

Diffusion interaction and quantitative analysis of zinc dialkyldithiophosphate content in lube base oils in terahertz regime

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We investigate the diffusion interaction and quantitative analysis of zinc dialkyldithiophosphate (ZDDP) mixed with lube base oil (LBO) at different concentrations using terahertz time-domain spectroscopy (THz-TDS). When the concentration exceeds 6.78%, the characteristic absorption peaks exhibit significantly shift, and the absorption coefficient peak value is nonlinear against concentration. Moreover, the absorption coefficients of mixed samples follow the Beer's law at a concentration below 6.78%. The quantitative analysis enables a strategy for monitoring the formulation of lubricating oil in real time.

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Zinc dialkyldithiophosphate (ZDDP), as a multifunctional additive and inhibitor in petroleum industry, works mainly as antiwear, antioxidant, and anticorrosion agent^[1,2]. ZDDP mixed with lube base oils (LBOs) has been used to study the effect of concentration on lubrication boundary and tribological properties^[3]. The concentration of ZDDP in LBOs plays a crucial role in formulation, which is a balance of many different aspects of performance. Lubricating formulation generally results from a molecular diffusion mechanism due to the relative motion of molecules. Molecular diffusion in a steady-state and nonequilibrium system is divided into molecular motion and interaction. Molecular motion, containing the electronic motion, molecular vibration, and molecular rotation, is complicated and multibody. The intermolecular and intramolecular modes of ZDDP and LBO determine the ability of the reactants to approach each other and products to separate from each other. The intermolecular and intramolecular interactions often have their characteristic frequencies in the region lower than 100 cm^{-1} .

Two major strategies can be used to investigate low-frequency diffusion between ZDDP and LBO. Femtosecond optical Kerr-effect (OKE) spectroscopy has been used over past decades to investigate molecular motion in liquids and liquid mixtures^[4]. The second technique is terahertz time-domain spectroscopy (THz-TDS)^[5,6], which is a promising and nondestructive analysis method for petroleum products. A unique attribute of THz-TDS is its ability to sensitively measure the induced molecular dipole moments of many petroleum products. Furthermore, the low photon energy of radiation allows propagation through flammable liquids without any danger of combustion. The past few years have witnessed a remarkable effort in employing THz-TDS for investigating

the properties of petroleum products, including gasoline, diesel, lubricating oil, lube base oil, water-oil complexes, and organic solvents^[7-9]. The absorption spectra of petroleum products show collective modes in the THz region.

In this letter, we described the interaction between ZDDP and LBO using THz-TDS. First, we measured the THz-TDS of polar liquid of ZDDP at different concentrations in LBO from Russia and calculated their absorption coefficients. We then investigated the usefulness of the standard absorption coefficient by comparing the calculated concentrations and the actual mixing ratios of the ZDDP in LBO from Korea. Investigating the quantitative analysis of lubricating oil formulation is important to find a strategic application in the field of real-time monitoring.

All measurements were performed with a conventional transmission setup for THz-TDS based on a ZnTe emitter for THz generation and electro-optic sampling^[10]. The ZDDP used was zinc nbutyl-isooctyl-dithiophosphate without further purification. ZDDP molecules can exist in solution not only as monomers, but also as dimers or even higher order oligomers; the zinc atoms are connected by two bridging DDP groups, and each zinc atom is chelated by one DDP group^[1]. The viscosity indices of LBOs from different countries have been studied^[11], and the absorption peak positions and spectral shapes of LBO have been shown to correspond very well with previous data. The collected THz-TDS of LBO contain the necessary analytical information to identify the viscosity index, such as spectral variations related to different chain lengths. For liquid spectroscopy, the accuracy of the absorbance and interaction determination depends directly on the precision of the concentration-dependent changes in the THz absorption coefficient. We mea-

sured the THz-TDS of polar liquid of ZDDP mixed with LBO of viscosity 150 from Russia (ZDDP-Russia150) and viscosity 70 from Korea (ZDDP-Korea70) at several concentrations. The interaction between ZDDP and LBO were divided into two broad categories: frequency shift and quantitative analysis. The sample in liquid phase was sealed in a polystyrene (PS) cuvette with a side thickness of less than 1 mm that is transparent for visible light. From our measured THz-TDS data, the transmittance of PS wafer substrate was calculated as 88.66%. Moreover, the empty cuvette was used as the reference measurement, and no macroscopic bubble was found in the sample. All the measurements were performed at room temperature and humidity was kept at less than 3.0%.

Figure 1 shows the THz absorption coefficient α of ZDDP-Russia150 with a variable concentration range of 0.18% to 20.01%. The vertical axis was offset to clarify with different concentrations. The absorption peaks shift significantly at the concentration of 20.01%, and the frequency shifts (Δf) are 0.073, 0.147, and 0.176 THz for peaks 1, 2, and 3, respectively. As shown in the inset of Fig. 1, in the ZDDP-Russia150 system, the concentration dependence of α follows the Beer's law in the concentration range from 0.18% to 6.78%. The intensity changes of molecular interaction at THz frequency region are thought of as peak shifts in intramolecular vibrations and/or the generation and disappearance of the peaks in direct intermolecular vibrations^[12]. Thus, the peak shift in our case is due to the intramolecular vibrations of alkanes and aromatics in LBOs.

To understand the absorption spectra, calculation was carried out using the GAUSSIAN 03 software package. The B3LYP method was used in conjunction with the 6-31G basis set. The hydrocarbons ranging in carbon number of 20–40 of LBO with different viscosity grades can be classified into a few broad categories: alkanes, alkenes, alicyclics, and aromatics. Alkenes are unsaturated molecules and comparatively rare in LBO. Figure 2 depicts the frequency-dependent vibrational modes of n-eicosane, 5-ethyloctadecane, eicosene, 4-ethyloctadecene, and dibenzo [a, h] pyrene representing alkanes, alkenes, alicyclics, and aromatics. Absorption peaks of LBO

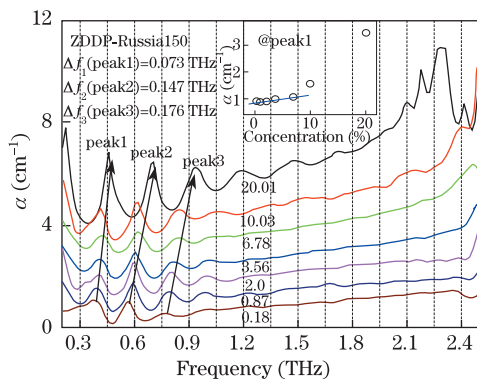


Fig. 1. THz absorbance spectra of ZDDP-Russia150, with concentration varying in the range of 0.18%–20.01%. The y -axis values have been offset for clarity. The inset shows the absorption coefficient of peak1 against concentration, which follows the Beer's law at the concentration below 6.78% (solid line).

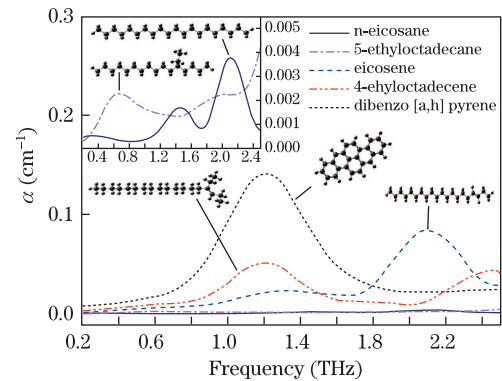


Fig. 2. Simulated absorption results of n-eicosane, 5-ethyloctadecane, eicosene, 4-ethyloctadecene, and dibenzo [a, h] pyrene.

located at lower frequency are affected by the motions of the alkyl chains, and the absorption modes are displayed as “collective modes”. However, the complicated composition of petroleum, which is a mixture of organic chemicals ranging in size from simple gaseous molecules to very high molecular weight asphaltic components, shows that the simulated absorption peaks in Fig. 2 are not perfectly consistent with experimental results in Fig. 1. The molecular modes of LBO thus play a crucial role in the interaction mechanism between ZDDP and LBO. Based on the calculated results at the B3LYP/6-31G level and with the aid of visualization of Gaussian View, the molecular modes of dominant alkanes and aromatics in the LBO are shown to correspond to collective torsional and vibrational ones, which give rise to the resonance of LBO in the 0.2–2.5-THz range.

The THz-TDS corresponds to Fourier transformation of the time-correlation function of the total dipole moment of the system, $M(t)$, which can be expressed as^[13,14]

$$\alpha(\nu) = \frac{2\pi}{3\hbar c n(\nu)} \nu [1 - \exp(-\hbar\nu/k_B T)] \times \int_{-\infty}^{\infty} dt \exp(-i\nu t) \langle M(t) \cdot M(0) \rangle, \quad (1)$$

where c is the speed of light, ν is the angular frequency, and $k_B T$ has its usual meaning. Two types of molecular motions in condensed phase contribute to the THz region: one is the reorientational relaxation of permanent and induced dipoles of the molecule, the other is the interaction between solute and solvent, which plays a role in interpreting the THz spectra. The total dipole moments of system can be expressed as the sum of the microscopic dipoles occurring in a liquid sample; the permanent and induced dipole moments contribute to the THz region. ZDDP has short chain structures, whereas LBO molecules have saturated linear or branched long chain structures and cyclic structures based on five- and six-membered rings or benzene rings. As shown at the right-hand side of Fig. 1, ZDDP dissolved in LBO is in the form of clusters, and the interaction between the ZDDP is negligible under the present experimental conditions. More surrounding ZDDP molecules collide with the LBO continuously in the solution, causing the increased strength of fluctuations of the dipole

moment^[15,16]. The frequency shift occurs more significantly at peak 3 than that at peak 1, with a decrease of interaction strength between the ZDDP and LBO molecules. The concentration of ZDDP in LBO has a significant effect on the performance of lubricating oils under boundary lubrication conditions; thus, ZDDP at lower concentrations (0.1%–5%) could be used in normal engine oils for maximum wear protection^[3].

To study the usefulness of the standard absorption coefficients of ZDDP-Korea70, the calculated concentrations from the $\alpha(\nu)$ was compared with the actual mixing ratio from 0.088% to 3.489%. Figure 3 shows the measured absorption coefficient (α_{obs}) of ZDDP-Korea70 as a function of frequency. The two relatively strong absorption peaks at 0.88 and 2.2 THz did not shift with the changes in concentrations. We selected the two peaks as marker bands and plotted the α_{obs} of those bands against concentration from 0.088% to 3.489%, as shown in the inset of Fig. 3. The adjusted R-squares were 0.838 and 0.973, which correspond to 0.88 and 2.2 THz, respectively. Thus, α_{obs} increased in close proportion to the concentration, indicating that the Beer's law can be applied to the present ZDDP-Korea70 system. The outstanding spectral stability of the measurements allowed us to obtain a quantitative analysis of the THz spectra.

To obtain a standard spectrum for quantitative analysis the absorption coefficient α_{calcd} , shown in Fig. 3, of ZDDP-Korea70 was calculated for a certain frequency region based on the α of ZDDP and Korea70 in the 0.5–1.8 THz frequency region, as shown in the inset of Fig. 4^[17,18]. Every α_{obs} shape was well reproduced by α_{calcd} . Figure 4 shows the calculated concentration C_{calcd} of ZDDP is best reproduced, matching the expected concentration C_T values with adjusted R-square greater than 0.954. The proposed method for real-time monitoring of formulation, in view of the data presented above, helps in the optimization of formulation process.

In conclusion, ZDDP mixed with LBOs of Russia150 and Korea70 at several concentrations are studied using THz-TDS. In the ZDDP-Russia150 system, the absorption peak positions shift significantly at 20.01% concentration. The surrounding ZDDP molecules that collide with LBO in solution cause the frequency shift at picosecond time scale. Moreover, in the ZDDP-Korea70 system, the quantitative analysis of system displays reproducibility, which can be used for real-time monitoring of formulation. All the results indicate that ZDDP is dissolved in cluster form to modulate the nature of

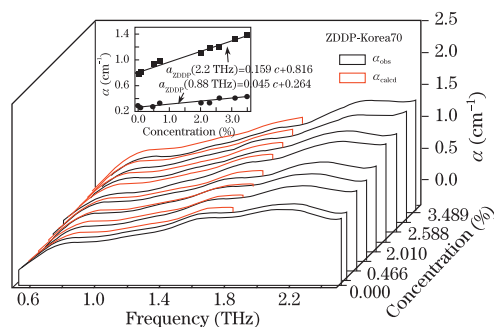


Fig. 3. THz spectra of ZDDP-Korea70 (α_{obs}) and calculated one (α_{calcd}). The inset shows the plots of α_{obs} at 0.88 THz (circle point) and at 2.2 THz (square point) against concentration following the Beer's law at the concentration of 0.088%–3.489%.

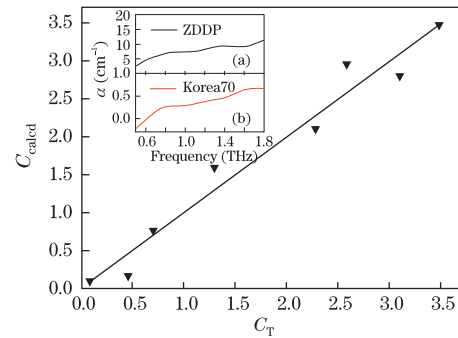


Fig. 4. True concentration C_T plotted against the calculated concentration C_{calcd} of ZDDP with adjusted R-square more than 0.954. The standard absorption coefficients of ZDDP and Korea70.

lubricating oil, and that the ZDDP-LBO system follows Beer's law at concentrations below 6.78%. The THz-TDS with data compression techniques can be used to monitor the formulation of lubricating oil in real time.

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References

- H. Spikes, *Tribol. Lett.* **17**, 469 (2004).
- N. J. Mosey and T. K. Woo, *J. Phys. Chem. A* **107**, 5058 (2003).
- S. J. Asadauskas, G. Biresaw, and T. G. McClure, *Tribol. Lett.* **37**, 111 (2010).
- N. T. Hunt, L. Kattner, R. P. Shanks, and K. Wynne, *J. Am. Chem. Soc.* **129**, 3168 (2007).
- E. Freysz and J. Degert, *Nature Photon.* **4**, 131 (2010).
- K. L. Nguyen, T. Friscic, G. M. Day, L. F. Gladden, and W. Jones, *Nature Material.* **6**, 206 (2007).
- F. M. Al-Douseri, Y. Chen, and X. Zhang, in *Proceeding of the Joint 30th International Conference on Infrared and Millimeter Waves and 13th International Conference on Terahertz Electronics* 598 (2005).
- S. Gorenflo, U. Tauer, I. Hinkov, A. Lambrecht, R. Buchner, and H. Helm, *Chem. Phys. Lett.* **421**, 494 (2006).
- M. Naftaly, A. P. Foulds, R. E. Miles, and A. G. Davies, *Int. J. Infrared Milli. Waves* **26**, 55 (2006).
- Q. Zhou, Y. Shi, B. Jin, and C. Zhang, *Appl. Phys. Lett.* **93**, 102103 (2008).
- L. Tian, Q. Zhou, B. Jin, K. Zhao, S. Zhao, Y. Shi, and C. Zhang, *Proc. SPIE* **7835**, 783513 (2009).
- N. Nagai, R. Kumazawa, and R. Fukasawa, *Chem. Phys. Lett.* **413**, 495 (2005).
- D. A. McQuarrie, *Statistical Mechanics* (University Science Books, Sausalito, 2000).
- B. N. Flanders, R. A. Cheville, A. Grischkowsky, and N. F. Scherer, *J. Phys. Chem.* **100**, 11824 (1996).
- P. Dutta and K. Tominaga, *J. Phys. Chem. A* **113**, 8235 (2009).
- A. Oka and K. J. Tominaga, *J. Non-cryst. Solids* **352**, 4606 (2006).
- T. Ohkulo, M. Onuma, J. Kitagawa, and Y. Kadoya, *Appl. Phys. Lett.* **88**, 212511 (2006).
- Y. Ueno, R. Rungsawang, I. Tomita, and K. Ajito, *Anal. Chem.* **78**, 5424 (2006).