引用格式：TIAN Lu, NI Hao. Molecular Dynamics of Lube Base Oil Subjected to Annealing, Ultrasonic and Magnetic Treatments in Terahertz Band[J]. Acta Photonica Sinica, 2022, 51(4):0430004
田璐,尼浩．基础油在热处理、超声和磁场作用下的太赫兹频段分子动力学[J].光子学报,2022,51(4):0430004

基础油在热处理、超声和磁场作用下的太赫兹频段分子动力学

田璐[1],尼浩[2]

(1 西北大学 物理学院,西安 710069)

(2 中国石油大学(华东)理学院,山东 青岛 266555)

摘　要:利用太赫兹时域光谱技术研究了基础油在热处理、超声和磁场作用下的动力学过程及相互作用机制。由于超声处理过程中声空化作用引起高温高压,而样品在热处理中的作用能量较低,基础油在超声处理后的折射率变化大于其在热处理和磁场作用下的变化。样品在1.7 THz和2.3 THz处有较明显的吸收峰,该吸收来源为分子间的相互作用,以这两处的吸收峰为研究对象,利用分子间相互作用的强弱变化分析了基础油与磁场的相互作用机制。研究结果表明太赫兹时域光谱技术能够实现有机化学物质在物理场作用下的降解机制研究,易操作,数据处理简单,重复性好。

关键词:太赫兹;分子动力学;超声;磁场;热处理

中图分类号:O439　　　**文献标识码**:A　　　**doi**:10.3788/gzxb20225104.0430004

0 Introduction

Currently, hydrocarbons remain the leading energy source. While the amount of conventional light crude oil becomes less and less available, an increasing number of heavy petroleum products, such as Lube Base Oil (LBO), are needed. These related petroleum products need to be upgraded using various microbial degradation, thermal and chemical methods to avoid potential hydrocarbon contamination[1]. The thermal method is slow and energy consuming and raises concerns about its environmental impact. In recent years, considerable attention has been given to the degradation of related petroleum products by various physical fields, such as electric[2-4], optical[5], ultrasonic[6-10] and magnetic methods[11-15].

Compared to thermal methods, ultrasound methods have the advantages of easy operation, low cost and high efficiency[9]. It is also reported that electric and magnetic methods may improve the rheological properties of crude oil, including asphalt base crude oil and paraffin crude oil[2-3]. However, the effect of the physical fields on the viscosity of related petroleum oil is very controversial[16]. Apart from this study, to our knowledge, no work studying the effects of the ultrasonic or magnetic treatment of LBO has been performed to date, and the interaction between the ultrasonic/magnetic fields and organic compounds needs further study.

To develop a fast method without any sample manipulation for the detection of the most common natural waxes, Terahertz Time-Domain Spectroscopy (THz-TDS) was used in this paper. To date, THz-TDS has received considerable attention with the expectation that it will provide new insights into complex petroleum systems, such as optical property and spectroscopic studies of the selected lubricating oil and probes of the disaggregation of crude oil[17]. Many rotational and vibrational spectra of organic molecules in natural waxes fall into the THz range. THz-TDS is a coherent technique in which both the amplitude and phase of a THz pulse

Foundation item: Scientific Research Fund of the Department of Education of Shaanxi Province, China (No. 14JK1758)

First author: TIAN Lu (1985—), female, associate professor, Ph. D. degree, mainly focuses on terahertz optoelectronics. Email: tianlu@nwu.edu.cn

Received: Oct.21,2021; **Accepted**: Dec.9,2021

are measured. Coherent detection enables direct calculations of both the imaginary and real parts of the refractive index.

In this paper, we report the difference between the annealing, ultrasonic and magnetic methods used to degrade LBO, and the treatment parameter dependence of the THz optical properties of LBO was experimentally characterized using THz-TDS. Moreover, the interaction mechanism between physical fields and organic molecules was determined, which is suitable for many important applications, such as oil transport via deep pipelines and oil degradation.

1 Experimental section

Commercial paraffin-based LBO obtained from Korea with a viscosity index of 105 (Korea105) was collected from Shell Tongyi (Beijing) Petroleum Chemical Co. Ltd. In our experiment, Korea105 is characterized by its high viscosity index, relatively high alkane content greater than 60%, and low alicyclic and alkene contents. Therefore, alkanes and aromatics are the main components in LBO. The samples were heated to a predetermined temperature at 110 °C in an ambient atmosphere, and after the temperature was maintained for 60 minutes, then cooled to room temperature.

An ultrasonic cleaner (KQ3200DB) with a 150 W power generating capacity and 40 kHz frequency was used for the sonication experiments. The samples were sealed in bottles to prevent the ingress of dust and then stored in a container with a certain water capacity. The ultrasonication times for the samples were 4 (us4h), 6 (us6h), and 12 hours (us12h). Notably, the sonication system was not sealed, so gaseous products such as low alkanes and hydrogen were not collected.

For the magnetic treatment, a set of permanent magnets were fixed on both sides of the Korea105 sample cell with a magnetic induction intensity of 1 T, and the magnetic treatment times were controlled at 4 (mag4h), 6 (mag6h), and 12 hours (mag12h). The color of the LBO after annealing, ultrasonic and magnetic treatments showed no significant difference. All samples were stored at room temperature in a laboratory for 1 week, and then THz-TDS measurements were carried out continuously.

A conventional transmission THz-TDS system with a mode-locked Ti:sapphire laser (MaiTai, Spectra Physics) was used for this study[17]. A Ti:sapphire laser with a center wavelength of 800 nm, a repetition rate of 80 MHz, a pulse width of 100 fs, and an output power of 960 mW was used. A standard THz-TDS setup based on a p-type InAs emitter for terahertz generation and ZnTe for electro-optic sampling were used to characterize the THz transmission spectra. LBO was sealed in a polystyrene cuvette that was transparent to visible light with a side thickness of less than 1 mm, and the THz waveforms transmitted through the cuvette were referred to as the sample signals[18]. The humidity was kept less than 1%, and the temperature was 20 °C.

2 Results and discussion

Fig. 1(a) shows the refractive index of Korea105 with no treatment, us4h, us6h, us12h and at 110 °C. Fig.1(b) shows the refractive index of Korea105 at mag4h, mag6h and mag12h was measured from 0.2 THz to 2.5 THz, the y-axis values have been offset to clarify. To facilitate the analysis of the variation in the refractive index, the vertical range for the sample spectra is from 1.44~1.5. Evidently, these materials exhibit almost no spectral dispersion in the 0.2~2.5 THz region. The refractive index can be accurately measured and used to correlate various important properties for multicomponent native petroleum, such as viscosity, density, carbon number, and other hydrocarbon properties, with high reliability[19]. The refractive index of shell oil without additives is proportional to the viscosity, and the parameters of the viscosity models are found to scale linearly with the molecular weight[20-21]. These results demonstrated that it is possible to correlate and predict the viscosity parameters of LBO.

Fig. 2 shows the absorption spectra of Korea105 under several conditions in the 0.2~2.5 THz region. The marker bands of the original LBOs are denoted as the absorption peaks. The y-axis values have been offset to clarify. The original Korea105 is identified by their absorption peaks at 1.7 THz and 2.3 THz in relatively higher frequency ranges. The absorption peaks of the samples varied significantly after annealing, ultrasonic and magnetic treatments. The assignment of these peaks was considered in this study, and recent theoretical predictions of the THz modes of samples have been improved using solid-state density functional theory calculations[22].

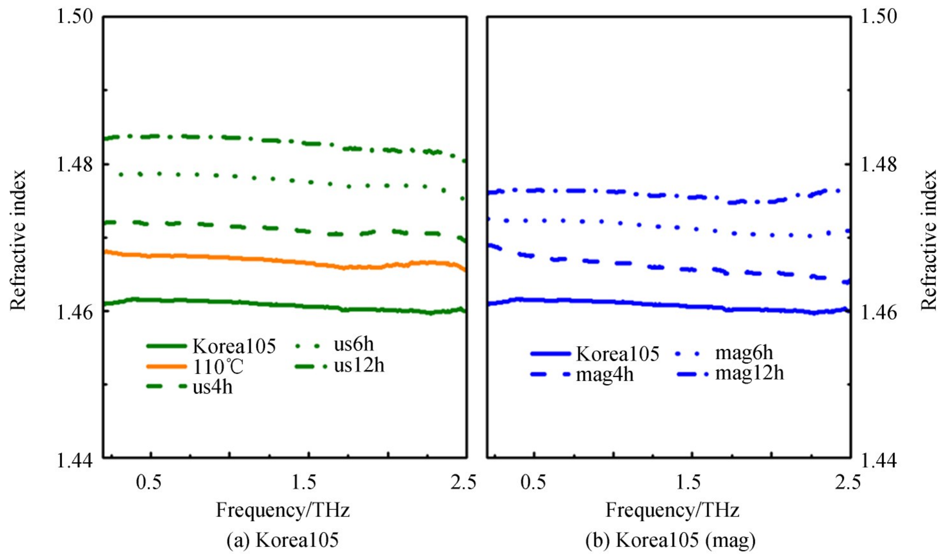

Fig. 1 The refractive indices as a function of frequency for each of the samples under several treatments

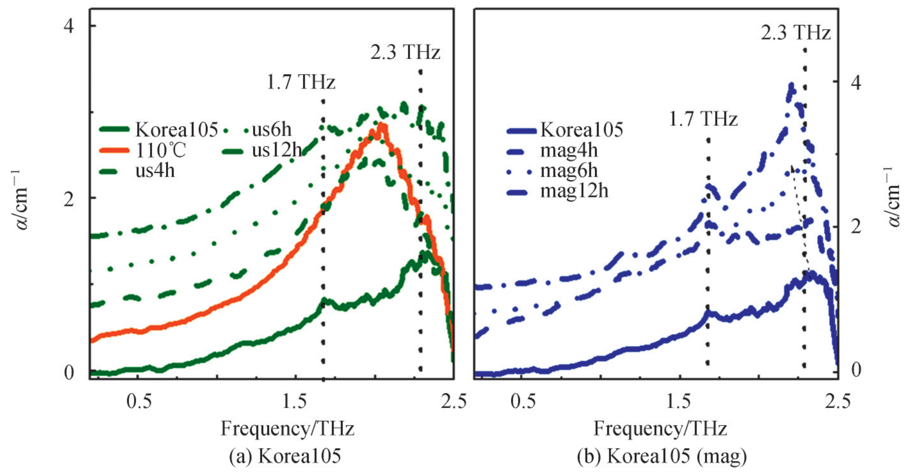

Fig. 2 The absorption coefficients of Korea105 in the 0.2～2.5 THz region

Analysis of THz spectra is often difficult owing to the broadened and overlapped nature of the vibrational peaks. The absorption peak at approximately 1.7 THz has been obtained in the THz-TDS measurements of grease, aviation kerosene, and many other substances[17-18,23]. In our previous papers, the molecular modes of the dominant alkanes and aromatics in LBO correspond to collective torsional and vibrational modes, which give rise to a resonance of LBO in the lower frequency range[18,22]. We are conducting a further in-depth study to accurately confirm the effect of the physical fields on the intermolecular forces in Korea105 by THz-TDS.

Moreover, an absorption peak of Korea105 was observed at 2.3 THz, which is close to the frequency of the B_{1u} translational lattice vibration observed in n-alkanes ($C_{19}H_{40}$, $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{30}H_{62}$, and $C_{36}H_{74}$)[22,24], paraffin waxes and liquid paraffin[25], as well as in calculations for n-paraffin crystals[36-37]. Based on these studies, the absorption peak at 2.3 THz assigned to the B_{1u} mode, which corresponds to the intermolecular interaction between parallel alkane molecules[25].

We selected two strong peaks corresponding to the intermolecular force as marker bands to illustrate the interaction mechanism between the physical field and petroleum organic molecules by comparing the absorption peaks before and after ultrasonic and annealing treatments. Changes in the molecular interaction intensity are observed as the generation and disappearance of peaks and/or the intensity changes in the peaks of direct intermolecular vibrations in the THz frequency region[27].

To obtain a reliable refractive index value n for qualitative and quantitative analysis, the average refractive index (n_{avg}) in the 0.2～2.5 THz range was selected to analyze the interaction mechanism and the molecular dynamics. The difference in the average refractive index (Δn) between n under various conditions and n_0 in the original state is defined as $n-n_0$. The Δn under annealing method is 0.001 1. Fig. 3 shows the Δn and $\Delta\alpha$ dependence on the ultrasonic and magnetic treatment times. Importantly, according to the viscosity estimation methods and the relationship between the refractive index and viscosity, the viscosity increased when Δn was greater than zero ($\Delta n>0$) and decreased in the opposite case ($\Delta n<0$). The Δn values subjected to ultrasonic treatments are larger than those of the sample subjected to annealing and magnetic treatment. This change is because the temperature and pressure rise due to ultrasound can reach over 5 273 K and several hundred atmospheres, whereas heat interacts on a longer time scale at lower energies[28-29].

Fig. 3 shows the Δn of Korea105 versus treatment time, and difference $\Delta\alpha$ values located at 1.0, 1.7 and 2.2 THz. The refractive index changes in the original Korea105 subjected to ultrasonic treatments are larger than those of the sample subjected to magnetic treatment. This change is because the temperature and pressure rise due to ultrasound can reach over 5 273 K and several hundred atmospheres. The time is 10^{-4}～10^{2} s, energy is less than 10^{-1} electron volts and pressure of thermochemistry is less than 1 atmosphere[28]. Therefore, the ultrasonic effect on viscosity is not simply achieved by a temperature increase; there are other effects, such as the cavitation effect and mechanical vibration[18,29].

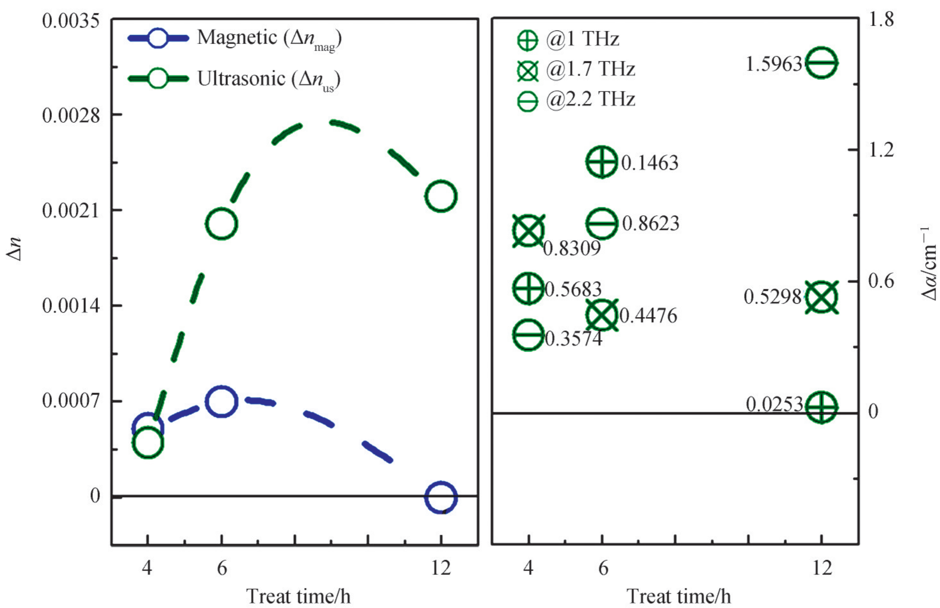

Fig. 3 The Δn and $\Delta\alpha$ of Korea105 versus treatment time

Considering the main components of alkanes and aromatics in Korea105, our method is illustrated in Fig. 4, in which the action of several methods is shown. As shown in Fig. 4(a), the vibration of alkanes and the "jumping jack" modes of aromatics are in field free space. During the annealing process, as shown in Fig. 2(a), the peaks at 1.7 THz and 2.3 THz disappeared, which is due to the attenuation of the interaction force. Notably, a new peak at 2.0 THz is generated, owing to the oxidation products formed in all the samples after degradation[30]. On the other hand, this can be attributed to a stronger variation in the Carbon-Carbon (C-C) axial interaction during the heating period for the degraded samples[11].

After ultrasonic degradation for an extended period, the peaks at 1.7 THz corresponding to the intermolecular interaction, and 2.3 THz corresponding to the parallel alkane interaction disappeared or shifted significantly (Fig. 2(b)). The first stage of the ultrasonic experiment was to confirm that the variation in the temperature and density was almost negligible[6].

In our previous papers, it was found that the ultrasonic effect on samples was not simply achieved by an increase in temperature; i.e., other effects existed, such as the cavitation effect and mechanical vibration[18,23,29].

As shown in Fig. 4 (b), the sonication of Korea105 proceeds by three categories of reactions: free radical generation, propagation, and termination. First, the primary step during the sonication of a high number of alkanes in Korea105 is C-C and carbon-heteroatom bond cleavage with secondary abstractions and rearrangements, which generates free radicals[31]. As C-C bond cleavage accelerated the decrease in alkane particle size, the properties of Korea105 with a higher alkane content changed continuously over an extended time period. The sonochemical degradation of a relatively small number of aromatic organic compounds in Korea105 was similar to that of asphaltenes[23]. The cracking of asphaltenes into gas oil and resins can be classified as free-radical reactions[28]. In the second step, the alkyl radical collides with another hydrocarbon and abstracts hydrogen, which yields lighter alkanes. The alkyl radical also eliminates a hydrogen radical, forming alkenes. Finally, two free radicals collide and recombine, which terminates the reaction.

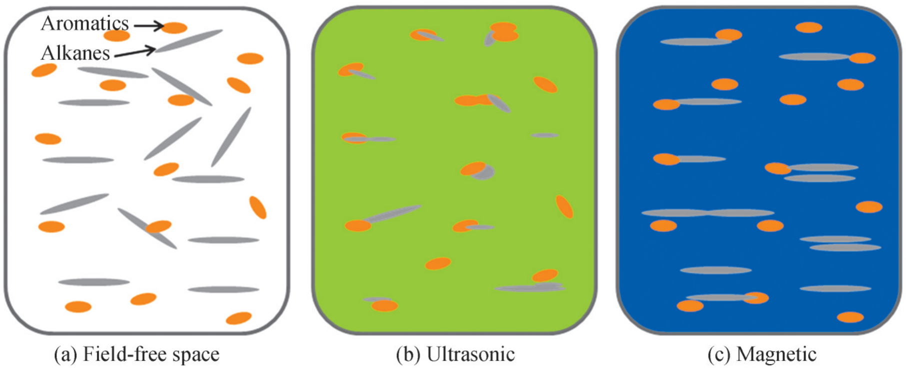

Fig. 4 Schematic illustrations of alkanes and aromatics molecules in Korea105

The study of the ultrasonication time control focused on the reaction time of the system is shown in Fig. 3. During an extended exposure time to an ultrasonic field, Δn_2 increased with increasing time. This can be attributed to the boiling effect and recombination[31], which is also observed in n-dodecane and paraffin oil[4]. The intensity of hot-spot ultrasound models increased as time increased. Studies have verified that the relative concentration of C_7-C_{10} fragments for n-dodecane and the insoluble sediment for diesel fuel during sonication varied linearly with time[6].

As shown in Fig. 2 (b), for Korea105 under magnetic treatment, the intermolecular forces between molecules at 1.7 THz increased slightly, which induced an increase in the absorption coefficient, and the peak located at 2.3 THz shifted to a lower frequency approximately 2.2 THz. Moreover, the $\Delta\alpha$ values located at 1.0, 1.7 and 2.2 THz, defined as $\alpha-\alpha_0$, are all above zero and have no significant relation with the magnetic treatment time. The Δn values were always above zero at 4, 6 and 12 h, which indicated an increasing viscosity (Fig. 3). It is known that an enhancement in the intermolecular strength results in an increased viscosity. Nevertheless, $\Delta\alpha>0$ suggests an enhancement in the intermolecular force at 1.7 THz and intermolecular interactions between parallel alkane molecules at 2.2 THz.

The effect of a magnetic field on the viscosity of related petroleum oil is very controversial, and the controversy was simplified to two aspects. Several researchers have determined that the viscosity of paraffin-based crude oil increases after exposure to a strong magnetic field at 1.5 T for an extended time[32]. In contrast, other studies have found that the magnetic field reduced the viscosity[3,13]. For paraffin-based crude oil, a magnetic field pulse at 0.38 T can effectively reduce its viscosity for several hours[3]. Our experiments regarding the increasing viscosity of Korea105 verified the first aspect.

As shown in Fig. 4 (c), the orientation and aggregation of organic molecules in Korea105 under a strong magnetic field were proposed in our paper. First, paraffin with high polydispersity alkanes ranging between C_{25} and C_{45} also aligns in a magnetic field (9 T) during crystallization from a melt, forming crystallites oriented with respect to the magnetic field[33]. This is especially true for liquid crystals, whose diamagnetic anisotropy is usually strongly dominated by aromatic rings[34]. Finally, several particles, such as alkane and aromatic particles, interlocked and aggregated with each other. When Korea105 was exposed to a strong magnetic field for an extended time, even when the magnetic measurement was removed for a long time, the orientation and aggregation of organic molecules were permanently maintained.

3 Conclusion

In summary, Korea105 subjected to annealing, ultrasonic and magnetic field treatments was characterized by THz-TDS, and the refractive index and absorption coefficient values were obtained. The absorption peaks of the original Korea105 at 1.7 THz and 2.3 THz corresponding to intermolecular interactions were selected as marker bands to illustrate the interaction mechanism. The degradation degree of petroleum macromolecules in Korea105 under an ultrasonic field is greater than that under a magnetic field and annealing treatment. The principle sonochemical process in LBO appears to be C-C bond cleavage and the recombination of alkanes and aromatics. The increase in the viscosity of Korea105 suggests that the strong magnetic field and long interaction time induced the orientation and aggregation of the organic molecules. It is found that the annealing, ultrasonic and magnetic methods used can effectively degrade samples.

References

[1] BHATT P, GANGOLA S, BHANDARI G, et al. New insights into the degradation of synthetic pollutants in contaminated environments[J]. Chemosphere, 2021, 268: 128827.

[2] TAO R, TANG H. Reducing viscosity of paraffin base crude oil with electric field for oil production and transportation[J]. Fuel, 2014, 118: 69-72.

[3] TAO R, XU X. Reducing the viscosity of crude oil by pulsed electric or magnetic field[J]. Energy Fuels, 2006, 20: 2046-2051.

[4] LOBRY L, LEMAIRE E. Viscosity decrease induced by a DC electric field in a suspension[J]. Journal of Electrostatics, 1999, 47: 61-69.

[5] HAN S, QIU C, CHEN X G, et al. Study of the reasons for discoloration of hydrotreated naphthenic lube base oil under ultraviolet radiation[J]. Industrial & Engineering Chemistry Research, 2005, 44: 250-253.

[6] GOPINATH R, DALAI A K, ADJAYE J. Effects of ultrasound treatment on the upgradation of heavy gas oil[J]. Energy Fuels, 2006, 20: 271-277.

[7] CHECK G R, MOWLA D. Theoretical and experimental investigation of desalting and dehydration of crude oil by assistance of ultrasonic irradiation[J]. Ultrasonics Sonochemistry, 2013, 20: 378-385.

[8] CHAKMA A, BERRUTI F. The effects of ultrasonic treatment on the viscosity of Athabasca bitumen and bitumen-solvent mixtures[J]. Journal of Canadian Petroleum Technology, 1993, 32: 48.

[9] AVVARU B, VENKATESWARAN N, UPPARA P, et al. Current knowledge and potential applications of cavitation technologies for the petroleum industry[J]. Ultrasonics Sonochemistry, 2018, 42: 493-507.

[10] PRICE G J, MCCOLLOM M. The effect of high-intensity ultrasound on diesel fuels[J]. Ultrasonics Sonochemistry, 1995, 2: S67-S70.

[11] SUSLICK K S, GAWIENOWSKI J W, SCHUBERT P F, et al. Alkane sonochemistry[J]. The Journal of Chemical Physics, 1983, 87: 2299-2301.

[12] SCHMELCHER P. Molecule formation in ultrahigh magnetic fields[J]. Science 2012, 337: 302-303.

[13] JIANG C, ZHAO K, ZHAO L J, et al. Probing disaggregation of crude oil in a magnetic field with terahertz time-domain spectroscopy[J]. Energy Fuels 2014, 28: 483-487.

[14] GONÇALVES J L, BOMBARD A J F, SOARES D A W, et al. Study of the factors responsible for the rheology change of a Brazilian crude oil under magnetic fields[J]. Energy Fuels, 2011, 25: 3537-3543.

[15] EVDOKIMOV I N, KORNISHIN K A. Apparent disaggregation of colloids in a magnetically treated crude oil[J]. Energy Fuels, 2009, 23: 4016-4020.

[16] GUO K, LV Y L, HE L M, et al. Experimental study on the dehydration performance of synergistic effect of electric field and magnetic field[J]. Chemical Engineering and Processing - Process Intensification, 2019, 142:107555.

[17] TIAN R H, BAO R M, TIAN L. Probing the liquid-solid transition of petroleum macromolecules with terahertz time-domain Spectroscopy[J]. Science China Physics, Mechanics & Astronomy, 2018, 61: 104221.

[18] TIAN L, NI H. Effects of ultrasonic irradation on the upgradation of lube base oil investigated using terahertz time-domain spectroscopy[J]. Vibrational Spectroscopy, 2021, 114: 103254.

[19] WANG J, BUCKLEY J S. Asphaltene stability in crude oil and aromatic solvents the influence of oil composition[J]. Energy Fuels, 2003, 17: 1445-1451.

[20] GUO S J, RUAN C J, KONG D Y, et al. Research on terahertz transmission characteristics of nonpolar liquid based on frequency-domain spectroscopy[J]. Journal of the Optical Society of America B: Optical Physics, 2020, 37: 1942-1947.

[21] TAN S P, ADIDHARMA H, TOWLER B F, et al. Friction theory and free-volume theory coupled with statistical

associating fluid theory for estimating the viscosity of pure n-alkanes[J]. Industrial & Engineering Chemistry Research, 2005, 44: 8409-8418.

[22] TIAN L, NI H. Sonochemical degradation of various lubricating oils investigated using terahertz time-domain spectroscopy [J]. Optik, 2020, 208: 164054.

[23] HUANG X, ZHOU C, SUO Q, et al. Experimental study on viscosity reduction for residual oil by ultrasonic [J]. Ultrasonics Sonochemistry, 2018, 41: 661-669.

[24] TANNO T, ASARI J, YODOKAWA S, et al. Terahertz spectroscopic study on order - disorder phase transition of nonadecane[J]. Chemical Physics, 2015, 461: 25-28.

[25] TIAN L, XU X L. Optical properties and crystallization of natural waxes at several annealing temperatures: a terahertz time-domain spectroscopy study[J]. Journal of Infrared Millimeter & Terahertz Waves, 2018, 39: 302-312.

[26] DUARTE L J, BRUNS R E. FTIR and dispersive gas phase absolute infrared intensities of hydrocarbon fundamental bands[J]. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2019, 214: 1-6.

[27] AMARLOO H, SAFAVI-NAEINI S. Enhanced on-chip terahertz vibrational absorption spectroscopy using evanescent fields in silicon waveguide structures[J]. Optics Express, 2021, 29 (11): 17343-17352.

[28] RICE F O. The thermal decomposition of organic compounds from the standpoint of free radicals. I. Saturated hydrocarbons[J]. Journal of the American Chemical Society, 1931, 53: 1959-1972.

[29] SHI C, YANG W Y, CHEN J, et al. Application and mechanism of ultrasonic static mixer in heavy oil viscosity reduction [J]. Ultrasonics Sonochemistry, 2017, 37: 648-653.

[30] ADHVARYU A, ERHAN S Y, SAHOO S K, et al. Thermo-oxidative stability studies on some new generation API group II and III base oils[J]. Fuel, 2002, 81: 785-791.

[31] DEHSHIBI R R, MOHEBBI A, RIAZI M, et al. Experimental investigation on the effect of ultrasonic waves on reducing asphaltene deposition and improving oil recovery under temperature control[J]. Ultrasonics Sonochemistry, 2018, 45: 204-212.

[32] JIANG C, GUO L Y, LI Y Z, et al. Magnetic field effect on apparent viscosity reducing of different crude oils at low temperature[J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2021, 629: 127372.

[33] KANG M K, CHA E J, SONG H H, et al. Interlayer structure and magnetic field-induced orientation of modified nanoclays in polymer aqueous solution[J]. Heliyon, 2019, 5: e02421.

[34] DE GENNES P G, PROST J. The physics of liquid crystals[M]. Clarendon, Oxford, 1993.

Molecular Dynamics of Lube Base Oil Subjected to Annealing, Ultrasonic and Magnetic Treatments in Terahertz Band

TIAN Lu[1], NI Hao[2]

(1 *School of Physics, Northwest University, Xi'an* 710069, *China*)

(2 *College of Science, China University of Petroleum Huadong, Qingdao, Shandong* 266555, *China*)

Abstract: The related petroleum products need to be upgraded using various microbial degradation, thermal and chemical methods to avoid potential hydrocarbon contamination. Although these techniques are commonly used, they have several limitations, such as high energy consumption, high cost, poor efficiency, and environmental pollution. To date, considerable attention has been paid to the degradation of related petroleum products by ultrasonic and magnetic methods. Ultrasound methods have the advantages of easy operation, mild conditions, high efficiency, low cost, and environmental friendliness. Comparatively, some authors have shown that magnetic and electric methods may improve the rheological properties of crude oil. Apart from this study, to our knowledge, no work studying the effects of the ultrasonic or magnetic treatment of Lube Base Oil (LBO) has been performed to date, and the interaction between the ultrasonic/magnetic fields and organic compounds needs further study. The use of these physical fields to treat and degrade petroleum products has sparked considerable controversy. Terahertz Time-Domain Spectroscopy (THz-TDS) has recently received considerable attention with the expectation that it will provide new insights into complex petroleum systems, such as optical property and spectroscopic studies of the selected lubricating oil and probes of the disaggregation of crude oil. In this paper, the degradation mechanism and molecular dynamics of LBO subjected to annealing, ultrasonic and magnetic treatments were compared and investigated using THz-TDS. The thermal degradation of the Korea105 was assessed by means of an annealing treatment at 110 °C. The ultrasonication times for the samples were 4 (us4h), 6 (us6h), and 12 hours (us12h). The magnetic treatment times were controlled at 4 (mag4h), 6 (mag6h), and 12 hours (mag12h). By comparison with reference and sample pulse, and use of a numerical fast Fourier transform, the refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$ of the samples were calculated. The change of refractive index of LBO under ultrasonic field is higher than that under annealing and magnetic treatment, owing to the high temperature and pressure rise due to ultrasound, whereas heat interacts on longer timescales at lower energies. Moreover, the absorption peaks of the original Korea105 at 1.7 THz and 2.3 THz corresponding to intermolecular interactions were selected as marker bands to illustrate the interaction mechanism. The absorption peaks of samples varied significantly after annealing, ultrasonic and magnetic treatments. The sonication of Korea105 proceeds by three categories of reactions, i.e., free-radical generation, propagation, and termination. The principle sonochemical process in LBO appears to be C-C bond cleavage and the recombination of alkanes and aromatics, according to the disappearance of or significant shift in the absorption peaks at the two positions corresponding to the intermolecular and parallel alkane interaction forces for all the LBOs after ultrasonic treatment. The effect of a magnetic field on the viscosity of related petroleum oil is very controversial and the controversy was simplified to two aspects. Several researchers have determined that the viscosity of paraffin-based crude oil increases after exposure to a strong magnetic field at 1.5 T for an extended time. In contrast, other studies have found that the magnetic field reduced the viscosity. Our experiments regarding the increasing viscosity of Korea105 verified the first aspect. The increase in the viscosity of Korea105 suggests that the strong magnetic field and long interaction time induced the aggregation and orientation of the organic molecules. The results obtained in this work demonstrate that THz-TDS is a powerful tool that can provide evidence for the degradation mechanism of organic molecules subjected to different physical treatment methods.

Key words: Terahertz; Molecular dynamics; Ultrasound; Magnetic; Annealing
OCIS Codes: 300.6495; 300.6390; 300.1030