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Effect of molecular structural isomers in thermal lens spectroscopy

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ABSTRACT

We explore the importance of molecular structure on thermal lens (TL) spectroscopy by measuring the effects of molecular isomerization on TL measurements. In particular, we present a case study for all the structural isomers of butanol, namely, normal-butanol (*n*-BuOH), secondary-butanol (*s*-BuOH), iso-butanol (*i*-BuOH) and tertiary-butanol (*t*-BuOH). We argue that the molecular isomerization influences the heat convection process in two possible ways: one being a change in the molecular surface area and the other being the steric hindrance. We show that *n*-BuOH has the highest capability to transfer heat by convection. Branching in the molecular structure renders the system sluggish as it makes the molecular motion successively retarded due to an increase in the mean free path. This we have defined as the molecular drift that slows under thermal conditions. In our studied isomers, therefore, *t*-BuOH drifts the slowest.

1. Introduction

Thermal lensing (TL) is a laser induced process that takes place when the laser energy is absorbed by a specimen under study and the absorbed radiation energy is partially or fully converted into heat [1–3]. The laser source is chosen such that its wavelength couples either the electronic or vibrational states of the sample under study. If the system relaxes via the radiationless mechanism, it transfers its absorbed energy completely to the system in the form of heat. This heating results in a hot spot, which has a different refractive index compared to the surroundings and the system behaves as a lens . The formation of TL starts with the absorption of the laser light and continues until the system reaches the thermal equilibrium state through heat transfer. TL spectroscopy is a popular, well-established, highly sensitive, non-destructive analytical technique [5–11]. Recently, this technique has been extensively used for thermal, optical, and chemical analysis of solids, liquids, and gases [12–16]. There has also been a recent proposal that this technique could be applied for cancer therapy through the irradiation of tumor cells, which would lead to temperature elevation. This rise in temperature promotes denaturation of the intracellular proteins and/or disrupt the cell membrane leading to cell death [17].

The thermal lens effect was first observed in 1965 by Gordon et al. [18] for the nearly transparent solvent used in a laser cavity experiment. Initially, the single beam TL technique [19] was commonly used for TL study until the advent of the dual beam TL technique [4,20]. However, the dual beam TL technique is more sensitive compared to the single beam technique. This is because, in the dual beam technique, one beam acts as the pump beam (absorbed by the sample) while the second beam acts as probe (does not have significant absorption in sample) contrary to the single beam TL technique where it becomes difficult to accurately estimate the TL signal. The dual beam technique is further classified as being mode-matched and mode-mismatched, respectively, depending upon the beam waist size and position [4]. The mode-mismatched version is more sensitive compared to the others and is commonly used to study the hydrodynamics relaxation and photochemical reactions [21–23].

In a recent study, we have shown that the alcohols strongly absorbed in the communication band around 1560 nm, where molecular heat convection becomes more important in the TL study [24]. We have also shown how the molecular chain length plays a critical role in this molecular heat convection. This implies that molecular size plays an important role in this type of study.

In the present Letter, we address the structural isomers of butanol, i.e., normal-butanol (*n*-BuOH), secondary-butanol (*s*-BuOH), iso-butanol (*i*-BuOH) and tertiary-butanol (*t*-BuOH). With this choice of samples, we show how branching changes the molecular heat convection. There are two principal factors that influence the molecular heat convection: One is the molecular surface area, which would decrease with increased branching (for the same molecular formula). The other is the steric hindrance, which increases with molecular branching. Since these two factors are opposing each other, it seemed interesting to observe how they impact the molecular heat convection when they are simultaneously present. For this particular study, we will utilized two-color

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pump–probe mode-mismatched Z-scan technique, where a High Repetition Rate (HRR) laser is used. It is important to note that although each femtosecond pulse deposits a small amount of heat in the sample, the amount of heat deposited by each pulse is insignificant. In case of a HRR laser, however, this heat accumulates to result in a long-time thermal lens effect. Such a pulsed laser source TL signal is within the error bar of an identical experiment performed with a continuous wave (CW) laser [25]. On the other hand, the TL signal from a pulsed laser has the advantage of a larger signal to noise ratio as compared to that of the CW laser experiment [25].

2. Experiment

Our experimental set-up (Figure 1) is a two-color pump–probe mode-mismatched Z-scan experiment set-up. The laser source used in this experiment is an Er-doped fiber laser (Femtolite C-20-SP, IMRA Inc.). This single laser serves as both the pump and probe beam source for the two color experiments since it generates femtosecond laser pulses centered at 1560 nm (fundamental wavelength) and its second harmonic at 780 nm. These two wavelength laser pulses are on top of each other at a repetition rate of 50 MHz. The laser pulses centered at 1560 nm are 300 fs wide with an average power of 12 mW at the sample while the laser pulses centered at 780 nm are of 100 fs width at an average power of 6 mW. The 1560 nm pulsed laser beam acts as the pump beam as it couples with the higher overtone and combination band of the hydroxyl group of the alcohols while the 780 nm pulsed laser beam acts as the probe beam. A lens L1 (Figure 1) is used to focus the pump beam. This same lens serves the purpose of collimating the probe beam also. A second lens, L2, is placed in the probe arm in such a manner that a combination of lens pair (L1 and L2) are in the telescopic arrangement. Another telescopic lens arrangement is independently used in the pump beam so that the size of the pump beam is well below the aperture size of the shutter (Figure 1). This shutter is used to study the hydrodynamics of the TL formation.

In our experiments, two types of TL signals are measured. In one type of TL signal, a stationary TL signal is measured with respect to the sample position. For such a TL signal at each sample position, a sufficient time is given so that there is a stationary TL. The sample

is taken in a 1 mm cuvette and scanned by a motorized translational stage (Newport: M-6 UTM150CC.1). The TL signal is measured by recording the transmittance of the probe through a 60% closed aperture located in the far field. The intensity of the probe beam is measured with the help of an amplified silicon photodetector (Thorlabs: PDA 100A-EC) with a 200 MHz oscilloscope (Tektronix TDS 224) interfaced to a computer with the National Instruments GPIB card. Data acquisition is done with code written in LabVIEW. The intensity fluctuation in the pump beam is measured with the help of an InGaAs photodiode (Acton Research) (Figure 1). This photodiode is also used to measure the absorption of the pump beam by the sample. The second type of TL measure is used to study the hydrodynamics of TL signal, where the respective sample is placed at the focal point of the pump beam. A shutter is opened and closed successively for a long time and transmittance of the probe beam is measured.

In this particular study, the isomers of butanol (*n*-BuOH, *s*-BuOH, *i*-BuOH and *t*-BuOH) are used as samples, which are of spectroscopy grade and are purchased from Sigma Aldrich India.

3. Result and discussion

In our previous study, we have shown that the molecular chain length has a significant effect on the molecular heat convection indicating that molecular size has an important role in this type of study [24]. In our present Letter, we focus on the TL study of the various isomers of butanol. The purpose of this Letter is to analyze the branching effect on the molecular heat convection. The hydroxyl group of alcohols is strongly coupled to the 1560 nm pump laser pulses due to the higher overtone and combination bands of the hydroxyl group [2]. This absorbed energy is transformed into heat, which results in the TL formation. As discussed, the stationary TL signal was measured with the two-color pump–probe mode-mismatched z-scan technique. The strength of stationary TL signal at each *z*-position of the sample is calculated by measuring the strength of the probe beam in the presence and the absence of the pump beam as:

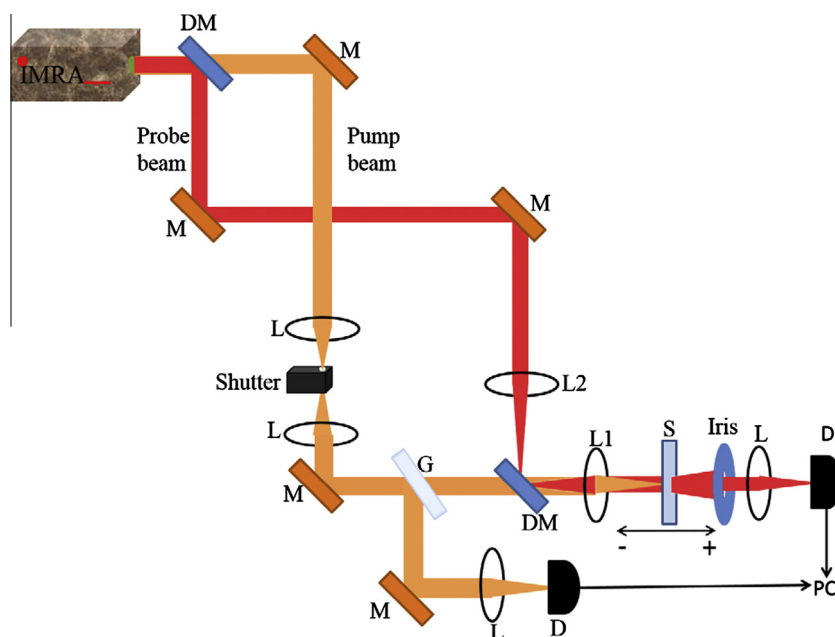$$S(z, t_\infty) = \frac{T(z, t_\infty) - T_0}{T_0} \tag{1}$$

Figure 1. Schematic diagram of experimental set-up: (DM) – dichroic mirror; (M) – mirror; (L) – lens; (G) – glass plate; (S) – sample; (D) – detector; (PC) – personal computer.

where, $S(z, t_\infty)$, is the strength of stationary TL signal at each z-position of the sample, and is measured after a sufficient time so that a stationary TL can form. $T(z, t_\infty)$ and T_0 are the probe beam transmittance through the aperture in the presence of the pump beam after a sufficiently long time and in the absence of the pump beam, respectively. The variation in TL signals for different isomers of butanol are shown in the Figure 2. The maximum TL is formed at the focal point of the pump beam in the mode-mismatched condition and this is observed in Figure 2. In this particular study, we have taken the TL signal at the focal point of the pump beam for our analysis. From Figure 3, we find that the TL signal for the isomers of butanol changes markedly from one isomer to the others, which is compared to the absorbance at the pump laser beam. It is interesting to explore the drastic changes in this TL signal with the changes in the branching within the molecule. The TL signal of a pure sample depends on a number of factors, such as, absorption coefficient (α), thermal conductivity (k), thermal expansion coefficient (β), thermo-optic coefficient (dn/dT), heat capacity (C_p) etc. It is important to note that though the absorption of the pump beam changes only slightly with changes in the isomer structure, other parameters may vary significantly with isomer structures. There are different theoretical models which connect these physical parameters with the TL signal. The widely used model for TL study is the model developed by Shen et al. [25]. This model was based on the assumption that heat generated in the system is transferred by conduction only. This is true when there is only a small absorption of the pump beam. In case of high absorption, the model based on the heat conduction is 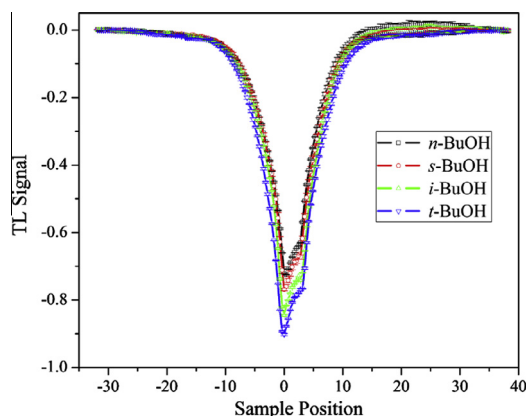not valid completely, so we have made appropriate changes in the existing models to include the heat convection. These changes are based on the principle that the amount of absorbed energy has two parts. One part of energy is transferred by conduction and the second part by convection. If the system has the absorption coefficient 'α' and 'P_e' is the laser power of the pump beam, then the amount of energy absorbed by the sample is 'αP_e'. The part of energy transferred by conduction is 'A' and remaining energy '$(\alpha P_e - A)$' is transferred by convection. The time dependency of the convection, on the principle of Linear time Invariant Theory, is taken as an exponential. This new model can be represented as [24]:

$$\frac{I(t)}{I(0)} = \left[1 - \frac{(\theta_1 + \theta_2)}{2} \tan^{-1} \left\{ \frac{2mv}{((1+2m)^2 + v^2)t_c/2t) + 1 + 22m + v^2} \right\} \right]^2 + F \left[\frac{(\theta_1 + \theta_2)}{4} \ln \left(\frac{[1 + 2m/(1+2t/t_c)]^2 + v^2}{(1+2m)^2 + v^2} \right) \right]^2 \quad (2)$$

Table 1
The experimental parameters used in this Letter.

Experimental parameter	Parameter value
w_e	110 μm
w_p	861.8 μm
z_p	10 cm
z	161 cm
P_e	12 mW
P_p	6 mw

Table 2
Sample physical parameters used in this Letter.

Sample	Thermal conductivity[a] (k) (Wm⁻¹ K⁻¹)	Thermo-optic coefficient (dn/dT) (K⁻¹) × 10⁴	Absorbance
n-BuOH	0.153	−4.1121[b]	0.194
s-BuOH	0.1344	−4.4111[c]	0.175
i-BuOH	0.1318	−3.6700[d]	0.193
t-BuOH	0.1158	−5.6260[c]	0.153

[a] From Ref. [26].
[b] From Ref. [24].
[c] From Ref. [27].
[d] From Ref. [28].

Figure 2. Calculated TL signals for isomers of butanol viz. n-BuOH, s-BuOH, i-BuOH, t-BuOH with respect to the z-position of the sample (see text for details).
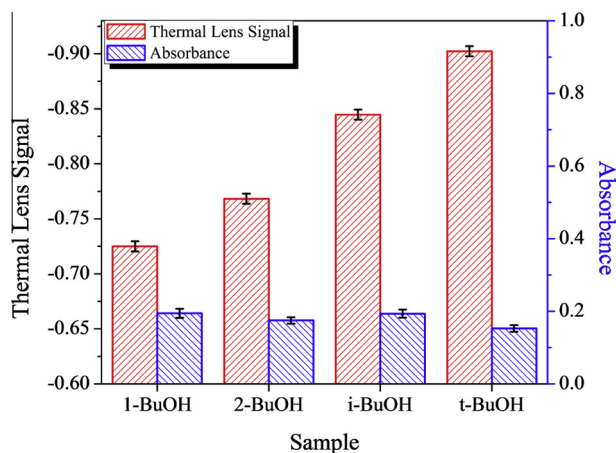

Figure 3. Plot of TL signals for isomers of butanol viz. n-BuOH, s-BuOH, i-BuOH, t-BuOH at the focal point of the pump beam compared to the respective molecular absorbance.
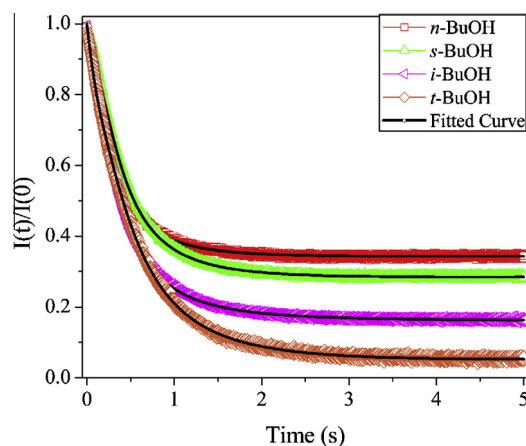

Figure 4. Time resolved profile of the intensity change of probe beam for the isomers of butanol, (n-BuOH, s-BuOH, i-BuOH, t-BuOH) with their respective fitted model.

Table 3
The model described in Eq. (2) fitted with the following parameters.

Sample	Θ_1	Θ_{conv}	h (w/m k)	F	t_c (ms)	t_d (ms)	Expected t_c (ms)	χ^2
n-BuOH	0.3475	0.81096	1.45024	0.2204	40	457.2	38.28	0.9988
s-BuOH	0.2766	0.98398	1.16768	0.1684	47	549.2	48.49	0.9991
i-BuOH	0.2947	1.05253	1.00076	0.0846	43	462.8	44.96	0.9995
t-BuOH	0.5039	1.08439	1.16558	0.0239	57	856.2	61.06	0.9991

where, $\theta_1 = -Al(dn/dt)/\lambda_p k$, $\theta_2 = -((\alpha P_e - A)l(dn/dt)/\lambda_p h)\exp(-t/t_d) = \theta_{conv}\exp(-t/t_d)$. P_e is power of the pump beam, λ_p is the probe beam wavelength, α is the absorption coefficient, dn/dT is the thermo-optic coefficient, k is the thermal conductivity and t_c is the characteristic time constant of the sample. The effectiveness of heat transfer for the system by convection is h, which depends on a number of factors, such as, molecular structure, temperature, type of heat source, etc. The time constant for heat convection is t_d. We placed the sample at the focal point of pump beam, i.e., 1560 nm beam, for this particular study. The parameters 'm' and 'v' are the experimental parameters defined by $m = (\omega_p/\omega_e)^2$, where ω_p and ω_e are the beam waists of the probe and the pump beams at their respective focal points; $v = z/z_p$, where z is the distance of the sample from the beam waist position of probe beam and z_p is Rayleigh range of probe beam. These parameters are measured at the focal points of the pump beam and are reported in Table 1 along with our other experimental parameters. The physical parameters of the samples studied are given in Table 2.

The model described in Eq. (2) is fitted to the time resolved TL data (Figure 4) and thermal information about the branched chain molecular isomers is extracted. The time resolved data was acquired by placing the sample at the focal point of the pump beam while the shutter was allowed to open and close successively for a sufficiently long time. This data is used to measure the dynamics of the TL formation and the corresponding fitted parameters are given in Table 3. As mentioned before, the two factors which play a vital role in molecular heat convection are molecular surface area and steric hindrance. For the same molecular formula, the surface area is decreased while the steric hindrance is increased with increased molecular branching. This can be quantified from Eq. (2), in terms of the 'h' factor, which defines the effectiveness of the system to convect heat. We find from Table 3 that the value of 'h' is highest for *n*-BuOH while the other isomers have lower values. Typically, the values decrease with branching. However, we find that the h value of *t*-BuOH is slightly higher than that of *i*-BuOH and nearly similar to that of *s*-BuOH. This could be conjectured as the small effect arising from the difference in the surface area of these isomers. The fitted parameters are given in Table 3, which also includes the experimental characteristic time constant (t_c). The characteristic time constant can also be theoretically calculated from the relation: $t_c = \frac{\omega_e^2 \rho c}{4k}$. From Table 3, we find that the values of t_c are in good agreement within the experimental errors. However, since heat convection is based on the drift of molecules, the convection time constant (t_d) strongly depends on molecular structure. Thus, t_d is the shortest for *n*-BuOH and the longest for *t*-BuOH. Our results, therefore, show that the branching of molecules makes the system sluggish in motion and thus more difficult to drift.

4. Conclusion

Our experiments show that the molecular heat convection strongly depends on the molecular structure as it a drift phenomenon. Thus, we are able to connect thermal lens to the molecular structure property in highly absorbing samples. In particular, we demonstrated our results on different structural isomers of butanol. The two contrasting effects of molecular surface area and steric hindrance highlight the importance of molecular structure in highly absorbing samples. In our Letter, *n*-BuOH has the highest capability to transfer heat by convection, while *t*-BuOH with its highest branching has the slowest molecular drift.

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