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Unusual behavior of thermal lens in alcohols

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ABSTRACT. We use a femtosecond pump-probe z-scan technique to measure the thermal lens (TL) signal in a homologous series of primary alcohols. The trend in these experimentally measured TL signals deviates in a counterintuitive manner from the ones calculated using theoretical models that are only based on the macroscopic parameters. Introspection shows that the present TL theories are based on heat conduction for low absorbing samples without considering any convective mode of heat transfer. Our studies on highly absorbing samples indicate the importance of convective mode of heat transfer in TL studies.

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1. INTRODUCTION

The Thermal Lens (TL) spectroscopy is based on the temperature rise in a sample undergoing laser excitation followed by nonradiative relaxation. In case of the TEM_{00} Gaussian beam profile, this temperature rise induces a refractive index gradient that behaves like an optical lens. This effect is probed by another laser beam propagating through the sample. Qualitative and quantitative information of the physical properties for the sample is obtained by measuring the variation in the center beam intensity of the probe laser at far field. TL effect was first observed by *Gordon et. al.* in a nearly transparent sample.[1] Thereafter, several developments in the TL measurement technique have evolved. Among the several available techniques, the mode-matched and the mode-mismatched dual beam techniques are comparatively more informative and, as such, more popular. In a mode-matched technique, the pump and probe beams have similar confocal parameters as well as waist positions. On the other hand, for the mode-mismatched condition, the pump and probe beam waist positions are different. Interestingly, even in between these two techniques, the mode-mismatched one is far more sensitive as compared to the mode-matched one.[2] This arises from the fact that within the first few milliseconds, the heat generated in the sample is equilibrated by the thermal diffusion resulting in a large radially distributed TL signal. This could have a much larger spread as compared to the interaction volume of the pump beam, which is not possible to be probed accurately with a mode-matched probe beam. Thus a relatively large collimated probe beam, which is the mode-mismatched condition provides better sensitivity. Such highly sensitive TL spectroscopy is used to study absorption co-efficient of samples as small as 10^{-6} cm^{-1} which is typically assumed to be transparent.[3] Presently, TL spectroscopy is a well-established, highly sensitive, non-destructive, and popular photo-thermal technique that can be used for thermal, optical, and chemical analysis of solids, liquids, and gases.[4-6] Recently, this technique has also being proposed for cancer therapy through the irradiation of tumor cells that would result in an elevation of temperature. This elevated temperature, in turn, would promote the denaturation of intracellular protein and/or disrupt the cell membrane leading to its death.[7]

In our particular TL experiments presented here, we focus on the two-color pump-probe mode-mismatched Z-scan technique. This approach is distinct from the single beam Z-scan experiments that are typically used to measure nonlinear optical properties, such as, multiphoton absorption, nonlinear index of refractive (n_2),[8] etc. Due to the instantaneous high power of the femtosecond pulses, they have become the popular choice for nonlinear studies using Z-scan technique. It is important to note that the femtosecond laser pulses can also result in a transient heating in the sample. However, TL due to a single femtosecond pulse is inconsequential since the TL effect occurs over a period of micro to millisecond timescales depending on the interaction of the laser beam on the sample. In case of high repetition rate (HRR) lasers, this transient heating accumulates in the sample resulting in a long time TL signal. The high peak power of femtosecond pulses provides the opportunity to measure the TL signal at fairly low powers without sample damage. Under such HRR conditions, TL effect can overwhelm the measurement of n_2.[9]

Alcohols are widely used for chemical, physical and biological applications depending on their physical and chemical properties[10]. Due to the high applicability of alcohols, it becomes important to study their thermal as well as other physical properties. TL signal of a sample depends on a number of parameters, namely, the thermal conductivity (k), thermo-optic coefficient (dn/dt) , heat capacity (c), density (ρ), absorption co-efficient (α), thermal expansion co-efficient (β), etc. High thermo-optic co-efficient and high thermal-expansion co-efficient make alcohols the appropriate candidate for TL study. We have used homologous series of primary alcohols starting from methanol (MeOH) ending at octanol (OcOH) where the successive member differs from the preceding member by a methylene group (CH_2). Previous studies on the third-order optical nonlinear susceptibility of the same series are also available[11].

2. EXPERIMENTAL SECTION.

Our experimental set-up involves a mode-locked femtosecond Er-doped fiber laser (Femtolite, IMRA Inc.), which generates pulses centered at the fundamental wavelength (1560nm) and its second harmonic (780nm) collinearly at 50MHz repetition rate. The 1560nm pulses are ~300fs wide with an average power of 10mW, whereas the 780nm pulses are ~100fs wide with an average power of 6mW at the sample. Our experimental set-up follows the mode-mismatched configuration, where 1560nm beam acts as the pump beam while 780nm beam acts as the probe beam as showed in Figure 1.

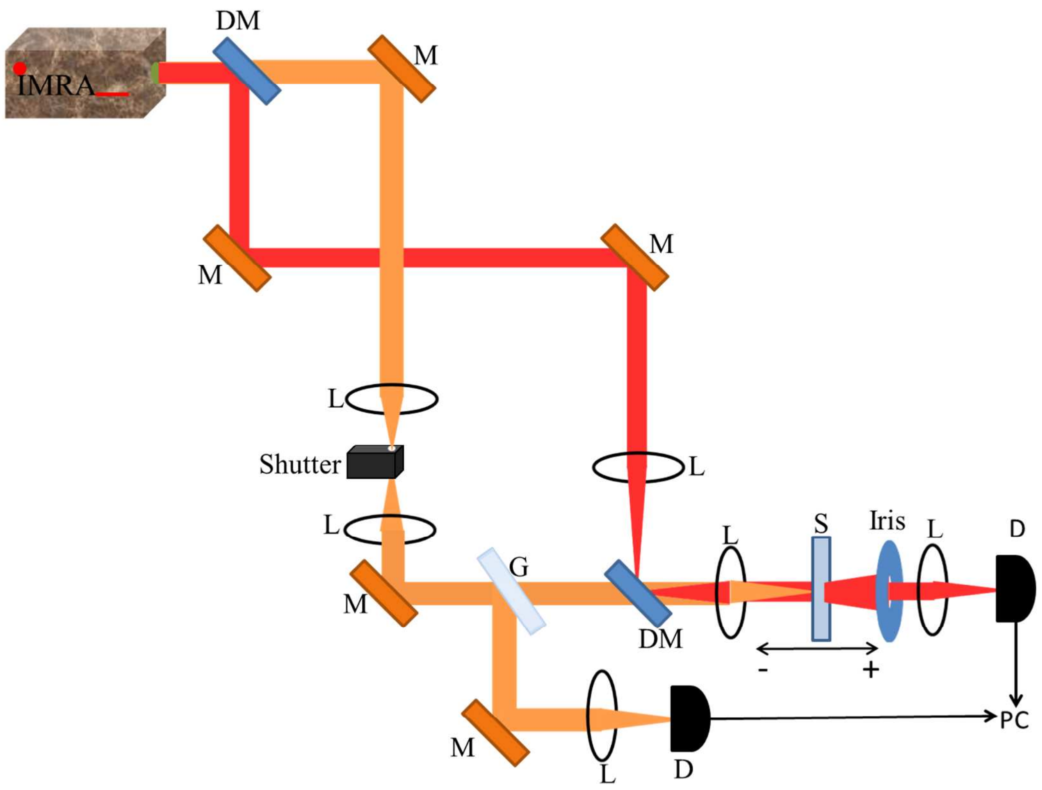

Figure 1. Schematic Diagram of the Experimental set-up, where: DM is Dichroic Mirror; M represent turning mirrors; L denote Lenses, G is the glass plate; S is the sample cell; D represent the Detectors connected to the computer through the oscilloscope (PC).

Sample is taken in 1 mm quartz cuvette and is scanned across the focal point of the pump beam. An amplified silicon photodetector (Thorlabs: PDA 100A-EC) is used to measure the transmittance of the 780nm probe beam through a 60% closed aperture at the far field allowing us to measure the TL signal in all samples. An InGaAs photodiode (Acton Research) is used to measure the fluctuations in the pump beam. This photodiode also measures the integrated absorption of 1560nm pulse (Figure 2(a)). Sample is scanned by a motorized translation stage (Newport: M-UTM150CC.1), controlled by the ESP300 Motion Controller (Newport), which can step at a maximum resolution 0.1μm. The transmittance of probe is recorded with a 200MHz oscilloscope (Tektronix TDS 224) interfaced to a computer with a National Instruments GPIB card. The sample is moved to a particular location with respect to the focal point where it waits for 5s before the data has taken. Data acquisitions are performed using a LabVIEW program. In order to measure the dynamics of the formation of TL, a shutter (SR-475) is placed in the pump arm, which has a rise time and fall time faster than 500μs. The transmittance of the probe is recorded as a function of time using 600MHz Oscilloscope (Lecroy Waverunner 64Xi) when an electronic shutter in the pump beam is opened.

We used spectroscopic grade methanol (MeOH), ethanol (EtOH), propanol (PrOH), butanol (BuOH), pentanol (PnOH), hexanol (HxOH), heptanol (HpOH) and octanol (OcOH) without further purification. The inherent sample purity is further confirmed by UV-Vis-NIR spectrum obtained from an UV-Vis-NIR spectrometer (Perkin-Elmer Lambda 900) using 1mm sample quartz cuvette. The absorption spectra around the central wavelength of the pump beam in shown in the Figure 2(b).

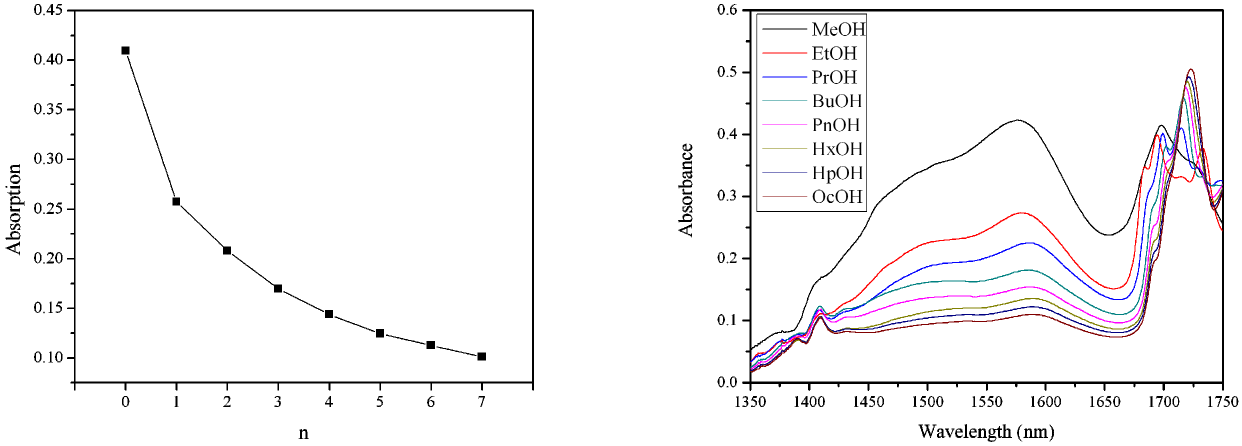

Figure 2. (a) Integrated absorption of pump beam measured by InGaAs photodiode (Acton Research) for different member of the homologous series of primary alcohols ($CH_3(CH_2)_nOH$, where n change from 0 to 7). **(b)** Absorption spectra of the alcohols near the central wavelength of pump beam 1560 nm obtained from UV/Vis/NIR spectrometer (Perkin-Elmer Lambda 900).

Closed aperture Z-scan traces are used to calculate the TL signal at each Z-position of the sample and is shown in Figure 3. The maximum TL signal is formed at the focal point of 1560nm since our experimental set-up is as per the mode-mismatched condition. The maxima of the TL signal is plotted along the alcohol series and is shown in comparison to the existing theoretical model of TL (Figure 4).

3. RESULTS AND DISCUSSIONS

We study the homologous series of primary alcohols through TL spectroscopy. Vibrational combination states of the alcohol hydroxyl group (OH) become coupled with femtosecond laser pulses at 1560nm. This coupling results in the non-resonant saturation absorption[11] of 1560nm. The excited molecule undergoes relaxation via a nonradiative relaxation process, which results in a transient thermal effect in the sample. In case of HRR laser, this transient thermal effect of the individual laser pulse accumulates to produce a cumulative thermal effect at a longer timescale. We measure the TL signal from this cumulative thermal effect with a femtosecond two-color pump-probe mode-mismatched Z-scan technique. The best approach to probe the TL signal is to measure the probe beam transmittance through a closed aperture placed at far field in the presence of the pump beam. Accordingly, we used a 60% closed aperture to detect the 780nm probe beam transmittance. From the closed aperture Z-scan traces of the sample, we measure the amplitude of the TL signal, ***S***, at various ***Z***-positions of the sample at a given time, ***t***, as[12]:

$$S(Z,t) = \frac{T(Z,t) - T_0}{T_0} \tag{1}$$

where, T(Z, t) is the transmittance of the probe beam through the aperture in the presence of the pump beam, while T_0 is the transmittance of the probe beam through the aperture in the absence of the pump beam. Using equation 1, we measured the TL signal for each member of the series at each z-position. Figure 3 shows the variation of the TL signals as a function of sample position for each member of the series.

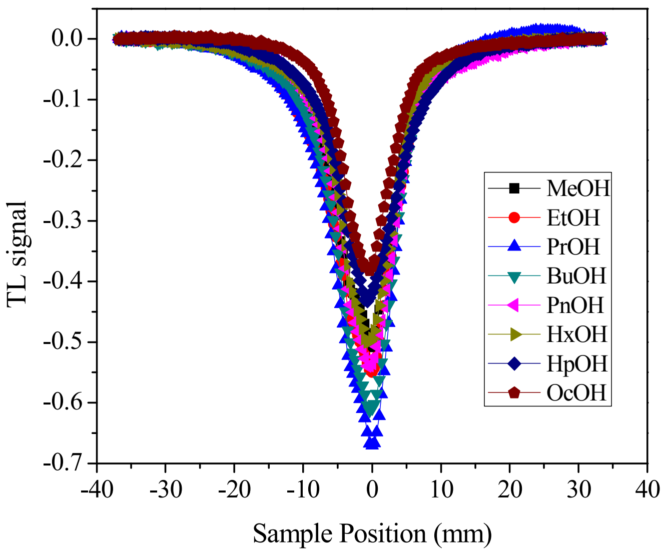

Figure 3. Thermal lens signal of homologous series of primary alcohols with respect to sample z-position.

As the maximum TL is formed at Z = 0, which is the focal point of 1560nm pump beam, we took it as the maximum value of TL signal for our analysis. The TL signal of a sample depends on a number of parameters, namely, the thermal conductivity (k), thermo-optic coefficient (dn/dt) , heat capacity (c), density (ρ), absorption co-efficient (α) (higher is the absorption, higher will be the heat generation), thermal expansion co-efficient (β), laser power and heat generation efficiency. If heat transfer is taking place only by conduction (which is the low absorption condition), the temperature distribution in the medium is governed by the equation[13]:

$$c\rho \,{}^{\partial}\!/_{\partial t}\left[\Delta T(r,t)\right] - k\nabla^{2}\left(\Delta T(r,t)\right) = Q(r,t) \tag{2}$$

where $Q(r,\ t) = 2\pi\alpha I(r)dr$, is the heat generated in the medium, and $I(r)$ in the intensity profile of laser source. The fundamental solution of this conductive heat transfer equation (equation 2) in the cylindrical co-ordinates (with boundary conditions ΔT(r, 0) = 0; ΔT (∞, t) = 0, t > 0) is given by the expression[1]

$\Delta T(r,t)=\int_0^{\infty}\int_0^{t} Q(r')G(r,r',t')dr'dt'$, where *G(r,r',t')* is the Green's function[13], i.e., $G(r,r',t')=\frac{1}{4\pi kt'}\exp\left(-\frac{r^2+r'^2}{4Kt'}\right)I_0\left(\frac{rr'}{2Kt'}\right)$, in which K = k/ρc is the thermal diffusivity, and I_0 is the modified Bessel function. The temperature change of the medium for the Gaussian intensity profile $\left(I(r)=(2P_e/\pi\omega_e^2)\exp(-2r^2/\omega_e^2)\right)$ is given by[2, 14,]

$$\Delta T(r,t)=\frac{2P_e\alpha}{\pi c\rho\omega_e^2}\int_0^t\frac{1}{1+2t'/t_c}\exp\left(-\frac{2r^2/\omega_e^2}{1+2t'/t_c}\right)dt' \qquad (3)$$

where, $\boldsymbol{P_e}$ is power of the pump beam, $\boldsymbol{\omega_e}$ are the beam waists, and $t_c=\omega_e^2/4K$ is the characteristic time constant of the sample. This distribution of temperature creates a change in refractive index of the medium, which changes the phase of the light passing through it. For small phase changes, the behavior of the probe beam intensity profile was given by Shen *et. al.* in the following form:[2]

$$\frac{I(t)}{I(0)}=\left[1-\frac{\theta}{2}\tan^{-1}\left\{\frac{2mv}{\left(\frac{((1+2m)^2+v^2)t_c}{2t}\right)+1+2m+v^2}\right\}\right]^2 \qquad (4)$$

where, ***I(t)*** and ***I(0)*** are the probe beam intensities in the presence or in the absence of the pump beam. The other parameters are: $\boldsymbol{\theta=-P_e\alpha l(dn/dT)/\lambda_p k}$, $\boldsymbol{\lambda_p}$ is the probe beam wavelength, $\boldsymbol{\alpha}$ is the absorption coefficient**,** ***dn/dT*** is the thermo-optic coefficient, and ***k*** is the thermal conductivity. The experimental setup defines the parameters '***m***' and '***v***' as: $\boldsymbol{m=(\omega_p/\omega_e)^2}$ and $\boldsymbol{v=z/z_p}$, where $\boldsymbol{\omega_p}$ and $\boldsymbol{\omega_e}$ are the beam waists of the probe and the pump at the focal point of the pump beam respectively. Similarly, ***z*** is the distance of the sample from the beam waist position of probe beam, while $\boldsymbol{z_p}$ is the Rayleigh range of probe beam. From the probe intensity ratio of equation 4, the TL signal for the Shen model is given as:

$$S(z,t)=\frac{I(t)}{I(0)}-1=\left[1-\frac{\theta}{2}\tan^{-1}\left\{\frac{2mv}{\left(\frac{((1+2m)^2+v^2)t_c}{2t}\right)+1+2m+v^2}\right\}\right]^2-1 \qquad (5)$$

For θ<<1, this simplifies to:

$$S(z,t) = -\,\theta \tan^{-1}\left\{\frac{2mv}{\left(\left((1+2m)^2+v^2\right)t_c/_{2t}\right)+1+2m+v^2}\right\} \qquad (6)$$

Another important model is developed by Marcano *et. al.*[12] as below (we use the subscript "m" for the TL signal to represent the Marcano model):

$$S_m(z,t) = \emptyset_0 \tan^{-1}\left\{\frac{2mv}{\left(\left((1+2m)^2+v^2\right)t_c/_{2t}\right)+1+2m+v^2}\right\} \qquad (7)$$

where, for liquid samples:

$$\emptyset_0 = P_e \alpha l (dn/dT)/\lambda_p k = -\,\theta \qquad (8)$$

All these parameters have been already defined previously for equation 4. In our particular TL experiments, we took each data point at an interval of 5s, which is an order of magnitude larger than $\boldsymbol{t_c}$. Consequently, we can consider a stationary thermal lens, which would allow us to rewrite equation 7 at the focal point of the pump beam (***Z* = *0***), as:

$$S_m(0,\infty) = \emptyset_0 \tan^{-1}\left\{\frac{2m(0)v(0)}{1+2m(0)+v^2(0)}\right\} \qquad (9)$$

To calculate the TL signal given by equation 9 (deduced from the Marcano model[12]), we extracted the necessary thermo-optic coefficient and thermal conductivity of the homologous series of primary alcohols from literature, which we present in Table 1 with appropriate references.

Table 1. Thermal conductivity and thermo-optic coefficient of the alcohols used in this study.

Sample	**Thermal Conductivity[a] (k) W/mK**	**Thermo-optics coefficient[b] 10^{-4} (dn/dt) K^{-1}**
MeOH	0.20	-3.98
EtOH	0.17	-4.38
PrOH	0.16	-4.34
BuOH	0.15	-4.11
PnOH	0.15	-4.04
HxOH	0.16	-3.95
HpOH	0.16	-3.91
OcOH	0.16	-3.83

a: Calculated from Ref. 21 by extrapolation of given data

b: Value calculated from data given in Ref. 22 by linear fit.

Table 2. Beam parameters of pump and probe beams.

Parameter	**value**
m(0)	50
v(0)	16.1
Pump beam power	10 mW

Probe beam power	6 mW

All experimental parameters needed for our TL calculation are from our particular experimental setup when the sample is placed at the focal point of the pump beam. All these parameters are listed in Table 2. Interestingly, Shen *et. al.* model (equation 5) can also be reduced to the stationary TL form at t=∞, which is as follows (we use subscript "s" to signify the Shen model):[2]

$$S_s(0,\infty)\left[1-\frac{\theta}{2}\tan^{-1}\left\{\frac{2m(0)v(0)}{1+2m(0)+v^2(0)}\right\}\right]^2-1 \qquad (10)$$

Using equations 8-10, we can relate both the Shen (S_s) and the Marcano (S_m) models for our particular experiments as follows:

$$S_s(0,\infty)=\left[1+\frac{S_m(0,\infty)}{2}\right]^2-1 \qquad (11)$$

We plot the theoretically calculated TL signals from equations 9 and 11 with respect to our experimentally measured TL signals in Figure 4.

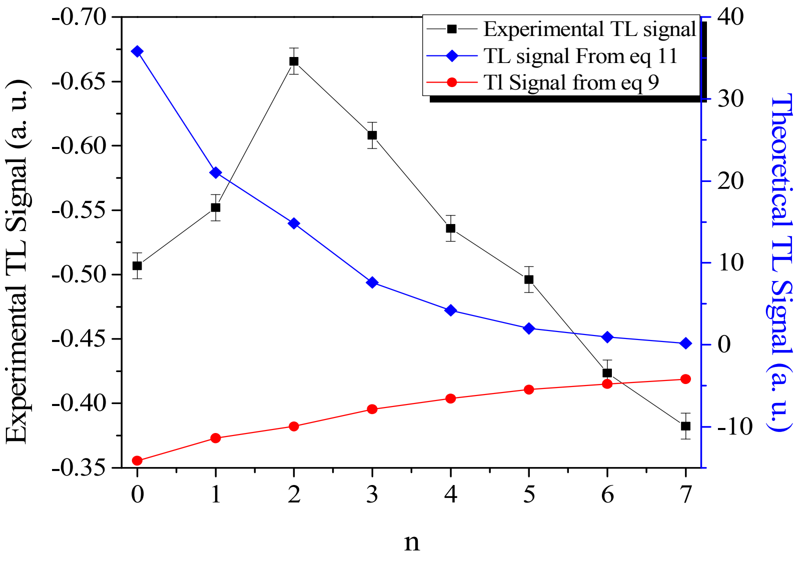

Figure 4. Comparison of calculated TL signals from the theoretical equation 9 (Marcano model) and equation 11 (Shen model) to the experimental TL signal measured in this experiment for different homologous primary alcohols of the form $CH_3(CH_2)_nOH$. (n represents the number of methylene group).

We note that the theoretically calculated TL signals are very different from the experimental values. In particular, the TL signals calculated by using either equations 10 or 11 even have the opposite sign in comparison to the experimentally measured TL. Overall, the theoretical models not only fail to predict the scale but also fail to match the trend of the experimental TL signal for the homologous series of primary alcohols. To further investigate into this unusual behavior of the TL signal along the homologous series, we measured the time resolved signal of the TL formation with help of a shutter as discussed in the experimental section. Among our primary alcohol homologous series, methanol and ethanol have the maximum absorption at the pump laser wavelength (Figure 2) and are also characterized by an inflection point in the time resolved TL signal (Figure 5).

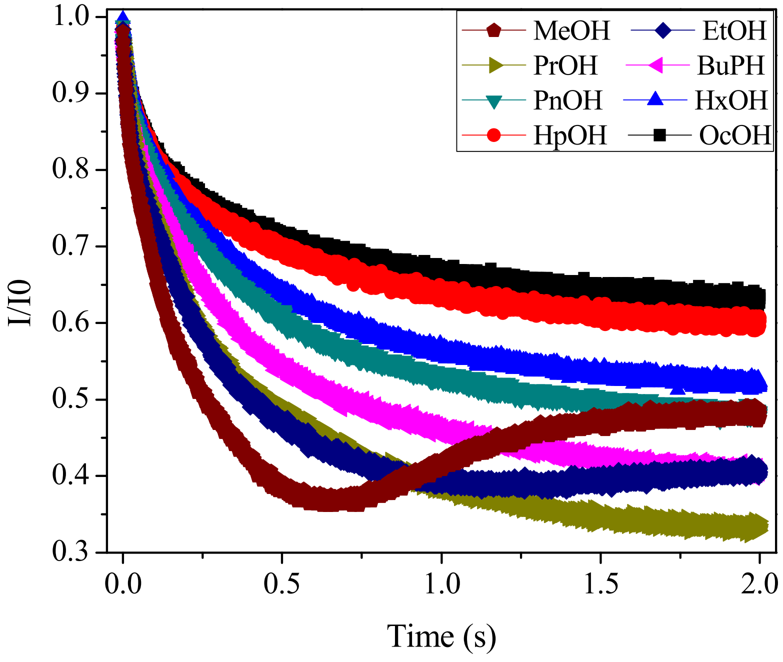

Figure 5. Temporal variation in the intensity ratios of the probe beam measured in presence (I(t)) and in absence (I(0)) of the pump beam for different alcohol samples ranging from methanol to octanol.

Such inflection points in time resolved TL measurements were earlier found for photochemical reactions or photo-degradations during TL measurements[15-18]. In our experiments, no such possibilities existed nor were detected (as confirmed through repeated absorption spectra measurements on the experimental samples before and after the experiment). These two alcohols showing the inflection points in the time resolved TL measurements also have lower steady state TL signals as compared to propanol, which has comparatively lower absorption at the pump laser wavelength. To address all these anomalies, we invoke the convective mode of heat transfer in addition to the existing conductive mode of heat transfer as used in the present TL models. Previous authors[1,2,19] have always considered their TL samples to have low enough absorption so that the convection process can be safely neglected. Thus, the present theoretical models for TL are only based on heat conduction and work for low absorbing sample. In the case of strong absorption, heat transfer through convection cannot be neglected. Convection in case of methanol and ethanol is higher as compared to the rest of the members in the homologous series (Figure 5) and thus the effect of conduction is most pronounced in these two cases. Consequently, these two alcohols show the characteristic inflection points in their time resolved TL measurements as well as have the lower steady state TL values as compared to next higher homologue in the series (propanol).

Let us now try to develop a simplistic approach to include the convective heat transfer process for the highly absorbing samples into the existing TL models. We start with equation 4 of Shen model. We plot the ratio of the intensities given by equation 4 as a theoretical measure of TL signal at the focal point of the pump beam and compare this to that of the experimental TL signal for different alcohols (Figure 6).

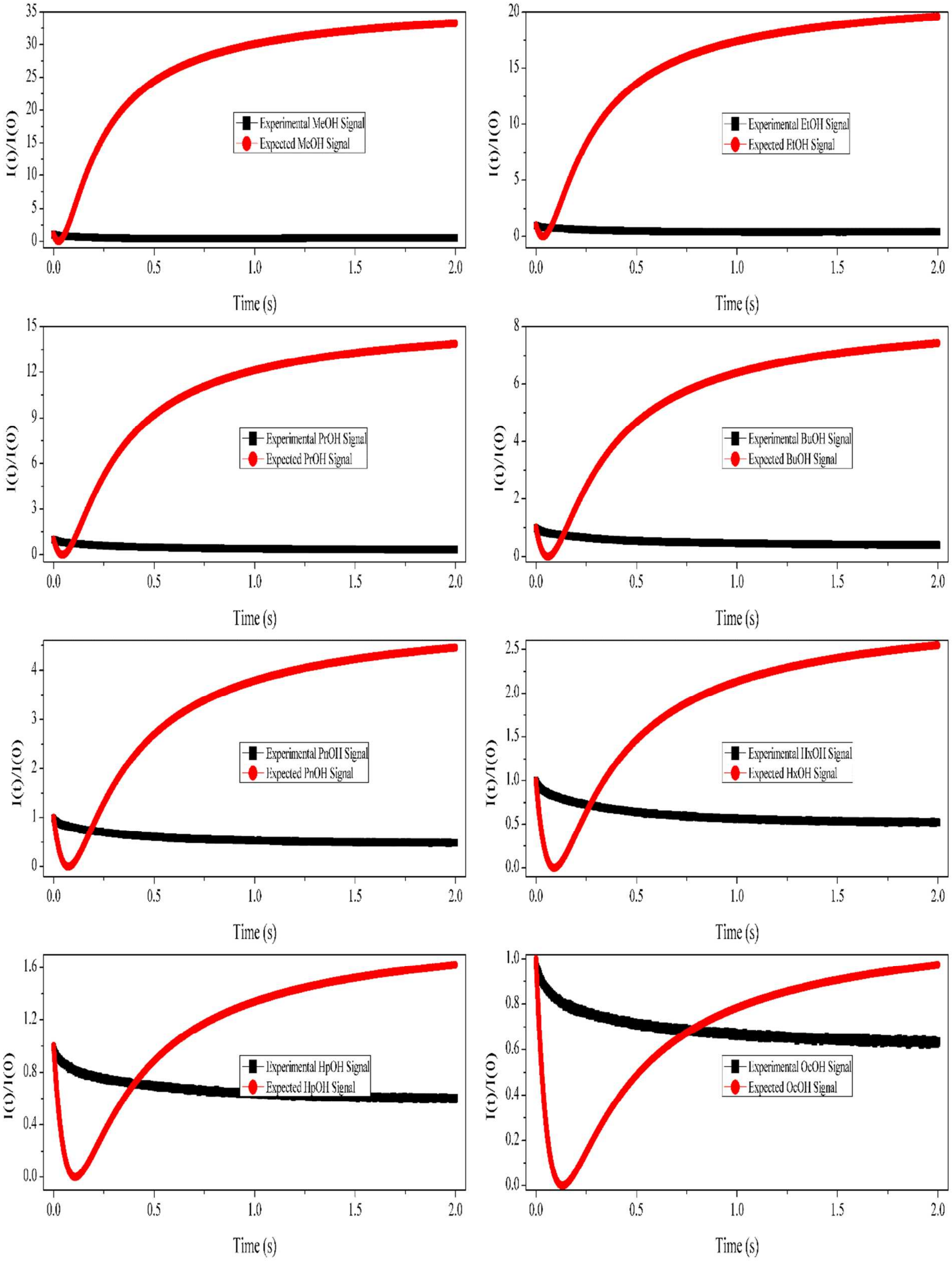
I(t)/I(0)
Time (s)
Experimental MeOH Signal
Expected MeOH Signal
Experimental EtOH Signal
Expected EtOH Signal
Experimental PrOH Signal
Expected PrOH Signal
Experimental BuOH Signal
Expected BuOH Signal
Experimental PnOH Signal
Expected PnOH Signal
Experimental HxOH Signal
Expected HxOH Signal
Experimental HpOH Signal
Expected HpOH Signal
Experimental OcOH Signal
Expected OcOH Signal
0.0
0.5
1.0
1.5
2.0
0
5
10
15
20
25
30
35
3
6
9
12
2
4
6
8
1
2
3
4
0.0
0.5
1.0
1.5
2.0
2.5
0.0
0.4
0.8
1.2
1.6
0.0
0.2
0.4
0.6
0.8
1.0

Figure 6. Temporal variation of intensity ratios of the probe beam in presence (I(t)) and in absence (I(t)) of the pump beam for the experimental TL measurement for alcohols from MeOH to OcOH in comparison to that of the theoretical model given by equation 4.

As expected, given the high absorbing nature of our alcohols, there is no match between the theory and experimental data. For such single molecular liquid samples as alcohols presented here, we argue that the convective mode of heat dissipation cannot ignored and although several parameters can be important in giving rise to the convective mode of heat transfer, the most important of them all would be the temperature difference that is caused due to absorption. We have used as our first line of approximation for understanding our data. So, we add an exponential convective correction term to equation 4 of the Shen model. This results in the following expression:

$$\frac{I(t)}{I(0)} = \left[1 - \frac{\theta_{con}}{2}\tan^{-1}\left\{\frac{2mv}{\left(\left((1+2m)^2+v^2\right)t_c/_{2t}\right)+1+2m+v^2}\right\}\right]^2 + \theta_{conv}\exp(-\frac{t}{t_d}) \qquad (12)$$

In this expression, we have argued that the absorbed energy transfer in the system has two parts. One parts of energy (*x*) is transferred by conduction and other parts of energy ($\alpha P_e - x$) is transferred by convection. Therefore, $\boldsymbol{\theta_{con} = -xl(dn/dT)/\lambda_p k}$ and $\boldsymbol{\theta_{conv} = -(\alpha P_e - x)l(dn/dT)/\lambda_p h}$**,** where h is the heat convective transfer factor. We fitted this simplistic model to our experimental data for the alcohols which is in Figure 7. There is a drastic improvement between the experiment and theory. The fitted parameters are given in table 3. This indicates that even with this simplest inclusion of the convective heat transfer contribution, there is a major improvement possible to the TL theory.

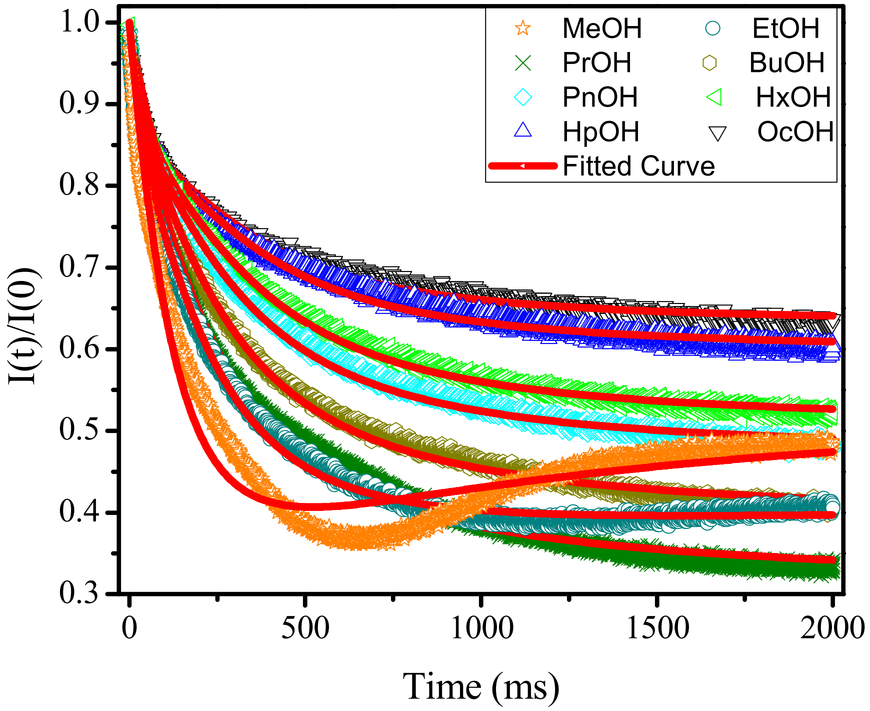

Figure 7: Temporal variation of intensity ratios of the probe beam in presence (I(t)) and in absence (I(t)) of the pump beam for the experimental TL measurement of alcohol fitted to our simplistic model including convection given by equation 12.

Table 3: The fitted parameters of equation 12 for alcohols

Sample	**θ_{con}**	**θ_{conv}**	**t_d (ms)**	**t_c (ms)**	**h (W/mK)**
MeOH	0.779	0.32965	800	50	0.20
EtOH	1.519	0.41933	162.9	114.8	0.17
PrOH	1.033	0.21619	180.3	101.3	0.16
BuOH	1.074	0.31219	191.8	112.9	0.15

PnOH	1.119	0.41078	212.7	127.1	0.15
HxOH	1.134	0.45472	235.3	140.6	0.16
HpOH	1.088	0.53051	245.9	138	0.16
OcOH	1.015	0.53336	229.3	123.4	0.16

To find out the exact model which include heat conduction and heat convection, a detailed model of TL need to be developed from the generalized heat transfer expression[20]:

$$c\rho \, {\partial}/{\partial t}\left[\Delta T(r,t)\right] - k\nabla^2\left(\Delta T(r,t)\right) + \vec{u}\, c\rho \nabla\left(\Delta T(r,t)\right) = Q(r,t) \qquad (13)$$

This generalized heat transfer expression (equation 13) has the additional term: $\vec{u}\, c\rho \nabla\left(\Delta T(r,t)\right)$ coming from convection in comparison to equation 2, which has been the basis of all the earlier TL models. The convective part of this heat transfer equation (equation 13) has the additional vector parameter $\vec{u}$ which is the convective velocity of the molecule under study. This shows the relevance of the molecular characteristic in TL under strongly absorbing condition. However, solution of equation 13 is not straight forward and we contained ourselves in this paper to show the importance of the convection correction even under the simplistic model.

4. CONCLUSIONS

We used femtosecond two-color pump-probe mode-mismatched Z-scan technique to measure the thermal lens (TL) signal of homologous series of primary alcohols. In this study, 1560 nm femtosecond beam was focused into the sample to act as the pump beam while a collimated 780nm femtosecond beam was used as a probe. The TL signal shows unusual behavior along the alcohol series when compared with the expected TL signal calculated from physical parameters. This is to be because of the fact that all the presently existing theories assume only low absorbing samples undergoing conductive mode of heat transfer. Our experiments also show a maximum in the TL signal for propanol in our TL trend of the homologous series of primary alcohols. Our time resolved TL studies indicate the importance of convective mode of heat transfer for highly absorbing samples.

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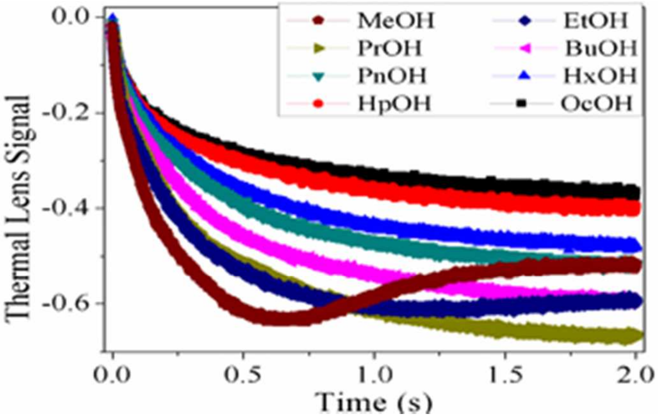

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