Fourier spectra of the sample pulse propagated through a 1 mm thick Crystal Violet pill (b) Absorption coefficient $a(n)$ of Crystal Violet from 0.2 to 2.5 THz at temperatures about 295 K

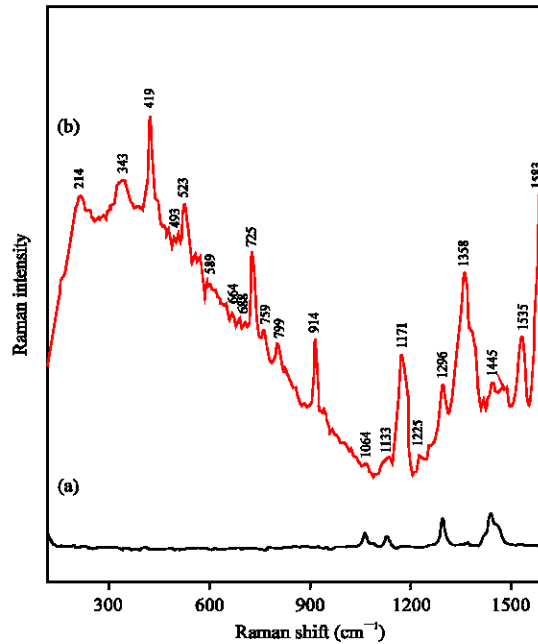


Fig. 7: Raman spectroscopy of polyethylene pill (a) and Crystal Violet pill intermingled with polyethylene (b)

signal-to-noise of Raman spectrum is determined by the scanning times. But we consider that different frequency band may play different role in the inducing fluorescence to occur. The strengthening of fluorescence restrains the activation of Raman modes.

CONCLUSIONS

Taking methyl red, crystal violet and Rhodamine B as examples, we improved an approach for non-destructive determination of dye molecules by Terahertz time-domain spectra and Raman spectra. These dye molecules exhibit strong absorption and dispersion for frequencies at THz region, especially notable that the Rhodamine B molecules present remarkable absorption behavior below the frequency of 1 THz which may bring forth potential applications in relative fields. The combined measurements provide a new field for the non-destructive inspection and much more information shown on the photo electronic and spectroscopic properties of materials.

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