Chemical Physics 441 (2014) 5–10

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Importance of molecular heat convection in time resolved thermal lens study of highly absorbing samples

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ARTICLE INFO

Article history:
Received 22 December 2013
In final form 11 June 2014
Available online 4 July 2014

Keywords:
Lasers
Thermal effects
Organic liquids
Thermo-optical materials
Photo-thermal effects

ABSTRACT

Our experimental study shows that in the case of strongly absorbing samples, the time resolved thermal lens (TL) signal has a distinctive new feature. Existing TL models that are only based on heat conduction cannot explain this behavior. We have therefore developed a more comprehensive model that can also explain this additional feature in the TL of strongly absorbing samples. Our model is also capable of explaining our experimental results that show how the molecular size affects the molecular heat convection.

1. Introduction

Alcohols are widely used in industry depending upon their physical and chemical properties as solvent, ingredients in cosmetics, in medicine, and as fuel [1] High applicability of alcohols, make it important to study their thermal as well as other physical properties. The thermo-optical properties—thermal conductivity (k) or thermal diffusivity (D), specific heat (Cp), and the temperature dependent refractive index (dn/dT) are important parameters of the samples, which are necessary to model, design, and for their suitable applications. High thermo-optic co-efficient and high thermal-expansion co-efficient make alcohols, suitable candidates for thermal lens study. Thermal Lens (TL) is the result of photo-thermal effect in light matter interaction. In absorbing samples, the absorbed photon's energy is partially or fully converted into heat resulting in a temperature rise. For the Gaussian beam absorption profile, this temperature rise induces a refractive index gradient that behaves like an optical lens. Depending on the thermo-optic coefficient, this optical lens formed can behave as a converging or a diverging lens [2]. In case of liquids, TL behavior is often diverging since most liquids expand on heating. The TL effect was first observed by Gordon et al. [3]. Thereafter, many developments in the TL measurement techniques have evolved, of which mode-matched and mode-mismatched dual beam techniques have become more popular as they are more informative. The mode-mismatched one is far more sensitive as compared to the mode-matched one [4]. In this technique, the pump and probe beam waist positions are different. On the other hand, in a mode-matched technique, the pump and probe beams have similar confocal parameters as well as waist positions [2]. The thermal diffusion equilibrates the heat generated in the sample within the first few milliseconds [5–7]. As a result, the stationary TL formed has a radial dimension much larger than the interaction volume of the pump beam. To probe such a TL, a relatively large collimated probe beam is used. Right now, TL spectroscopy is a well-established, non-destructive, highly sensitive, popular photo-thermal technique that can be used for applications in thermal, optical, and biological systems, as well as in chemical analysis of solids, liquids, and gases [8–11].

In our particular TL study for high absorbing sample, we used two-color pump–probe mode-mismatched Z-scan technique. This is different from the single beam Z-scan experiments that are typically used to measure nonlinear optical properties, such as, multi-photon absorption, nonlinear refractive index [12], etc. It is important to note that femtosecond laser pulses can also result in a transient heating in the sample. Typically, TL due to a single femtosecond pulse is insignificant. This is because, depending on the interaction of the laser beam with the sample, the TL effect occurs over a period of micro to millisecond time scales. However, in the case of high repetition rate (HRR) lasers, this transient heating accumulates in the sample to eventually result in a long time TL signal. In fact, it has been shown that in case of HRR lasers the cumulative TL effect overwhelms the measure of individual pulse nonlinear refractive index [13]. The high peak power of femtosecond pulses provides the opportunity to measure the TL signal at fairly low average powers without sample damage.

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http://dx.doi.org/10.1016/j.chemphys.2014.06.008
0301-0104/

We have used homologous series of primary alcohols starting from methanol (MeOH) ending at octanol (OcOH) where the consecutive members differ from each other by a methylene group (CH_2). Previously, the third-order optical nonlinear susceptibility of this series was also measured [14]. In this paper, we report the time resolved signal for the TL at the focal point of the pump beam, which corresponds to the maximum of TL formed. Our results show how molecular heat convection plays an important role in TL study.

2. Experiment

Our experimental set-up (Fig. 1) involves a mode-locked femtosecond Er-doped fiber laser (Femtolite) IMRA Inc. It generates pulses centered at the fundamental wavelength (1560 nm) and its second harmonic (780 nm) collinearly with a repetition rate of 50 MHz. The 1560 nm pulses are ~300 fs wide, whereas the 780 nm pulses are ~100 fs wide. The average power of 1560 nm beam is 10 mW whereas the average of 780 nm beam is 6 mW at the sample. Our experimental set-up follows the mode-mismatched configuration. In this experiment set-up, 1560 nm laser beam acts as the pump beam while 780 nm laser beam acts as the probe beam as showed in Fig. 1. An amplified silicon photo-detector (Thorlabs: PDA 100A-EC) is used to measure the transmittance of the 780 nm probe beam through a 60% closed aperture located in the far field to measure the TL signal in all samples. An InGaAs photodiode (Acton Research) is used to measure the fluctuations in the pump beam. Sample is taken in 1 mm quartz cuvette and is scanned across the focal point of the pump beam (Fig. 2) with a motorized translation stage (Newport: M-UTM150CC.1), controlled by the ESP300 Motion Controller (Newport), which has a maximum resolution of 0.1 μm. The transmittance of probe is recorded with a 200 MHz oscilloscope (Tektronix TDS 224) interfaced to a computer with a National Instruments GPIB card and data acquisition is performed using LabVIEW program.

For studying the dynamics involved in TL formation, we put a mechanical shutter (Fig. 1) in the pump arm which has an activation time of 500 μs. As our pump beam size is around 6 mm and the aperture size of shutter is 3 mm, we made a telescope arrangement in the pump beam to fit the shutter. This has two advantages, viz. we decrease the size of the pump beam to ~200 μm. This helps us to save the power loss and secondly, we are able to achieve faster activation time as activation time depends upon the beam size. Since, the maximum TL signal is formed at the focal point of the pump beam; we placed the sample at the focus and measured the time resolved signal of TL. For measuring the time resolved signal, we opened and closed the shutter for a long time until the TL signal reaches the steady state. Fig. 3 shows the transmittance of the probe beam through the aperture for the representative cases of methanol and octanol respectively. For data acquisition, time

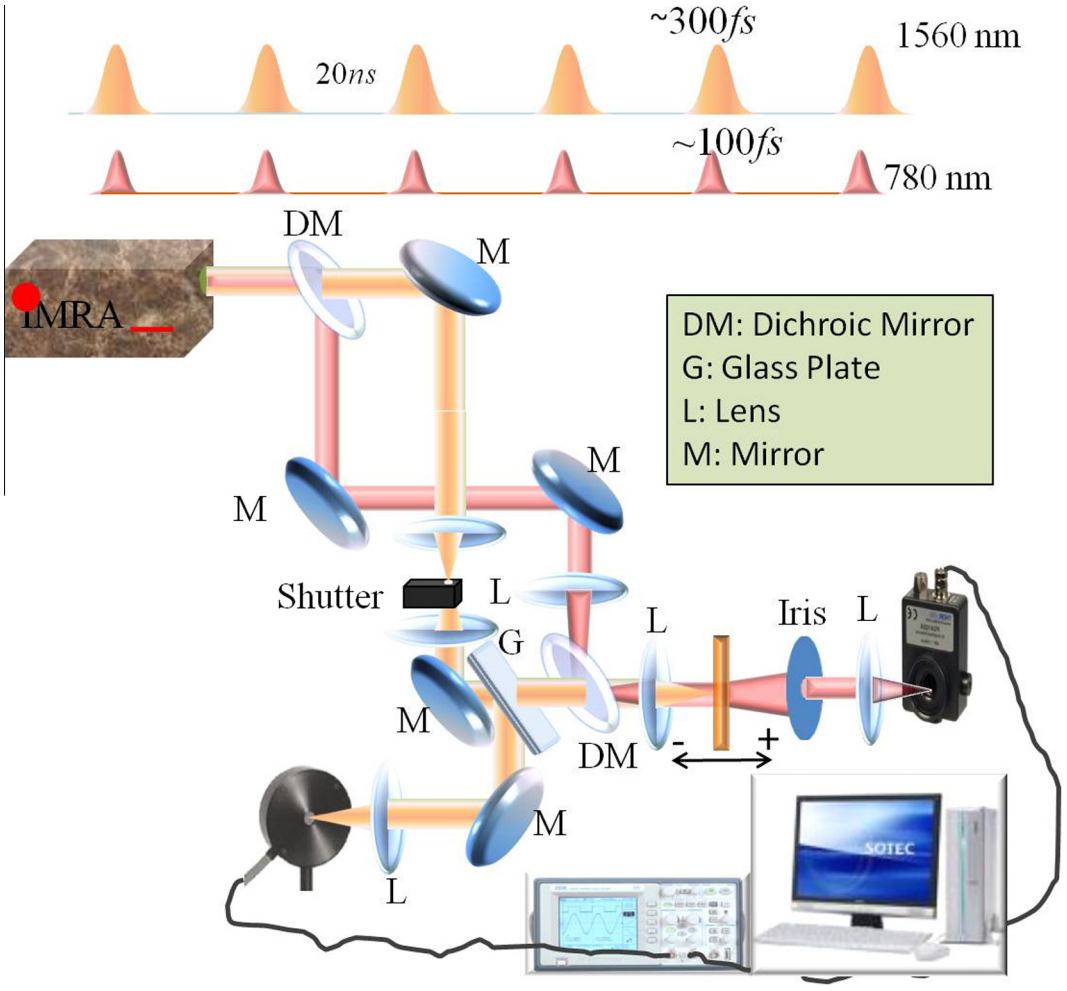

Fig. 1. Schematic diagram of experimental set-up.