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Absorption coefficient of nearly transparent liquids measured using thermal lens spectrometry

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We use an optimized pump-probe mode-mismatched thermal lens scheme to determine the optical absorption coefficient and thermal diffusivity of ethanol, benzene, acetone, methanol, toluene and chloroform. In this scheme the excitation beam is focused in the presence of a collimated probe beam. The agreement between experimentally obtained results and values reported in the literature is good.

Key words: *thermal lens, absorption coefficient, transparent liquids, thermal diffusivity*

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1. Introduction

Optical absorption in bulk materials is usually determined by measuring the beam transmission using a commercial spectrophotometer [1] with low precision and a calorimetric method [2] with higher precision. For measuring low absorption coefficients multi-pass cells [3] and cavity integration methods [4] have been also developed. The sensitivity of these methods is of the order of $10^{-3} - 10^{-4}$ cm^{-1}. An alternative technique for measuring low absorption values is the thermal lens (TL) method. TL spectrometry is a photo-thermal technique which has been widely used for the determination of absorption of different materials with high sensitivity and versatility [5–10]. Since its discovery in 1964 the method has been used for the intracavity measurements of absorption of nearly transparent materials [5,6]. When a beam of light with a Gaussian intensity profile propagates in an absorbing medium, the heat generated, as a consequence of optical absorption, causes the sample temperature to rise. Because the refraction index depends on the temperature, a spatial distribution of the refraction index of similar extension is generated in the absorbing medium (TL stationary generation). The thermal diffusion expands this lens over a volume much larger than the volume defined by the pump beam within the sample. The TL induces phase shifts in the beam wave-fronts of the probe beam. In this two-beam experiment, the TL signal is usually defined as the relative probe transmission change through a small aperture located at the far field and on the optical beam axis.

Marcano et al. have developed a simple calibrated TL method for measuring low absorption values based on a pump-probe scheme with a collimated probe beam and a focused pump beam [7–9]. The method not only optimizes the TL response but also allows a simple calibration and simple data interpretation. In this work we use this method for obtaining the values of the absorption coefficient and the thermal diffusivities of a series of nearly transparent organic solvents. Our results are in good agreement with previously reported values.

2. Theoretical considerations

We consider that the pump beam and the probe beam are Gaussians with Rayleigh parameters z_e and z_p, waist positions a_e and a_p and wavelength λ_e and λ_p for the pump and probe beam respectively. The method supposes that the pump beam is focused and the probe beam is collimated giving a beam spot constant and more than two orders of magnitude larger that the pump beam spot. Due to the presence of the TL generated by the pump beam the spatial distribution of the probe beam changes. The signal can be recorded by measuring the transmission of the probe light power passing through a small aperture located at the far field. In this regard the signal is defined as

$$S(z,t) = \frac{[T(z,t) - T_0]}{T_0}\,, \tag{2.1}$$

where T_0 is the probe light transmittance through the aperture after passing the sample cell with no pump beam present and $T(z,t)$ is the probe beam transmittance in the presence of the pump beam, z is the position of the sample cell and t is the time. When scanning the sample around the excitation beam focal point, a single peak (Z-scan) is obtained if $z_p \gg z_e$. In the stationary situation ($t \to \infty$) we obtain a simple equation for determination of the TL phase amplitude Φ_0 [9]

$$S_{\max} = \pi\Phi_0/2, \tag{2.2}$$

$$\Phi_0 = \frac{\alpha\; l\; P_0(\mathrm{d}n/\mathrm{d}T)}{\kappa\lambda_p}\,, \tag{2.3}$$

where $S_{\max}$ is the maximal value of the TL signal which is obtained for position $z = 0$, (excitation beam waist position), P_0 is the impinging pump light power, α is the absorption coefficient, $\mathrm{d}n/\mathrm{d}T$ is the thermal gradient of the refraction coefficient,κ is the thermal conductivity and l is the sample length.

The described equation (2.2) provides a simple relation between the maximum value of the signal and TL phase amplitude, which value is used for absorption determination if the rest of the photo-thermal parameters are known.

Shen et al. have pointed out that it takes longer time to carry out steady-state measurements when the mode mismatched between pump and probe beams is bigger [11]. We report a similar effect for the proposed configuration with collimated probe beam and focused excitation beam [9]. From the practical point of view this time is of the order of several seconds (7 to 10). This time-span can be easily achieved in a real experimental situation using appropriate mechanical shutter.

The thermal diffusivity is $D = \kappa/\rho C_\nu$, where ρ is the sample density and C_ν is its heat capacity. The thermal diffusivity can be determined by fitting the time dependence of the TL signal using the theoretical model previously described in [7,8].

3. Experimental method

The experimental set-up is similar to the ones described previously [7–9]. The excitation beam is generated by a 500-mW CW green diode pumped Nd–YAG laser ($\lambda_e = 533$ nm, Intelite Inc.)). The probe light is coming from a 4-mW CW He-Ne laser (632 nm, PMS Electrooptics). The resulting probe power at the sample position is 0.5 mW. This light passes through 1-cm and 30-cm focal length lenses resulting in a near collimated probe beam of 6-millimeter diameter. The excitation beam is directed collinearly with the probe using a dichroic beam splitter. This light is focused onto the sample (1-cm path-length) using a converging lens with 40-cm focal length. Behind the sample the excitation beam is canceled by using interference filters and a dichroic mirror. The probe beam is directed toward a 100-microns aperture and a diode detector (Melles Griot) located at a distance of 80 cm measured from the position of the excitation beam waist. The signal from the detector is then pre-amplified using a current amplifier (SR570 Stanford Research Systems) and then directed toward a digital oscilloscope (TDS3052 Tektronix) for recording.

To determine the absolute value of the TL signal the use of a shutter (Sh) is required. The shutter (846 Newport Corporation) is put on for a period of 10 seconds, after which the signal reaches a maximum. Then, it is turned off for another ten seconds for allowing the system to relax. The cycle is repeated 30 times and the averages are computed. The time evolution of the signal is used to determine the sample thermal diffusivity. Using this method we determine the absolute value of the TL signal according to the definition given by equation (2.1). We use different samples such as: ethanol, benzene, acetone, methanol, toluene, and chloroform. The liquids are contained in a quartz cell of 1-cm path-length.

4. Results and discussion

In figure 1a we show the TL signal for ethanol as a function of time as measured for an excitation power of 46 mW. Superimposed we show the theoretical fitting estimated using the model described

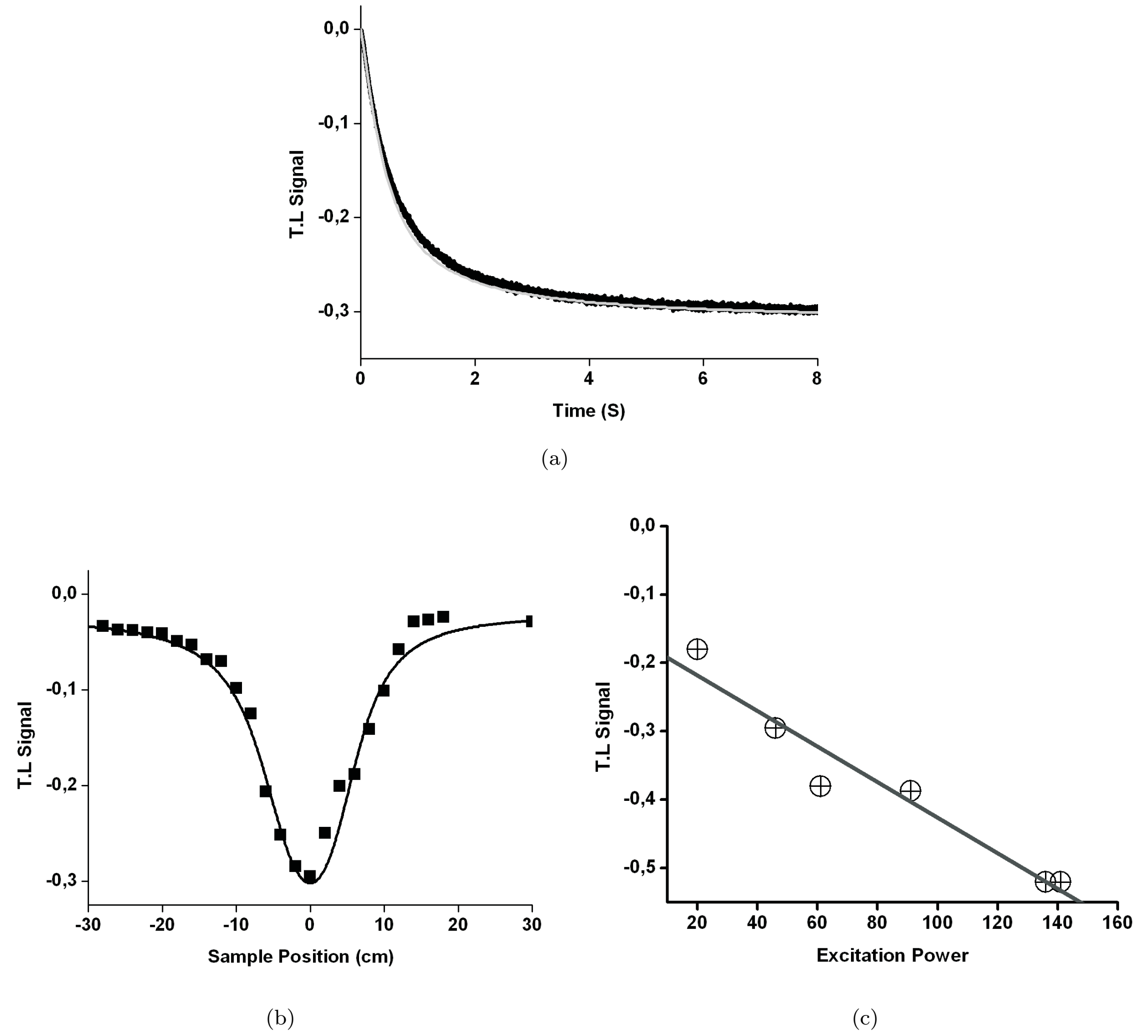

Figure 1. (a) Experimental TL signal for ethanol calculated using equation (2.1) ($z = 0$); (b) Z-scan curve for ethanol; (c) Excitation power(mW) versus maximum of TL signal.

in [7], a diffusivity coefficient of 0.89×10^{-3} cm^2/s and a phase amplitude value $\Phi_0 = -0.20$. The rest of the parameters for this fitting are λ_e=533 nm, λ_p=632 nm, z_p = 10000 cm, z_e = 0.25 cm,

$z = 0$, $L = 80$ cm, $a_e = 0$, $a_p = 0$, and $t = 10$ s. The value of the thermal diffusivity of ethanol agrees well with previous reports [10].

We also perform Z-scan measurements for the value of the excitation beam Rayleigh parameter obtained. The results are plotted in figure 1b. The solid line corresponds to the theoretical fitting performed using the same parameters as in figure 1a. We have measured the TL signal at the maximum for different values of the excitation power. The result is shown in figure 1c. The result is a linear dependence as corresponds to a one-photon absorption process. From the slope of this dependence and from equations (2.2) and (2.3) we obtain for the absorption coefficient of the ethanol

$$\alpha = \frac{0.0026}{10^{-3}} W^{-1} \frac{\kappa \lambda_p}{l(\mathrm{d}n/\mathrm{d}T)} \,. \tag{4.1}$$

Using the values of the photo-thermal parameters for ethanol $\mathrm{d}n/\mathrm{d}T = -4 \times 10^{-4}$ °C^{-1} and $\kappa = D/C_\nu = 1.67 \times 10^{-3}$ W cm^{-1}°C^{-1}, we obtain for the absorption coefficient α=$(6.8 \pm 0.5) \times 10^{-4}$ cm^{-1}.

Performing the same procedure we determine the absorption coefficient and thermal diffusivity of the rest of the liquids, the results are shown in table 1.

Table 1. Measured optical absorption coefficient (α) and thermal diffusivity (D) of several liquids.

Parameters	Ethanol	Benzene	Acetone	Methanol	Toluene	Chloroform
$\alpha \times 10^4$ cm^{-1}	6.8 ± 0.5	4.0 ± 0.4	1.89 ± 0.10	5.9 ± 0.5	2.8 ± 0.2	1.52 ± 0.10
D$\times 10^3$(sec^{-1}cm^2)	0.89 ± 0.01	0.90 ± 0.01	1.09 ± 0.01	1.04 ± 0.01	0.92 ± 0.01	0.81 ± 0.01

5. Conclusions

This work demonstrates the usefulness of the optimized method for measurement of optical and thermal properties of nearly transparent liquids. Results obtained agree quite well with those reported in the literature. We have measured the absorptivity of six organic liquids at 532-nm. The absorptivities do not exceed 10^{-4} cm^{-1}. The accuracy of this experiment (5.3 to 10%) is only limited by the fluctuations of the excitation light power. We have also measured the thermal diffusivity of these liquids with high precision.

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Коефіцієнт поглинання майже прозорих рідин, виміряний методом спектрометрії термічної лінзи

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Ми використали оптимізовану схему термічної лінзи з неузгодженням нагнітаючої і зондуючої мод для визначення коефіцієнтів поглинання і термічної дифузії етанолу, ацетону, метанолу, тоулену і хлороформу. У цій схемі збуджуючий промінь фокусувався в присутності колімованого зондуючого променя. Узгодження між отриманими результатами і значеннями, які повідомлялись в літературі є добрим.

Ключові слова: *термічна лінза, коефіцієнт абсорбції, прозорі рідини, термічна дифузія*

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