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Anomalous effects of ultradilute impurities on heat diffusion in liquids



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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 timeconstant and the magnitude of the transmittance change, heat diffusivity, thermal conductivity and specific heat of the sample can

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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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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 singleand 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 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 dve 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 π -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 $\sim 10^4\,cm^{-1}$ 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 ~ 12 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 µs. 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 µm 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, ~ 100 fs wide and ~ 12 ns interpulse separation. In the timescale of our measurement this appears as continuous illumination.

wavelength λ is essential. For this we measure the beam size at a few points along the beam axis (z-direction) near the focus by the conventional knife-edge method [24]. The laser power (P_T) transmitted over a knife-edge was measured for different positions of the knife-edge as it was moved across the beam (say in x-direction) for a given z-position near focus [Fig. 3(a)]. The zero of the *x*-axis is arbitrarily set to a point outside the beam. Numerically calculated derivative of P_T with respect to x is plotted in Fig. 3(b). It is fitted well with a Gaussian: $G(x) = G_0 \exp[-2(x-x_c)^2/r^2]$. This gives an estimation of the beam radius *r* [defined as the $1/e^2$ point of G(x)] at that particular z-position. Further, we obtain the same beam radius at the same z-position when measured in the orthogonal direction (along y-axis). This shows that we have a nice Gaussian beam (TEM₀₀). Beam radius r measured in this way at a few z-positions near focus is plotted in Fig. 3(c). We have taken beam propagation direction along positive z-axis. Thus, the positions before focus correspond to negative z and positions beyond focus correspond to positive z. The zero of the z-axis is initially set to an approximately determined focus of the laser beam. The data in Fig. 3(c) clearly show that the laser spot size increases symmetrically on either side of the focus (z=0). We fit the beam radius data along z-axis by $r(z) = r_0 \sqrt{1 + [(z - \delta)/z_0]^2}$ where r_0 is the beam waist, δ is the correction to the approximately estimated focal position, and z_0 is the Rayleigh length. Best fit to the data yields $r_0 = 30 \ \mu m$, $\delta = 2 \ mm$, and $z_0 = 3.6$ mm. For $\lambda = 780$ nm used in our experiment, estimated values of r_0 and z_0 are consistent with each other. Hereafter we shall denote the sample position by $\zeta = z/z_0$.

3. Results and discussion

In transient TL measurements the time-trace of transmitted intensity is usually recorded for the sample positions $\zeta \sim \pm 1$, where the TLE is expected to be maximum. We present in Fig. 4(a) the time-evolution of transmitted intensity for pure chloroform and for 10^{-5} molar solutions of S-A and S-B in chloroform for $\zeta = 1$. The



Fig. 3. (a) Laser power (P_T) transmitted over a knife-edge at z = -5 mm for different *x*-positions of the knife-edge as it was moved across the beam. (b) Numerically calculated derivative of P_T with respect to *x* along with a Gaussian fit to estimate the beam radius *r*. (c) *z*-dependence of beam radius near focus. Solid line is a fit by $r(z) = r(0)\sqrt{1 + [(z - \delta)/z_0]^2}$ with $r_0 = 30 \,\mu\text{m}$, $\delta = 2 \,\text{mm}$, and $z_0 = 3.6 \,\text{mm}$.

data are normalized to unity at t=0 when the laser illumination starts. All the data presented in this paper are recorded at the average laser power P=200 mW. For chloroform, transmittance remains independent of the duration of laser illumination, indicating negligible TLE. This is attributed to the negligibly small absorption coefficient of chloroform near 780 nm [23]. However, addition of very little amount of dye impurity, S-A or S-B, improves light absorption by the solution resulting in sample heating and measurable TLE as seen from the time-evolution of the transmittance for S-A and S-B. Decrease in transmittance with time for postfocal position $\zeta = 1$ indicates divergence of the laser beam caused by the sample i.e., negative lensing effect (temperature coefficient of refractive index. dn/dT < 0 is observed. If the addition of dve impurity had only affected the optical absorption and had not modified the thermal property of the mixture, then identical timeevolution of transmittance should have been observed for both S-A and S-B and the heat diffusivity extracted from the measured timeconstant should have been assigned to that of the chloroform. But a clear difference in time-constants of build-up of the lensing effect between S-A and S-B is seen in our data in Fig. 4(a). This shows that addition of even very dilute impurities not only affects the optical absorption but also significantly alters the thermal properties of the solvent.

Unlike most of the studies of the TLE available in the literature where the TL transients are recorded only at one sample position, we went ahead to measure TL transients at several sample positions on both sides of the focus. Fig. 4(b) shows data from such measurements for S-A as an example for a few sample positions, $\zeta = \pm 1$ and ± 3 , symmetrically chosen around the focus. Data are also shown at $\zeta = -8$, far away from the focus where the laser intensity is not concentrated and the lensing effect is not pronounced. As a result, almost no variation in transmittance with time is seen there. However, for positions near the focus where the laser intensity becomes very high, we observe a considerable variation in transmittance over a millisecond time-scale due to TLE. This is consistent with the expectation that for dn/dT < 0, transmittance should increase [decrease] with time for prefocal ($\zeta < 0$) [postfocal ($\zeta > 0$)] positions. Similar data (not



Fig. 4. (a) Time-evolution of normalized transmittance, $I_{\rm T}(t)/I_{\rm T}(0)$ at $\zeta = 1$ is compared for pure chloroform and 10^{-5} molar solutions of S-A and S-B in chloroform. (b) Time-trace of normalized transmittance for S-A at a few sample positions, $\zeta = \pm 1, \pm 3$, and -8.

shown) were obtained for S-B. Data for chloroform show no lensing effect and remain independent of time and position. Two main observations from Fig. 4(b) are: (i) a pronounced asymmetry in the time-evolution at positions symmetrically situated at two sides of the focus and (ii) different time-constants at different positions. The reason behind this asymmetry in data about focus is not clear at the moment. Asymmetry in the beam size on two sides of the focus is ruled from the data in Fig. 3(c). Different timeconstants at different sample position do not allow a straightforward calculation of heat diffusivity of a sample from transient TL measurements. We have checked that the time-constants do not scale with the increasing beam size away from the laser focus.

We construct a three-dimensional plot [Fig. 5] of normalized transmittance, $T_N(\zeta, t) = I_T(\zeta, t)/I_T(10, t)$ for S-B using the time-traces of transmittance at different sample positions. It gives a complete picture of the spatial and temporal evolution of the lensing effect. Peak-to-valley nature of the z-scan curves is evident even at early times, but it becomes more prominent, i.e., difference in transmittance between peak and valley (ΔT_{P-V}) increases with increasing time. It approaches to a steady-state value over a millisecond timescale. Qualitatively similar behavior was observed for S-A, though the time-evolution was faster and the steady-state value of ΔT_{P-V} was more for S-A.

For further quantitative analysis, we take slices of the data from the three-dimensional graphs at fixed times for S-A and S-B and plot it in Fig. 6. Typical z-scan curves with prefocal peak and postfocal valley is seen to evolve with time (ΔT_{P-V} increases with time). Amplitude of lensing effect (given by ΔT_{P-V}) is more for S-A. Steady-state z-scan data (under continuous illumination) for an empty cuvette and for pure chloroform [Fig. 6(a)-inset] show no measurable lensing effect. We use a model of TLE under parabolic approximation [5] for analyzing the experimental data. The model considers that the focused laser beam heats up the sample locally through light absorption. The diffusion of heat is assumed to take place only in the radial direction. Axial flow of heat as well as heat transfer by convection is neglected. According to this model, the normalized transmittance $T_N(\zeta, t)$ as a function of the sample position (ζ) and laser irradiation time (t) is given by

$$T_N(\zeta, t) = \left[1 + \frac{2\zeta}{1 + \zeta^2} |\theta(t)| + \frac{1}{1 + \zeta^2} \theta^2(t)\right]^{-1}$$
(1)

where the time-dependent phase-shift $\theta(t)$ is given by

$$\theta(t) = \frac{\theta_0}{1 + t_c/2t}.$$
(2)

The diffusion time-constant t_c and the on-axis phase-shift θ_0 (phase difference between the center and the edge of the beam) are related to various thermal parameters of the material as $t_c = r_0^2/4D$ and $|\theta_0| = (\alpha_0 LP/\kappa\lambda)(dn/dT)$, where $r_0 =$ beam waist, $D = \kappa/\rho C_p$ is the thermal diffusivity, $\kappa =$ thermal conductivity, $\rho =$ density, $C_p =$ specific heat at constant pressure, $\alpha_0 =$ linear absorption coefficient, L = sample thickness, P = incident laser power, and dn/dT = temperature coefficient of refractive index. Estimation of t_c and θ_0 through fitting of the TR-z-scan data can be used to evaluate various thermal constants of the sample.

The position dependence of the normalized transmittance at a few selected times is fitted with Eq. (1) (solid lines) in Fig. 6. At a given time, $\theta(t)$ is treated as a fit parameter. The fits are reasonably good but deviations are seen around the valley at positive ζ , particularly at longer times when phase-shift is large. Phase-shift $\theta(t)$ obtained from such fits is plotted in the inset of Fig. 6(b) for S-A and S-B. It increases with time to approach a steady-state value over a millisecond timescale. The $\theta(t)$ data are very well-fitted with Eq. (2) to yield t_c = 1.2 and 2.4 ms, respectively, for S-A and S-B. Using these values of t_c along with r_0 = 30 µm, we estimate thermal



Fig. 5. Three-dimensional plot of normalized transmittance $T_N(\zeta, t)$ for S-B.



Fig. 6. Steady-state z-scan data for an empty cuvette and for pure chloroform in the inset of (a) show no lensing effect. Example of normalized z-scan curves for S-A (a) and S-B (b) at different illumination times. The data are fitted (solid lines) with a model of TLE [Eq. (1)] to obtain the time-dependent phase-shift $\theta(t)$. Time-evolution of $\theta(t)$ fitted with Eq. (2) in the inset of (b) gives t_c =1.2 and 2.4 ms, respectively, for S-A and S-B.

diffusivity $D = 1.85 \times 10^{-7}$ and 0.93×10^{-7} m² s⁻¹, respectively, for S-A and S-B. We may compare these values of *D* with that of chloroform reported in the literature [25] as 0.8×10^{-7} m² s⁻¹. We have used very dilute solutions (10^{-5} M) of S-A and S-B. Estimated values of *D* in this case were expected to reflect that of the solvent chloroform. Difference in estimated values of *D* for S-A and S-B, from that of chloroform may be attributed to their different absorption coefficients near 780 nm [Fig. 1 (inset)] and it is clearly a nonlinear heat transport effect. Peak temperature of the solution for S-A is expected to be higher than that for S-B, because S-A has higher absorption coefficient than S-B near 780 nm [26]. Thermal diffusivity may depend on temperature [11,18] and also the effect of convection (which is neglected in the model) may be different for different temperatures. In fact, we observed in Figs. 4(a) and 6(b)- inset that the thermal equilibration time-constant for S-A is significantly smaller than that of S-B. This suggests that other heat transport mechanisms such as convection may be effective for S-A. Our data show that addition of different dyes can differently modify the thermal properties of the solvent [20].

4. Summary and conclusion

We investigated the effects of very dilute impurities on heat transport in liquids in time-resolved (TR) z-scan experiments. Pure chloroform did not show any thermal lens (TL) effect. But addition of a very little amount of dye impurity in it showed pronounced lensing effect. This is attributed to the significantly higher optical absorption of the dyes compared to that of chloroform at the measurement wavelength of 780 nm. Contrary to the expectation, dye impurities not only affect the optical properties of the solution, but also significantly alter the thermal properties of the solvent. Solutions of two dyes used here showed significantly different time-evolution of the TL. For a given solution, different time-evolution of TL is observed for different sample positions. A pronounced asymmetry is present in time-evolution of TL between sample positions symmetric about the focus. Though the thermal properties of very dilute solutions are expected to be governed by the solvent only, we measure quite different thermal diffusivity for two dye solutions and the measured values are also different from that of chloroform reported in the literature. This anomaly in heat diffusion is attributed to an order of magnitude different absorption coefficient for the two dyes near 780 nm, leading to different peak temperatures of the two solutions. Apart from non-negligible effects of convective heat transport at high temperatures, heat diffusivity may itself be temperature-dependent, leading to the observed anomalous behavior. Our results clearly demonstrate the important effects of nonlinear heat transport in TR-TL z-scan experiments.

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Appendix A. Saturable absorption

Active participation of the dye molecules in optical absorption is also evident from our open-aperture (OA) z-scan measurements which probe the nonlinear absorption processes [27,28]. Negligible effect of thermal lensing on nonlinear absorption is observed from the time-independence of the OA transmittance in Fig. A1(a) for both S-A and S-B. Magnitude of OA transmittance at long times $(\sim 1.5 \text{ ms})$ is plotted in Fig. A1(b) for S-A and S-B. The data are normalized to unity at $\zeta = 10$. A symmetric peak observed at the focus ($\zeta = 0$) for S-A signifies saturable absorption. This is fitted very well with a model [27,28] of saturable absorption to yield a saturation intensity of 1.95×10^{12} W/cm², smaller than the intensity of 5.8×10^{12} W/cm² used in our measurements. Data for S-B show no nonlinear absorption. Observation of saturable absorption in S-A and not in S-B independently supports our earlier observation that S-A has stronger linear absorption than S-B near the measurement wavelength of 780 nm. Being very dilute solutions, there are only limited number of absorbing molecules which gets saturated at the measurement intensity for S-A because it has a larger linear absorption [29].



Fig. A1. Open-aperture z-scan transmittan3ce normalized to unity at $\zeta = 10$ for S-A and S-B; (a) Time-evolution at $\zeta = 1$ and (b) position dependence at t = 1.5 ms. A peak in the data for S-A in (b) fits (solid line) well with a model of saturable absorption.

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relaxation and more heat generation. Fluorescence quantum yield measurement was carried out for S-A and S-B for excitation at the respective low energy absorption peaks (around 500 nm) using quinine sulfate as a standard [22]. These results may not be directly applicable for excitation at 780 nm as the radiative and nonradiative relaxation processes depend on excitation energy. However, if we extrapolate the fluorescence quantum yield data measured at about 500 nm excitation to 780 nm, and normalize it with respect to the respective absorption coefficients (at 780 nm), we get values of 0.3 and 1, respectively, for S-A and S-B. This supports our assumption that the heat generated in the solution of S-A is more than that in S-B.

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