

Terahertz spectral properties of melamine and its deuterated isotope, melamine-d₆

HE Mingxia^{1,*} LI Meng¹ TIAN Zhen¹ CAO Wei² HAN Jianguang¹

¹Center for Terahertz Waves and College of Precision Instrument and Optoelectronics Engineering, Tianjin University, Tianjin 300072, China

²School of Electrical and Computer Engineering, Oklahoma State University, Stillwater, Oklahoma 74078, USA

Abstract The far-infrared optical properties of melamine and its deuterated isotope, melamine-d₆ were experimentally and theoretically investigated in the frequency range from 0.2 to 3.0 THz. Under the room temperature and dry air nitrogen conditions, three absorption bands were observed at 2.0, 2.3 and 2.6 THz in the melamine sample by use of terahertz time-domain spectroscopy. Whereas, in the melamine-d₆ sample, the observed absorption bands shift towards lower frequencies and the relative intensity of the absorption bands reduces. Numerical simulation results based on the Parameterized Model number 3 (PM3) were compared with the experimental data and the observed vibration spectra were assigned according to the PM3 calculations. The absorption bands of the measured melamine samples at terahertz frequencies are highly correlated with the intermolecular hydrogen bond stretching and π-π stacking vibration. Also, the red shift of the absorption bands is due to hydrogen/deuterium substitution.

Key words THz time-domain spectroscopy, melamine, deuterium, hydrogen bond stretching, π-π stacking vibration.

1 Introduction

Recently, there has been considerable interest in applying terahertz (THz) technology in chemical examinations, because THz radiation is sensitive to the low-frequency vibration modes usually caused by inter- or intra-molecular interactions. THz technology has great advantages in distinguishing different phases of samples by their spectra^[1–3], recognizing certain samples with fingerprint-like spectra^[4–6], and analyzing mixture components quantitatively^[7–9]. Studying vibration spectra of molecules often makes it possible to understand crystal structures and monitor the undergoing structure changes. The vibration mode frequencies provide information about hydrogen bonding, conformational changes, effects of hydration, neighbor effects, and so on. However, unlike IR spectroscopy, no specific molecular structures can be identified using THz spectroscopy modality, such as the existence of chemical bond C=C in a substance.

In this paper, THz time-domain spectroscopy is used to study hydrogen bond and π-π stacking in the

THz region, taking melamine and deuterated melamine-d₆ as the model molecular systems.

Melamine, C₃N₆H₆, is an important organic material of nitrogen heterocyclic ring for industrial applications. It is quite ideal for THz experiment, because of its simple molecule structure and the crystal structure having only two types of common inter-molecular interactions: hydrogen bond and π-π stacking. The hydrogen bond plays an important role in the crystal structure, any change in hydrogen would alter the spectral properties.

In this article, we study spectral characteristics of melamine and its deuterated isotope, melamine-d₆, in the frequency range of 0.2 to 3.0 THz. The THz spectra are acquired by use of an 8-F confocal THz-TDS system, and the spectral analysis is conducted with the Gaussian 03 software. The origin of each absorption band is revealed in the scale of inter-molecular interaction and the difference between melamine and melamine-d₆ is distinguished.

* Corresponding author. E-mail address: hhmmxx@tju.edu.cn

Received date: 2012-02-17

2 Experimental

2.1 Sample preparation

The melamine ($C_3H_6N_6$, 2,4,6-Triamino-1,3,5-triazine, sym-Triaminotriazine) and melamine-d₆ ($C_3D_6N_6$, 1,3,5-triazine-2,4,6-triamine-d₆) samples, from Sigma-Aldrich, were used without further purification. Their molecular structures are shown schematically in Fig.1. In the experiments, the two samples were in powder form and placed in a silicon cell with two parallel 0.64-mm-thick windows, which were 0.64-mm-spaced. The experiments were done at room temperature.

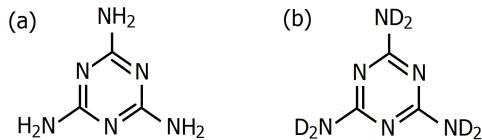


Fig. 1 Molecular formula of melamine (a) and melamine-d₆ (b).

2.2 THz-TDS system

The 8F THz-TDS system to characterize the melamine samples is shown in Fig.2. The photoconductive switch-based transmitter and receiver modules are gated by 30 fs 800 nm pulses generated from a self-mode-locked Ti:sapphire laser. THz waves emitted from the GaAs transmitter are spatially gathered by a hyper-hemispherical silicon lens and collimated by the 8F confocal system to enable a $\Phi 3.5$ mm frequency-independent beam waist for sample characterization. The system works at 0.1–4.5 THz and the single-scan amplitude signal-to-noise ratio is over $10^4:1$ ^[10,11].

2.3 Data analysis

Power absorption of the pure melamine powder is extracted based on transmitted THz pulses. Because of the clear separation between the transmitted and the first reflected pulses in the time domain, the multiple reflection effect of the cell is neglected in the data analysis^[11]. Defining $E_{ref}(\omega)$ and $E_{samp}(\omega)$ as the Fourier transformed spectra of the transmitted THz pulses from the reference and melamine sample, respectively, we have

$$E_{ref}(\omega) = E_{in}(\omega)t_{sa}t_{as}e^{ik_0d} \quad (1)$$

$$E_{samp}(\omega) = E_{in}(\omega)t_{sm}t_{ms}e^{ikd-0.5ad} \quad (2)$$

where, $E_{in}(\omega)$ is the incident pulse spectrum; $k_0=2\pi/\lambda_0$

and $k=2\pi n_m/\lambda$ are wave vectors for air and the sample, respectively; n_m is the refractive index of the melamine sample; d is the sample thickness; λ_0 is the free-space wavelength; and α is the power absorption coefficient of melamine; and $t_{sa}=2n_s/(1+n_s)$, $t_{as}=2/(1+n_s)$, $t_{sm}=2n_s/(n_s+n_m)$ and $t_{ms}=2n_m/(n_s+n_m)$ are the Fresnel transmission coefficients of the THz pulses propagating through silicon-air, air-silicon, silicon-melamine, and melamine-silicon interfaces, respectively. The t_{sm} and t_{ms} are the complex, frequency-dependent transmission coefficients related to the powder form melamine samples.

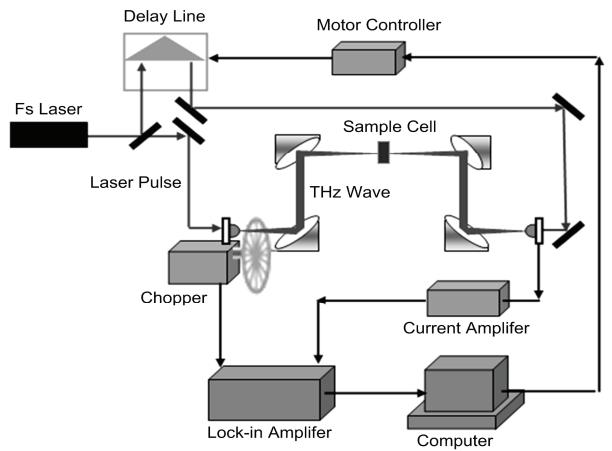


Fig.2 Schematic diagram of the 8-F confocal THz-TDS system.

Based on the obtained temporal waveforms and Eqs.(1) and (2), the power absorption coefficients and refractive index can be extracted. Since the measured powder sample is a melamine/air composite, the effective power absorption coefficients α_{eff} and effective refractive index n_{eff} of the powder samples are extracted from the measurements. To obtain these parameters of the pure powder samples, a simple effective medium theory (EMT) is employed,

$$\epsilon_{eff}(\omega) = f\epsilon_{pure}(\omega) + (1-f)\epsilon_h \quad (3)$$

where, f is the filling factor defining the volume fraction of the pure melamine and can be measured; and ϵ_{pure} and ϵ_h are the dielectric constants of the pure melamine and the host medium, respectively^[12,13]. The frequency-dependent complex dielectric function $\epsilon_{eff}(\omega)$ can be calculated as follows by the measured power absorption α_{eff} and refractive index n_{eff} ,

$$\epsilon_{eff} = n_r^2 - (\alpha\lambda_0/4\pi)^2 \quad (4)$$

$$\varepsilon_{\text{effi}} = \alpha n_r \lambda_0 / 2\pi, \quad (5)$$

where, $\varepsilon_{\text{effr}}$ and $\varepsilon_{\text{effi}}$ are the real part and imaginary part of the complex dielectric functions ε_{eff} , respectively. In our case, $\varepsilon_h = \varepsilon_{\text{air}} = 1.0$, $f_m = 0.83$, and $f_{md6} = 0.56$.

3 Results and discussion

The power absorption spectra of melamine and melamine-d₆ are shown in Fig.3. Three absorption bands are observed in both samples in the frequency range of 0.2–3.0 THz. The bands at 2.0 and 2.3 THz for melamine were reported in Ref.[14], while the 2.6 THz band is observed in our THz-TDS measurement. In the melamine-d₆ spectrum, one finds a red-shift for each of the three bands, from 2.0, 2.3 and 2.6 THz to 1.9, 2.2 and 2.3 THz, respectively. Also, one sees a significantly enhanced absorption baseline and reduced relative intensity of absorption, in the melamine-d₆ spectrum. The red shift of the absorption bands is due to the hydrogen/deuterium substitution. According to the harmonic oscillator model in quantum chemistry, bigger mass and weaker interactions lead to lower frequency absorption bands [15]. For melamine-d₆, the neutron in deuterium atom provides extra mass of the molecule, and about 15% reduction in N–D hydrogen bond energy is found during the simulation with a double-molecule model, hence the red shift.

In order to correlate the THz absorption features of melamine and melamine-d₆ to their molecular structures, calculations based on the Parameterized Model number 3 (PM3) method were performed by use of the Gaussian 03 software. Being widely used for spectral features prediction, the Gaussian 03 can optimize molecular structures and calculate the theoretical positions of spectral absorption bands with a given structure. The PM3 method is based on the Neglect of Differential Diatomic Overlap integral approximation and a semi-empirical method for the quantum calculation of molecular electronic structure in computational chemistry [16]. Of all methods available in the software, the PM3 method provides the closest optimum structure to the known structure of melamine.

The optimized single-molecular structures of melamine and melamine-d₆ have the same geometrical

molecular structure (Fig.4a). The calculated results reveal that all the vibration frequencies of the isolated melamine or melamine-d₆ molecule are above 6.0 THz, which indicates that the observed absorption bands are not due to the intramolecular interactions.

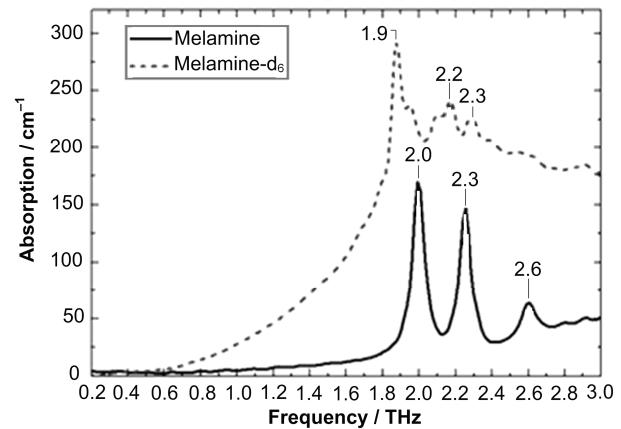


Fig. 3 Power absorption spectra of melamine (solid line) and melamine-d₆ (dash line).

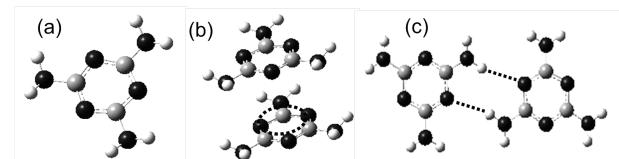


Fig. 4 Optimized structure of single-molecule model (a), inter-layer interactions of nearby melamine molecules(b) with the dashed circles being big π bonds, and intra-layer interactions of nearby melamine molecules (c) with the dashed lines being hydrogen bonds.

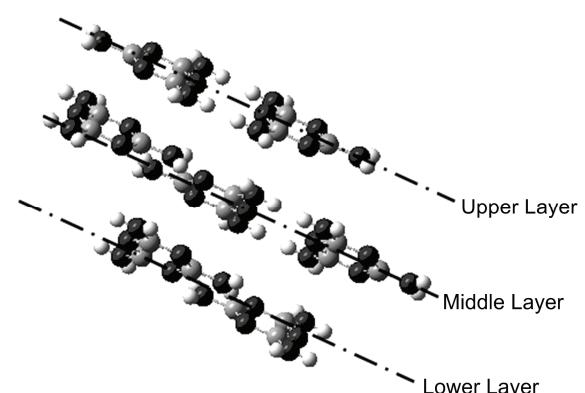


Fig. 5 The 11-molecule model of melamine.

Melamine is in fact a molecular crystal with a layered structure^[17]. It is the π - π stacking interaction and the hydrogen bond connecting nearby molecules (Figs.4b and 4c). An 11-molecule model is constructed

to simulate the real crystal. In this model, one melamine molecule is surrounded by 4 molecules from middle layer, 3 molecules from upper layer and 3 molecules from lower layer. All possible interactions between nearby molecules are contained (Fig.5).

The results of vibration simulation are listed in Table 1. There are 5 strong vibration modes from 1.8 to 3.0 THz. In Fig.6, the 2.0 THz band of melamine, and the 1.9 THz band of melamine-d₆, is attributed to the translational lattice vibration caused by the 6 hydrogen bonds stretching between intra-layer molecules (left). The 2.6 THz band of melamine and the 2.5 THz band of melamine-d₆ are due to the translational lattice vibration caused by the π-π stacking vibration between the center molecule and a molecule from lower layer (right). The 2.2-THz, 2.3-THz and 2.4-THz bands of melamine and the

2.1-THz, 2.2-THz and 2.3-THz bands of melamine-d₆ are much more complicated. They can be referred to the rotation and torsion lattice vibration, resulted by the combination of hydrogen bonds, including inter-layer ones, stretching and π-π stacking vibration. Comparing the simulated band positions of melamine with those of melamine-d₆, the red shift is also seen.

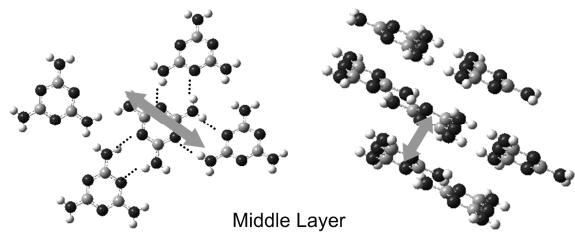


Fig.6 The vibration direction of the center molecule in the 11-molecule model at 2.0/1.9 THz mode (left) and 2.6/2.5 THz mode (right).

Table 1 Absorption band (in THz) list of melamine and melamine-d₆.

Melamine		Melamine-d ₆		Assignment
Calculated	Measured	Calculated	Measured	
>6.0	none	>6.0	none	Intramolecular
2.0	2.0	1.9	1.9	Intra layer hydrogen bonds stretching
2.2	2.3	2.1	2.2	Coupled hydrogen bonds stretching and π-π stacking vibration
2.3		2.2		
2.4		2.3	2.3	
2.6	2.6	2.5	none	π-π stacking vibration

A comparison of the simulated and measured spectrum is shown in Fig.7. For the melamine measurement, the 2.0 THz band is due to 2.0 THz mode calculation; the 2.2 THz band is due to the combination of 2.2, 2.3 and 2.4 THz modes in calculation; and the 2.6 THz band is due to 2.6 THz mode calculation. For the melamine-d₆ measurement, the 1.9 THz band is due to 1.9 THz mode calculation; but the 2.2 and 2.3 THz bands are quite difficult to determine. Possibly, the 2.2 THz band is due to the combination of 2.1 and 2.2 THz mode calculation, and the 2.3 THz band is due to 2.3 THz mode calculation. However, no visible band in the measured melamine-d₆ spectrum can be related to the 2.5 THz mode. We suppose that temperature may have something to do with this phenomenon that some modes cannot be observed.

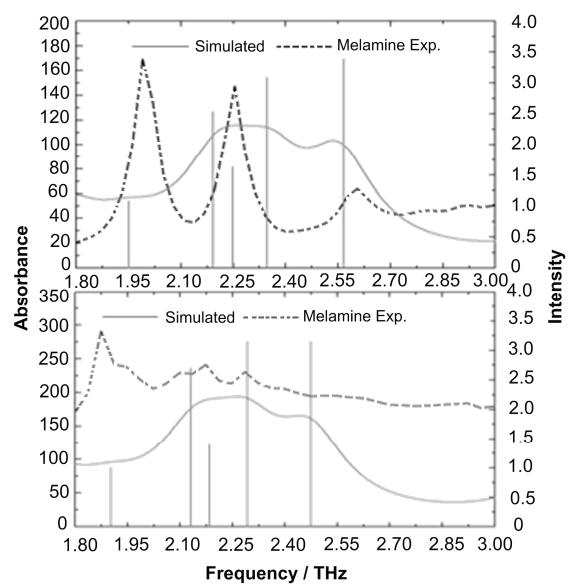


Fig.7 Comparison of the simulated and experimental THz spectrum of melamine and melamine-d₆. The simulated spectrum is in orange, the vertical lines represent the calculated infrared intensity of each predicted mode. The melamine spectrum is in black, and the melamine-d₆ is in red.

A number of recent studies demonstrated that temperature plays a role in THz spectrum. Higher temperature may merge some modes, which can be distinguished into one band, and depress the absorption peak, because of the intense molecular thermodynamic movements. Day G. M. *et al.*^[18] worked on carbamazepine and found that the carbamazepine form I had 7 sharp peaks at 7 K but 5 of them became weak peaks at room temperature, while carbamazepine form III had 5 sharp peaks at 7 K but 3 weak peaks at room temperature. In the experiment with MECH·HCl, Hakey P. M. *et al.*^[19] observed 7 peaks at 78.4 K but just 4 weak peaks at room temperature. Our samples were measured at room temperature, and only strong features can be observed in THz spectra for the use of identifying certain molecular structures.

4 Conclusions

Spectral properties of melamine and deuterated melamine-d₆ ranging from 0.2 to 3.0 THz are studied by applying an 8-F confocal THz-TDS characterization. Three bands are found in two samples, 2.0, 2.3 and 2.6 THz of melamine and 1.9, 2.2 and 2.3 THz of deuterated melamine-d₆. The bands at 2.0 and 2.3 THz of melamine are consistent with previous work, and the 2.6 THz band is the first observation by THz-TDS. The vibration modes of every absorption band are explained in the scale of inter-molecular interactions. The 2.0/1.9 THz band is due to the intra-layer hydrogen bonds stretching, the 2.2/2.3 THz band is due to the co-interaction of hydrogen bonds stretching and π-π stacking vibration, and the 2.6 THz band is due to the π-π stacking vibration. The red shift of the melamine-d₆ bands is clearly observed in both experimental and simulated results, proving again the significant effect of the hydrogen bond. This study demonstrates that the absorption bands of melamine and similar compounds in the THz region are mainly resulted from the hydrogen bond stretching and the π-π stacking vibrations, and the band shift is originated from the hydrogen/deuterium substitution. Our study also indicates that THz technology is an ideal modality to determine the existence of the hydrogen bonds and the π-π stacking interactions in certain compounds, and to

fingerprint or distinguish between molecules or compounds and their isotopes.

Acknowledgements

This work was partly supported by the Major Project of the National Natural Science Foundation of China (Grant Nos. 60977064 and 61028011) and Tianjin Sci-Tech Program (Grant No. 07ZCGHHZ01100, Grant No. 09ZCKFGX01500, and Grant No. 10JCYB JC01400). The authors also thank Dr. Zhu Miaoli with Institute of Molecular Scicence of Shanxi University for providing the parameters of melamine crystal structure.

References

- Zeitler J A, Kogermann K, Rantanen J, *et al.* Int J Pharm, 2007, **334**: 78–84.
- Zeitler J A, Newnham D A, Taday P F, *et al.* J Pharm Sci, 2006, **95**: 2486–2498.
- Ge M, Zhao H, Ji T, *et al.* Sci China Ser B, 2005, **35**: 204–208.
- Dobroiu A, Sasaki Y, Shibuya T, *et al.* P IEEE, 2007, **95**: 1566–1575.
- Cao B, Hou D, Yan Z, *et al.* J Infrared Millim W, 2008, **27**: 429–432.
- Li J, Li J, Zhao X. J Chin Univ Metrol, 2009, **20**: 131–134.
- Strachan C J, Taday P F, Newnham D A, *et al.* J Pharm Sci, 2005, **94**: 837–846.
- Wang Y, Kang K, Chen Z, *et al.* J Tsinghua Univ (Sci. & Tech.), 2009, **49**: 161–164.
- Zhang Z, Xiao T, Zhao H, *et al.* Spectrosc Spect Anal., 2008, **28**: 1990–1993.
- Grischkowsky D, Keiding S, van Exter M, *et al.* J Opt Soc Am B, 1990, **7**: 2006–2015.
- Azad A K, Zhao Y, Zhang W, *et al.* Opt Lett, 2006, **31**: 2637–2639.
- Han J, Zhang W, Chen W, *et al.* J Phys Chem C, 2007, **111**: 13000–13006.
- Han J, Zhu Z, Ray S, *et al.* Appl Phys Lett, 2006, **89**: 031107–1–031107–3.
- Harsha S S, Laman N, Grischkowsky D. High resolution waveguide THz-TDS of melamine, conference on lasers and electro-optics/quantum electronics and laser science conference and photonic applications systems technologies, San Jose, CA, USA, May, 2008, JWA40.

- 15 Settle F A. *Handbook of instrumental techniques for analytical chemistry*, Upper Saddle River: Prentice Hall, 1997.
- 16 Stewart J JP. *J Comp Chem*, 1989, **10**: 221–264.
- 17 Li X, Jing B, Li L, *et al.* *J Shanxi Datong Univ (Nat Sci)*, 2009, **25**: 37–39.
- 18 Day G M, Zeitler JA, Jones W, *et al.* *J Phys Chem B*, 2006, **110**: 447–456.
- 19 Hakey P M, Allis D G, Ouellette W, *et al.* *J Phys Chem A*, 2009, **113**: 5119–5127.