Consistency-dependent optical properties of lubricating grease studied by terahertz spectroscopy*

Tian Lu(田 璐)[a)b)], Zhou Qing-Li(周庆莉)[c)], Zhao Kun(赵 昆)[a)b)†], Shi Yu-Lei(施宇蕾)[c)], Zhao Dong-Mei(赵冬梅)[c)], Zhao Song-Qing(赵嵩卿)[b)], Zhao Hui(赵 卉)[b)], Bao Ri-Ma(宝日玛)[b)], Zhu Shou-Ming(朱守明)[b)], Miao Qing(苗 青)[b)], and Zhang Cun-Lin(张存林)[c)]

[a)] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing* 102249, *China*
[b)] *College of Science, China University of Petroleum, Beijing* 102249, *China*
[c)] *Beijing Key Laboratory for Terahertz Spectroscopy and Imaging, Key Laboratory of Terahertz Optoelectronics, Ministry of Education, Department of Physics, Capital Normal University, Beijing* 100048, *China*

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The optical properties of four kinds of lubricating greases (urea, lithium, extreme pressure lithium, molybdenum disulfide lithium greases) with different NLGL (National Lubricant Grease Institute of America) numbers were investigated using terahertz time-domain spectroscopy. Greases with different NLGL grades have unique spectral features in the terahertz range. Comparison of the experimental data with predictions based on Lorentz–Lorenz theory exhibited that the refractive indices of each kind of lubricating grease were dependent on the their consistency. In addition, molybdenum disulfide (MoS_2) as a libricant additive shows strong absorption from 0.2 to 1.4 THz, leading to higher absorption of MoS_2-lithium grease than that of lithium grease.

Keywords: terahertz, lubricating grease, molybdenum disulfide, refractive index
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1. Introduction

Lubricating grease is used in a great variety of situations to reduce the wear and friction between movable (metal) joints.[1] A typical multipurpose lubricating grease is the multiphase system that consists of about 85% base fluid, 10% thickener and 5% 'other ingredients imparting special properties' (ASTM, 1961). Different greases can be produced by using different soaps and some performance additives.[2] For example, the soap of urea compound can yield urea grease. The main alkalis used for grease-making are lime (calcium hydroxide), sodium and lithium hydroxide. These in turn produce calcium, sodium and lithium soaps which give grease a set of distinctive properties. Extreme pressure and molybdenum disulfide lithium greases which are mainly used in the market exhibit a low coefficient of friction. Because of the importance of molybdenum disulfide (MoS_2) as a dry lubricant additive, it has been the subject of considerable research of both fundamental and applied interests.[3−5]

The importance of optical measurement methods in various technologies is increasing. The refractive index (RI) has been shown to represent various important properties of multicomponent native petroleum, processed fuels, as well as their respective components.[6] Spectral analysis of lubricating materials originally used for research can be traced back to the 20th century. In recent years, much attention has been paid to the terahertz (THz) spectroscopic studies of petroleum products.[7−10] Terahertz time-domain spectroscopy (THz-TDS), compared with conventional spectroscopic techniques, can provide both absorption coefficient and refractive index of a sample with high signal-to-noise ratio (SNR) and without using the Kramers–Kroning relation.[11,12] However, there is no THz spectroscopic study on the lubricating grease with different soap and additive. Hence, the expeimental and theoretical investigation on lubricating grease is truly important for greases identification and on line monitoring.

In this paper, the four kinds of lubricating greases

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†Corresponding author. E-mail: zhk@cup.edu.cn
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and MoS_2 were studied based on the THz-TDS, and the optical constants of greases were also calculated. Furthermore, comparison of the experimental data based on Lorentz–Lorenz theory shows that the RI is related to the consistency of the greases. The present results suggest that the THz spectroscopy can be used to characterise the type and consistency of lubricating greases.

2. Experimental methods and materials

All measurements were performed with a conventional transmission setup for THz-TDS based on a ZnTe emitter for terahertz generation and electro-optic sampling.[13] Oils are classified in the SAE system, so greases are classified in the NLGL (National Lubricaint Grease Institute of America) by means of penetration. As shown in Table 1, the different kinds of lubricating greases were collected from Shell Tongyi (Beijing) Petroleum Chemical Co. Ltd. The samples listed in Table 1 are urea grease (UG) with NLGL number 0# (UG0), 1# (UG1) and 3# (UG3), lithium grease (LG) with NLGL number 1# (LG1), 2# (LG2), and 3# (LG3), extreme pressure lithium grease (EPLG) with NLGL number 0# (EPLG0), 1# (EPLG1), and 2# (EPLG2), and molybdenum disulfide lithium grease (MoS_2-LG) with NLGL number 1# (MoS_2-LG1) and 3# (MoS_2-LG3). All samples were in semi-solid phase and without further purification. The as-supplied MoS_2 powder from Tianjin Guangfu Fine Chemical Research Institute had a purity of 98.21% and a partical size of 78 μm.

Table 1. The NLGL number and worked penetration of four kinds of lubricating greases.

lubricating grease	state and colour	NLGL number	worked penetration
LG	semi-fluid yellow	1	315
		2	265
		3	234
EPLG	semi-solid blue	0	380
		1	319
		2	270
UG	semi-solid blue	0	369
		1	330
		3	245
MoS_2-LG	semi-fluid black	1	310
		3	224

Due to the different absorption of samples within THz range, in order to improve SNR, the thickness was fixed at 1 cm for UG, LG and EPLG, and 0.3 cm for MoS_2-LG. UG, LG and EPLG were sealed in polystyrene (PS) cuvette, which was transparent for visible light with a side thickness of less than 1 mm. In our experiment, as calculated from measured THz time-domain spectra, the transmittance of PS wafer substrate was 88.66%. As shown in Fig. 1, it can be seen that $n_{\rm PS}$ is nearly unchanged with the value of about 1.48 in the 0.5–2.5 THz region. Moreover, $\kappa_{\rm PS}$ is rather low, indicating the low absorption in this waveband. By visible inspection, any macroscopic bubble, which would have influence on the results, was not found in the samples. Empty cuvette was used as a reference for the lubricating greases' measurement. The MoS_2 powder was pressed to form thin circle slices with a diameter of 13 mm and thickness of 0.5 mm. The signal in N_2 was used as reference for MoS_2 measurement. All the samples were investigated at room temperature and humidity was kept less than 3.0%.

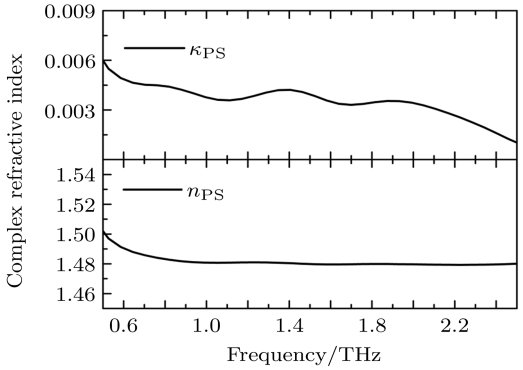


Fig. 1. The frequency dependence of the complex refractive index of polystyrene wafer.

3. Rusults and discussions

The reference pulses of free cell 1 and 2 are shown in Fig. 2, respectively. Although the optical path length of MoS_2-LG is shorter, due to the strong polar of MoS_2-LG, the signals of MoS_2-LG (Fig. 2(b)) show more drop in amplitude than LG, EPLG and UG (Fig. 2(a)).

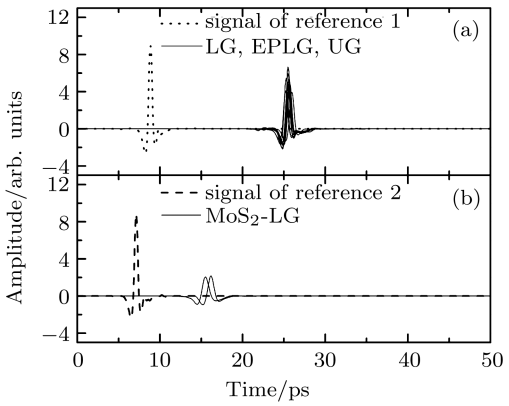


Fig. 2. THz time-domain spectra of reference and sample pulses.

By a numerical fast Fourier transform (FFT), the optical constants of greases were calculated. The frequency-dependent refractive indices and absorption coefficients of LG, EPLG and UG are shown in Fig. 3. There is no sharp absorption peak in greases' spectra in the range between 0.2–2.5 THz. Materials suitable for the production of lubricating grease are composed principally of hydrocarbons containing carbon numbers from C_{25} to C_{40}. The join of absorption peaks of each component comes into rectilinear form. The absorption spectra of each kind sample with different NLGL grades are not equal in the slope of the curve. The right panel of Fig. 3 also gives the refractive indices varying from 1.489 to 1.515 with average values of 1.499, 1.500 and 1.503 for LG1, LG2 and LG3, 1.493, 1.506 and 1.505 for EPLG0, EPLG1 and EPLG2, 1.491, 1.498 and 1.514 for UG0, UG1 and UG3, respectively.

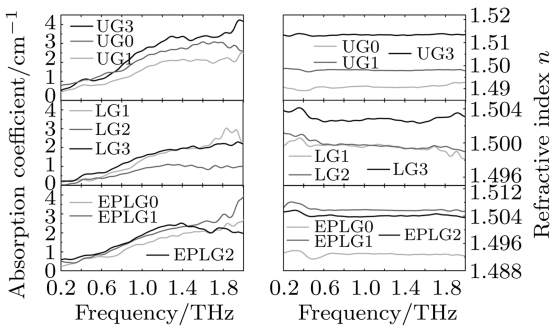


Fig. 3. THz absorption coefficients and refractive indices of LG, EPLG and UG, as depicted separately.

Greases with different NLGL grades can be identified and predicted using the Lorentz–Lorenz relation. The deviation of the refractive index for greases with different grades can be described on the basis of the Lorentz–Lorenz formula. The Lorentz-Lorenz relation for simple systems relates the RI to the polarisability of the molecules in the following way

$$\mathrm{RI} = \left(\frac{n^2-1}{n^2+2}\right) = \frac{N_\mathrm{a}\alpha\rho_\mathrm{m}}{3M}, \tag{1}$$

where N_a is the universal Avogadro's number, ρ_m the density, α the polarisability, n the refractive index, and M the molecular weight of the material. For homogeneous multicompinent systems, the effective refractive index is described by volume mean refractive index

$$n_\mathrm{e} = \sum_i f_i n_i, \tag{2}$$

where f_i, n_e and n_i are the volume fraction, effective refractive index and the partial refractive index of the i components, respectively.[14] In order to increase consistency of greases, additional dissolved substance of the i components will change Eqs. (2) in the following way

$$\Delta n_i \approx \frac{\left(n_i^2+2\right)^2}{6n_i}\frac{1}{3\varepsilon_0}N_{ix}p_{ix} \propto N_{ix} \equiv c_{ix}. \tag{3}$$

The effective additional refractive index of multicomponent systems are given by

$$\Delta n_\mathrm{e} = \sum_i \Delta n_i = \sum_i c_{ix}. \tag{4}$$

In this relation, we suppose that the molecule polarisability is constant, and this is only valid for small concentration of each component.[8] The variation of refractive index with consistency is depicted in Fig. 4. The average refractive indices of LG and UG increase because of the complex mixture of components, while that of EPLG decreases at the grade of 1–2 due to the scattering error.

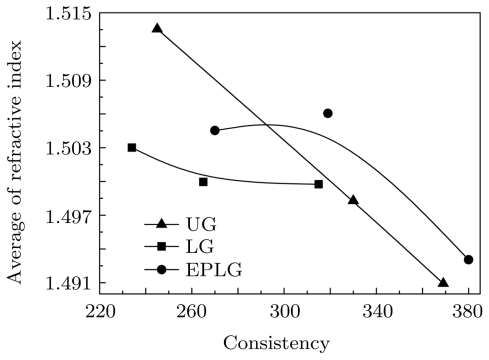


Fig. 4. Plots of average refractive index as a function of consistency.

To study the optical properties of MoS_2-LG in THz range, we also performed the THz spectrum measurement of MoS_2 thin circle slice, as shown in Fig. 5. Due to the high absorption of MoS_2, the effective spectral range is 0.2–1.4 THz. There are no obvious absorption peaks in the absorption spectra of LG, MoS_2-LG and MoS_2; and the absorption coefficients increase with increasing frequency. The absorption coefficient of MoS_2 is higher than 120, leading to a higher absorption of MoS_2-lithium grease than that of lithium grease. The layer structure is the origin of the characteristic spectrum of MoS_2. In the case of MoS_2 the important layers are made up of the MoS_2 molecules and are of three atom layers thick. These layers have strong covalent bonding within them, the bonding between the layers is of the weak van der Waals type.[15] It is along this plane of weak bonding that the shearing takes place to result in the low friction. MoS_2 is an indirect band gap material with lowest indirect band gaps of 1.23 and 1.69 eV, as determined by photocurrent measurements in an electrochemical cell.[16] The electronic spectra of bulk and cluster MoS_2 have been studied in the 200–1040 nm region, which consist of a series of absorption thresholds. Photochemical property of MoS_2 is strongly related to the nature of the gap in the near infrared.[17−19] The photo energy of terahertz is about 4 meV, which is larger than the weak van der Waals energy between the layers, thus giving rise to the resonance with each other, as well as to the vibration of their own layers just like the collective modes of graphite studied by Ji *et al.* using THz-TDS. Graphite also has a layered structure.[20] As shown in the right panels of Fig. 5, the refractive indices of LG and MoS_2-LG display a little variation with frequency. The average refractive indices are 1.500, 1.502, 1.835 and 1.904 for LG1, LG3, MoS_2-LG1 and MoS_2-LG3, respectively. The refractive index of MoS_2-LG lies between those of LG and MoS_2. As the same content of MoS_2 is added into LG, the average refractive index of MoS_2-LG1 is higher than that of MoS_2-LG3. Each grade of MoS_2-LG is characterised by a specific refractive index and absorption coefficient.

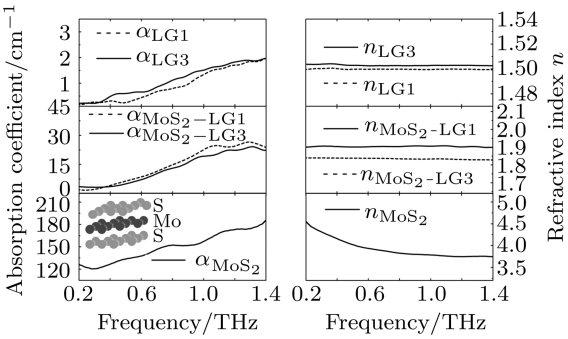


Fig. 5. THz spectra of MoS_2, MoS_2-LG1 and MoS_2-LG3.

4. Conclusions

In summary, the four kinds of lubricating greases and MoS_2 have been studied using terahertz TDS technology. Analysis of the optical properties of lubricating greases at different consistency permits the determination of the refractive index and the absorption coefficient. The specific kinds and grades of lubricating greases can be characterised according to their different refractive index based on Lorentz–Lorenz theory. The dielectric behaviour of MoS_2-LG complexes is found to be fundamentally different from that of MoS_2 and LG. The interaction of layers and resonance in them give rise to the strong absorption of MoS_2, as well as the high absorption of MoS_2-LG.

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