Terahertz spectroscopy studies of far-infrared optical and dielectric signatures of melamine

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We report on the far–infrared optical properties of melamine characterized by terahertz time–domain spectroscopy (THz–TDS). Transmission measurement reveals three low–frequency vibration modes at 1.99, 2.25, and 2.61 THz, which may provide fingerprints for direct melamine detection. By combining THz–TDS with Fourier transform infrared (FTIR) spectroscopy, an overall low–frequency optical response of melamine is presented in an extended spectral range of 0.2–6.2 THz. In this range, the low-frequency vibration mode at 3.96 THz is recorded via FTIR. The measured THz spectra are well fit by the multiple–oscillator model, thereby demonstrating that the low–frequency THz response of melamine is a consequence of the lowest four vibration modes.

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Melamine or $C_3N_6H_6$, is described as a trimer of cyanamide with three cyanamide units joined in a ring. It is harmful when swallowed, inhaled, or absorbed through the skin[1]. In recent years, the detection and monitoring of melamine levels in dairy products have attracted enormous attention worldwide. Useful techniques, such as high–performance liquid chromatography, liquid chromatography–mass spectrometry, electrospray ionization methods coupled with mass spectrometry, and ultrasound-assisted extractive electrospray ionization mass spectrometry, have been adopted to determine the quality and safety of milk foods[2]. In this letter, we study the characteristic signature of melamine using terahertz time–domain spectroscopy (THz–TDS), which has provided us with powerful modality and high sensitivity in exploring the low-frequency properties of materials[3−5]. In recent reports[6,7], two low absorption peaks at 1.99 and 2.25 THz have been addressed in the THz regime. By employing a broadband THz–TDS system, we characterize the power absorption and refractive index of a powder–form melamine sample in the frequency range of 0.2 to 3.0 THz. To underscore the THz–TDS measurements, the optical resonance of melamine is also characterized by Fourier transform infrared (FTIR) spectroscopy, which shows an obvious complementary characteristic. A complete low–frequency optical response of melamine is depicted in a broad spectral range (0.2–6.2 THz) upon combining THz–TDS with FTIR spectroscopy. Our results reveal that the optical response of melamine recorded by THz–TDS is dominated by the four lowest optical vibrational modes at 1.99, 2.25, 2.61, and 3.96 THz. The presented THz spectral signatures may lead to potential applications in detecting or monitoring melamine.

The sample prepared for this research is a white crystalline powder, with a purity of 99.5% and 0.5% of the cyanide. For THz characterization, the melamine powder was naturally placed without applying additional pressure in the silicon transparent material in the THz band, with the cell composed of two parallel 0.64-mm-spaced and 0.64-mm-thick windows of certain distances to avoid the effect of THz multi-reflection. An identical empty cell was used as reference in the data acquisition. This approach enabled direct characterization of the natural form of powder samples with possible broadband width, and avoided the interference of added diluent media, such as polyethylene powder in pellet samples. The measurements were performed at room temperature in a photoconductive switch–based THz–TDS system (Fig. 1), which consists of four parabolic mirrors in an 8–F confocal geometry, a useful bandwidth of 0.1 to 4.5 THz,

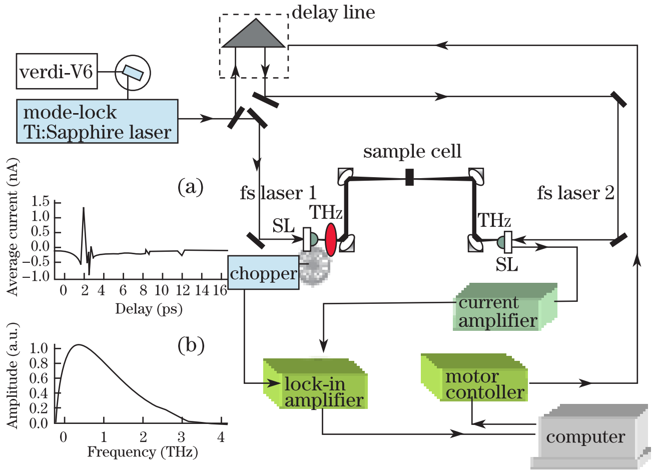

Fig. 1. Schematic of a THz–TDS system.

and an amplitude signal–to–noise ratio greater than 1.5×10^4: 1[3,8]. The resolution of both the THz–TDS system and the FTIR spectrograph used in the following is better than 0.01 THz.

The power absorption of the pure powder melamine is extracted based on transmitted pulses. The waveform is obtained in the time–domain and a fast Fourier transform can be performed to convert power absorption coefficients and the refractive index to obtain spectral information at room temperature[4,5,8,9]. Because the measured powder sample is a melamine/air composite, the experimentally determined initial parameters contain contributions from both air and the pure melamine, that is, we have effective power absorption coefficients α_{eff} and effective refractive index n_{eff} of the powder. To obtain the parameters of pure melamine, a simple effective medium theory, $\varepsilon_{\text{eff}}(\omega) = f\varepsilon_{\text{pure}}(\omega) + (1-f)\varepsilon_{\text{h}}$, was employed, in which the filling factor f defined the volume fraction of the pure melamine and was measured directly in the experiments; $\varepsilon_{\text{pure}}$ and ε_{h} were the dielectric constants of the pure melamine and the host medium, respectively[4,5]. The frequency–dependent complex dielectric function $\varepsilon_{\text{eff}}(\omega)$ can be obtained employing the measured data of power absorption α_{eff} and refractive index n_{eff} through the relationship $\varepsilon_{\text{effr}} = n_{\text{r}}^2 - (\alpha\lambda_0/4\pi)^2$ and $\varepsilon_{\text{effi}} = \alpha n_{\text{r}}\lambda_0/2\pi$, where $\varepsilon_{\text{effr}}$ and $\varepsilon_{\text{effi}}$ are the real and imaginary parts of the complex dielectric function ε_{eff}, respectively. In this letter, $\varepsilon_{\text{h}} = \varepsilon_{\text{air}} = 1.0$. The dash–dotted line, in Fig. 2 represents the experimentally determined power absorption and refractive index of the pure melamine with a filling factor of $f = 0.83$.

As shown in Fig. 2(a), three distinguishable power absorption peaks of the melamine sample are observed at 1.99, 2.25, and 2.61 THz. The presence of the absorption

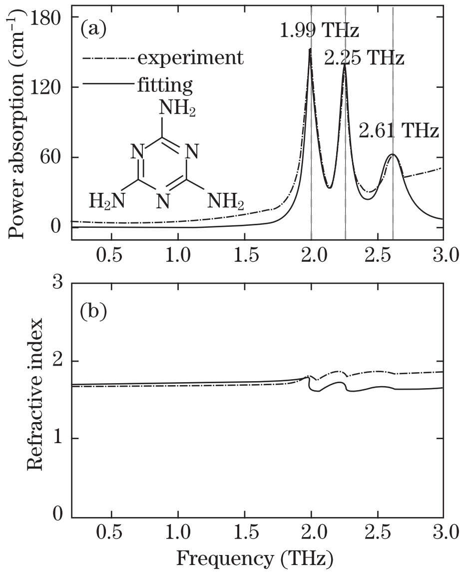

Fig. 2. (a) Power absorption α of pure melamine (dash-dotted curve) measured by THz-TDS and theoretical fitting through the multiple-oscillator model (solid curve); (b) measured refractive index (dash-dotted curve) and theoretical fitting (solid curve). The fitting parameters used with three vibrational modes are: ε_∞=2.80, $\varepsilon_{\text{st}_1}$=0.031, $\omega_1/2\pi$= 1.99 THz, $\Gamma_1/2\pi$=0.1 THz, ε_{st2}=0.016, $\omega_2/2\pi$=2.25 THz, $\Gamma_2/2\pi$=0.08 THz, ε_{st3}=0.015, $\omega_3/2\pi$=2.61 THz, and $\Gamma_3/2\pi$=0.22 THz.

peak is further confirmed in the corresponding refractive index curve in Fig. 2(b), in which a noticeable signature occurs at the same frequency. The far–infrared THz absorption of molecules is attributed to the interactions of a radiation field with the inter–or intra–molecule vibrational modes, and these modes can mostly be described using a multiple–oscillator model and summing up the various oscillators[4,5], thus:

$$\varepsilon_{\text{pure}}(\omega) = \varepsilon_\infty + \sum_j \frac{\varepsilon_{\text{st}_j}\omega_j^2}{\omega_j^2 - \omega^2 - i\Gamma_j\omega}, \qquad (1)$$

where ε_∞ is the high–frequency dielectric constant, $\varepsilon_{\text{st}_j}$ represents the oscillator strength, Γ_j denotes the oscillator damping constant, and ω_j is the frequency of the jth resonance.

Based on the directly obtained data from THz–TDS measurement (as illustrated by the solid curves in Figs. 2(a) and (b)), the experimental power absorption and refractive index of pure melamine were initially fit by a three–oscillator model calculation using Eq. (1). The theoretical fittings indicate that the THz response of melamine is a consequence of three resonant vibrational modes located at $\omega_1/2\pi$=1.99 THz, $\omega_2/2\pi$=2.25 THz, and $\omega_3/2\pi$=2.61 THz[10]. Around third vibrational mode ω_3, however, the obvious divergence in magnitude between the theoretical fitting and the THz–TDS measurement can be found in both the power absorption and the refractive index. This is an indication that a strong resonance may occur at a higher frequency, which essentially contributes to the THz–TDS measured optical response.

To facilitate in–depth understanding of the far–infrared spectra of pure melamine characterized by THz–TDS at low frequencies, FTIR spectroscopy was used as a complement to THz–TDS to extend the spectral range to higher frequencies. Compared with the coherent THz–TDS measurement, FTIR is a non–coherent method, but it is most useful in identifying chemicals that are either organic or inorganic, and is perhaps the most powerful tool for identifying types of chemical bonds[11]. Figure 3(a) shows complete optical response processes over a frequency range of 0.2 to 6.2 THz upon combining THz–TDS and FTIR measurements. The solid curve illustrates the THz–TDS spectrum of melamine at lower frequencies, while the dotted curve represents the data recorded via FTIR beginning from 3.0 THz. Figure 3(a) shows that the FTIR spectrum reveals a strong optical resonance at 3.96 THz. The further theoretical fitting based on the proceeding three vibrational modes ω_1 through ω_3, and the fourth resonance $\omega_4/2\pi$ = 3.96 THz is updated, as shown by the solid curve in Fig. 3(b). The good agreement between fitting and measurements confirms that aside from $\varpi_1/2\pi$= 1.99 THz, $\varpi_2/2\pi$=2.25 THz, and $\varpi_3/2\pi$=2.61 THz, the higher resonance $\varpi_4/2\pi$=3.96 THz contributes to the dielectric and optical response of melamine at low THz frequencies characterized by THz–TDS. This resonance has an especially remarkable influence on the higher frequency response in the THz–TDS spectrum.

In conclusion, we have investigated the low–frequency dielectric and optical properties of melamine. Using THz–TDS, we characterize the far–infrared power

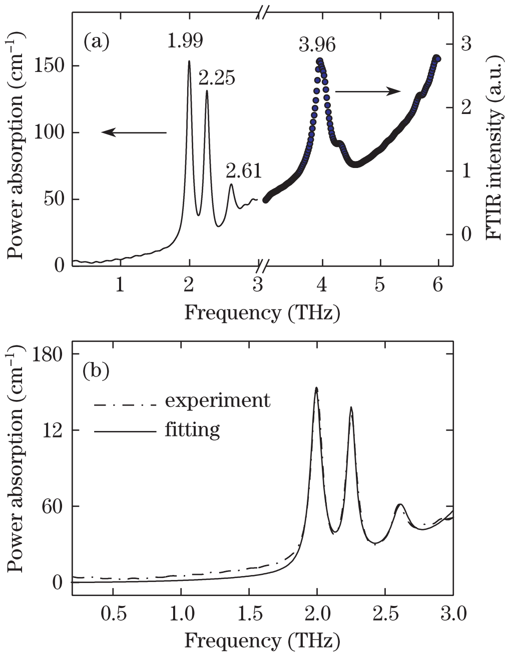

Fig. 3. (a) Complete low-frequency optical response of melamine. the solid curve is measured by THz–TDS in the frequency range 0.2 to 3.0 THz, and the solid–dots represent the FTIR spectrum recorded at 3.0–6.2 THz. (b) Comparison of THz–TDS measured power absorption with theoretical fitting using four vibrational modes with parameters: ε_∞=2.80, $\varepsilon_{\mathrm{st}_1}$=0.031, $\omega_1/2\pi$=1.99 THz, Ti/2π=0.1 THz, $\varepsilon_{\mathrm{st}_2}$=0.016, $\omega_2/2\pi$=2.25 THz, $\Gamma_2/2\pi$=0.08 THz, $\varepsilon_{\mathrm{st}3}$=0.0065, $\omega_3/2\pi$=2.61 THz, $\Gamma_3/2\pi$=0.15 THz, $\varepsilon_{\mathrm{st}4}$=0.32, $\omega_4/2\pi$= 3.96 THz, and $\Gamma_4/2\pi$=0.5 THz.

absorption and refractive index of powder-form melamine in the frequency range of 0.2 to 3.0 THz. The THz–TDS study directly indicates that the THz optical response of melamine is highly correlated with the three lowest optical vibration modes at 1.99, 2.25, and 2.61 THz. Further exploration by FTIR spectroscopy reveals a high frequency vibration mode at 3.96 THz, and confirms that this resonance contributes to the optical response revealed in the THz–TDS spectrum. The results are well fit by the multiple–oscillator model. The combination of THz–TDS and FTIR has been demonstrated as a powerful approach in exploring the low–frequency optical properties associated with optical resonances in various materials. The presented results provide a fingerprint of melamine at THz frequencies, and can lead to possible applications in dairy product analysis using state–of–the–art THz technology.

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