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Terahertz absorption spectra of 8-hydroxyquinoline and its some metal complexes

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ABSTRACT

The room temperature terahertz (THz) absorption spectra of 8-hydroxyquinoline (8HQ) and tris(8-hydroxyquinolino)aluminum, bis-(8-hydroxyquinolinato)zinc and copper 8-hydroxyquinoline were clearly measured from 0.3 to 1.8 THz. 8HQ has absorption peaks which occur at 1.02, 1.48, and 1.77 THz. Density functional theory (DFT) was used to predict the vibration frequencies of 8HQ in the frequency range 0–10 THz. Metal complexes have various absorption peaks in the THz region, which may be related to different metal ions and used to distinguish them. These results show that THz-TDS are sensitive tools for characterization of metal complexes.

1. Introduction

Advances over the last ten years in laser and semiconductor technology are now allowing terahertz technology to be applied to many fields such as the semiconductor, chemicals, medical and pharmaceutical, defence and space industries [1–5]. Terahertz time-domain spectroscopy (THz-TDS) is a developed technique, which enables us to acquire much information, such as absorption coefficients, vibration, rotation and refractive indices. THz-TDS provides us with a powerful tool and technology for discussing metal–ligand complexes. Nishizawa [6] presented the transmission spectra of metallocene (Cp2Fe, Cp2Ni, Cp2Ru) and decamethyl metallocene in the range of 0.7–6.2 THz measured by GaP Raman terahertz spectrometer. Yang [7] recorded THz absorption spectra of some saccharides and their metal complexes and the results show that THz methods may be more sensitive tools than mid-IR technique for characterization of metal–sugar complexes. Yuan [8] have studied optical properties of cubic ZrW_2O_8 and HfW_2O_8, and trigonal $ZrMo_2O_8$ and $HfMo_2O_8$ with THz-TDS. However, to our knowledge, no study has reported on the use of THz-TDS spectrometer for 8-hydroxyquinoline (8HQ) and related metal complexes.

8HQ is a monoprotic bidentate chelating agent and has been used for the extraction and analytical determination of metal ions due to the ability to coordinate with metal ions [9]. Metal 8HQ (Mq_n) chelates have been extensively studied in theoretical and experimental aspects. Tris(8-hydroxyquinolino)aluminum (Alq3) is the mile stone for the development of organic light-emitting diode (OLED) because of its good electronic conductivity and strong electroluminescence emission [10,11]. Bis(8-hydroxyquinoline) zinc(II) (Znq2) as an electroluminescent material has been investigated by Hamada [12] in 1993. Since then, OLEDs based on Znq2 were well studied [13] to find new insight to design improved electroluminescent molecules. Copper 8-hydroxyquinoline (Cuq2) is a good antimycoltic agent, and the β-form is known to be more thermally stable. Since M–O vibrations appear in the FIR region, which makes FIR a common used method to characterize metal–ligand complexes. Here 8HQ and some metal complexes were investigated using THz-TDS method, and each complex has characteristic absorption bands from 8HQ in the THz region, which indicates that THz-TDS can be an effective tool to detect these complexes and to identify the formation of metal–ligand complexes.

2. Materials and methods

2.1. Sample preparation

8-Hydroxyquinoline (8HQ), tris(8-hydroxyquinolino)aluminum (Alq3), bis-(8-hydroxyquinolinato)zinc (Znq2) and copper 8-hydroxyquinoline (Cuq2) were obtained from commercial sources and used as supplied. Their chemical structures are shown in Fig. 1. 8HQ, Znq2, Cuq2 and Alq3 were rapidly prepared by weighing 80 mg of each solid, and were gently ground in a mortar and pestle to reduce particle size as much as possible and therefore minimize Mie scattering. Each sample was thoroughly mixed with polyethyl-

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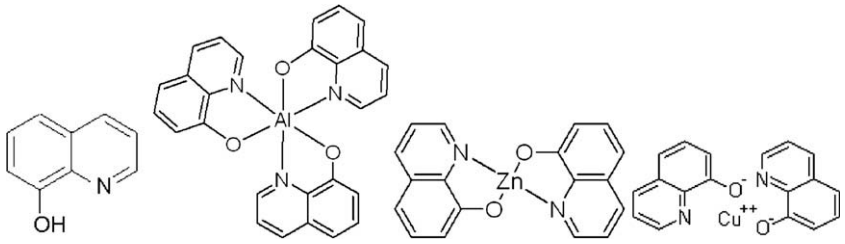

Fig. 1. The chemical structures of 8HQ, Alq3, Znq2 and Cuq2.

ene (PE) powder at a mass ratio of 1:1 and pressed as a pellet in a 13 mm diameter vacuum die at possible pressures of 3 ton with an oil press. Since PE is nearly transparent in THz spectral region and is a suitable filling material for spectroscopic applications. The thickness of pellet is about 1.2 mm, which is sufficient to eliminate etaloning artifacts.

2.2. THz-TDS

Our transmission THz-TDS system has been described elsewhere [14]. Briefly, the femtosecond laser source generates 100 fs pulses at 80 MHz and 700 mW of average power. A beam splitter separates the laser beam into pump and probe pulses. The pump pulse illuminates the THz emitter GaAs crystal to generate a THz beam, while the probe beam collinearly with the THz pulse transmitted the sample, passing through the 2-mm-thick ⟨110⟩ ZnTe crystal. Pulsed THz radiation was detected via electro-optical sampling [15]. Signal noise ratio (SNR) was higher than 1000:1, and the spectral resolution was better than 40 GHz. The entire THz beam pathway is purged with dry-nitrogen purged to reduce the absorption of the residual water vapor that can cause interference in the THz spectrum.

2.3. Density functional theory (DFT)

Recently, density functional theory (DFT) has been accepted as a popular approach for the computation of molecular structures, vibrational frequencies, energies of chemical reactions, etc. There is sufficient evidence that DFT has proven to be surprisingly successful in predicting accurate vibrational frequencies for medium size molecules in the mid-infrared. However, several groups are beginning to predict and try to understand THz spectra using DFT. For example, Allis et al. [16] have analyzed the THz spectrum of HMX with isolated-molecule and solid-state DFT calculations.

DFT calculations using B3LYP functions, along with 6-31G* base set, were performed on 8HQ using the program package GAUSSIAN03 [17]. The resulting non-negative vibrational frequencies confirmed that the calculated minimized structures of 8HQ were found. The calculated vibrational frequencies of 8HQ agree with those from experiments. All calculated vibrational frequencies are scaled by 0.960, which is cited from NIST computational comparison and benchmark database (CCCBDB).

3. Results and discussion

3.1. THz spectra of 8HQ

The field of a THz pulse transmitting through a sample is modified by dispersion and absorption of the sample. Fig. 2(a) shows the waveform of the THz signal through the reference and the sample of 8HQ. Fig. 2(b) presents the Fourier transforms of the waveforms in Fig. 2(a). The measured pulse is delayed because of the different refractive index of 8HQ and reference. The amplitude of

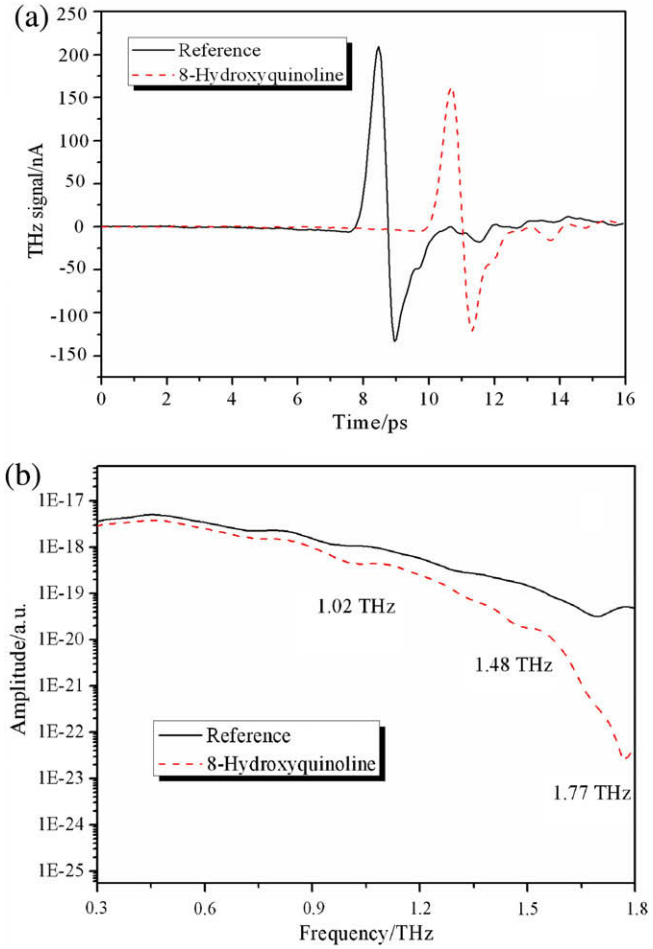

Fig. 2. THz time-domain spectra (a) and THz frequency-domain spectra (b) of 8HQ.

the measured pulse decreased is due to the absorption of 8HQ. This graph indicates that 8HQ has absorption peaks which occur at 1.02, 1.48, and 1.77 THz. Fig. 3 shows the absorption coefficient of 8HQ between 0.5 and 1.8 THz. It can be seen that 8HQ exhibits one prominent absorption peak at 1.77 THz and two weak ones at about 1.02 and 1.48 THz. A detailed assignment of the vibrational modes in the THz region is a challenging task. We limited ourselves to a description of the spectra observed in the 0.5–1.8 THz range. As is well known that inter- or intra-molecular vibrational modes or lattice vibration contribute to the low-frequency spectrum and result in obvious absorption. Comparison of mid-IR of 8HQ between experiment and calculation is shown in Fig. 4. The calculated O–H stretching vibration (νO–H) is found at 3418 cm^{-1} and being sharp, while there appears a broad absorption at 3400–3100 cm^{-1} in the measured FT-IR spectrum. The in-plane deformation modes of O-H (δO–H) appears at 1456 cm^{-1} in the experiment,