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Experimental measurements of water content in crude oil emulsions by terahertz time-domain spectroscopy*

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Abstract: We measured the water content (0.01%–0.25% w/w) in crude oil emulsions using terahertz time-domain spectroscopy (THz-TDS). To improve the precision and range of the measurements, we used 1 and 10 mm thick quartz cells. The experiments were performed at 20 °C and the THz wave was transmitted vertically to the samples and detected on the other side. The experimental results suggest linear relation for the THz absorption coefficient and the water content of the crude oil emulsions in the observed range. The linear dependence facilitates high-precision measurements of the water content of crude oil. This suggests the potential of THz-TDS in determining the water concentration in crude oil and borehole fluid identification.
Keywords: water content, crude oil emulsions, terahertz spectroscopy

Introduction

Terahertz radiation, which is in the frequency gap between infrared radiation and microwaves, has been used in astronomy and analytical sciences. However, recent technological innovations in photonics and nanotechnology made possible the application of THz research results in information technology and communications, biology and medical sciences, nondestructive evaluation, homeland security, environmental monitoring, ultrafast computing, etc. (Tonouchi, 2007). Terahertz time-domain spectroscopy (THz-TDS) gives the amplitude and phase composition of various materials by using the transmission or reflection mode from 0.1 to 10 THz. Consequently, THz-TDS has been used to study the dielectric properties of oil–water complexes (Gorenflo et al., 2006). THz radiation was also used to study the moisture content and distribution in various materials, such as paper, biomolecules, food wafers, and plant leaves (Banerjee et al., 2008; George et al., 2008; Hadjiloucas et al., 1999).

We performed laboratory experiments to study the THz absorption of crude oil emulsions. We used two thick quartz sample cells with water-in-oil emulsions from 0.01% to 25%. The experiments show that the relation between the absorption coefficient and water content of the emulsions is linear. We anticipate that the results

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of this study will help develop watercut meters and improve the application prospects of THz technology in the petroleum industry.

Sample preparation and experiment

THz-TDS gives the amplitude and phase composition of samples based on coherence measurements of THz light. An 800 nm femtosecond Ti:Sapphire laser was used to generate THz pulses (Löffler et al., 2005). The pulse duration, repetition rate, and average power were 100 fs, 80 MHz, and 800 mW, respectively. The femtosecond laser beam was split into pump and probe parts. The chopped pump beam was focused on a GaAs crystal to generate THz pulses. The emitted THz pulses were collimated and focused by a pair of off-axis parabolic mirrors. The samples were placed right at the THz focus point, perpendicularly to the incident THz beam. The transmitted THz beam was collected and focused using another pair of off-axis parabolic mirrors onto a ZnTe crystal, in which the probe beam detected the THz field by electro-optic sampling. To minimize the influence of moisture, the measurements were performed at 20 °C under dry nitrogen. The emulsion samples were prepared by adding water to crude oil. The crude oil sample was obtained from China National Petroleum Corporation and dehydrated with electric methods. After dehydration, the water concentration in the crude oil measured with Karl Fischer titration was 0.01%. We prepared emulsions with different water concentrations from 0.01% to 25% (w/w) in 10 ml vials by using a high-precision electronic scale.

To reduce absorption, high-purity quartz cuvettes were used as sample cells because of their small absorption, which makes them practically transparent in the target THz frequency range (Grischkowsky et al., 1990). Moreover, because water is a strong absorber of THz radiation (Vij et al., 2004; Kristensen et al., 2010), the thickness (Withayachumnankul et al., 2008) of the sample cell affects the spectrum measurements and analysis. In the measurements, 1 mm and 10 mm thick quartz cuvettes were used as sample cells. In each measurement, the THz wave was vertically incident to the surface of the quartz cuvettes.

Stable and homogeneous emulsions are critical for accurate and reliable measurements. Thus, each emulsion sample was thoroughly mixed using a homogenizer for more than ten minutes. Figure 1 shows the sample cell and the uniform distribution of the water droplets in crude oil emulsions after stirring. The uniform distribution ensures that each emulsion sample is a representative of the whole emulsion.

In particular, for emulsion samples with water content less than 10%, we selected quartz cuvettes with thickness of 10 mm. For emulsions with water content more than 8%, we used 1 mm thick cells to ensure the transmission of the THz radiation through the water–oil emulsions and acceptable signal-to-noise ratio (SNR).

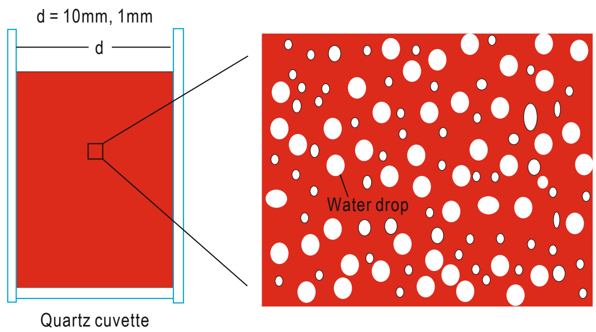

Fig.1 Sample cell and water droplets distribution in crude oil emulsion.

Results and discussion

The THz time-domain spectrum of emulsions with different water content (0.01%, 0.2%, 0.4%, 0.6%, 1%, 1.5%, 2%, 3%, 6%, 8%, and 10%) was successively measured using a 10 mm thick quartz cell. For emulsions with higher water content (8%, 10%, 15%, 20%, and 25%), we used a 1 mm thick quartz cell. The THz waveforms for path lengths of 1 and 10 mm are shown in Figure 2. The intensity of the THz waveform decreases as the water content of the emulsions increases. In addition, the increase in water content causes the THz waveform to shift in time. Therefore, THz-TDS can provide information on the water content of emulsions by using the amplitude and phase change. Figure 3 shows the amplitude changes in the transmitted THz pulse as a function of the water content of the emulsions in two different, thick quartz cells. The data for the 10 mm thick sample cell exhibit exponential damping of the THz pulse amplitude as the water content in the emulsion increases. When the water content exceeded 5%, the peak intensity of the transmitted THz pulse dropped and the SNR decreased. Consequently, the 1 mm thick quartz sample cell was used to improve the accuracy of the measurement and increase the measured water content range in crude oil emulsions. In general, thicker cells (e.g., 10 mm) are suitable for emulsions with water content less than 5%, whereas 1 mm thick sample cells are preferred when the water concentration is higher than 8%.

Emulsions with different water content have different absorption intensities. Figure 4 shows the absorption coefficients of crude oil emulsions with water content from 0.01% to 25% for 1 and 10 mm thick cells. The absorption coefficient depends on the frequency of the THz radiation and increases with increasing frequency from 0.2 to 1.5 THz. Because of the absorption coefficient fluctuations with THz frequency, the absorption coefficient was linearly fitted, as the black dotted lines shown in Figure 4, to determine the exact water content in crude oil.

Figure 5 shows the linear relation of the absorption coefficient and the water content of the emulsions at four selected frequencies (0.5, 0.75, 1.0, and 1.25 THz). The inset map gives the amplification details of the absorption coefficients of emulsions with water content from 0.01% to 0.6%; the colored arrows denote the absorption coefficients of pure crude oil. The linear dependence can be explained by the fact that the terahertz wave penetrates into a greater volume of

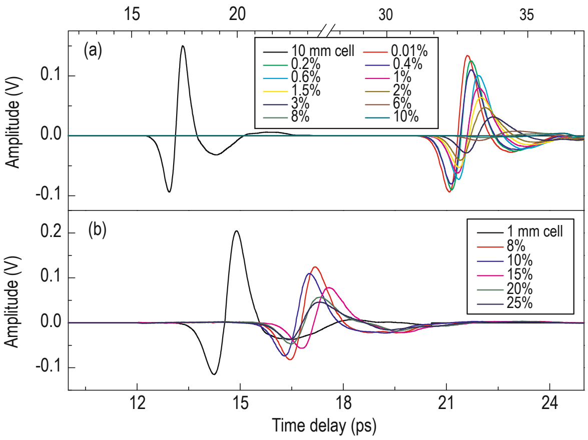

Fig.2 Time-domain spectra of (a) 10 mm and (b) 1 mm thick emulsion samples.

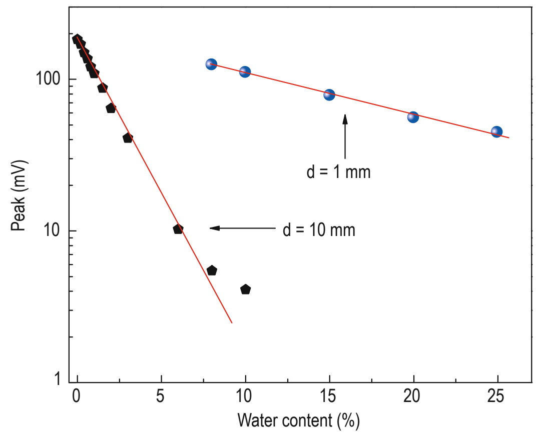

Fig.3 Peak amplitude vs water content for 1 and 10 mm thick emulsions.

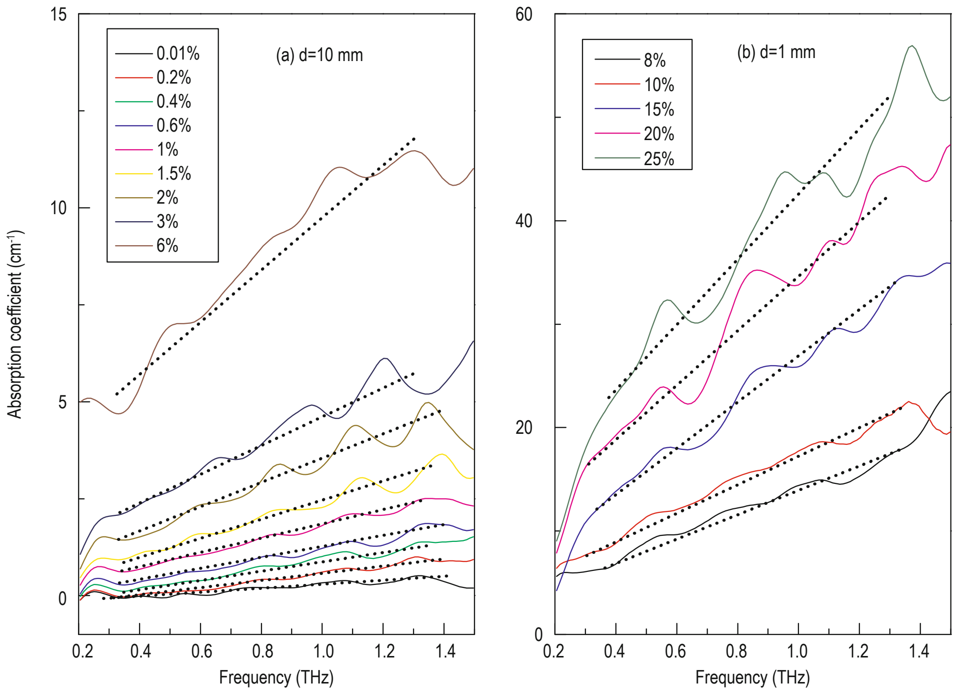

Fig.4 Absorption spectrum of emulsion samples (water content ranges from 0.01% to 25% w/w).

water when the water content of the crude oil emulsions is from 0.01% to 25%. The results suggest that THZ transmission spectroscopy not only can be used to determine the water content in crude oil emulsions but also evaluate the stability and uniformity of the emulsions by measuring the water content at different points in the emulsions.

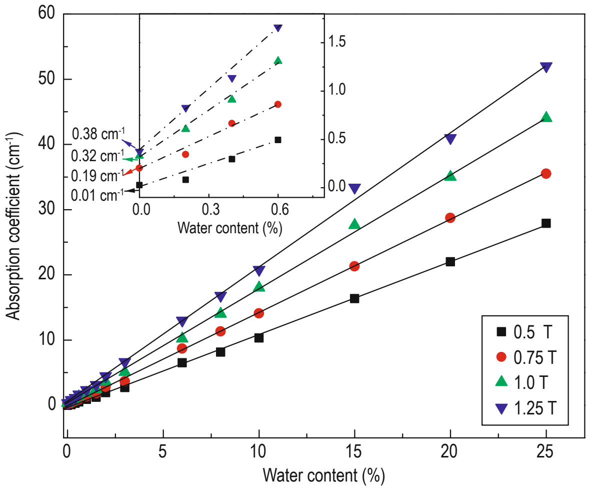

Fig.5 Absorption coefficient of emulsion sample as a function of the water content at selected frequencies.

Conclusions

We investigated the potential of THz transmission spectroscopy to accurately determine the water content in crude oil. By employing sample cells with different thicknesses, crude oil emulsions with water content from 0.01% to 25% (w/w) were measured using THz-TDS. The experimental results suggest that both the amplitude and absorption coefficient of the THz pulse can be used to calculate the water content in the emulsions. The absorption coefficient of the THz radiation and the water content in crude oil are strongly and linearly correlated in the examined range. This linear relation will probably minimize the calibration complexity of the measurements. Although thinner cells could be used for more than 25% water content, high-power THz emitters will be necessary to improve the SNR of the measured signal. We successfully used THz time-domain spectroscopy to measure the water content in crude oil emulsions. We anticipate that THz technology will be a powerful tool in measuring the water content of crude oil as terahertz science and technology as well as the miniaturization and integration of instruments improve.

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