Detecting Marine Kerogen from Western Canada Basin Using Terahertz Spectroscopy

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ABSTRACT: In this paper, terahertz time-domain spectroscopy was employed to study the properties of marine kerogen from Western Canada Basin at various temperatures. On the basis of terahertz absorption coefficients of samples, the evolution model of oil and gas generation in kerogen was established, explained, and verified by IR and principal component analysis. In addition, the molecular models of kerogen were simulated by means of the quantum chemistry. Then the vibration characteristics of functional groups in terahertz band were analyzed, and the reasons for different absorptions of kerogen at different temperatures were explained. This study will provide a reference for thermal evolution kinetics of kerogen, as well as an effective complement to the potential evaluation of oil and gas resources.

1. INTRODUCTION

The Western Canada Basin is a massive sedimentary basin with an area of 1.4 × 10^6 km^2, including southwestern Manitoba, southern Saskatchewan, Alberta, northeastern British Columbia, and southwestern corner of Northwest Territories. The rock formation is about 6 km thick below the Rocky Mountain, rich in shale and with a high abundance of organic matter.1 In sedimentary rock, ~95% of the organic matter is composed of kerogen, the key intermediate in the formation of oil and gas.2 Studying the thermal evolution of kerogen will help to better understand the mechanism of oil generation in kerogen and provide the basis for further improvement of the modern oil generation theory.

Various methods have been applied to study kerogen, such as thermal analysis, chemical degradation, infrared (IR) and Raman spectroscopy, gas chromatography–mass spectrometry, and solid-state nuclear magnetic resonance (NMR) spectroscopy. Hu Haiyan3 et al. characterized kerogen by 13C NMR spectroscopy and obtained the structural parameters of kerogen, revealing the thermal evolution and hydrocarbon generation of kerogen. By the Fischer assay experimental approaches, Deng guo Lai4 et al. found that most of the aliphatic carbons in kerogen generated oil and gas, and the aromatic carbons were mainly converted into a coke residue. Our group adopted terahertz time-domain spectroscopy (THz-TDS) to probe the evolution of kerogen with temperature in a semiclosed and semiopen system. Terahertz spectrum has been employed to obtain information of materials by many investigators and efforts were made to apply the terahertz approach to detect kerogen in this work.5–12 Terahertz technology is a nondestructive testing technique compared to other means that are routinely used by organic geochemists. However, the absorption change caused by the weak motions of molecules plays an important role in analyzing the evolution of kerogen, which can be a supplement in the abovementioned studies. In the electromagnetic spectrum, some activities correspond to the terahertz range, such as weak interactions (such as hydrogen bonds) between organic molecules, slow movement and rotation of macromolecules, skeleton vibration of macromolecules (configuration bending), dipole rotation, and vibration transition.13 Therefore, it is of some significance to study the mechanism of action between the terahertz wave and kerogens.

In this work, kerogens at different temperatures were characterized by THz-TDS, and the evolution model of hydrocarbon generation was established. Then the relationship between THz absorption and chemical bond fracture was analyzed by IR. The kerogen functional molecule was modeled by Gaussian software using the quantum chemistry method, and motion modes of the molecules in the terahertz range were
observed visually through Gauss View video function. In this way, the weak vibration and the large skeleton vibration of different functional groups were identified at different frequencies.

2. RESULTS AND DISCUSSION

Figure 1 shows terahertz time-domain spectra of samples after terahertz wave passing through kerogens and the illustrations is frequency-domain spectroscopy. As shown in Figure 1, kerogens at different temperatures had different terahertz absorptions. Therefore, amplitude of terahertz wave was found to be various after passing through different samples. The terahertz refractive index of the sample was higher than the refractive index of N₂, resulting in different propagation speeds of terahertz waves through different samples, which caused diverse time delay. In terahertz frequency-domain spectra obtained by fast Fourier transformation of time-domain spectra for samples and reference, terahertz radiation was mainly concentrated in the frequency range of 0.3–1.45 THz. Different kerogen samples corresponded to different frequency-domain spectra.

Figure 2 shows terahertz absorption coefficient spectra of the samples. As shown in Figure 2, compared with the absorption curves of the samples with different temperatures, the evolution model of kerogen was established (Figure 3). As shown in Figure 3, it can be found that the absorption curves of the samples at various evolutionary temperatures had different trends. Absorption coefficients of the samples at 310, 425, and 450 °C reached the maximum at 0.8 THz. As seen from Table 1, at 310, 425, and 450 °C, carbon–oxygen double bond disappeared or appeared again, showing that 0.8 THz is the sensitive frequency of carbon–oxygen double bond cleavage. The maximum absorption varied with frequency at different temperatures, indicating that the changes are not the same. For example, the wave number of carbon–carbon double bonds changed at 350 and 400 °C. A large number of carbon–hydrogen bonds appeared at 350 °C, and the wave number of carbon–hydrogen bonds decreased obviously at 375 °C.

According to the theory of oil generation, the hydrocarbon evolution of organic matter can be divided into five stages. As shown in Figure 3, it can be seen that there was a certain relationship between terahertz optical parameters of kerogen and stages of hydrocarbon evolution by comparing kerogen absorption curves and evolution temperatures at different frequencies. At early mature stage (225 °C ≤ T < 300 °C), the functional groups did not change significantly and terahertz optical constants showed little change. During the middle mature stage (300 °C ≤ T < 375 °C), methyl, methylene, and oxygen-containing functional groups were separated from kerogen, producing a large amount of oil and gas.

**Table 1. Wave Number of Functional Groups Corresponding to Kerogen Samples at Different Temperatures by Fourier Infrared Spectra**

| temperature °C | −CH₃ | −CH₂ | C=O | C=C | clay mineral | C–H |
|----------------|------|------|-----|-----|--------------|-----|
| RT             | 2920, 2848, 1449, 1376 | 1696 | 1617 | none | none |
| 200            | 2920, 2848, 1446, 1373 | 1700 | 1620 | none | none |
| 225            | 2917, 2848, 1446, 1373 | 1693 | 1621 | none | none |
| 250            | 2924, 2851, 1449, 1376 | 1696 | 1614 | none | none |
| 275            | 2917, 2851, 1449, 1376 | 1696 | 1607 | 1096, 1036 | none |
| 300            | 2920, 2848, 1446, 1373 | 1693 | 1604 | 1109, 1043 | none |
| 310            | 2917, 2848, 1449, 1373 | none | 1607 | 1109, 1036 | none |
| 325            | 2914, 2848, 1442, 1376 | none | 1597 | none | none |
| 350            | 2920, 2851, 1442, 1376 | none | 1594 | none | 3043, 861, 809, 749 |
| 375            | 2917, 2845, 1439, 1376 | none | 1594 | none | 865, 812, 746 |
| 400            | 2917, 2845, 1432, 1373 | 1693 | 1584 | none | 3043, 868, 805, 746 |
| 425            | 2914, 2845, 1439, 1376 | 1693 | 1587 | none | 3046, 868, 812, 749 |
| 450            | 2914, 2845, 1439 | none | 1587 | none | 3049, 868, 805, 746 |
Furthermore, the corresponding terahertz absorption changed significantly. This stage was the peak of oil generation of kerogen. During this period, there were peaks of clay minerals due to the pyrolysis effect of rock, while clay minerals have an obvious effect on the amount and composition of organic hydrocarbons.\textsuperscript{15,16} As the simulated temperature increased, the remaining kerogens agglomerates into large molecules with aromatic nuclei during the late mature stage of evolution \((T \geq 375^\circ C)\).\textsuperscript{17} This stage produced a large number of C–H bonds (Table 1), mainly generating methane. The condensation and cleavage of the molecules increased terahertz absorption coefficients again.

In this study, principal component analysis (PCA) was used to analyze the relationship between temperature and absorption coefficient as well. On the basis of the idea of dimensionality reduction, the multi-index was transformed into a few comprehensive indexes [i.e., principal components (PCs)]. PCA is a mathematical method, which reduces the number of dimensions within the data while retains as much of the overall variations as possible based on uncorrelated projections. The calculation of PCA results in several variables called PCs. PCs are a set of new maximized variables, which are uncorrelated and expressed as a linear combination of original variables.\textsuperscript{11} The results showed that the first PC (PC1) accounted for 91.4% of the total and contributed the most to kerogen. The second PC (PC2) accounted for 4.6%, making the second contribution to kerogen. As shown in Figure 4, kerogen at different stages can be classified by PC1 and PC2. PC1 and PC2 were related to original variables\textsuperscript{18,19} while kerogen at the same maturity stage got together, which was consistent with the evolution model of kerogen oil and gas generation.

In order to further investigate the absorption characteristics of kerogen molecules, the dielectric functions of the samples were studied. The optical properties of the matter can be uniquely determined by the dielectric function, which is related to the microscopic electromagnetic interaction of the matter.\textsuperscript{20} When an external electric field is applied to the sample, the phenomenon will appear. After removing the electric field, this phenomenon will disappear and the molecules relax and return to their original state. The time of relaxation process is called relaxation time \(\tau\), which is in picosecond and can be detected by the terahertz wave.\textsuperscript{21} As shown in Figure 5, the real part of dielectric constant \(\epsilon'(\omega)\) was calculated, \(\epsilon'(\omega) = n^2(\omega) - k^2(\omega)\), in which \(n\) is the refractive index and \(k\) is the extinction coefficient. As the frequency increased, the real part of dielectric constant showed a decreasing trend. When the electric field frequency increased, the intermolecular rotation became more and more difficult because of the restriction of polymer chain bonds and covalent bonds between carbon atoms and hydrogen atoms, and the polarization rate does not change with increasing frequency.\textsuperscript{14} As shown in Figure 6, the imaginary part of dielectric constant \(\epsilon''(\omega)\) was calculated, \(\epsilon''(\omega) = 2nk\); they had a large difference before 0.5 THz, but they became stable after 0.5 THz, which showed that the dielectric properties of kerogen had significant changes at low frequency.

Intermolecular collision can cause transient dipole moment, and the relaxation process occurs after interaction with the electric field.\textsuperscript{22,23} The reason that differences existed in the dielectric properties of samples with different temperatures was that the collision probabilities of the sample molecules with different evolution temperatures were various and that the shorter hydrocarbon chain was conducive to inducing the dipole moment of a single molecule.\textsuperscript{24} As the temperature increased, the carbon chains of kerogen continued to fall off to form hydrocarbons and became shorter and shorter, which affected the relaxation process and time. Therefore, the optical parameters of kerogen with different temperatures were inconsistent.

The interaction between kerogen and terahertz wave was based on the change of functional groups.\textsuperscript{25} In order to demonstrate the change of functional groups in the terahertz range during the evolution of kerogen, the function groups of kerogens were modeled by Gaussian software and the molecular vibrational spectra were obtained after structure optimization and frequency calculation in the terahertz range. Studying macromolecular compounds with a small molecule model was considered as an effective method. The principle of selecting small molecules from a macromolecular structure was that compositional elements and chemical bond types should be consistent.\textsuperscript{26–28} \(C_{21}H_{30}O\), \(C_{24}H_{48}O\), \(C_{14}H_{16}O\), and \(C_{14}H_{32}O_2\) were simulated as shown in Figure 7a–d. By Gauss View video function of Gaussian software, the \(C_{21}H_{30}O\) molecule of six vibrational modes at 9.02, 23.84, 25.77, 28.4, 37.05, and 46.54 cm\(^{-1}\) was observed, and the corresponding
kerogen particles of different zones were treated with HCl and HF to remove inorganic impurities at 200 °C. However, the functional groups of the kerogen samples showed that the vibrational modes of aromatic rings and carbon chains had some differences. The aromatic rings have three kinds of oscillation modes: plane swing, nonplane swing, and nonplane twist. The inherent frequency of a molecule was determined by the overall oscillatory modes of the molecule. Resonance absorption occurred when the terahertz wave interacted with molecules, which explained the difference of kerogen absorption with different frequencies. However, the functional groups of the kerogen samples changed because of the generation of oil and gas, and inherent frequencies were different; hence, the kerogen samples at different temperatures had different absorption coefficients.

3. CONCLUSIONS
In this paper, THz-TDS was utilized to study the evolution of kerogen with different simulated temperatures, and the evolution model was established. Furthermore, the interaction between kerogen and terahertz wave was studied by the dielectric function, and the modes of vibration and rotation of kerogen molecules in the terahertz range were explored by means of quantum chemistry. The results showed that differences of kerogen molecules on the absorption of terahertz wave were resulted from the transient dipole moments induced by collisions between molecules, as well as the different modes of vibration of kerogen molecules at different frequencies.

4. EXPERIMENTAL METHODS
4.1. Sample Preparation. Kerogen was isolated from shales in the Western Canada Basin. Conventional chemical isolation method was used. First, the shale was smashed, and 100 mesh particles were taken after sieving. Soxhlet isolation was done with chloroform for 72 h to remove residual soluble organic matter in rocks, the samples were heated to different temperatures (200–450 °C) in an aluminum crucible after drying, and the pyrolysis products in different temperature zones were treated with HCl and HF to remove inorganic minerals and then washed with distilled water to obtain kerogen particles of different maturities. In final, the purity of the kerogens was verified by a thermogravimetric analyzer with a loss on ignition of more than 90%. After analysis, the type of kerogen was type II. The kerogens were named after the pyrolysis temperatures.

4.2. Terahertz Time-Domain Spectroscopy. The terahertz instrument is CIP-TDS. In the THz-TDS system, the terahertz waves are generated by a photoconductive antenna which is triggered by a femtosecond laser. Ti-sapphire femtosecond mode-locked pulsed laser generates femtosecond laser pulses with the center wavelength of 800 nm, the repetition frequency of 80 MHz, and the pulse width of 100 fs. Experiments need to be conducted in the N2 environment, with the humidity below 1%.

4.3. Fourier Transform Infrared (FTIR) Spectroscopy. The testing instrument is VERTEX 70 + HYPERION 2000, including the FTIR spectrometer and IR microscope. The signal-to-noise ratio of the normal test is higher than 55 000:1, and the signal-to-noise ratio of the micro test is 7000:1. The wave number accuracy is better than 0.005 cm⁻¹, and the light transmittance accuracy is better than 0.07% T. The best space accuracy of automatic scanning table is 1 μm, with the measurement area of 250 μm and the working distance of 24 mm.

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Notes
The authors declare no competing financial interest.

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Figure 7. Simulation structures of kerogen molecules, (a) C21H30O, (b) C24H48O, (c) C14H16O, and (d) C11H12O2.
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