

Thermal diffusivity measurements in organic liquids using transient thermal lens calorimetry

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Abstract. Thermal diffusivity measurements are carried out in certain organic liquids using the pulsed dual beam thermal lens technique. The 532 nm pulses from a frequency doubled Q-switched Nd:YAG laser are used as the heating source and an intensity stabilized He-Ne laser serves as the probe beam. Experimental determination of the characteristic time constant of the transient thermal lens signal is verified theoretically. Measured thermal diffusivity values are in excellent agreement with literature values. © 1998 Society of Photo-Optical Instrumentation Engineers. [S0091-3286(98)00510-8]

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1 Introduction

Recently, there has been renewed interest in the development of new methods of determining the thermal properties of materials in different forms. This is largely a result of the availability of novel experimental techniques in the context of the rapid advances in materials technology and the many new applications of materials under very severe environmental conditions. Thermal diffusivity of a material is a very important parameter and it is closely related to thermal conductivity, specific heat and thermal expansion. An extensive review of thermal diffusivity of materials had been presented by Touloukian¹ and a number of methods for determining the diffusivity are discussed. There are a number of presently existing steady-state and non-steady-state methods of measuring thermal parameters.¹⁻⁸ There is, however, some dissatisfaction with the length of the time required to make reliable measurements, and in some cases, with respect to the large sample sizes required by these techniques to impose intolerable limitations.

Methods based on photothermal effects are eminently suited for the effective measurement of thermal properties of materials.⁷⁻¹⁰ Photothermal effects are generated by deposition of heat in a sample due to nonradiative deexcitation following absorption of radiation.^{11,12} Laser based photothermal methods such as the photoacoustic effect^{7,8} for the determination of thermal diffusivity of materials have become very popular due to the many advantages offered by such techniques.

Among the various photothermal spectroscopic methods based on the thermal relaxation of excited species, thermal lens spectroscopy has appeared to be very powerful.^{13,14} The thermal lens (TL) technique was successfully used for the absorption spectroscopy of liquids and in particular for studying weak electronic transitions.^{14,15} The applications of the TL technique include calorimetric trace analysis,¹⁴ multiphoton absorption studies^{15,16} and investigation of the photochemical rate and absolute quantum yield.¹¹

The TL method can be successfully employed for the determination of thermal diffusivity, especially in the liquid

phase. With a pulsed laser as the excitation source we get a transient TL, and by monitoring this transient TL, the thermal diffusivity can be determined. The work of Gordon et al.¹⁷ on the thermo-optical effect in a liquid provides a basis for linking the rate of dissipation of the TL to a quantitative measure of thermal diffusivity. Using a single-beam TL technique, Calmettes and Laj¹⁸ measured thermal diffusivity values for certain liquids and solid polymethacrylate. In this paper, we show that a dual beam TL technique can be effectively utilized for the determination of thermal diffusivity of certain organic liquids.

2 Experimental Setup

The schematic diagram of the experimental setup is shown in Figure 1. The 532 nm radiation from a frequency doubled Q-switched Nd:YAG laser (9 ns, maximum energy 110 mJ) was used as the pump beam. An intensity stabilized He-Ne laser was used as the probe beam. The pump and probe beams are combined by using a dichroic mirror and are made collinear by carefully adjusting the optical components in the x, y, and z planes. The collinearity of the experimental setup was verified using the z-scan technique. The sample was taken in a 0.5 cm quartz cuvette. The pump beam was focused into the quartz cuvette containing the sample by a convex lens with a focal length of 20 cm. The TL effect was detected by monitoring the intensity fluctuations in the beam center of the probe He-Ne laser. The position of the cuvette was adjusted to achieve the maximum value for the TL signal. The TL signal was detected by sampling the intensity of the center portion of the probe beam through a small aperture. In this work, the intensity of the central portion of the transmitted probe beam was detected by using an optical fiber. The optical fiber also serves as the limiting aperture. The output of the optical fiber was detected by a PMT that was coupled to a McPerson monochromator, which further filtered out the scattered light from the excitation beam. The time depen-

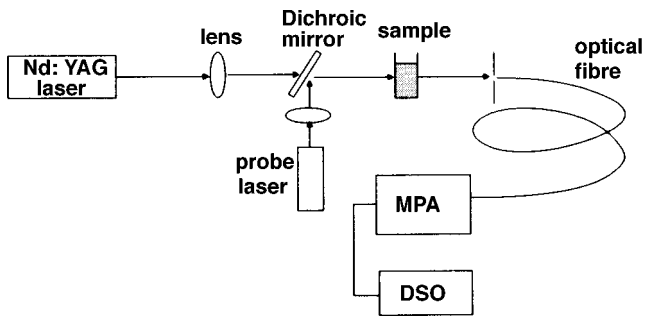


Fig. 1 Pulsed TL setup used in this experiment: MPA, monochromator, to photomultiplier tube (PMT) assembly; DSO, digital storage oscilloscope.

dent TL signal was processed with a digital storage oscilloscope. All the measurements were made at a room temperature of 22°C.

3 Results

In the case of pulsed laser excitation, the pulse width of the heating laser is very small (~ 9 ns) and the rate of the radiationless transition is very fast in comparison with the decay rate of the TL effect. The signal strength reaches the maximum value almost instantly and it decays with a characteristic time constant. A typical transient TL signal is given in Figure 2. The pulsed TL system has distinct advantages with respect to large enhancement factor and its background subtraction capability. Quantitative analysis of this transient phenomenon is given by Twarowski and Klinger¹⁹ along with experimental verifications.

The focal length of the induced TL by pulsed laser irradiation is given by¹⁶

$$\frac{1}{f} = \frac{1}{f_0} \left(1 + \frac{2nt}{t_c} \right)^{-2} \quad (1)$$

Here

$$\frac{1}{f_0} = \frac{4lDN\sigma h\nu Hn^2}{kJ\omega^{2n+2}} \frac{d\eta}{dT} \left(\frac{2}{\pi} \right)^n, \quad (2)$$

where $D = (k/\rho c)$ and $H = \int_0^t P(t)dt$, l is the thickness of the TL, N is the number of molecules per cubic centimeter, D is the thermal diffusivity, k is the thermal conductivity, ρ is the density, c is the specific heat, η is the refractive index of the medium, ν is the frequency of the pump beam, $P(t)$ is the pulsed laser power as a function of time, ω is the beam radius, J is Joule's constant, σ is the cross section for n photon absorption, and n is the number of photons absorbed. Since the temperature coefficient of the refractive index is negative for most liquids, Eqs. (1) and (2) predict that the TL will be divergent.

If another laser is used to monitor this TL, then intensity at the beam center of the probe beam can be expressed by

$$S = \frac{I_t - I_\infty}{I_t} = S_{t=0} \frac{1}{[1 + 2n(t/t_c)]^2}, \quad (3)$$

where

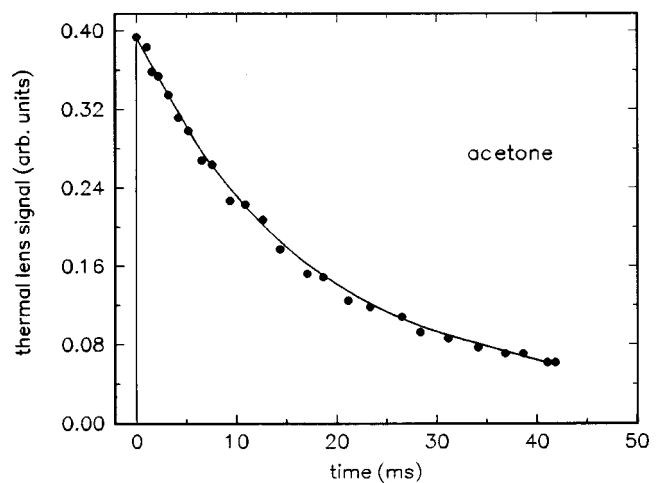
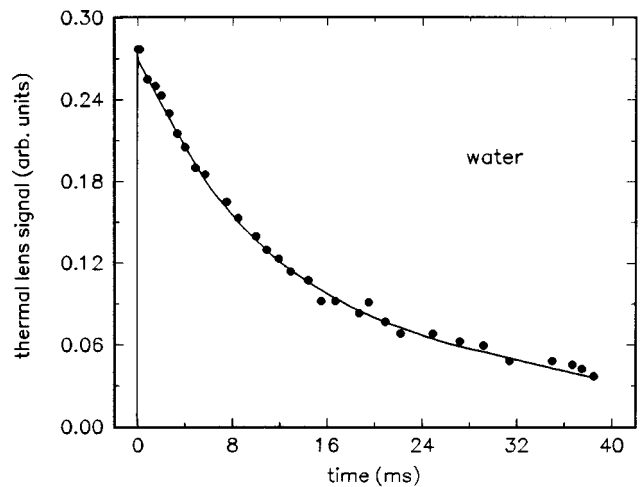


Fig. 2 Transient decay curve measured by the pulsed TL technique. The points in the figures represent the experimental data. The solid curves represent the theoretical fit obtained using Eq. (3). The theoretical fits were made with measured values of t_c obtained from Figure 3 ($t_c^{\text{acetone}} = 60$ ms and $t_c^{\text{water}} = 45$ ms).

$$S_{(t=0)} = \frac{I_\infty - I_0}{I_0} \quad (4)$$

where I_∞ , I_0 , and I_t are the steady-state TL signal, the signal at time $t=0$, and the signal at time t , respectively.

Equation (3) leads us to the prediction that a plot of $S^{-1/2}$ will be a linear function of time. Verification of this prediction is shown in Figure 3. From the slope and intercept, the value of n/t_c can be determined. One can determine the value of n from measurements of the dependence of TL signal on laser energy E of the pump laser pulse, using the relationship¹⁹

$$\frac{I_t - I_{t=\infty}}{I_t} \propto E^n. \quad (5)$$

The variation of TL signal with laser power for all the liquids studied showed a linear dependence, suggesting one photon absorption ($n=1$). From these measurements, we calculated the values of characteristic time constant corresponding to each organic liquids. We have verified mea-

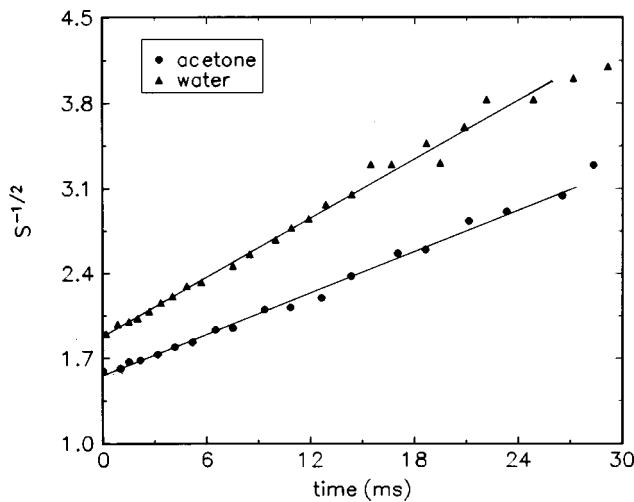


Fig. 3 Typical linear plots of experimental data obtained using Eq. (3). From the slope and intercept of these plots value of t_c is evaluated.

sured t_c with theoretical fit using Eq. (3). The smooth curve in the Figure 2 gives such a theoretical fit obtained from Eq. (3), assuming t_c , which was obtained from the slope and intercept of the linear plot (Figure 3). The agreement between the theoretical and experimental data is good.

The characteristic time constant t_c is related to the thermal diffusivity and beam radius (ω) through the relation

$$t_c = \frac{\omega^2}{4D}. \quad (6)$$

To eliminate the uncertainty in the determination of beam radius, a reference sample with known thermal diffusivity is used to determine the thermal diffusivity of the unknown sample. In our case, water was used as the reference sample. Thus,

$$D = D_{\text{water}} \frac{t_c^{\text{water}}}{t_c}. \quad (7)$$

The time dependence of the lensing phenomenon gives a detailed account of the thermal history of the sample medium. Clearly the magnitude of the TL effect depends on the competition between the rate of creation of the lens and the rate of decay of the lens, and these are related to the thermal diffusivity of the medium.

To demonstrate the applicability of the method, we measured the thermal diffusivity of several transparent liquid samples. Using the presented setup, the thermal diffusivities of different organic samples were determined with water as the reference. Trace amounts of the dye rhodamine 6G were added to increase the absorption of the pulsed laser beam, thereby increasing the TL signal intensity. This level of impurity does not affect the solvent thermal conductivity since adding trace amounts of dye affect only the optical properties and not the thermal properties of the solvent.²⁰

The results also show that water reaches thermal equilibrium faster than all other liquids studied in this work

Table 1 Thermal diffusivity values for different organic liquids studied using dual beam TL lens calorimetry. Reported literature values are also given.

Sample	Value of D Obtained using TL method	Literature value ^{21,22}
Acetone	$1.07 \pm 0.01 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$	$1.07 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
Toluene	$1.09 \pm 0.01 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$	$1.04 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
Methanol	$1.07 \pm 0.01 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$	$1.08 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
Benzene	$9.95 \pm 0.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	$1.01 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
Glycerol	$9.98 \pm 0.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	$1.00 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
Ethanol	$9.47 \pm 0.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	$9.33 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$
Ethylene glycol	$9.66 \pm 0.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	$9.71 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$

(Figure 3). Hence the thermal diffusivity of water ($1.43 \times 10^{-3} \text{ cm}^2/\text{s}$) should be higher than that of the other liquids. In Table 1, we summarize the results for the thermal diffusivities for various samples. Thermal diffusivity values obtained using the presented experimental setup are in excellent agreement with reported literature values^{21,22} of the same for these organic liquids.

4 Conclusion

In this paper, the usefulness of the TL technique for obtaining the thermal diffusivity of transparent liquid samples has been demonstrated. The thermal blooming technique offers a novel means of measuring thermal diffusivity. The method is simple and accurate. The obvious advantage of this method is that only small sample volumes are required to make such measurements. Also only a very short time is required for the measurements and accurate results can be obtained with TL method.

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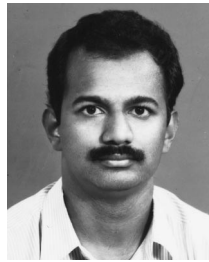
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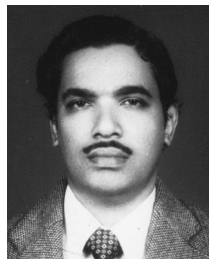
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