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RESEARCH ARTICLE

Characterizing $PM_{2.5}$ in Beijing and Shanxi Province using terahertz radiation

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Abstract Particles of aerodynamic diameter⩽2.5 μm ($PM_{2.5}$) caused extremely severe and persistent haze pollution is of concern in many cities. In this study, samples of $PM_{2.5}$ were collected from atmosphere environment of Beijing and Shanxi Province, and analyzed using terahertz (THz) radiation. The transmission spectrum of $PM_{2.5}$ in Shanxi Province had two distinct absorption peaks at 6.0 and 6.7 THz, and the curve was increasing on the whole. However, the transmission spectrum of $PM_{2.5}$ in Beijing had obviously different variation tendency and the absorption peak was studied by monitoring $PM_{2.5}$ masses in conjunction with two-dimensional correlation spectroscopy (2DCOS). By comparing the pollutant species and concentrations of Shanxi Province and Beijing over the time of collecting samples, the concentrations of sulfate and ammonium were similar, which contributed to emerge absorption bands in the same position. While the concentrations of organic matter (OM), nitrate, chloride and elemental carbon (EC) were different. Furthermore, dust and some other inorganic ion are unique to Shanxi province, which lead to different variation tendency of the transmission spectrum of $PM_{2.5}$. These results will be of importance for environmental monitoring and for controlling PM emissions. According to this research, optical techniques, and especially spectral methods, should be considered for $PM_{2.5}$ monitoring.

Keywords $PM_{2.5}$, terahertz, two dimensional correlation spectroscopy (2DCOS)

1 Introduction

With the rapid development of industrialization and urbanization in China, particulate pollution has frequently occurred over the country and attracted worldwide attention, which is influencing air quality, human health, global climates and leading to huge economic losses [1]. The economic losses caused by $PM_{2.5}$ (particles of aerodynamic diameter⩽2.5μm) only in Beijing area has reached 1.86 billion CNY in 2010 and it is increasing enormously year by year [2]. The incidences of cardiovascular and respiratory diseases are rising in the world. In hospital emergency room visits, $PM_{2.5}$ is often linked to adverse health effects. Therefore, efforts need to be made to prevent and control PM pollution.

$PM_{2.5}$ is the primary pollutant causing haze. Particularly, the severe haze pollution event is mainly driven by secondary constituents of $PM_{2.5}$, which account for 30%–77% [1]. The composition of $PM_{2.5}$ is complex including organic carbon, nitrate, sulfate, ammonium, chloride, trace elements, elemental carbon (EC), etc. And it includes components from various sources including industry, vehicle emissions, residences, biomass burning and other human activities [3]. Finding the main source of pollutants and distinguishing the main types of pollutants are conducive to taking more practical and feasible measures. At the moment, tapered element oscillating microbalance (TEOM) and β-ray absorption method are often used to detect $PM_{2.5}$ automatically. TEOM method can reflect the particulate matter concentration, but it also has complex instrument structures which need to be maintained troublesomely. Meanwhile, β-ray absorption method is simple and it can realize automatic and continuous monitoring. Because of huge land area and complex climate characteristics in China, some existing technology has some limitations. Some direct detection of $PM_{2.5}$, such as spectrum detection and spectral analysis, can effectively make up for these problems [4–6]. It has also been proven that optical techniques, especially spectral methods, can be considered for $PM_{2.5}$ monitoring. Terahertz (THz) wave bridges the gap between microwave and infrared in the

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electromagnetic spectrum [7,8], which has been used for characterization of natural gas, qualitative identification of crude oils, determination of the principal components of natural gas and so on [9–12]. THz spectra with the dust environment showed the relationship between absorbance and mass of $PM_{2.5}$ [13,14], suggesting that THz spectroscopy is effective and feasible for the characterization of atmosphere environment.

In this work, a set of $PM_{2.5}$ samples from Changping in Beijing and Taigu in Shanxi Province, China were studied, and the pollutant species and concentrations in two areas were characterized using THz spectroscopy with two-dimensional correlation spectroscopy (2DCOS).

2 Experiment

$PM_{2.5}$ particulate was collected by the Minivol Tactical Air Sampler (TAS) from October 2 to October 19, 2015. Air was drawn through a particle size separator which had a 10-cut-point and a 2.5-cut-point, and $PM_{2.5}$ was collected on the filter medium (made of quartz with a diameter of 47 mm). The speed of air drawn was set as 8 L/min. To reduce the impact of changes in external environmental conditions, blank filters were treated in constant temperature and humidity before and after the sampling process.

The absorption spectra of the $PM_{2.5}$ samples in THz range were measured by a Fourier transform infrared spectrometer (FT-IR) [15,16]. And a pre-configured program was used to preprocess the spectra to make the multivariate statistical analysis of spectra data [17,18]. Absorbance of the FT-IR spectrum analysis was adjusted to 0–676 cm^{-1}. At the same time, each spectrum was normalized to the same area to minimize experiment errors to standardize baseline correction.

2DCOS enables cross-correlation analysis of spectral series of systems that change with any physical variable [14]. The spectrum resolution can be improved and the spectrum which contains many overlapping peaks can be simplified. 2DCOS provides two different correlation maps. The synchronous map displays correlations between all spectral bands changing in phase in the experiment and shows whether they increase or decrease relative to each other. The asynchronous correlation map, in contrast, relates spectral bands that change at different rates and also contains information about the sequence of the events occurring [19]. The cross-correlation function including the real and imaginary parts is called the synchronous and asynchronous spectra, respectively. A cross peak, in the asynchronous spectrum, provides a tool to visualize independently changing bands when two spectral features change out of phase or at a different rate. The synchronous spectrum, on the other hand, provides information on the overall similarity or coincidental trends between two separate intensity variations measured at different spectral variables.

3 Results and discussion

The frequency-dependent spectra of samples (filters with $PM_{2.5}$ collected from Beijing and Shanxi Province) and references (blank filters) were shown in Fig. 1 and the maximum peak value occurred at 4.5 THz. The amplitude of reference was higher than that from Beijing and Shanxi. The curves appeared significant differences at 4.5, 6.5 and 7.0 THz. Hence more attention was paid to the frequency from 4.0 to 7.5 THz. According to Beer-Lambert Law, the spectra were processed by Fourier transform and the absorbance spectra were calculated using $A = \ln(I_0/I)$, where I_0 and I were the signal intensities of the reference and sample.

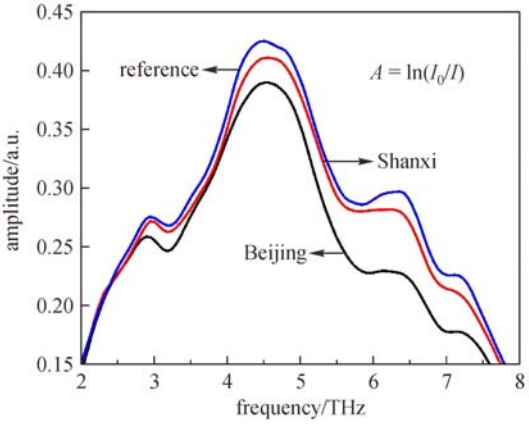

Fig. 1 Frequency-dependent spectra of $PM_{2.5}$ from Beijing as well as Shanxi and reference (blank filters)

The THz absorption spectra of $PM_{2.5}$ in 4.0–7.5 THz were presented in Fig. 2. A Savitzky–Golay filter was applied to pre-process the absorption data, which could reduce instrument noise and smooth curve but did not

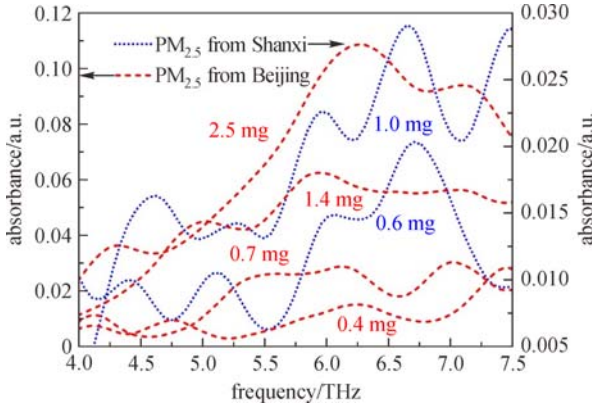

Fig. 2 Frequency dependence of the absorbance spectra of the $PM_{2.5}$ samples collected in the atmospheric environment from Beijing and Shanxi, respectively. The mass of $PM_{2.5}$ collected from Beijing ranged from 0.4 to 2.5 mg. And the mass of $PM_{2.5}$ collected from Shanxi ranged from 0.6 to 1.0 mg

distort the spectral waveforms and absorption features [20]. Two prominent peaks were identified at 6.0 and 6.7 THz for the samples from Shanxi. At 6.7 THz, with increasing $PM_{2.5}$ mass from 0.6 to 1.0 mg, the absorbance changed from ~0.020 to ~0.030. Meanwhile, two peaks were observed at ~4.6 and 5.2 THz with lower amplitude. The absorbance of 1.0-mg $PM_{2.5}$ reduced to ~0.015 and that of 0.6 mg $PM_{2.5}$ was merely ~0.010 at 5.2 THz. With the increasing of frequency, the THz waveform of $PM_{2.5}$ from Beijing also reflected a similar tendency of rising. It was necessary to point out that there was almost no sharp absorption peak over the entire frequency range. One prominent band was identified in the 5.7–7.5 THz region. To accurately determine the characteristics of the $PM_{2.5}$ in Beijing, 2DCOS was used to extract more detailed information about the spectral changes and identify the overlapped peaks or unobvious peaks in Fig. 2.

2DCOS was used to enhance spectral resolution by spreading peaks along the second dimension. Synchronous 2-D correlation plot of all the samples over the frequency range from 4.0 to 7.5 THz was showed in Fig. 3. In 2DCOS models, the absorbance spectra from 4.0 to 7.5 THz were employed as the input and the mass of all samples were used as the perturbation. If the sign of a cross peak was positive, intensities at corresponding frequency were increasing or decreasing together; otherwise, one was increasing while the other was decreasing. The large-scale correlation for the auto-peak showed a high extent of dynamic fluctuations. Positive correlation was observed over the entire frequency range (Fig. 2), which indicated that the absorption increased with $PM_{2.5}$ mass over the entire frequency (4.0–7.5 THz). An auto-peak (the peak on the diagonal) at 6.48 THz in the synchronous map reflected the overall spectral change, while there was no symmetric cross peak at the other correlation square. This indicated 6.48 THz was the center of the absorption band and there was only one absorption peak. The results were in agreement with what was got about atmosphere environment before [13,14].

Asynchronous 2DCOS figure was plotted in Fig. 4. Several strong cross peaks were observed in the range 6.0–7.5 THz. While positive or negative correlation in the asynchronous plot reflected the special asynchronous characteristics of the signal intensities at different frequency, and the information revealed from positive and negative correlation was different. In asynchronous correlation spectrum, cross peaks developed only if the intensity varies out of phase with each other for some Fourier frequency components of signal fluctuations [21]. More information from original spectra could be obtained in asynchronous plot. According to the absorption status at ~6.48 THz, positive correlation was found at 6.31, 6.42 and 6.89 THz, respectively. The cross peaks in the asynchronous plot indicated that the absorption band, centered at ~6.42 THz, was composed of these three overlapping peaks. Besides, absorbance at 6.42 THz was stronger, which contributed more to the absorption band at 6.48 THz in Fig. 3. Furthermore, according to the 2DCOS analysis, three cross peaks were also observed at 5.03, 5.68 and 7.35 THz in Fig. 4, indicating weak or unobvious absorption peaks in the original spectra. All of the positive correlation illustrated the sequencing of intensity changes at the two frequencies. The band at 6.42 THz changed prior to that at 5.03 THz, and the band at 6.89 THz lagged behind compared with the bands at 6.31 and 7.35 THz. As was shown in 2DCOS, some characteristic absorption peaks of spectra reflecting $PM_{2.5}$ in Changping, which might not be well identified through original spectra, had been acquired. Thus the comparison of $PM_{2.5}$ between two regions could be proceeded.

This study focused on the differences between THz spectra of $PM_{2.5}$ collected from two areas. Absorption

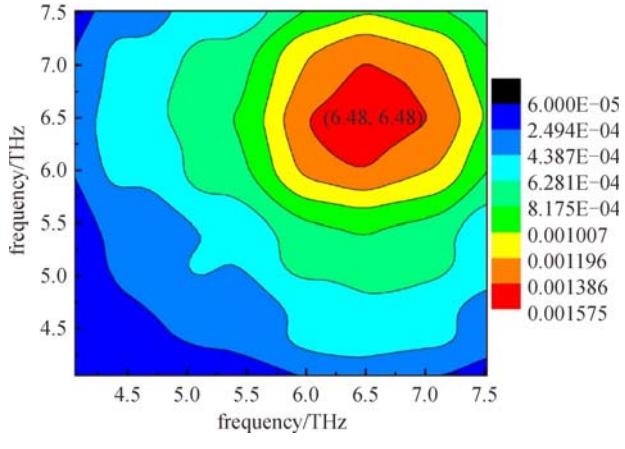

Fig. 3 Synchronous 2-D correlation plot over the frequency range from 4.0 to 7.5 THz. The numbers represent the coordinates of the peaks in synchronous data. Positive correlation is indicated that the absorption increased with $PM_{2.5}$ mass over the entire frequency (4.0–7.5 THz)

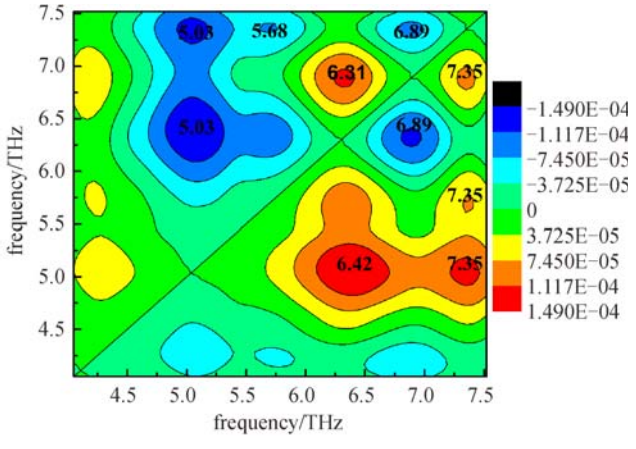

Fig. 4 Asynchronous 2-D correlation plot over the frequency range from 4.0 to 7.5 THz. The numbers represent the horizontal ordinates of the peaks in asynchronous data. Cross peaks develop only if the intensity varies out of phase with each other for some Fourier frequency components of signal fluctuations

curves of Taigu in Shanxi showed a rising tendency as a whole and a prominent peak was identified at 6.7 THz in the image. Characteristic peaks of absorption spectra of $PM_{2.5}$ in Changping at 6.31, 6.42 and 6.89 THz could be classified as 6.7 THz. That was on account of the small deviations from this frequency and the coherence reflected in the asynchronous plot. Hence, additional difference in absorption spectra was showed in the range 4.0–7.5 THz. The absorption peaks in the spectra of $PM_{2.5}$ from Taigu, Shanxi lay at 6.0, 5.2 and 4.6 THz. In contrast, some weak or unobvious absorption peaks at 5.03, 5.68 and 7.35 THz were found in the spectra of $PM_{2.5}$ from Changping, Beijing.

Due to a similar response of THz radiation to the similar concentrations of sulfate and ammonium in two areas, both of spectra emerged absorption peak at ~6.7 THz. Nevertheless, by comparing the pollutant species and concentrations of Shanxi Province and Beijing over the time of collecting samples, the concentrations of organic matter (OM), nitrate, chloride and elemental carbon (EC) were different [22]. Besides, dust and some other inorganic ion were unique to Shanxi province. These differences led to different variation tendency and different peaks of the $PM_{2.5}$ absorption spectra. According to the survey, air pollution sources were complicated in Beijing. Except for traffic and coal burning, complex weather conditions and impacts of human activities made air pollution more severe. Because the sources of $PM_{2.5}$ in Beijing were complex, some weak or unobvious characteristic peaks of THz absorption spectra were showed at different frequencies. These results indicate THz measurements can be employed and required for the application in characterizing $PM_{2.5}$. And THz absorption spectra can be used to identify different pollutant sources. What's more, rapid, direct and correct identification of pollutant sources can be found using THz fingerprint database. These results will be of importance for environmental monitoring and for controlling PM emissions.

4 Conclusions

In summary, this study focused on the different responses between $PM_{2.5}$ from two areas under THz radiation. By comparing the pollutant species and concentrations of Shanxi Province and Beijing over the time of collecting samples, the concentrations of sulfate and ammonium were similar, which contributed to emerge absorption peak at 6.7 THz, while, the concentrations of organic matter (OM), nitrate, chloride and elemental carbon (EC) were different. Furthermore, dust and some other inorganic ion were unique to Shanxi province. These differences led to different variation tendency and different peaks of the $PM_{2.5}$ absorption spectrum. Because atmospheric pollutants in different areas were distinctly different, THz absorption spectra would show different tendency and absorption features. It was proved that THz radiation could identify pollutants in different areas.

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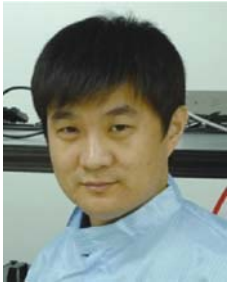

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