Identification of terahertz fingerprint spectra extracted from Gas-Fat coal

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Abstract: The absorption spectra of gas-fat coal (GFC) in the frequency range 1 to 9 *THz* have been studied by experiment and computer simulation. The Gaussian lineshape fingerprint spectra were exfoliated from the Terahertz absorption curve by a fast method of curve fitting, and the corresponding low frequency vibrational modes were identified with the aid of Gaussian©, one piece of quantum chemical computer software. It is found that there are 2 absorption peaks by experiment, which is in good agreement with those by computer simulation, and both of them point to bending vibrations in the plane of aromatic rings. It indicates that the in-plane bending energy is less affected by interactions between the basic structural units (BSUs) of coal. On the other hand, there are 2 pairs of discrepant peak positions by experiment and computing, which respond to out-of-plain bending vibrations of methyl and hydroxyl. It is believed to derive from interactions between the BSUs, which are not be considered in computer simulation. The sensitivity of out-of-plain bending energy to entire molecule structure and environment is essential for fingerprint identification of macromolecules.

Keywords: Terahertz, Coal chemistry, Gaussian lineshape, Fingerprint spectra.

1. Introduction

Terahertz (THz) waves are recognized of great importance in the chemical and physical analysis due to the uniqueness of THz range from other frequency ranges of electromagnetic waves. Rotational and vibrational modes of organic molecules such as aromatic compounds fall into the THz range. Thus THz spectra are of sensitive response, which can provide robust fingerprinting features, to isomers and even slight differences of the molecular structure of materials. Moreover, the low photon energy (4 *meV* @ 1 *THz*) of the THz radiation allows propagation through flammable materials or body tissues without causing any danger of combustion or ionization [1]. Therefore, THz spectroscopy has attracted greater interest in some specific fields of such as public security, biomedicine, energy chemistry, etc [2-6].

We focus on the primary energy sources. F. M. Al-Douseri, *et al* reported the results of THz wave sensing for petroleum industrial applications, which was regarded as pioneering work on THz spectroscopy applied in the field of energy chemistry [1, 6]. The similar task on coal has not

yet been carried out due to the more complexity of coal with properties of solid polymer and mixture. Still, in this letter, the THz spectra of gas-fat coal (GFC) during 1 to 9 *THz* have been studied. GFC belongs to the rank of high volatile bituminous coal (HVBC) with medium degree of coalification [7]. It is appropriate for coal blend coking and destructive distillation to generate gas as clean fuels [8, 9]. To improve the conversion efficiency, it is necessary to get more information about the molecular structure of GFC with the aid of THz waves. THz spectroscopy analysis on coal will be a new significant method in Coal Chemistry.

2. Experimental and computational methods

The GFC samples from a mine in Taiyuan, Shanxi province are ground into particles with diameter <0.15 *mm*, then tableted with thickness 1 *mm* and diameter 12 *mm* by a pressure of 30 *tons*. Due to the complexity of coal chemical components, there has been little information gotten by THz time-domain spectroscopy (THz-TDS) with range of 0.2 to 3.0 *THz* limited at present. Then a Fourier transform infrared (FTIR) spectrometer, BRUCK VERTEX 80 *V*, has to be applied to sense the GFC samples. When the phase measurements are not discussed, the absorption coefficient can be defined by [4]

$$\alpha(v) = -\frac{1}{d}\ln\left[\frac{E_s(v)}{E_r(v)}\right] \tag{1}$$

Where $E_s(v)/E_r(v)$ is the field transmitted through the sample/reference, and d is the thickness of sample.

The THz absorption spectra are overlapped seriously due to the property of coal mixture. The fingerprint information that includes the positions and intensities of absorption peaks have to be extracted from the composite spectra by a spectrum exfoliating method.

IR including THz spectra are recorded theoretically in Lorentzian lineshape but experimentally in Gassian lineshape [10],

$$Y(v) = E\exp\left[-\frac{(v-v_0)^2}{2\sigma^2}\right] \tag{2}$$

Where E, v_0 and σ are peak height, peak frequency and half-peak width respectively. Then the first and second-order derivatives are

$$Y' = -\frac{(v-v_0)}{\sigma^2}E\exp\left[-\frac{(v-v_0)^2}{2\sigma^2}\right] \tag{3}$$

$$Y'' = \left[\frac{1}{(\nu - \nu_0)} - \frac{(\nu - \nu_0)}{\sigma^2} \right] Y' \tag{4}$$

The following parameters are obtained

$$\sigma^2 = \frac{(\nu - \nu_0)^2 Y'}{Y' - (\nu - \nu_0) Y''} \tag{5}$$

$$E = -\frac{Y' \sigma^2}{(\nu - \nu_0)} \exp\left[\frac{(\nu - \nu_0)^2}{2\sigma^2} \right] \tag{6}$$

In the numerical computing process

$$Y'_n = (\alpha_{n+1} - \alpha_n) / (\Delta \nu) \tag{7}$$

$$Y''_n = (\alpha_{n+1} - 2\alpha_n + \alpha_{n-1}) / (\Delta \nu)^2 \tag{8}$$

Where α_n is absorption coefficient corresponding to the discrete frequency ν_n, and $\Delta \nu$ is the sampling frequency interval. The peak frequency ν_0 is acquired to satisfy $Y'=0$ and $Y'' < 0$. A set of $[\sigma_i^2, E_i]$ is computed point by point from the peak to the both sides up to $Y''=0$. Finally the parameters of Gaussian line are obtained as the mean values $\sigma = \sqrt{\overline{\sigma_i^2}}$ and $E = \overline{E_i}$.
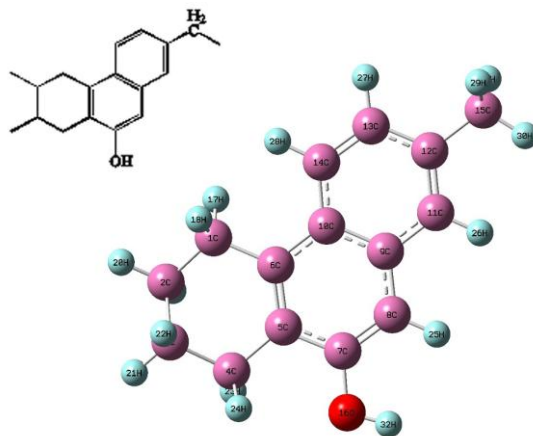

Fig. 1 The optimized molecular model together with structure formula of the BSU of GFC

In order to identify the corresponding vibrational modes of the absorption peaks, Gaussian©, a piece of quantum chemical software, is applied to compute simulation. The periodic structures in polymer macromolecule of coal are named Basic structural units (BSUs). The BSUs are composed of aromatic nucleus and kinds of side chains and bridges. It is shown in fig.1 that

the approximate BSU of GFC is formed with 1, 2, 3, 4-tetrahydrophenanthrene as the aromatic nucleus together with a methyl and a hydroxyl side chains [11]. Density functional theory (DFT) with the method of B3LYP/6-311+G (d, p) is adopted to simulate the BSU of GFC.

3. Fingerprint spectra and vibrational modes

It shows in fig.2 that the spectra limited in the range of 1 to 9 *THz* are effective to discuss because the Signal-to-noise ratio (SNR) is too low beyond the range. Then the original THz absorption curve and the exfoliated fingerprinting spectra compared with the simulated results are plotted together in fig 3. Meanwhile, the data of the fingerprinting spectra and the simulated spectra together with the corresponding vibrational modes are listed in table 1. There are 7 peaks obtained by experiment and 8 by computing simulation, where 5 pairs of peaks match with each other. Moreover, in this range there are no stretching modes except bending modes: (1)Scissoring, symmetrical bending in plane; (2) rocking, asymmetrical bending in plane;(3) wagging, symmetrical bending out of plane; and (4) twisting, asymmetrical bending out of plane.
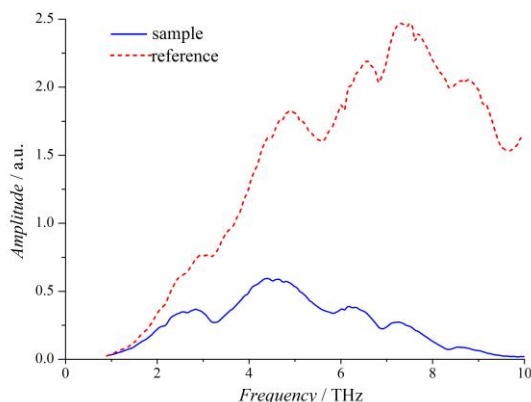

Fig. 2 Terahertz frequency domain spectra of GFC's sample and reference

The 4th and 6th peaks by experiment (5.86 and 8.33 *THz*) are in best agreement with simulation. Both of them are identified that they are originated from the in-plane vibrational modes (scissoring) of the hydrogenated ring, methyl or hydroxyl group. It indicates that the in-plane THz vibration of side chain in coal molecule is little affected by interactions between the BSUs, because the simplified model of isolated BSU is adopted in simulation without considering the interactions.

In contrast, there is a significant distance between the 5th peak 6.93 *THz* by experiment and 7.39 *THz* by simulation, which is corresponding to the out-of-plain vibrational mode of the hydroxyl and methyl group. The discrepancy may be derived from the model simplification of simulation. Therefore, it reveals that the out-of-plain vibrational energy of side chains in coal molecule is sensitive to the structure of high polymer or the variance of environment. Even the

3rd peak 3.84 *THz* exhibits a similar appearance. It will provide more information for fingerprinting identification of polymers.
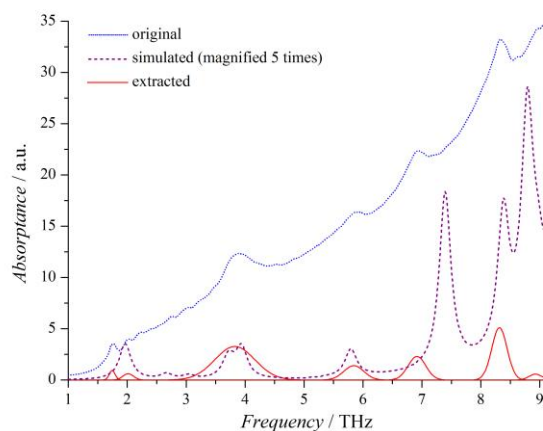

Fig. 3 Gaussian lineshape fingerprinting spectra extracted from original Terahertz absorption comparing with computer simulation

Tab. 1 Data of absorption peaks by experiment and simulation with vibrational modes

No.	Experimental		Simulated		vibrational modes
	Position /THz	Intensity /a.u.	Position /THz	Intensity /a.u.	
1	1.76	0.93			
2	2.03	0.61	1.94	0.75	Wagging of the entire aromatic nucleus around the minor axis
3	3.84	3.27	3.70	0.45	Twisting of the hydrogenated ring
			3.92	0.65	Synergetic twisting of the hydrogenated ring and methyl group
4	5.86	1.39	5.78	0.58	Synergetic scissoring of the hydrogenated ring and the methyl group
5	6.93	2.31			
			7.39	3.67	Synergetic twisting of the hydroxyl group and methyl group
6	8.33	5.10	8.38	2.82	Synergetic scissoring of the hydroxyl group and methyl group
7	8.91	0.57	8.79	4.58	Synergetic twisting of the hydrogenated ring and hydroxyl group
			8.96	0.89	Wagging of the entire aromatic nucleus around the major axis

4. Conclusions

The THz absorption spectra of gas-fat coal have been studied by experiment and computer simulation. It has been found that the energy of bending vibrations of the hydrogenated ring and side chains causes strong THz absorption peaks. The THz fingerprint spectra have been collected and identified that the out-of-plain vibrations of side chains are more sensitive to the entire

structure of high polymer or the variance of environment. It results in characteristic performance of THz fingerprinting for coal chemistry.

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