Thermal Lens Study of NIR Femtosecond Laser-Induced Convection in Alcohols

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ABSTRACT: We use time-resolved thermal lens (TL) experiments to examine the convective heat transfer at microscale in the first eight members of the homologous series of primary alcohols. TL measurements enable a direct study of these primary alcohols without adding any chromophore as a function of varying heat loads created via femtosecond laser pulses at 1560 nm. Convective heat transfer leads to the asymmetrical and reduced thermal gradient, which substantially weakens the TL signal. The inflection in the time profile of the TL signal of methanol at higher powers is attributed to the greater molecular convection in methanol compared to other samples. This inflection dies out with a decrease in laser power. Our results demonstrate that the convection is more prominent at higher laser powers in all samples, and it modifies the trend in the steady-state TL signal of different alcohols with pump laser power. Methanol also has the highest steady-state TL among the primary alcohol series at low laser powers. The maxima in the TL signal are shifted systematically from methanol to ethanol and then to propanol as the laser power increases. Semiempirical analysis of time-resolved TL signal by using the latest theoretical TL model enabled us to extract the coefficient of convective heat transfer in methanol at different laser powers. In addition to that, analysis of other members of alcohol series at the highest (7.3 mW) laser power shows that convection is more facile in short-chain alcohols compared to the long-chain alcohols.

1. INTRODUCTION

Alcohols are extensively used in chemical, pharmaceutical, medical, and industrial sectors depending on their physical and chemical properties. Therefore, the study of the chemical and physical properties of alcohols has always been an active area of research. Alcohols, water, and their binary mixtures also play a crucial role as heat transfer fluids in different industrial subdivisions, such as chemical and power plants, refrigeration and air-conditioning units, transportation, and microelectronics. With the aim of device miniaturization and process intensification at industrial scale, performance improvement of heat transfer fluids has been an objective of various investigations for a long time. Heat removal methodology in numerous engineering disciplines, such as cooling of electronic devices, relies on heat transfer by natural convection due to its simplicity and reliability.

Convection is the transfer of heat by collective motion of fluid driven by buoyancy force and/or external forces. The convection led by buoyancy forces is called natural convection, i.e., denser fluids sink while lighter fluids rise. Natural convection has been studied extensively due to its presence in various phenomena in nature. Convective heat transfer is more difficult to characterize than conduction because not a single intrinsic property of the material, like thermal conductivity for conduction, can be defined to scale the process. Both thermal properties of fluids and hydrodynamic characteristics of flow govern heat dissipation by convection. In practice, convective heat transfer is often analyzed empirically (by experimental measurement). Lasers can achieve contactless regulated local heating with controlled intensity and beam profile. Natural convection induced that way can be investigated using the thermal lens (TL) technique. This technique relies on the measurement of the refractive index gradient build up in the samples. When an absorbing sample is irradiated with a laser, constituent molecules get excited to higher-energy states. Nonradiative relaxation of these molecules back to the ground states produces heat in the medium.

Consequently, the temperature of the irradiated spot becomes higher than that of its surrounding. Since refractive index of a medium changes with temperature, a refractive index gradient is also formed in the sample. Thus, the sample acts like a lens, which is called the thermal lens. It can be probed by monitoring the alteration of the wavefront of the light beam passing through it. Thermal lens effect was first observed by Gordon et al., who used a single laser beam for both pump and probe purposes. Over the years, thermal lens spectroscopy has emerged as a highly sensitive tool to study photochemical reactions, thermo-optical properties, quantum yield, low absorbance, trace analysis, nonlinear optical properties, and thermophoresis. Since the first observation of the thermal lens effect, many different experimental configurations and theoretical models have been developed to improve the sensitivity of TL apparatus and the analysis of the experimental signal. Unfortunately, these
models are valid only for small phase change of the probe beam and only for the conductive mode of heat transfer. Only a few reports in the literature address the effects of natural convection on thermal lens signal. Recently, our group has shown the influence of molecular size and structure on convective heat transfer. In so doing, we showed the effect of molecular size on convection by changing the chain length of primary aliphatic alcohols and the effect of molecular structure on convection by taking different structural isomers of the butanol. Convection has also been exploited in a variety of experiments in the last few decades, for instance, for the guided motion of an oil droplet on the surface of water using a laser beam and for DNA trapping and DNA stretching. Other than the above biophysical applications, convection has also been utilized for tailoring and manipulating two-dimensional colloidal crystals. Besides these diverse applications of convective flow induced in the system via laser heating, convective heat transfer needs to be explored as a function of laser parameters.

In our previous report, a new semiempirical TL model was proposed and tested on a homologous series of primary alcohols at one particular laser power where molecular size was the major factor in the systematic study of convective heat transfer. The low thermal conductivity of alcohols makes them a suitable candidate for the thermal lens study. However, as the heat load changes at different laser powers, the heat transfer process can be different—a possibility that was not explored in our previous work. In the present study, the rate of heat generation has been investigated as the key factor in the systematic study of convective heat transfer. Thus, this study explores an important missing parameter from our last study and is not an extension of our previous work. It is an exploration that builds on the understanding gained from the previous work. In keeping with this perspective, we choose the same series of alcohols as before and study both the steady-state and time-resolved thermal lens signals to explore the impact of laser intensity on convective heat transfer. Light intensity provides us the necessary control over the rate of heat generation in the sample. We show that the higher rate of heat generation with increasing laser power is counterbalanced by an increased convective heat transfer. Thus, the emphasis here is more on the rate of heat generation. Convective heat transfer characterized by thermal lens spectroscopy may be useful for future optothermal applications. This study also explores the reliability of TL model for both low- and high-absorbing samples. We find that the study works well for both weak and strong thermal lensing systems.

2. EXPERIMENTAL SECTION

In this thermal lens study, the dual-beam-mode-mismatched pump–probe scheme is used, in which one beam acts as a pump beam, while the other beam is used as a probe beam. Figure 1 shows the experimental setup used in this study. A mode-locked femtosecond Erbium-doped fiber laser is employed, which generates femtosecond laser pulses of the central wavelength at 1560 nm with 50 MHz repetition rate. It also simultaneously produces laser pulses centered at wavelength 780 nm through the second harmonic generation of 1560 nm pulses. Pulse widths for 1560 and 780 nm pulses are measured to be ~300 and ~100 fs, respectively. The 1560 nm beam serves the purpose of a pump beam, whereas the 780 nm laser beam acts as a probe beam. The average power of the pump beam at the sample position is varied from 1.2 to 7.3 mW by using half-wave plate and polarizer combination, whereas the average power of the probe beam is kept fixed at 6 mW.

In our mode-mismatched configuration, the probe beam passes through the sample collinearly with the pump beam. The probe beam is kept nearly collimated, while the pump beam is focused using a 5 cm lens. The sample is taken in a 1 mm quartz cuvette, and it is put at the focus of the pump beam. The central portion of the probe beam is selected using a partially closed aperture placed at the far field from the sample position. The intensity of the probe beam after the aperture is detected by an amplified silicon photodiode (Thorlabs: PDA 100A-EC). The signal is recorded by a 600 MHz digital oscilloscope (LeCroy Waverunner 64xi). A mechanical shutter (SR-475) of <500 μs rise and fall time is placed in the pump arm to measure time-resolved TL signal. Open and close time windows of the shutter are sufficiently long (∼5 s) so that the equilibrium condition could be reached. The <500 μs rise and fall time is too short to have any consequential impact on the details of the TL signal that arises in the order of milliseconds. Similarly, the individual laser pulse

Figure 1. Experimental setup for dual-beam thermal lens spectroscopy with 1560 nm thermal pump and 780 nm probe.
width of 300 fs does not affect our measurement as the TL signal is the cumulative effect of millions of pulses within our measurement window of the shutter open and close times.

Direct determination of Rayleigh parameters of the pump and probe beams is usually tedious and cannot be performed within the sample. So, we calibrated our experimental setup using pure water as a reference sample. However, the beam radius \((\omega_{\text{p}})\) of the collimated probe beam at the sample position is measured to be \(\sim 1\) mm using the knife-edge technique. All samples are of spectroscopic grade and used without further purification. Absorption spectra of these samples are measured by a spectrophotometer (PerkinElmer Lambda900) to measure the absorption coefficient of the samples.

3. RESULTS AND DISCUSSION

TL signals of homologous series of primary alcohols starting from methanol to octanol are measured at different pump laser powers ranging from 1.2 to 7.3 mW. Each alcohol shows strong absorption bands in the near-IR region that originates from

Figure 2. Near-IR absorption spectra of water and homologous series of primary alcohols.

Figure 3. Steady-state TL signal of homologous series of alcohols at three different pump laser powers.

Figure 4. Steady-state TL signal of homologous series of alcohols measured with different pump laser powers at the focus.

Figure 5. Time-resolved TL signal of methanol and water at 7.3 mW pump laser power.

Figure 6. Experimentally obtained time-resolved TL signal of water at 7.3 mW laser power (black curve) and fits with eq 2 (solid red curve).
overtones of fundamental and combination vibrations of the −OH group.43 The absorption spectra of all of the samples are shown in Figure 2. Absorbance in alcohols at 1560 nm wavelength is the highest for methanol, and it goes down along the homologous series, whereas there is negligible absorption at 780 nm wavelength. So, we use femtosecond laser pulses centered at 1560 nm wavelength to excite these samples. Excited molecules relax back from their excited state to ground state via nonradiative relaxation pathway. A significant amount of heat generated in this whole process creates a thermal lens in the sample. In our case of high-repetition-rate lasers, the time between two successive pulses is 20 ns, which is very short such that the heat generated by individual pulse accumulates to a significant amount and gives rise to a very strong TL signal. The thermal lens formed into these samples generates a thermal lens in the sample. In our case of high-repetition-rate lasers, the time between two successive pulses is 20 ns, which is very short such that the heat generated by individual pulse accumulates to a significant amount and gives rise to a very strong TL signal. The thermal lens formed into these samples.

Table 1. Fixed Parameters for Different Alcohols

| Alcohols | Thermal conductivity (k) (mW/(cm K)) | Thermo-optical coefficient (dn/dT) (K⁻¹) | Absorption coefficient (α) (cm⁻¹) |
|----------|--------------------------------------|------------------------------------------|----------------------------------|
| Methanol | 2.0                                  | -3.98 x 10⁻⁴                             | 312                              |
| Ethanol  | 1.7                                  | -4.38 x 10⁻⁴                             | 350                              |
| Propanol | 1.6                                  | -4.34 x 10⁻⁴                             | 380                              |
| Butanol  | 1.5                                  | -4.11 x 10⁻⁴                             | 400                              |
| Pentanol | 1.5                                  | -4.04 x 10⁻⁴                             | 399                              |
| Hexanol  | 1.6                                  | -3.95 x 10⁻⁴                             | 370                              |
| Heptanol | 1.6                                  | -3.91 x 10⁻⁴                             | 374                              |
| Octanol  | 1.6                                  | -3.83 x 10⁻⁴                             | 377                              |

Table 2. Fits Parameters for Methanol at Different Laser Powers

| Power (mW) | H (mW/(cm K)) | t₁ (ms) | θ₁ (ºC/ºC) | F |
|------------|--------------|----------|------------|---|
| 7.3        | 1.139 ± 0.005| 222 ± 3  | 3.882 ± 0.029 | 15.87 ± 0.03 |
| 6.8        | 1.017 ± 0.005| 241 ± 2  | 3.65 ± 0.025 | 16.22 ± 0.03 |
| 5.9        | 0.87 ± 0.004 | 248 ± 2  | 3.106 ± 0.024 | 18.16 ± 0.03 |
| 4.7        | 0.513 ± 0.004| 330 ± 2  | 3.186 ± 0.016 | 22.08 ± 0.02 |
| 3.4        | 0.249 ± 0.004| 420 ± 3  | 2.741 ± 0.012 | 31.98 ± 0.02 |
| 2.2        | 0.129 ± 0.005| 450 ± 4  | 1.93 ± 0.012 | 57.49 ± 0.05 |
| 1.2        | 0.033 ± 0.008| 739 ± 15 | 1.158 ± 0.012 | 164.5 ± 0.2  |
Table 3. Fits Parameters for Alcohol Series at 7.3 mW Laser Power

| alcohol    | $h$ (mW/(cm K)) | $t_{01}$ (ms) | $\theta_1$ | $F$    |
|------------|-----------------|---------------|------------|--------|
| CH$_3$OH   | 1.139 ± 0.005   | 222 ± 3       | 3.882 ± 0.029 | 15.87 ± 0.03 |
| C$_2$H$_5$OH | 0.774 ± 0.003 | 335 ± 3       | 3.527 ± 0.014 | 11.46 ± 0.01 |
| C$_3$H$_7$OH | 0.611 ± 0.003 | 349 ± 3       | 3.186 ± 0.016 | 08.79 ± 0.01 |
| C$_4$H$_9$OH | 0.191 ± 0.003 | 479 ± 4       | 3.30 ± 0.01   | 11.69 ± 0.01 |
| C$_5$H$_{11}$OH | 0.146 ± 0.003 | 510 ± 4       | 2.866 ± 0.011 | 14.18 ± 0.02 |
| C$_6$H$_{13}$OH | 0.044 ± 0.004 | 437 ± 4       | 2.405 ± 0.013 | 17.64 ± 0.02 |
| C$_7$H$_{15}$OH | 0.043 ± 0.006 | 434 ± 5       | 2.123 ± 0.019 | 20.59 ± 0.04 |
| C$_8$H$_{17}$OH | 0.042 ± 0.004 | 439 ± 4       | 1.83 ± 0.012  | 23.82 ± 0.03 |

Figure 11. Convective heat transfer coefficients $H_i$ for alcohol series (methanol to octanol) at 7.3 mW laser power.

is defocusing in nature due to the negative value of the thermooptic coefficient (d$n$/dT) of the samples. In our model-mismatch dual-beam technique, thermal lens is probed using another femtosecond laser beam centered at 780 nm wavelength by passing through TL and then through a partially closed aperture placed at far field. The intensity of the probe beam after aperture changes, as TL modifies its spatial phase. TL signal is defined as the relative change in the probe beam intensity when the pump beam is “on” to the probe beam intensity when the pump beam is “off”.

(time resolved TL signal, $S(t) = \frac{I(t)}{I(0)}$)

(steady state TL signal, $S(\infty) = \frac{I(\infty) - I(0)}{I(0)}$)

where $I(t)$ and $I(0)$ are the intensities of probe beam transmitted through an aperture when pump beam is on and off, respectively. Until time $t = 0$, the pump beam is off, i.e., shutter is closed, and then the shutter opens for time $t = t$, when the pump beam is on.

3.1. Steady-State TL Study. Figure 3 shows the steady-state TL signal of the first eight members of the homologous series of primary aliphatic alcohols measured at the focus of the pump beam for three different pump laser powers. Steady-state TL signal at 1.2 mW laser power is maximum for methanol and decreases along the higher members of the series. Interestingly, the maximum of steady-state TL signal shifts to ethanol at 2.9 mW power and, in turn, shifts to propanol among alcohol series at 7.3 mW laser power. It indicates that the TL signal does not hold the linear relationship with pump laser power. It can be inferred more clearly from Figure 4 showing the plot of steady-state TL signal of individual samples vs laser power. Here, we can see that the steady-state TL signal of the lower members of the alcohol series tends to saturate at high laser power. This saturation suggests that the refractive index gradient, as well as temperature gradient, remains same in spite of greater heat generation with higher laser power.

It is because the heat generated in liquids can be transferred by both conductive and convective modes of heat transfer. Conductive heat transfer mode is predominant when the thermal load in the sample is small. But the thermal load is very high at high pump power. Therefore, convective heat transfer also contributes significantly to heat dissipation, which diminishes the temperature gradient and results in lesser TL signal. Newton’s law of cooling relates convective heat transfer per unit time and temperature difference, which is given as

$$q = h_c \times A \times \frac{dT}{dt}$$  \hspace{1cm} (1)

where $q$ is the amount of heat transfer (Joules), $h_c$ is the convective heat transfer coefficient (W/(m$^2$ K)), $A$ is the area (m$^2$), and $dT$ is the temperature difference. Temperature gradient induced through laser heating will increase with laser intensity to match heat transfer rate with heat generation rate if $h_c$ and $A$ are constant. In our experiment, $A$ is constant as it is imposed by the spot size of the probe beam at the sample position. But heat transfer coefficient “$h_c$” is generally temperature-dependent in the case of convection unlike thermal conductivity “$k$” in the case of conduction process. So, both temperature gradient and convective heat transfer coefficient can vary with laser intensity. When $dT$ becomes constant, the rate of heat transfer varies only due to changes in the heat transfer coefficient. This situation is encountered in methanol at laser power more than 4 mW, where TL signal remains nearly same. In a similar situation of laser-induced heating, z-integrated radial temperature profile measurements for several laser powers using fluorescence thermometry have been performed in water. 44 They also found that the temperature rise at the beam center is linear at low laser powers and temperature starts to saturate at higher laser powers. They rationalized transition from low to high laser power regime by correlating the change in Peclet number ($Pe_c$), which is the ratio of convection to conduction of heat, between low-power and high-power regimes.

3.2. Time-Resolved TL Study. Time-resolved TL signal can give more insight into the heat transfer process. In time-resolved TL experiments, a mechanical shutter/chopper is used in the pump arm. As the shutter opens at $t = 0$, TL starts to build up in the sample, and consequently, probe beam intensity changes until steady-state TL is formed. Time-resolved TL signal of methanol at 7.3 mW pump laser power is...
The TL signals are recorded for 5 s. This figure clearly shows the inflection in the time-resolved TL signal profile of methanol. Recently, we have revealed that this unusual thermal lens profile of alcohols cannot be explained by the most widely applicable TL model given by Shen et al.\textsuperscript{21} The mathematical expression of the TL signal derived by Shen et al. is given as

\[
\frac{I(t)}{I(0)} = \left[ 1 - \frac{\theta}{2} \tan^{-1}\left( \frac{2mV}{((1 + 2m)^2 + V^2) \frac{\ell}{2z} + 1 + 2m + V^2} \right) \right]^2
\]

where \( \theta = -\frac{\alpha p m n / \Delta T}{k_p} \). \( \theta \) contains all properties of a sample on which the strength of TL depends, where \( dn/dT \) is the thermooptic coefficient of the sample, \( \lambda_p \) is the wavelength of the probe beam, \( l \) is the sample path length, \( \alpha \) is the absorption coefficient, \( P_e \) is the average power of the pump beam, and \( m \) and \( V \) are the geometrical parameters that are defined as

\[ m = \left( \frac{\omega_{1p}^2}{\omega_{tc}^2} \right) \text{ and } V = \frac{z_1}{z_c} + \frac{z_2}{z_c} \left( 1 + \frac{z_1}{z_2} \right) \]

where \( \omega_{1p} \) is the pump beam radius and \( \omega_{tc} \) is the probe beam radius at the sample position; \( z_c = \pi \omega_{tc}^2 / \lambda_p \) is the Rayleigh range of Gaussian beam; \( t_c = \omega_{tc}^2 / 4D \) is the characteristics time constant; and \( D \) is the thermal diffusivity.

Shen’s model considers only the conductive mode of heat transfer. However, a distinctive feature in the time profile of TL signal in liquids and gases, as in methanol, shown in Figure 5, is attributed to convective flow induced as a result of a large temperature gradient formed in the sample. High absorption at 1560 nm and low thermal conductivity of alcohols lead to a large temperature gradient. Robust theoretical models have been proposed in the literature to accommodate the effect of convection in thermal lens spectroscopy. But these models require numerical treatment to calculate the TL signal. However, in many cases, it is advantageous to have an analytical expression that substantially reduces the complexity and required effort and still offer useful anticipation of the nature of experimental TL signals. It is sometimes possible to adopt rather pragmatic treatment based on some valid approximations. So, a new mathematical expression incorporating both conductive and convective modes of heat transfer was introduced by little modification in Shen’s model.\textsuperscript{28} The following equation gives the resulting expression for the time-resolved TL signal

\[
I(t) = I(0) \left[ 1 - \frac{\theta_1 + \theta_2}{2} \right]^2
\]

\[ \tan^{-1}\left( \frac{2mV}{((1 + 2m)^2 + V^2) \frac{\ell}{2z} + 1 + 2m + V^2} \right) \]

\[ + \frac{\theta_1 + \theta_2}{4} \ln \left[ \frac{1 + 2m/(1 + 2m) \frac{\ell}{2z} + V^2}{(1 + 2m)^2 + V^2} \right]^2 \]

where \( \theta_1 = -\frac{\alpha p m n / \Delta T}{k_p} \) and \( \theta_2 = -\frac{(\alpha p - \lambda_p) m n / \Delta T}{h_p} \exp \left( -\frac{\ell}{T} \right) \).

The quantities \( m, V, \theta_1, \theta_2, A, \lambda_p, dn/dT, \alpha, P_e, F, k, h, t_d \) involved in the above expression are discussed in detail elsewhere.\textsuperscript{28} The value of convective heat transfer factor “h” for alcohols is obtained by fitting time-resolved TL signals into eq 3. It is important to note that \( h \) is the magnitude of heat transfer rate per unit length. So, the magnitude of heat transfer per unit area would be “h^2”, which is equivalent to heat transfer coefficient “h^2” in eq 1. The quantity \( h^2 \) is more relevant than \( h \) itself as \( h^2 \) relates convective heat transfer rate with dT. To ensure dimensional consistency for the heat transfer coefficient \( h_{tc} \) we consider a constant normalization of \( h^2 \) by the ratio of the ideal temperature that is equivalent to the specific laser intensity used for different laser powers. This additional step ensures that we can now consider a scaled \( h_{tc} \) (referred to as “H_{tc}”) as being equivalent to \( h^2 \) with the appropriate dimensionality of \( h_{tc} \) which we refer to in our subsequent sections.

3.3. Setup Calibration. In our experiments, instead of calculating the value of \( m \) and \( V \) via measuring the beam radius \( \omega_{1p}, \omega_{tc}, \omega_{pp} \) and confocal parameters, we prefer to obtain \( m \) and \( V \) directly from transient TL signal of water used as a reference sample. Time-resolved TL signal of pure water along with methanol is depicted in Figure 5. In spite of having larger absorption at 1560 nm than methanol, water gives very less TL signal than methanol. The high value of thermal conductivity of water renders low thermal gradient that causes weak TL signal in the water. Therefore, Shen’s model is fitted into the time-resolved TL signal of water to obtain the values of \( m \) and \( V \) from best fitting. The values of \( m \) and \( V \) were found to be 8 and 66.96, respectively. The Shen model fitted into time-resolved TL signal of water is shown in Figure 6.

3.4. Time-Resolved TL Signal of Methanol. The time-resolved TL signal of methanol measured at different laser powers is shown in Figure 7. It can be observed in Figure 7 that the inflection in the TL signal of methanol decreases with decrease in laser power. The value of \( h \) at different laser powers is obtained for methanol by fitting these TL signals into eq 3. The fixed quantities needed for fitting are given in Table 1. The values of \( h \) along with other parameters obtained from fitting are listed in Table 2. Figure 8 illustrates the variation of \( h \) with pump laser power.

As we mentioned above, \( H_{tc} \) is equivalent to the convective heat transfer coefficient; therefore, we also plot \( H_{tc} \) vs laser power in Figure 9. Linear fit at laser power above ~4 mW is expected since dT is constant, which is inferred from the saturation of steady-state TL signal of methanol after ~4 mW.
in Figure 4. The larger rate of heat generation at higher powers (>4 mW) is balanced with the larger rate of heat transfer through enhancement of convective heat transfer coefficient. However, both temperature gradient (steady-state TL signal) in Figure 4 and $H_c$ in Figure 9 vary with laser power below ~4 mW.

3.5. Time-Resolved TL Signal of the Alcohol Series.

We also determine $H_c$ for different members of homologous series of alcohols at 7.3 mW laser power to rationalize the trend of steady-state TL signal in Figure 3. Time-resolved TL signal of alcohol series measured at 7.3 mW pump laser power is shown in Figure 10. The values of $h$ at different laser powers are obtained for alcohols by fitting TL signals into eq 3. Parameters available for fitting are given in Table 1. The values of $h$ along with other parameters obtained by fitting are given in Table 3. The convective heat transfer coefficient $H_c$ for different alcohols is plotted in Figure 11. One can see from this figure that the convective heat transfer coefficient is largest for methanol and decreases along with chain length in series. That is because convection relies on the directional flow of fluids where heat is carried by the constituent molecules by transit from one place to another. The motion of molecules is highly dependent upon molecular size, shape, and intermolecular interactions. Small chain molecules can drift more efficiently and lead to a considerable amount of convection. Consequently, $H_c$ decreases along the homologous series of the primary alcohols. Due to a large amount of convection in short-chain alcohols, the steady-state TL signal is reduced by a sizable amount for methanol at 7.3 mW laser power and in turn for ethanol, propanol, and so on.

4. CONCLUSIONS

Convective heat transfer process reduces the strength of the TL signal, which limits the maximum TL at high pump laser power. The inflection in the time profile of the TL signal of methanol at high power arises because of high convection, which increases with pump laser power. Methanol shows the highest TL signal at low pump power, whereas the TL signals of methanol and ethanol get reduced at high power and hence, the maximum of the TL signal is shifted to propanol because of high convection in the short-chain alcohols.

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