Characterization of Kuwait Crude Oil via Terahertz Fourier Transform Spectroscopy

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Abstract. We report the experimental and theoretical terahertz (THz) absorption characteristics of unprocessed crude oils from Kuwait oil wells. Using THz Fourier transform spectroscopy technique and semi-empirical computational chemistry calculation, five of the 30 crude oils revealed characteristic absorbance spectra. Experimental data showed absorption peaks at 6.0 THz, 7.7 THz, 13 THz, and 16 THz. On the other hand, the calculated spectral bands of 10 nonane molecules were found at around 2.8 THz, 7.7 THz, 10 THz, and 16 THz. Although only two bands were predicted by the calculation, adding alkane molecules of different lengths (pentane to decane) resulted in the formation of new bands. These preliminary results suggest that there is a mixture of different alkanes present in the investigated samples, a typical characteristic of unprocessed crude oil.

1 Introduction

Crude oil is an unprocessed, combustible mixture of hydrocarbons combined with other elements such as oxygen, sulfur, and nitrogen, among others. These viscous liquids or semi-solid substances with varying colors from brownish-black to dark green undergo preliminary treatment before being transported to refineries via pipelines, oilers, or other oil transportation methods. One of the most effective tools for characterizing crude oils is by determining its boiling point also known as the true boiling point technique; a batch distillation process that is widely used in the oil industry. A relatively new technique to further characterize petrochemical products is the use of terahertz (1×10^{12} Hz, THz) radiation, a part of the electromagnetic spectrum between the microwave and the infrared regions, which corresponds to the wavelength range of 30 μm to 3 mm. This low-energy radiation resonates with the weak interaction between molecules, macromolecular skeleton vibration, dipole rotation, vibration transition, and phonon dynamics in the lattice of semiconductor crystals.[1] Due to this, THz spectroscopy has been used to identify, classify, and to some extent quantitatively analyze petrochemical products.[2] In this work, unprocessed crude oils from the fields in Kuwait were obtained and characterized using THz Fourier transform spectroscopy (FTS) technique between the frequencies from 1.5 – 18 THz (50 – 600 cm^{-1}). Among 30 crude oils measured, five (SA121T, SA-151TS, SA108T, SA-120T, SA159T) were shown to have absorption peaks in this frequency region. We employed semi-empirical chemistry calculation to obtain their vibrational modes. Comparison between the experimental THz spectra and the theoretical results suggests a blend of different alkane lengths, which is conventionally found in unprocessed crude oils.

2 Experiment

The schematic diagram of THz FTS spectrometer is shown in Figure 1. A heated blackbody source emits broadband radiation that includes the THz. It is collimated and directed by parabolic mirror (PM) to the beam splitter (BS) of the interferometer. The radiation divided by the BS reflects back from the two mirrors M1 and M2. M1 is stepwise adjusted to generate a path difference between the two radiation beams and interference is created. The radiation leaves the interferometer towards another mirror (M3) and irradiates the cuvette containing the sample, where part of the THz radiation is absorbed, which is then finally registered with the pyroelectric detector. The detector senses the interfering radiation with the information about the sample as an electrical signal dependence on the moving mirror position. A beam of continuous wave laser (red trace) is also made to interfere in the setup which gives the precise measurement of M1 position by measuring the interferogram nodes of monochromatic radiation with the photo diode (PD).

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The LDPE zip-bags were filled with different crude oils extracted from Kuwait oil wells and placed in the cuvette for exposure to THz radiation through the aperture in the cuvette to measure the interferograms in transmission configuration. From 30 crude oils tested, five (SA121T, SA-151TS, SA108T, SA-120T, SA159T) were shown to have absorption peaks in this frequency region.

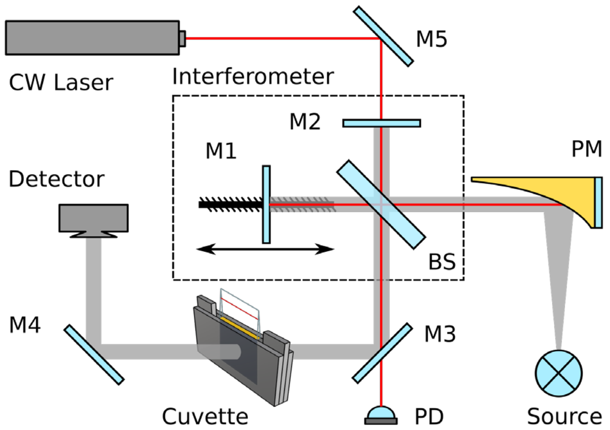

Fig. 1. Schematic diagram of THz FTS set-up.

3 Theoretical Calculations

The open-sourced computational chemistry program Firely820 was used to optimize the geometry of the n-alkane molecules as well as to calculate the Hessian matrix to depict the normal modes of the structures.[3,4] Due to the long-chain nature of the hydrocarbons, we opted to use parametric method 3 (PM3), a semi-empirical method for the quantum calculation of the molecular electronic structure, as a preliminary approach for this work. A single molecule of nonane (C_9H_{20}) was increased to 10, and a molecule of pentane, hexane, heptane, octane, nonane, and decane was added separately with five molecules of nonane.

4 Results and Discussion

The experimental absorbance spectra from Figure 2 (a) shows four peaks detected at 6.0 THz, 7.7 THz, 13 THz, and 16 THz. On the other hand, the calculated spectral bands are at around 2.8 THz, 7.7 THz, 10 THz, and 16 THz. Although having a similar number of peaks as that of the experimental data, the peak positions do not match except for two, and the calculated main peak of nonane at around 10 THz is way off compared to the experimental data. The effect of adding molecules in the calculation resulted only in the increase of the amplitude of absorption bands but not in its position, i.e., there was no shift in the absorption peaks. When normal modes of five nonanes and a pentane molecule were calculated, new absorption peaks emerged at 5 THz and 15 THz. These additional bands may be assigned to the intermolecular interaction between the nonane and pentane molecules. The accompanying vibrational modes were also obtained showing the parts of the molecules that are in motion at these frequencies (not shown here).

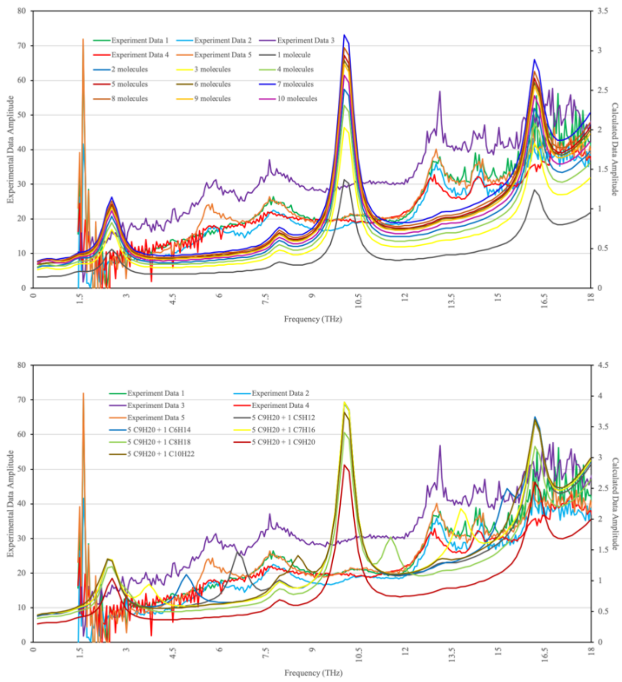

Fig. 2. Experimental absorbance spectra and calculated modes of nonane. (a) increasing number of nonane from one molecule to 10 molecules and (b) five nonane molecules with pentane, hexane, heptane, octane, nonane, and decane molecule.

Similarly, adding a heptane molecule resulted in bands at 4 THz, 10 THz, and 14 THz, while adding one molecule of nonane and octane ensue modes at 8 THz and 11 THz, respectively. These results suggest that the crude oil measured is a mixture of different alkane lengths, typical for unprocessed crude oils.

Summary

Unprocessed crude oils from Kuwait oil fields were characterized using the THz Fourier transform spectroscopy technique. By using semi-empirical quantum chemistry calculation, the vibrational modes were obtained. A comparison of the experimental and calculated THz spectra indicates a mixture of alkane chains present in the crude oils, a typical observation of unprocessed oils. Our follow-up work would focus on adding and or mixing other lengths of alkane molecules to depict the experimental absorbance data more accurately.

References

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