Femtosecond Laser-Induced Photothermal Effect for Nanoscale Viscometer and Thermometer

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Abstract

A new method of utilizing photothermal effect at nano-volume dimensions to measure viscosity is presented here that can, in turn, provide the surrounding temperature. Our measurements use high repetition rate, low average power, femtosecond laser pulses that induce photothermal effect that is highly influence by the convective mode of heat transfer. This is especially important for absorbing liquids, which is unlike the typical photothermal effects that are due to such ultrashort pulses. Typical thermal processes involve only conductive mode of heat transfer and are phenomenological in nature. Inclusion of convective mode results in additional molecular characteristics of the thermal process. We measure traditional thermal lens with femtosecond pulse train through geometric beam divergence of a collimated laser beam co-propagating with the focused heating laser beam. The refractive index gradient in the sample arising from a focused heating laser creates a thermal lens, which is measured. On the other hand, the same heat gradient from the focusing heating laser beam generates a change in local viscosity in the medium, which changes the trapped stiffness of an optically trapped microsphere in its vicinity. We use co-propagating femtosecond train of laser pulses at 1560 and 780 nm wavelengths for these experiments. We also show from the bulk thermal studies that use of water as sample has the advantage of using conductive mode of heat transfer for femtosecond pulse train excitation.

Keywords

Femtosecond laser pulses • Optical trapping • Heat flow • Viscosity

1 Introduction

Since thermal processes occur typically in sub-millisecond timescales [1], a single femtosecond laser pulse is rarely of any concern for photothermal effects. For a train of high repetition rate femtosecond pulses, however, a residual cumulative thermal effect is often seen. Several distinct behaviors resulted from such indirectly induced photothermal effects. However, it was found that the thermal dissipation process in case of a femtosecond pulse train induced thermal effect does not follow the expected heat dissipative behavior based on thermal conduction model [2]. Instead, it was influenced appreciably by thermal convection mode of heat transfer [3–5]. This additional heat transfer channel introduces molecular characteristics to the thermal process, in contrast to the phenomenological material properties only necessary for thermal behavior. In comparison to the slow cumulative effect of the pulse train due to the impulsive nature of the instantaneous interaction of the individual pulses, a lot more heat deposition occurs for the high

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repetition rate (HRR) femtosecond laser pulses. This furthered the need of heat dissipation process through convective mode in addition to the conductive mode. Such drastic changes result in strong viscosity correlations that correspond to local temperature changes over laser interaction regions. We have taken advantage of the molecular nature of the thermal studies as discussed here in furthering some features of traditional thermal lens spectroscopy. We have also used a trapped microsphere as a sensor to measure the changes in viscosity and temperature over nanoscale volumes within the liquid interaction zone as a result of thermal effect. We measured the traditional thermal lens signal from the geometric beam divergence of a collimated laser beam co-traveling with the focused heating laser beam that generated the refractive index gradient in the sample. The same heat gradient process generates a change in local viscosity and temperature in the medium that was measured from the changes in trap stiffness of an optically trapped microsphere. We are able to correlate photothermal effects into measuring viscosity and temperature at nanoscale.

2 Experimental Setup

We used in all our experiments a mode-locked femtosecond Erbium-doped fiber laser, which generates femtosecond pulses simultaneously at 1560 nm and its second harmonic at 780 nm at 50 MHz repetition rate. Typical pulse widths are ~300 fs and ~100 fs for 1560 nm and 780 nm pulses, respectively.

2.1 Thermal Lens Setup

Measure of thermal lens signal using dual beam technique [5] is very sensitive to beam configurations. Earlier demonstrations [6] have shown that the detection of thermal lens signal under mode-mismatched condition [7–12] is more sensitive than the mode-matched detection. Later studies [10] further optimized the thermal lens with a collimated probe beam using mode-mismatched condition. Given this background, we use mode-mismatched thermal lens studies. To measure the thermal lens signal in water, we separate the two outputs from the femtosecond laser operating at 1560 nm and 780 nm, respectively as the thermal pump and probe for water (Fig. 1).

Water strongly absorbs at 1560 nm and as such acts as the thermal pump, which, in turn, produces high thermal lens signal in the sample. Water is transparent at 780 nm (Fig. 2),

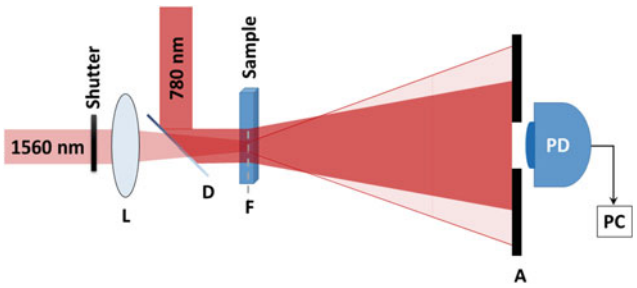

Fig. 1 Dual—beam thermal lens measurement setup schematic, where L: Lens, D: Dichroic Beamsplitter, F: 1560 nm beam focal point, A: Aperture, PD: Photodiode; PC: Computer

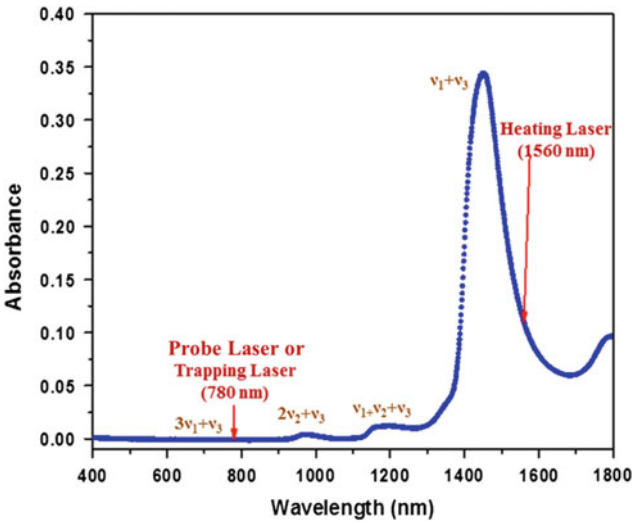

Fig. 2 Absorption spectra of pure water indicating the laser wavelengths

which therefore, acts as an ideal probe. A collinear mode-mismatched beam configuration is used. In this configuration, the probe beam is recombined with the pump beam at the sample, where the pump beam is focused with a 5 cm lens while the probe beam is collimated. The respective average powers of the pump and probe beams at the sample are ~7.3 mW and ~6 mW.

The sample is taken in a 1 mm quartz cuvette and placed at the focal point of the pump beam estimated from the Z-scan trace. An aperture is placed on the probe beam detection line in the far field in order to select the central portion of the probe beam.

The intensity of the selected portion of the probe beam passing through the aperture is detected by an amplified large area silicon photodiode (Thorlab: PDA 100A-EC), which is connected to a 600 MHz digital oscilloscope

(LeCroy Waverunner 64xi). Throughout the experiment, we use spectroscopic grade water without further purification, whose spectra is shown in Fig. 2 using a Perkin Elmer Lambda 900 spectrophotometer.

2.2 Optical Tweezers Setup

Dual collinear output from the laser is used directly onto an oil immersion objective (UPlanSApo, 100X, 1.4 NA, OLYMPUS Inc. Japan) to achieve tight focusing (Fig. 3). The forward scattered light was collected with a second oil immersion objective (60x, PlanAapo N, 1.42 NA, OLYMPUS Inc. Japan) and focused onto a quadrant photodiode (QPD) (2901, Newport Co. USA), which was connected to a digital oscilloscope (Waverunner 64Xi, LeCroy USA) interfaced with a personal computer through a GPIB card (National Instruments, USA).

We suspended 1 µm diameter polystyrene microsphere (T8883, Life technology, USA) in phosphate buffer saline solution. The trapping event video was monitored with a CCD camera (350 K pixel, e-Marks Inc. USA). The 780 nm trapping laser power was measured with a power meter (FieldMate, Coherent USA) as well as a silicon amplified photodiode (PDA100A-EC, Thorlabs USA), while the 1560 nm heating laser power was measured with a calibrated biased InGaAs detector (DET10C/M, Thorlabs USA).

3 Results and Discussions

Due to the overtone and coupled vibrations of OH group, water shows significant absorption at 1560 nm and thus shows high thermal lens signal under the present experimental condition. We explore both cases of bulk as well as at nanoscale volumes.

3.1 Bulk Liquid Thermal Lens Studies

The steady state thermal lens signal at different Z positions along the Z-scan axis is measured. This Z-scan is important as it enables us to determine the focal point of the pump beam. The signal goes through a minimum, which indicates the focal point of the pump beam. For recording the time-resolved thermal lens evolution, the sample is kept at the 1560 nm focal point and the start and stop of time for the process is achieved with the help of a shutter as shown in our experimental setup (Fig. 1). The time-resolved thermal lens signal so recorded is shown in Fig. 4. In the specific case of water which has high heat conductivity and high specific heat, the heat dissipation process is very efficient, and most of the heat deposition studies can be modeled based on conduction model of heat dissipation [2]. The distinguishing feature from the higher absorbing sample of alcohol samples lies in any inflection point in the time-resolved TL data (Fig. 4).

Given this advantage of water as a model system for thermal relaxation through conduction only, we are able to use it effectively as the sample of choice for measuring local viscosity at nanoscale using an optical tweezer.

3.2 Viscosity Measurements from Optical Tweezers Setup

We have trapped 1 µm diameter polystyrene microsphere under femtosecond 780 nm laser with 7 mW average power. The trapping laser has nominal heating effect on the trapped bead because of very low absorption coefficient of water at the trapping wavelength (Fig. 2). Water has high absorption coefficient due to strong vibration combination band ($\nu_1 + \nu_3$) at 1560 nm [3], which is utilized to control the trapping volume temperature which is directly reflected on

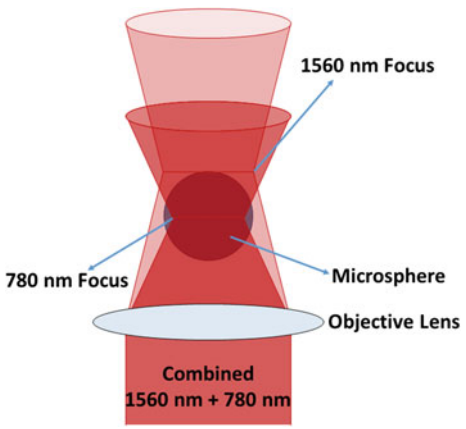

Fig. 3 Schematic of a dual beam femtosecond optical tweezers setup where 780 nm beam acts as tweezer for the microsphere in water while the 1560 nm beam acts as a heating source

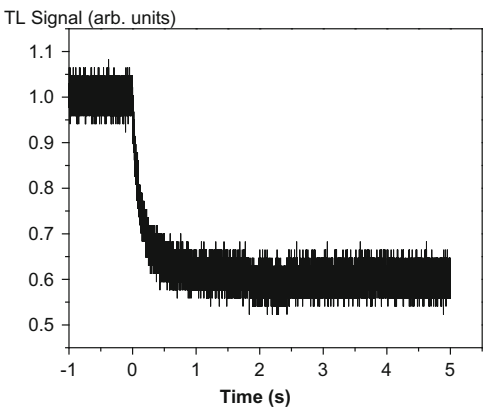

Fig. 4 Time resolved thermal lens (TL) signal at the focal point of the 1560 nm pump beam measured as a divergence in the 780 nm probe laser beam

trapped polystyrene microsphere. The low power illumination of femtosecond high repetition rate 1560 nm can change focal volume temperature as well as viscosity. Theoretical model [13] also supports our experimental data. Some slight deviation from theoretical model can be seen towards high temperatures as our model is only based upon conduction. The forward scattered data of 1 μm trapped bead was collected with QPD in 20 kHz sampling rate and all the data are analyzed with MATLAB program. The acquired data of channel X and Y is de-correlated by removing cross talk [14, 15] between them. The processed power spectrum density is fitted with the following Lorenzian function of frequency *f*:

$$P_x(f) = \frac{A}{\left(f_c^2 + f^2\right)} = \frac{D}{2\pi^2\left(f_c^2 + f^2\right)}, \tag{1}$$

where A is a fitting parameter in which diffusion coefficient (D) information is interposed. The cutoff frequency or corner frequency (f_c) is the 3 dB corner (a frequency for which the output signal is −3 dB of the maximum). Experimentally, this was achieved by measuring the power spectra of the trapped microsphere in comparison to the case when there was no particle present in the trap center (Fig. 5).

In order to correlate these experimental measurements to the effect of thermal perturbation as generated by the co-propagating heating laser at 1560 nm. We calculate spot sizes for the two color-focused beam generated by a single focusing objective lens that do not focus to a single point, using simple ray optics geometry (Fig. 3). We can use the geometric model [13] to calculate effective beam waist spot size of 1560 nm laser at focus as 1360 nm and that of 780 nm laser at focus as 680 nm. These effective beam radii can be used to calculate the pump laser (1560 nm) fluence at the 780 nm beam focus, where the polystyrene bead is trapped, with the help of the following equation:

$$F_0 = \frac{Pulse\ Energy}{\pi\left[\left\{\left(\frac{\sin 67^0}{\sin 23^0} \times 1.6\right) + 0.68\right\} \times 10^{-6}\right]^2} \tag{2}$$

The total fluence absorbed by water is $\mathcal{A}.\left(1-|r_f|^2\right).F_0,$, where F_0 is laser fluence before the sample chamber and r_f is the reflection coefficient that is calculated from the refractive index, n, using relation: $r_f = (n-1)/(n+1)$. $\mathcal{A}$ is the water absorbance in thin sample chamber. The viscosity change as a result of this heating can be calculated using the equation [16]

$$\eta(T) = 2.414 \times 10^{-5} \times 10^{\left(\frac{247.8}{T-140}\right)} \tag{3}$$

We find that the calculated viscosity decreases linearly with increase in power of 1560 nm laser due to the inverse relationship between them in a small interval change (Fig. 6). This linear scaling may be due to the change in trap stiffness or change of viscosity of the solvent, which is directly dependent on solvent temperature as a result of local heating due to non-radiative relaxation process. As our trapping power is fixed and probe power is very small, we can mainly concentrate on the viscosity change due to local heating.

The pump 1560 nm laser power is directly proportional to the focal point temperature. As calculated from our theoretical model [13], viscosity linearly decreases with temperature for small temperature intervals (Fig. 6). Under this condition, we calculate the viscosity at different powers relative to 0.89×10^{-3} Pa.s (corresponding to f_c = 131 Hz at 298 K) [17], which is the water viscosity at 298 K when

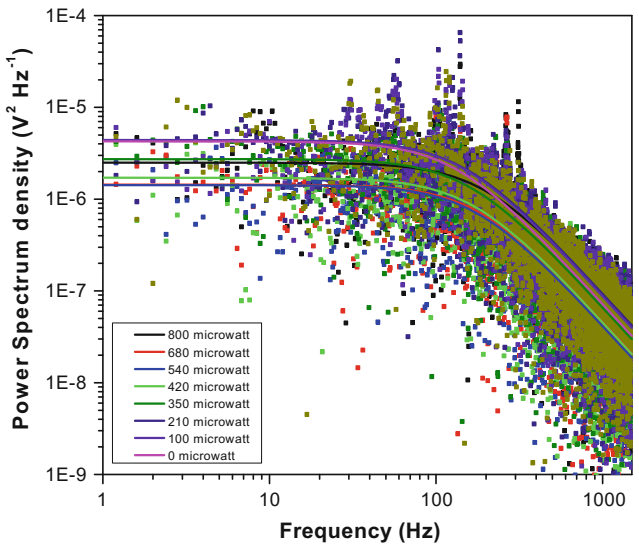

Fig. 5 Experimentally measured power spectrum (Scatter point) and respective fitted data (*Solid line*) with Lorenzian of 1 μm fluorophore coated polystyrene bead

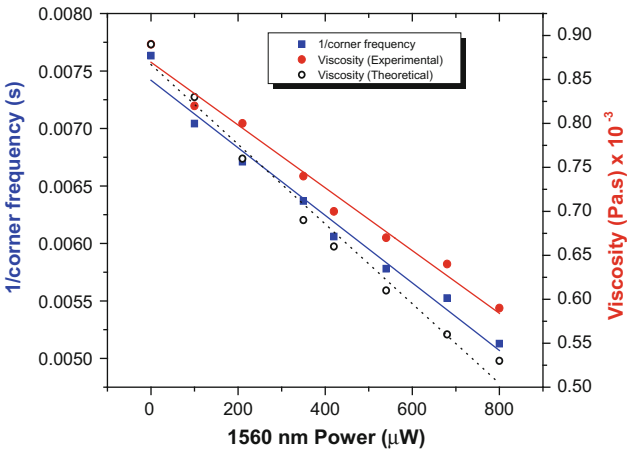

Fig. 6 Plot of Inverse corner frequency (*blue square*), as well as viscosity for experimental (*red circle*) and simulated case (*black circle*) and their respective linear fits; all plotted with respect to 1560 nm femtosecond laser power

1560 nm laser is absent. Within the range of our experimental conditions, we approximate that f_c . η as a constant [18, 19]. We find that the maximum viscosity decrease (Δη) is 0.30 × 10^{-3} Pa.s, which is observed at 800 μW power of 1560 nm. This observed value is within ∼5% error bar.

When we calculate trap stiffness ($\kappa = 2\pi\gamma f_c$), with viscous drag coefficient ($\gamma = 6\pi\eta r$) of polystyrene bead of radius r, we find that κ is almost a constant although the temperature is increasing. Our calculated trap stiffness from power spectrum κ_{ps} is 0.0068 ± 0.0001 pN/nm. As far as we know, this is the first report on resonantly excited optical trap by femtosecond Megahertz repetition rate pulses, which results in an accurate measure of viscosity at the trapping nano-focal volume.

4 Conclusions

Using a mode-mismatched pump-probe thermal lens approach to measure thermal Lens in water, we show that even for femtosecond laser pulses, water follows the conduction mode of heat transfer. We use the non-radiative relaxation of water with resonant excitation that sharply changes its temperature around the optical trap center. Femtosecond high repetition rate, 1560 nm, laser having high peak power and very low average power can be useful for altering temperature and viscosity for highly absorbing solvents, which relax through non-radiative relaxation. In the vicinity of trapped polystyrene bead, viscosity decreases linearly with increase of 1560 nm laser power, which we map with high sensitivity with a 780 nm trap acting as a nano-viscometer.

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