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# Anomalous effects of ultradilute impurities on heat diffusion in liquids



Deepak K.S. Ambast<sup>a</sup>, Richarj Mondal<sup>a</sup>, Palas Baran Pati<sup>b</sup>, Sanjio S. Zade<sup>b</sup>,  
Bhavtosh Bansal<sup>a</sup>, Bipul Pal<sup>a,\*</sup>

<sup>a</sup> Department of Physical Sciences, Indian Institute of Science Education & Research Kolkata, Mohanpur, Nadia 741252 West Bengal, India

<sup>b</sup> Department of Chemical Sciences, Indian Institute of Science Education & Research Kolkata, Mohanpur, Nadia 741252 West Bengal, India

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## ABSTRACT

We analyze the applicability of transient thermal lens (TL) z-scan technique as a sensitive tool to measure heat diffusivity of liquids. Suitable dyes at very low concentrations were added to the host liquid to enhance the TL effect through improved optical absorption. We investigate if these dye impurities, besides improving light absorption, have any effect on the thermal properties of the host liquid. We find that even a trace amount of impurity significantly alters the thermal properties of a solvent. Time-evolution of TL showed pronounced asymmetry about laser focus revealing anomalous behavior in thermal blooming of the laser beam. Heat transport was strongly dependent on the rise in sample temperature by light absorption. Important effects of nonlinear heat transport in time-resolved TL z-scan experiments were revealed.

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## 1. Introduction

Investigation of thermal properties of materials through accurate measurements of heat diffusivity, thermal conductivity, specific heat, etc. is essential [1] for the rapid growth of material research and for the search of novel materials with targeted applications. Among various calorimetric methods, photothermal techniques based on the thermal lensing effect (TLE) have become very popular [2]. The origin of the TLE lies with the radial refractive index gradient imparted in a material by a spatially varying temperature field induced by the heat deposition in the sample from a Gaussian laser beam [3–5]. Most common implementation of the TLE for photothermal calorimetry is through the measurement of transient change in the laser beam divergence (thermal blooming) resulting from the interaction with a material [3,6–11]. Closed-aperture time-resolved (TR) z-scan technique is well suited for this [12,13]. In this measurement, the sample is placed near the focus of a Gaussian laser beam and the transmitted light intensity is measured through a small aperture placed in the far field as a function of laser illumination time. The thermal lens developed in the sample changes the laser beam divergence which is mapped to a change in the transmittance depicting the build-up of the TLE in real time. From the time-constant and the magnitude of the transmittance change, heat diffusivity, thermal conductivity and specific heat of the sample can

be calculated [3,10,11]. Some of the advantages [14,6] of this technique are high sensitivity, very fast, non-contact optical measurement, small sample volume, suitable for liquids and gases, and very little perturbation to the sample. Techniques based on the TLE have been successfully applied for many sensitive measurements [15] including photothermal microscopy [16], photoinduced reaction kinetics [8], absolute luminescence quantum yields [7], ultralow values of single- and multi-photon absorption coefficients [4,6], flow velocity in liquids [17], and thermal coefficients, e.g., heat diffusivity, thermal conductivity etc. [10,11,14,18]

However, as this technique relies entirely on setting up a spatially varying temperature field in the sample, applying this becomes difficult for materials where the absorption of light and resultant rise in the sample temperature is negligible. In such cases, a small amount of a suitable dye may be added to the host material to improve light absorption to increase the temperature of the mixture [11,19]. It is expected that a very dilute concentration of dye will change the optical absorption of the mixture, but it will not affect the thermal properties of the host material [7,10]. However, it is rarely tested experimentally [20]. Interpretation of the z-scan experimental data has always been difficult and is heavily dependent on theoretical models [21]. Many simplifying assumptions made in these models [3,5] of TLE may not be fully satisfied in usual experiments.

In this paper we investigate the effects of very dilute impurities on heat transport in liquids. Applicability of TR-z-scan experiments in photothermal calorimetry is reevaluated. We show that only a trace amount (a few parts per million) of impurity can significantly alter the heat diffusivity of a liquid. We find that the

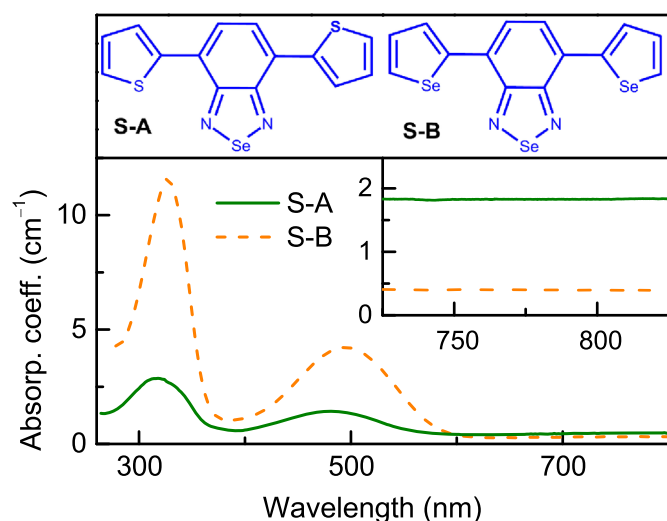
\* Corresponding author.

E-mail addresses: [dambast@iiserkol.ac.in](mailto:dambast@iiserkol.ac.in) (D.K.S. Ambast), [bhavtosh@iiserkol.ac.in](mailto:bhavtosh@iiserkol.ac.in) (B. Bansal), [bipul@iiserkol.ac.in](mailto:bipul@iiserkol.ac.in) (B. Pal).

experimental results strongly depend on the rise of the sample temperature due to laser absorption. Straightforward calculation of heat diffusivity from the thermal time-constant measured in TR-z-scan experiments can be misleading and should be cautiously interpreted.

## 2. Experimental

We probe heat diffusion in pure chloroform and chloroform with a trace amount ( $10^{-5}$  molar) of added impurity using TR thermal lens (TL) z-scan experiments. All our measurements are carried out at room temperature. Two organic dyes, thiophene and selenophene capped benzoselenadiazole, labeled respectively as S-A and S-B, were used as impurities. These two dyes have very similar molecular structures as shown in Fig. 1. Details of the synthesis of and the characterization measurements on S-A and S-B are available in Ref. [22]. The only difference between S-A and S-B is at the two end-rings, where S-A has thiophene and S-B has selenophene. This leads to slightly different donor–acceptor character of the two molecules. Selenium being more electronegative than sulfur, S-B has stronger donor–acceptor character compared to S-A. This is reflected in their linear absorption spectra presented in Fig. 1. The spectra were measured in the UV-visible range for  $10^{-5}$  molar dye solutions in chloroform using a standard absorption spectrometer. Absorption spectra for both S-A and S-B show two peaks, one around 300 nm related to the  $\pi$ -conjugation, and a second peak around 500 nm, related to the donor–acceptor nature. Slight redshift in the absorption spectrum of S-B compared to that of S-A observed here is due to its stronger donor–acceptor character. We have measured absorption spectra for solution of S-A and S-B in chloroform with varying concentration up to  $10^{-4}$  molar and no redshift in the absorption spectra was observed with increasing concentration. This confirms absence of any aggregation at  $10^{-5}$  molar concentration. The wavelength of 780 nm was chosen for our z-scan measurements to avoid strong resonant absorption of light by the dye molecules. Though we have relatively small absorption coefficient of  $\sim 1 \text{ cm}^{-1}$  for the  $10^{-5}$  molar dye solutions, compared to e.g., that of bulk GaAs of  $\sim 10^4 \text{ cm}^{-1}$  near 780 nm, a careful measurement using a precision spectrometer and high sensitive charge coupled device (CCD) detector shows [Fig. 1 (inset)] that S-A has somewhat larger absorption coefficient compared to that of S-B around 780 nm. This has important consequences on our experimental results.

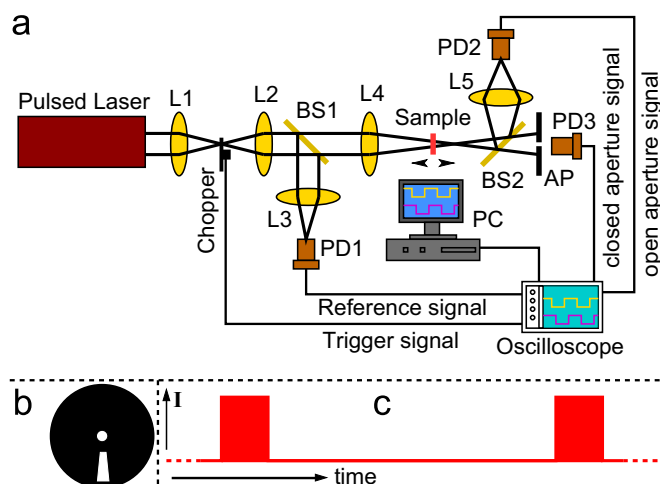


**Fig. 1.** Molecular structures and absorption spectra of the two dyes, S-A and S-B. Inset: Absorption spectra measured with a sensitive CCD spectrometer near 780 nm.

Compared to the dye solutions, chloroform has a significantly smaller absorption coefficient of  $\sim 0.002 \text{ cm}^{-1}$  near 780 nm [23].

A schematic diagram of our TR-z-scan setup is shown in Fig. 2(a). We use a mode-locked Ti:Sapphire laser operating at 80 MHz leading to a time spacing of  $\sim 12 \text{ ns}$  between successive laser pulses. This is much smaller than the thermal timescales (typically in the millisecond range). Laser pulse width is about 100 fs and its wavelength is tuned to 780 nm. The laser beam is modulated by a mechanical light chopper placed at the focus of an unity gain telescopic arrangement made by the lens pair L1 and L2. The especially designed light chopper [Fig. 2(b)] used here gives different ‘OFF’ and ‘ON’ time for laser light passing through it, leading to an asymmetric duty cycle ( $\sim 3\%$ ) ‘pulse’ train [Fig. 2(c)] for sample illumination. Chopper frequency is set to 15 Hz. This results to a sample illumination for about 1.5 ms in every 50 ms. Due to finite size of the laser beam at the chopper position, beam opening rise time on the sample is about  $20 \mu\text{s}$ . After the light chopper arrangement, a beam splitter BS1 splits the beam in two parts. One part of the beam is focused by a lens L3 on to a Si p-i-n fast-photodiode PD1 to record a reference signal. The response (rise and fall) time of the Si p-i-n fast-photodiodes is about 1 ns at the bias voltage of 10 V. The other part of the beam after BS1 is focused by a 10 cm focal length lens L4. The laser beam power is controlled by a neutral density filter. The sample taken in a quartz cuvette is moved along the laser beam (z-axis) across the focus (created by the lens L4) by using a motorized translation stage having  $1 \mu\text{m}$  resolution. Laser beam transmitted through the sample is again split in two parts by another beam splitter BS2. One part of it is focused by a lens L5 on to a second Si p-i-n fast-photodiode PD2 to detect the open-aperture z-scan signal. Other part of the transmitted beam is sent through an aperture AP of 1 mm diameter placed at a distance of  $\sim 1 \text{ m}$  from the laser focus (created by the lens L4) to ensure the far-field condition. A third Si p-i-n fast-photodiode PD3 placed behind AP detects the closed-aperture z-scan signal. Signals from PD1, PD2 and PD3 are recorded as time-traces in a 500 MHz digital oscilloscope. A trigger signal from the light chopper is fed to the oscilloscope to synchronize it to the sample illumination pattern [Fig. 2(c)] created by the chopper. Our setup is capable of measuring both closed- and open-aperture z-scan signals simultaneously in real time for different sample positions around the laser focus.

In the z-scan experiment, estimation of the beam waist  $r_0$  (beam radius at the focus) and the Rayleigh length  $z_0 = \pi r_0^2 / \lambda$  for the



**Fig. 2.** (a) Schematic of our TR-z-scan setup. L1, L2, L3, L4, L5 are lenses; PD1, PD2, PD3 are photodiodes; BS1, BS2 are beam splitters; AP is an aperture. (b) Front view of the light chopper. (c) Schematic of the laser illumination profile after the chopper. The solid shaded region consists of  $\sim 10^5$  laser pulses,  $\sim 100 \text{ fs}$  wide and  $\sim 12 \text{ ns}$  interpulse separation. In the timescale of our measurement this appears as continuous illumination.

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