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# Thermal Lens Technique as a Potential Optical Tool

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**Abstract:** *The spectroscopic characterization of materials involves the use of various optical tools. Spectrometers, interferometers etc, are some of the examples of optical tools. Thermal lens technique is one of the potential optical tools for the thermal characterization of different materials. The thermal lens effect is a photothermal effect which results when energy from a laser beam is absorbed by a sample, causing heating of the sample along the beam path. In this paper an overview of thermal lensing, its significance as potential optical tool and its applications are discussed.*

**Index Terms:** *Optical tool, Photothermal spectroscopy, TLS application, Thermal diffusivity*

## I. INTRODUCTION

The thermal lens effect is a photothermal effect which results when energy from a laser beam is absorbed by a sample, causing heating of the sample along the beam path. The sample acts like a lens as a result of gradient in the refractive index corresponding to the temperature gradient in the sample. The invention of thermal lensing in the field of optics has replaced many of the conventional method where the accuracy falls on the probability part. Thermal lensing has got a wide range of applications as its high sensitivity and simpler setup could be relayed for the study of many chemicals and materials where the conventional method was a failure.

## II. BASIC OPTICAL CHARACTERIZATION TECHNIQUES

### A. Absorption Spectroscopy

Absorption refers to the decrease in intensity of light as it passes through a substance. It can be defined as the transfer of energy of a wave to the matter as the wave passes through it. Absorption spectrum shows the specific wavelengths absorbed by the given sample.

#### Principle

Beer Lambert's law states that the quantity of light absorbed by the substance dissolved in a fully transmitting solvent is directly proportional to the concentration of substance (c) and the path length of the light (l) through the solution [1].

$$A = \epsilon cl$$

Where,

$\epsilon$  = molar absorption coefficient

If (i) is the intensity of emitted light and ( $i_0$ ) is the intensity of absorbed light, then absorbance can also be given by,

$$A = \log \frac{i}{i_0}$$

### B. Photoluminescence Spectroscopy

Photoluminescence is the process in which a molecule absorbs a photon in the visible region, exciting one of its electrons to a higher electronic excited state, and then radiates a photon as the electron returns to a lower energy state. In this case molecules undergo internal energy redistribution when photon absorption. Fluorescence and Phosphorescence are two types of photoluminescence.

1) **Fluorescence:** It is the phenomenon where an excited electron after absorbing energy (photons) move to higher excited state and release energy in radiative form which is of longer wavelength during the process of de-excitation. Using Jablonski diagram, it can be said as when excited electron jump from higher state to singlet state without any inter system crossing, but due to internal conversion, fluorescence takes place.

a) **Fluorescence Quantum Yield:** It is simply the efficiency. Particularly the ratio between the total no of photons released to the total no of photons absorbed by the solution after absorption and de-excitation process.

b) **Phosphorescence:** This is similar process to fluorescence but this happens when an inter- system crossing take place. In this the electrons jump from higher energy state to triplet state after inter – system crossing. The persistence of re-emitted light so that it lasts several seconds or minutes after incident light is turned off. In this wavelength will be longer according to stokes theorem [2]-[4].

### III. PHOTOTHERMAL SPECTROSCOPY

Photo thermal generation refers to the heating of sample due to absorption of electromagnetic radiation in other words photons. In this technique the sample is illuminated using a Gaussian beam having intensity distribution across the beam. As Photothermal spectroscopy is a modulation measurement technique, which implies periodic perturbation of some parameter of the material under study by modulated (pulsed) laser radiation. Photoinduced absorption increases with an increase in the laser intensity. Photothermal techniques can be implemented in two ways. In the first version, a sample is exposed to continuous wavelength (cw) laser radiation periodically modulated in amplitude (so-called photothermal modulation spectroscopy). The second version is the pulsed photothermal spectroscopy, where periodically repeated laser pulses are used. [3]- [5]. Depending on the way of detecting modulated signal, the most widespread methods are photo acoustic spectroscopy techniques, photo thermal deflection spectroscopy (mirage effect), thermal lens technique (thermal lens spectroscopy), photo thermal radiometry and photo thermal interferometry, and thermo reflectance technique.

#### A. Different Photothermal Spectroscopic Techniques

- 1) *Photo Acoustics Effect*: Modulated laser is passed through the sample, which fully or partially absorbs and the sample gets heated up. The heat released by the sample is transferred to the gas medium in an acoustic cell. So, pressure change is measured using microphone.
- 2) *Photothermal Deflection (Mirage Effect)*: Excited radiation heats the surface of the sample. Heat transfer cause periodic change in temperature gradient leads to change in refractive index. So, the deviation of probe beam from plane parallel of sample surface called mirage effect.
- 3) *Thermal Lens Technique*: Excited radiation heats the whole sample causing temperature gradient and change in refractive index causing the sample to act as lens depending upon the temperature coefficient of refractive index of the sample. It is more sensitive compared to any other photo thermal techniques. It has got single beam setup, double beam, associated with mode matching and mode mismatching (which is more sensitive) [9] configuration. The thermal lens technique is widely used to measure weak absorption in solids and liquids, to analyse trace amounts of materials and kinetics of chemical processes, in nonlinear spectroscopy, etc.
- 4) *Surface Thermal Lensing*: Similar to thermal lensing technique where only the surface is mainly focused. This technique is an alternative to the deflection photothermal spectroscopy. It depends and varies with diameter of probe beam and pump beam. Used for finding the sensitivity and absorption of thin film coating.
- 5) *Photo Thermal Radiometry*: This method eliminates influence of any unwanted background radiation. Partial absorption of laser radiation and the corresponding heat release led to modulation of the sample surface temperature and the recorded heat flux at the pulse repetition (modulation) frequency. This method is used for remote measurement of the temperature of bodies and their thermo physical parameter, to investigate electronic properties of semiconductor materials and monitor their defect structure, for remote spectral analysis in different technological problems when studying surfaces of materials and coatings, and in thermal-wave microscopy and thermography.
- 6) *Photo Thermal Reflectance Technique*: For finding energy structure of semiconductors, using the reflectance of sample after absorbing energy from laser.
- 7) *Photo Thermal Interferometry*: In the technique the phase change is detected and used in interferometry. Variations in the refractive index of irradiated medium change the phase of a radiation wave passing through it. Apart from this the measurement of light induced absorption for lower intensity cases and for higher intensity cases have difference in their experimental setup, which is modified and advanced. This makes the photo thermal techniques to be more sensitive [6].

### IV. THERMAL LENS SPECTROSCOPY(TLS)

The photo thermal lens effect was discovered by Gordon et al, in 1965. The Thermal lens technique is based on measurement of the temperature rise that it is produced in an illuminated sample as a result of nonradioactive relaxation of the energy absorbed from a laser. If a laser beam is passed through a liquid sample small fraction of incident power is always absorbed by the medium. This gives rise to a temperature profile, causing gradient of density and refractive index and it changes the optical properties of the sample. The divergence of the probe beam when it is passed through a sample excited due to pump beam is known as thermal blooming. Fig 1 shows how the thermal blooming occurs when probe beam probes through the sample. TL is one of the techniques among different techniques of photo thermal spectroscopy.

This technique is more prominent and important because of the high sensitivity. The unique characteristics of lasers, namely low-beam divergence, pure polarization, high spectral and spatial resolution, and its ability to be focused to a diffraction-limited spot, have been fully exploited to use the thermal lens as a detection technique for microfluidic devices. As a consequence of these developments, the thermal lens technique has been established as a highly sensitive technique.

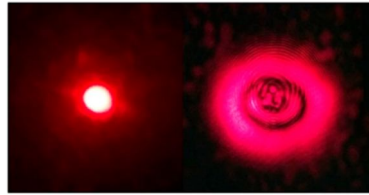


Fig 1: Photograph showing the thermal blooming of probe beam [17]

A. Measurements Schemes

Main types of thermal lens setup, used for the experiment are:

1) *Single Beam*: Where a single laser beam is used for the setup and it act as both the pump and probe beam that is to excite and to probe the thermal lens signal. In a single-beam thermal lens instrument, the laser beam is focused with a lens and modulated by a chopper or a shutter. After passing the sample, the beam center intensity is usually measured in the far field with a photodiode placed behind a pinhole. The photodiode output is amplified and fed into a storage oscilloscope, which facilitates a recording of transient changes in the beam center intensity (Fig 2). Single beam TL has got high sensitivity, but due to some disadvantages of using single beam for pumping and probing, the sensitivity is restricted to some extent. Still is used more widely because of the ease of setting up it for TL experiment.

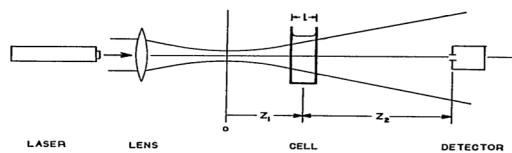


Fig 2: Thermal lensing components (single beam). [9]

2) *Dual Beam*: In a dual-beam instrument, the generation and the detection of the thermal lens are achieved separately by a modulated pump beam and a non-modulated probe beam. This can be setup either by collinear way or by transverse coaxial way. Arranging the dual beam in collinear way requires more accurate setup. So most commonly used method is through transverse method, which indeed specifically helps in mode mismatched method. The collinear configuration provides better absolute sensitivity because of the longer interaction length of the two beams. In a transverse thermal lens experiment (Fig 3), the excitation beam is focused into the sample perpendicularly to the probe beam (crossed beam configuration). This alignment is useful in small volume liquid sample and liquid chromatography and capillary electrophoresis. Two sorts of dual-beam thermal lens experimental arrangements have been developed. In a conventional dual-beam TL experimental configuration the sample cell is located at the confocal position of both excitation beam and probe beam, and the radii of these two beams are nearly the same. This is called the mode-matched dual-beam thermal lens configuration. In a mode-mismatched dual-beam experiment the sample cell is put at the waist of the excitation beam, where its power density and the thermally produced refractive-index gradient are maximum, and an additional signal enhancement can be observed. The probe beam, in this situation, may be wider than the excitation beam in the sample. [7]

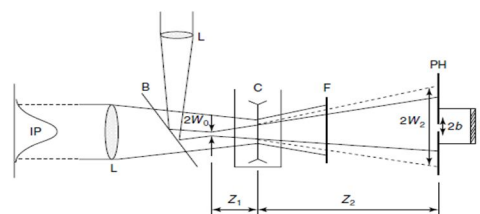


Fig 3: Scheme of the geometric position of laser beams in a mode-mismatched dual beam thermal lens experiment IP: intensity profile of the pump beam L: dichroic mirror C: Sample cell F: optical filter pH: pinhole; D: photodiode;  $w_0$ : radius of the probe beam in the waist;  $w_2$ : radius of defocused probe beam at pinhole position; Z: distance between the focal point of the probe beam and the sample cell; Z2: distance between the sample and the pinhole; b: radius of the pinhole [7]

**B. Dual Beam Thermal Lens Experimental Setup**

In the mode-mismatched dual-beam thermal lens experiment, a cw Gaussian beam illuminates a weakly absorbing sample, causing a thermal lens. A weak Gaussian beam, which is co-linear to the excitation beam, is incident to the sample to probe the thermal lens. The position of the waist of the probe beam is taken as the origin along the axis.

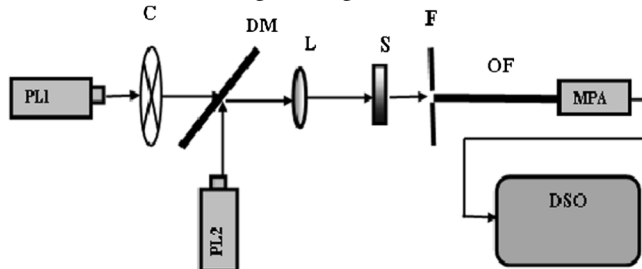


Fig 4: Schematic representation of the experimental set-up PL1 pump Laser (DPSS, 532 nm), C chopper, L lens, DM dichroic mirror, S sample Cell, OF optical fiber, PL2 probe laser (He-Ne, 632 nm), MPA monochromator, DSO digital storage oscilloscope. [18]

In the experimental setup a pump beam is allowed to pass through the chopper to arrange or modulate the frequency of the beam. Then the probe beam is used, which is reflected to the lens using a dichroic mirror. After that a convex lens is used to focus the beam of light to the sample kept behind the lens. A filter is kept in front of the probe beam to collect probe beam then optical fiber is kept which is connected to an oscilloscope (Fig 4). [8-10]

**C. Measurement of Thermal Diffusivity and Quantum Yield using Thermal Lens Technique**

1) *Thermal Diffusivity*: Thermal diffusivity refers to the rate of transfer of heat through a given sample. Thermal lens technique is commonly used for the thermal diffusivity measurements of materials like dyes, quantum dots, nanoparticles etc. [11-17] The thermal diffusivity can be found out using the following equation.

$$D = \frac{w^2}{4t_c}$$

Where,

D = thermal diffusivity

w = beam radius at sample position

tc = relaxation time constant

Figure 5 shows a curve fitted thermal lens signal from which the relaxation time constant can be found out.

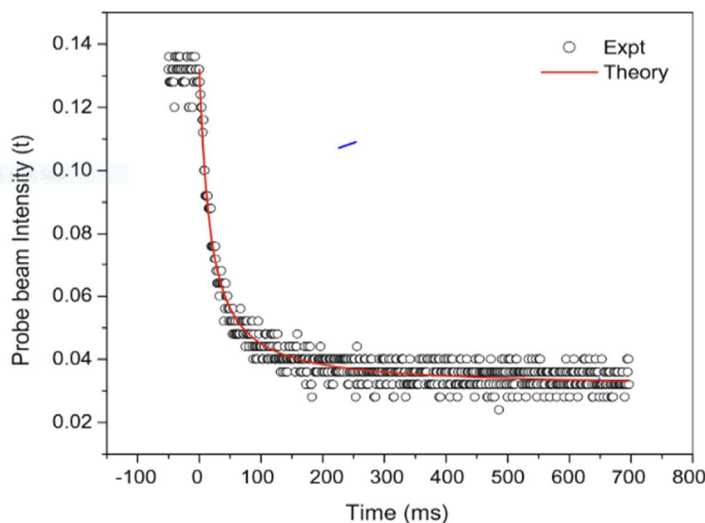


Fig 5: Relaxation time curve fitting of thermal blooming (used to find the thermal diffusivity) [16]

- 2) *Quantum Yield*: Other than finding the thermal diffusivity of the sample, thermal lensing can also be used to find the quantum yield of the sample. This helps to study the different chemical properties of the samples.

$$Q_f = \left( \frac{\lambda_f}{\lambda} \right) \left( 1 - \frac{\eta}{\eta_\infty} \right)$$

Where,

$\eta$  = thermal lens signal

$\lambda_f$  = fluorescence wavelength

$\lambda$  = excitation wavelength

$\eta_\infty$  = thermal lens signal for the concentration at which the fluorescence intensity is quenched completely.

#### D. Applications of TLS

- 1) *TL- A Spectroscopic Tool*: The thermal lens technique is proved to be useful to measure excited-state lifetimes of non-emitting states. Most work in pulsed thermal lens experiments have assumed instantaneous lens buildup followed by a lens decay which is determined by thermal characteristics of the sample. It is also used in the study the thermal properties of polymer and other plasma studies. Hence it is said as spectroscopic. [19]
- 2) *TLS - Calorimetric Application to Chromatographic Detection*: The laser-induced thermal lens effect has been applied to the calorimetric detection of absorbing samples having negligible fluorescence quantum yields. Hence in the chromatographic detection of sample. [20]
- 3) *TLS- Food Analysis and Environmental Research*: The TLS technique has found many applications in the analysis of environmental and food samples, which vary in complexity from drinking water to analytically very demanding samples of oils, fruit juices and extracts from biological fluids and tissues. Various organic pollutants, heavy metals and biologically active compounds can be detected with high sensitivity, which enables their determination at ppb concentration levels. [21]
- 4) *TLS – To Assess oil Biodiesel Blend*: The goal of this experiment is to evaluate the behavior of the thermal and mass diffusivity that arose when oil was added to biodiesel and to verify the capabilities of the method to identify small concentration of triglycerol. The configuration used is dual beam TLS. Heat effects on the sample of biodiesel and oil blend were also obtained apart from the experiment. [22]
- 5) *TLS – Electron – Probe Microanalysis of Surface of Glass with Bonded Organic Dye*: Thermal lensing and electron-probe microanalysis were used for studying surfaces of quartz glass samples with chemically bonded Reactivot B5A organic dye. Thermal lensing was used for determining thermal stability of dye covers. Using thermal lensing more uniformity can be obtained in determining stability of the dye in its surface. [23]
- 6) *TLS -Techniques in the Near- and Middle-Infrared Region*: Thermal lens measurements are based on the use of laser as the excitation source. Therefore, the spectral range in which measurements can be performed is dependent on the availability of lasers in that region. After the introduction of advanced lasers which enable the near and middle –infrared region in the spectra. The high sensitivity of the thermal lens technique makes it possible to use it to measure higher overtone spectra, which is not possible with dispersive or FTIR instruments. [24]
- 7) *TLS-Capillary Electrophoresis*: Capillary electrophoresis is another example of the advantageous use of TLS as a highly sensitive technique in which TLS can overcome the problem of short optical path length and small-volume samples, governed in CE by the dimensions of capillaries. The capability of TLS to probe small volume samples is indeed exploited the best in capillary electrophoresis, resulted in the determination of  $1.8 \times 10^{-7}$  M dabsylated arginine, histidine, leucine, alanine, glycine, and glutamic acid in a detection volume of 50 pL. Thermal lens has been emerging with advanced technology and development, which widens it angle of application. Other applications of thermal lensing include determination of physical properties of solvents (water), Effects of Surfactants and Electrolytes on Structure of solvents, Microscopic TLS, Foodstuff analysis, Trace detection, Measurements of absolute absorption coefficients, etc. [25],[26]

## V. CONCLUSION

Thermal lens spectroscopy is a highly sensitive optical technique that can be applied in the study of various properties of samples induced due to a temperature gradient. It is attractive because it is neither destructive nor invasive. With its simple set up, high sensitivity and modification, it has got a wide range of applications. The present study exploded the said features of Thermal lensing as a potential optical tool.

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