Thermal lens spectroscopy - An overview

This chapter introduces different photophysical processes taking place in an illuminated medium. Various photothermal phenomena that characterize the photo-induced thermal state of materials are also briefly described in the introduction. The relevant theoretical treatment of photo-induced thermal lens effect that forms the foundation of this work is discussed in this chapter. Recent advancements in the field of thermal lens spectroscopy and it’s applications are also outlined.
1 Thermal lens spectroscopy

1.1 Introduction

The science and technology of photonics is an edifice resting on two strong pillars viz., (1) the theory of light-matter interaction and (2) synthesis and characterization of photonic materials. The fifth generation computer which fuses information technology and logical programming demand fast computation and parallel processing, leading to dense connectivity. It is an accepted fact that photon-based photonic technology will provide a helping hand in this regard through the development of appropriate photonic materials and their characterization. Materials, which exhibit efficient optical nonlinearities, fluorescence quantum yield and large thermal diffusivity are potential candidates for efficient photonic materials.

The knowledge about thermal and optical properties of materials can be achieved through a systematic study of light-matter interaction. Such studies can be made by monitoring radiative or nonradiative processes taking place in a medium, which contain a number of excited state atoms or molecules. This chapter gives a brief introduction to various processes taking place due to light-matter interaction with special reference to thermo-optic effects.

1.2 Processes of light-matter interaction

The absorption of photon by a molecule (A) of a sample in accordance with their spectroscopic properties may follow a variety of effects so that the excited state molecule will lose its energy either by radiative processes or by non-radiative deactivation processes. If the photon energy is sufficient enough, direct photochemical decomposition of the molecule can be achieved. Schematic representations of relevant processes are given below.
1.2.1 Fluorescence

When a molecule in the excited state returns to the ground state radiatively, the emission probability is maximum from the lowest vibrational level of the first excited singlet state, regardless of the vibrational levels or the electronic states to which the molecule is originally excited (figure 1.1). Therefore the fluorescence maximum occurs at lower energy due to the Stokes' shift. This is the difference between the energy of the excitation and emission maxima that indicates the energy dissipated during the lifetime of the excited state before returning to the ground state. Stokes' shift can be represented as

\[
\text{Stokes' shift} = 10^7 \left( \frac{1}{\lambda_{\text{ex}}} - \frac{1}{\lambda_{\text{em}}} \right) \text{nm}^{-1}
\]  

(1.1)

where \(\lambda_{\text{ex}}\) and \(\lambda_{\text{em}}\) are the maximum wavelength for excitation and emission.

The rate of emission depends on the molecular environment and the structure of molecule.

1.2.2 Non-radiative Transition

Once the molecule is in an exited state \((S_1)\) it has a lifetime in the range of nano seconds, which depends upon a number of competing factors. It may non-radiatively return to the ground state by internal conversion (IC), or may undergo intersystem crossing (ISC) to the triplet state, as shown in figure 1.1.
However, IC cross-section is prominent factor in the case of de-excitation from $S_n$ to $S_1$ ($n>1$) and it has low probability for transition between $S_1$ and $S_0$. It should be noted that direct absorption to triplet state is spin forbidden. Major component of nonradiative relaxations appears through de-excitation to various vibronic levels, ISC etc.

*Figure 1.1 Energy level diagram of typical dye molecule illustrating several optical and kinetic processes (A-absorption, IC-internal conversion, F-fluorescence, P-phosphorescence and ISC-intersystem crossing)*
1.2.3 Energy transfer

Energy transfer represents another channel whereby the excited molecule can dispose its energy. The excited molecule \((D^*)\) may transfer its energy to another molecule \(A\), so that

\[ A + D^* \rightarrow D + A^- \]

This process can be considered as either quenching of the excited state molecules \(D^*\) \((A\) is called the quencher) or to generate \(A^-\) indirectly rather than by optical excitation. The molecule \(D\) is said to be the donor while \(A\) is the acceptor molecule. For the transfer of energy to occur, \(A^-\) should be lower in energy than \(D^*\) and it must takes place within the excited lifetime of the donor. Of the two types of transfer, in trivial process, the light emitted by the donor travels through the solution and is absorbed by the acceptor. In the other type of transfer, removal of energy from \(D^-\) occurs simultaneously with its appearance in \(A\). In this process of nonradiative transfer, absorption spectrum of \(A\) must overlap with the fluorescence spectrum of \(D\).

Most of the spectroscopic techniques are based on the detection of photons so that only radiative relaxation processes are monitored directly. Information regarding the nonradiative process is extracted indirectly from the data of radiative transitions. However the results obtained thus may not be reliable as far as nonradiative processes are concerned. Direct information about such process can be obtained by employing techniques of the thermo-optic effect. An added advantage is that this method will provide both optical and thermal properties of the medium directly. Salient features of the thermo-optic spectroscopy are described in the following section.
1.3 Photothermal Spectroscopy

Photothermal Spectroscopy belongs to a class of highly sensitive techniques, which can be used to measure optical absorption and thermal characteristics of a sample. The basis of photothermal spectroscopy is photo-induced changes in the thermal state of the sample due to optical absorption by molecules and the subsequent nonradiative relaxation processes that results in heating of the sample, which in turn modifies its thermal state. Photothermal signals will not be affected by scattered or reflected light unlike conventional optical signal detection. Hence photothermal spectroscopy measures optical absorption more precisely in scattering solutions, solids and at interfaces. The large signal to noise ratio of thermo-optic techniques makes it an effective tool to study the surface and absorption properties of materials, particularly for solids. There are different photothermal mechanisms that can be used for the physical and chemical analyses of materials, such as photoacoustic spectroscopy, photothermal deflection, photothermal lens spectroscopy etc. These are briefly described in the following sections.

1.3.1 Photoacoustic spectroscopy

![Photoacoustic effect diagram]

*Figure 1.2 Photoacoustic effect*
When light (short light pulse or modulated light beam) is absorbed by the sample, non-radiative relaxation produces local heating. This induces local expansion in the irradiated region. This thermal energy is coupled to the coupling gas in the photoacoustic cell, which causes a transient or periodic pressure change in this cell. This generates acoustic signal that can be detected using a sensitive microphone. Photoacoustic effect has been applied to detect phase transitions, fluorescent properties of laser dyes, nonlinear optical properties of materials, imaging, depth profiling etc. A good treatment of this topic is available in standard books [1].

1.3.2 Photothermal deflection

Photothermal deflection method or mirage technique is a sensitive method to evaluate the thermal, optical and transport properties of matter in all its states. In this method, the sample is excited with a mechanically modulated optical radiation. The nonradiative de-excitation of molecules produce periodic local heating of the specimen which in turn produces refractive index variation in the coupling medium.

![Diagram of Photothermal deflection](image)

*Figure 1.3 Photothermal deflection*
This refractive index variation can be probed using a low power laser radiation (probe beam), the deflection of which depends on the optical and thermal properties of the sample. Depending on the pump-probe configuration, photothermal deflection technique can be employed in two ways, either in transverse photothermal deflection method or in collinear photothermal deflection method. Photothermal deflection technique has been successfully used to evaluate thermal properties of materials, surface imaging, phase transition studies etc [2].

1.3.3 Thermal lens effect

The first photothermal spectroscopic method to be applied for sensitive chemical analysis was photothermal lens spectroscopy. The photothermal lens effect was discovered by Gordon et al. in 1965 [3]. In this technique the sample is illuminated using a gaussian beam having intensity distribution across the beam as

\[ I_r = I_0 e^{-2r^2/\omega^2} \]  

(1.1)

where \( \omega \) is the beam radius. A part of the incident radiation is absorbed by the sample and subsequent nonradiative decay of excited state population results in local heating of the medium. The temperature distribution in the medium mimics the beam profile of the excitation beam and hence a refractive index gradient is created in the medium. Due to this modification in refractive index, the medium mimics a lens, called thermal lens (TL). Figure 1.4 shows the schematic diagram of TL effect. The thermal lens generally has a negative focal length since most materials expand upon heating and hence have negative temperature coefficient of refractive index. This negative lens causes beam divergence and the signal is
detected as a time dependent decrease in power at the center of the beam at far field.

![Block diagram of Thermal lens effect](image)

**Figure 1.4 Block diagram of Thermal lens effect**

### 1.4 Historical developments of thermal lens studies

Gordon and his coworkers observed TL effect quite accidentally during their study of laser Raman scattering of pure liquids. The resulting investigations predicted the most important application of the measurements of small absorbance. The first use of the intra-cavity thermal lens to measure the absorptivity of liquids was reported by Leite et al [4] in 1964. Solimini (1966) [5] refined the apparatus and measured the absorption coefficients of 27 organic liquids. In 1967 Callen et al [6] reported the observation of a pattern of concentric rings, which is now recognized as arising due to spherical aberration of the thermal lens. Similar observations were reported by Dabby et al in 1970 [7] and
Akhmanov et al [8]. Carman and Kelly [9] studied the time evolution of thermal lens and recorded the growth of thermal lens by a movie camera. But the problem with the intra-cavity method was that the beam propagation altered the character of the photothermal lens element and the intra-cavity apertures. The first extra-cavity photothermal lens apparatus was used by Rieckhoff in 1966 [10]. However, he misinterpreted the results as nonlinear sample absorption.

The most important advance in thermal lens technique was introduced by Hu and Whinnery in 1973 [11,12]. The authors demonstrated that maximum divergence of the laser beam could be obtained for a given sample by positioning the sample at a distance of one confocal length from the minimum beam waist of the laser, which results in sensitive absorbance measurements. Later, an extensive application and refinement of the thermal lens technique were carried out by Dovichi and Harris [13-16]. They introduced procedures needed for reliable and reproducible measurements of thermal lens signal. The authors constructed a differential thermal lens spectrophotometer for canceling the back absorbance of the sample matrix or the solvent. When the sample, with negative thermal coefficient of refractive index, is placed beyond the beam waist, a diverging beam is created and when it is placed at an equal distance before the beam waist, a converging beam is resulted. Therefore, when two cells filled with identical samples are placed symmetrically about a beam waist, a cancellation of about 99% of TL signal is observed. Hence, signal due to the matrix or solvent can be optically subtracted from that of the sample automatically, if blank sample is placed $\sqrt{3}$ times confocal distance before and after the beam waist. Using this experimental arrangement, an improved sensitivity was reported.

All the works described above used the single beam TL measurement method. The first reports of dual beam thermal lens measurements were from the
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work of Grabiner et al [17] and Flynn [18] (1974) who used a He-Ne laser to probe the time resolved formation of thermal lens. The first application of dual beam TL technique to spectroscopic absorption measurements was the work of Long et al [19] who used repetitively chopped (13 Hz) tunable cw dye laser. The 13 Hz modulation frequency was selected on the basis of the practical low frequency limit for lock-in amplifier. Several other optical arrangements for the dual beam thermal lens technique have been suggested. Moacanin et al showed the counter propagating pump and probe beams through the sample. But in this arrangement care should be taken to avoid pump beam from entering probe laser cavity. Rojas et al [20] developed a dual beam thermal lens optical fibre spectrometer which is capable of measuring sensitive TL spectra at a location remote from the pump laser such as in an environmentally-controlled glove box for actinide chemistry studies and remote environmental analysis. Franko and Tran [21] constructed a cw dual-wavelength pump-probe configuration TL spectrometer that was capable of measuring thermal lens signal at two different wavelengths. The advantage of this dual-wavelength setup included its ability to correct for solvent background absorption and its improved selectivity. Swofford et al [22-24] investigated the dependence of the magnitude of thermal lens on the parameters of the experimental design in a dual beam TL setup. The authors observed very good agreement between measured and calculated signal in the repetitively chopped TL experiment.

A novel fiber optic modified thermal lens detector in combination with capillary electrophoresis that facilitate the use of microlitre volumes of samples was demonstrated by Seidel and Faubel [25]. Imasaka et al [26] constructed TL spectrophotometer [TLS] consisted of a couple of optical fibers. Franko and Tran described various analytical thermal lens instruments such as differential thermal lens, multiwavelength and spectral tunable instruments, circular dichroism
spectropolarimeters and miniaturized instruments. Recently Franko demonstrated differential IR TLS and microscopic TLS, with improved sensitivity [27-35]. Leach and Harris [36,37] and Amador-Hernandez et al demonstrated sensitivity of three orders of magnitude in supercritical fluids [38,39], which opened new possibilities for using TLS in combination with supercritical fluid extraction or chromatography.

The pulsed laser thermal lens has made possible the study of a wide variety of nonlinear optical effects. One of the important phenomena is two-photon absorption, by which a molecule is promoted to an excited state at twice the frequency of the incident light as a result of simultaneous absorption of two photons. Since the rate of this weak process depends on laser intensity, the use of pulsed laser combined with a sensitive detection method is required. Long et al [19] was the first to recognize TL technique as a possible detection scheme for two-photon absorption. Twarowski and Kliger studied two-photon absorption of benzene with a pulsed nitrogen pumped dye laser [40,41]. Rasheed et al recorded fifth CH overtone spectra of some organic molecules using dual beam TL method [42]. Bindhu et al investigated some novel applications of TL effect [43-50]. This includes the study of multiphoton absorption processes occurring in liquids, optical limiting properties of C_{60} and C_{70}, fluorescence quantum yield of dyes in different organic solvents, thermal diffusivity of organic liquids and seawater. The details of the theory and experimental arrangement for two-photon absorption are given in chapter 5.

### 1.5 Theory of Thermal lens effect

The thermal lens effect has been theoretically derived under a variety of experimental conditions [51-73]. Existing theoretical models range from relatively simple formulations to complex and sophisticated versions. These models cover...
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Thermal lens effect, which are generated under different excitation conditions (pulsed and cw excitation), different pump/probe geometries (single and dual beam, collinear and crossed beam configuration, pump–probe displacements) and different sample conditions (stationary and flowing samples). The thermal lens effect has been theoretically derived under aberrant and parabolic models. Sheldon et al [51] were the first to consider the aberrant nature of the thermally induced lens. They used the diffraction theory to find the intensity at the beam center in the far field. Parabolic and aberrant lens models were both derived for single beam or coaxial two beam experiments in which the probe beam and pump beam radii are same in the sample cell. These models of thermal lens describing its effect upon the propagation of the probe beam assume that the sample is thick and hence the surrounding medium has no influence on the heat flow away from the probed region of the sample. Therefore for thin samples these assumptions are not valid. Wu and Dovichi [52] developed a Fresnel diffraction theory for steady state thermal lens in thin films. Fang and Swofford [24] postulated mismatched configuration and in this two beam configuration maximum sensitivity was predicted when the sample is placed at \( \sqrt{3} \) times the confocal distance from the beam waist. Shen et al [53] and others modified the theory for mode mismatched configuration and constructed a dual beam mode-mismatched TL spectrometer that can be used for steady-state measurements and time resolved studies. With this apparatus they determined the trace of copper in water. Viyas and Gupta modified the theory for flowing samples [59-61].

The theoretical procedure can be divided into three parts. (1) The heat equation must be solved for the particular boundary conditions of the system to generate a temperature distribution within the sample. (2) The temperature
distribution must be converted into a refractive index profile. (3) The interaction of
the beam with the refractive index profile is used to predict a change in the beam
intensity profile. The different models differ primarily in the last step. A simple
paraxial approximation theory is usually used to predict changes in the beam
centre intensity and in the beam spot size [3, 11,12]. This paraxial approximation
is a closed-form solution of ray tracing through a parabolic temperature rise near
the beam axis.

1.5.1 Background

In a thermal lens experiment, a Gaussian laser beam illuminates a weakly
absorbing sample. Nonradiative decay of excited states within the sample
produces a temperature field that mimics the intensity profile of the laser beam.
Expansion of the heated sample leads to a change in refractive index that acts to
defocus the laser beam. Either the change in the beam spot size or the change in
the beam centre intensity may be monitored to estimate the strength of the
thermal lens.

1.5.2 Assumptions

A number of assumptions are involved in the model of the thermal lens.

(1) The laser beam is in the TEM$_{00}$ mode so that the beam cross section
is gaussian.

(2) The spot of the laser beam remains constant over the length of the sample
cell.

(3) The sample is homogeneous and satisfies Beer's law.

(4) The thermal conduction is the main mechanism of heat transfer and the
temperature rise produced within the sample does not induce convection.
(5) Refractive index change of the sample with temperature, \( \frac{dn}{dT} \), is constant over the temperature rise induced by the laser.

(6) Detection of the intensity profile of the laser beam is undertaken in the far field.

(7) The strength of the thermal lens is not sufficient to induce a change in the beam profile within the sample.

Consider a gaussian beam passing through an element of an absorbing sample in which the heat flow is radial and the beam is turned on during the time interval \( 0 \leq t \leq t_o \). The heat generated per unit length [54]

\[
Q(r)dr = \frac{2\alpha E_0}{\pi \omega^2} \exp\left(-\frac{2r^2}{\omega^2}\right)
\]

(1.2)

where \( \alpha \) is the absorption coefficient of the medium. \( E_0 \) is the total energy in each laser pulse and \( \omega \) is the beam radius at time \( t = 0 \).

The temperature rise of the laser-irradiated region [57,58] is obtained as

\[
T(r,t) = \frac{2\alpha E_0}{\pi \rho c_p (\omega^2 + 8Dt)} \exp\left(-\frac{2r^2}{\omega^2 + 8Dt}\right)
\]

(1.3)

where \( D \) is the thermal diffusivity given as

\[
D = \frac{\omega^2}{4\tau_c}
\]

(1.4)

The solution of equation for cw excitation is given as [60, 61]

\[
T(r,t) = \frac{2\alpha P(1 + \cos \omega t)}{\pi \rho c_p (\omega^2 + 8Dt)} \exp\left(-\frac{2r^2}{\omega^2 + 8Dt}\right)
\]

(1.5)
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Due to nonuniform radial temperature distribution, time dependent refractive index gradient formed inside the sample can be expressed as

\[ n(r, t) = n_0 + \left( \frac{\partial n}{\partial t} \right) T(r, t) \]  \hspace{1cm} (1.6)

where \( n_0 \) is the refractive index at time \( t=0 \)

Consequently, the irradiated sample acts like a lens, which affects the laser beam intensity profile by altering the radius \( \omega \). The relative change in the beam intensity is proportional to the relative changes in power of the beam reaching the detector and hence is a direct measure of the thermal lens strength.

The photothermal lens signal is obtained by monitoring the probe laser power that passes through a pinhole placed far from the sample. The photothermal lens will either focus or defocus the probe laser beam so that the power at the center of the beam will either increase or decrease. This change in power is maximized when the sample is placed at one confocal distance,

\[ z_0 = \frac{\pi \omega_0^2}{\lambda} \]  \hspace{1cm} (1.7)

where \( \omega_0(0) \) is the radius of the beam at time \( t=0 \) and \( \omega_2(t) \) is the time dependent radius of a beam induced by a thermal lens given as [74,75]

\[ \omega_2^2(t) = \omega_0^2 \left[ \left( 1 - \frac{z_2^2}{f(t)} \right)^2 + \frac{z_2^2}{z_0^2} \left( 1 - \frac{z_1^2}{f(t)} \right)^2 \right] \]  \hspace{1cm} (1.8)

\( f(t) \) is the focal length of the thermal lens.
Considering the approximation \( Z_2 \gg Z_1 \),

\[
1.9 \quad s(t) = \frac{2 z_1}{f(t)}
\]

The steady state focal length of the induced lens is given as [11,12]

\[
1.10 \quad f_{\infty} = \frac{\pi k \omega^2}{PA \left( \frac{dn}{dt} \right)}
\]

where \( k \) is the thermal conductivity (W cm\(^{-1}\) K\(^{-1}\)), \( P \) is the laser power (W), \( A \) is the sample absorbance, and \( dn/dt \) is the refractive index change with temperature.

The thermal lens signal for pulsed excitation [36,60-62]

\[
1.11 \quad S_p = \frac{4 \ln(10) \Delta E_0 Z_1}{\pi k \omega^2 t_c} \left( \frac{\partial n}{\partial T} \right) \frac{1}{\left(1 + 2t/t_c\right)^2}
\]

For cw excitation

\[
1.12 \quad S_c = \frac{2 \ln(10) \Delta P Z_1}{\pi k \omega^2} \left( \frac{\partial n}{\partial T} \right) \frac{1}{\left(1 + t_c/2t\right)^2}
\]

### 1.6 Sensitivity of Thermal lens technique

The sensitivity of TL signal can be understood by comparing it with conventional spectrophotometric measurements. Consider the transmission of optical radiation through an absorbing medium and let \( I_0 \) be the incident intensity, then the transmitted intensity, \( I_t \) is given as

\[
1.13 \quad I_t = I_0 e^{-\alpha l}
\]
where \( c \) is the concentration of the solution and \( l \) is the length of the medium.

The transmittance of the medium can be defined as

\[
T = \frac{I}{I_0} = 10^{-A}
\]  

(1.14)

Hence absorbance is given by

\[
A = 1 - T
\]

(1.15)

\[
= 1 - 10^{-A} \approx 2.303A
\]

(1.16)

In TL technique the thermal gradient established after optical absorption and thermal relaxation of the sample results in a change in intensity at the beam center owing to the induced beam divergence. The thermal lens signal is expressed as the relative change in power

\[
S = \frac{I_0 - I}{I} = \frac{\Delta I}{I} = \frac{2.303AP(-dn/dT)}{\lambda k}
\]

(1.17)

where \( I_0 \) and \( I \) are the transmitted power before and after the formation of the thermal lens respectively, \( A \) is the absorbance, \( P \) is the laser power, \( \lambda \) is the pump laser wavelength, \( k \) is the thermal conductivity and \( \frac{dn}{dT} \) is the sample's temperature coefficient of refractive index. Equation (1.17) is written as [32]

\[
\frac{\Delta I}{I} = 2.303AE
\]

(1.18)

where \( E = \frac{P(-dn/dT)}{\lambda k} \)

(1.19)
Comparing eqn. (1.16) and (1.18) for the same absorbance, the thermal lens signal is increased by a factor \( E \), called the enhancement factor. The enhancement factor is a function of the thermodynamic and optical properties of the medium and on the power used to excite the sample. Thus the sensitivity of the photothermal method can be increased by using solvents with high refractive index gradient and low thermal conductivity for a given power.

With both cw and pulsed excitation, water is a poor solvent while organic solvents like carbon tetrachloride induce larger enhancement factors [74,75]. The TL signal is inversely proportional to the square of the excitation beam waist, while the sensitivity is independent of the beam size. The selectivity of TLS is hindered by the limited wavelength range of available lasers and is most frequently confined to single wavelength only. The selectivity of TL technique can be improved by using OPO based TL setup, the details are given in chapter 5.

1.7 Measurement approach

1.7.1 Single beam Thermal lens configuration

Figure 1.5 shows the schematic representation of single beam thermal lens setup. In single-beam TL spectrometer, the same laser is used to excite the sample and to probe the thermal lens created. The first analytical application of single beam thermal lens spectroscopy was the trace level determination of Cu(II) with an EDTA complex reported by Dovichi and Harris [13]. This method is perhaps the most well known and used of all the photothermal spectroscopy methods. In single beam TL spectrometer, the laser beam is focused with a lens and modulated with a chopper or a shutter. After passing through the sample, the beam center intensity is usually measured in the far field with a photodiode.
placed behind the pinhole. The photo diode output is fed into storage oscilloscope, which gives the transient change in the beam center intensity.

The single beam measurement method can be used to produce a differential TL experiment. Reference and unknown samples are located on opposite sides of the beam waist so that TL strength of the two samples are

![Diagram of single beam thermal lens setup]

*Figure 1.5 Schematic representation of single beam thermal lens setup.*

subtracted by their opposite effects on the far field beam spot size. The differential configuration has immunity from laser power fluctuations but is limited to weak TL. The sensitivity of TL can be enhanced by keeping the sample at one confocal distance past the probe beam waist. Since one beam is used to probe the TL, there is decrease in power at the beam radius. The relative simplicity of the apparatus coupled with the low solution absorption detection limits, make it highly attractive for trace analysis applications.
1.7.2 Dual beam thermal lens configuration

The two-laser photothermal lens apparatus was used before the extra-cavity single laser method was invented. Dual beam instrumentation can be of two types, collinear and transverse configuration. In collinear configuration, good spatial overlapping of both beams is necessary for optimal sensitivity. The pump beam is used to generate the thermal lens in the medium. Another laser of low intensity is used to probe the lens formed. The pump beam is modulated while the probe is not. Separate lenses are used to focus the beams. The alignment and combination of the two beams is facilitated by a dichroic mirror.

The generated TL produces fluctuations in the intensity of the probe beam that can be sensitively monitored by signal averaging devices like lock-in amplifier and boxcar averager.

In transverse thermal lens experiment, the excitation beam is focused on to the sample perpendicular to the probe beam. The monitored volume is defined by the intersection of two laser beams and is usually of the order of picolitres. This alignment is useful for samples, which are available in a very low concentration and in small volume and for chromatographic detection. Franko and Tran [34] using this configuration detected amino acids at a femtomole level, which corresponds to only 50 molecules. The authors used a prism to ensure a good overlap and counter propagation between the pump and probe beams.

Dual beam thermal lens setup is given in chapter 2. Dual beam technique is more advantageous since only a single wavelength (probe) is always detected.
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and no correction for the spectral response of the optical elements and detector are required. Moreover TL spectra can be recorded only by dual beam setup.

1.8 Advantages in using Photothermal Lens Spectrometry

- Photothermal signals are relatively linear and independent of excitation and probe laser beam focus geometries
- Excitation energy or power dependent signals may be easily measured and modeled, yielding information regarding ground and excited state absorption cross sections and relaxation rate constants
- Data is complimentary to relaxation kinetic measurements but yield more information
- Sensitivity allows the use of thin optical cells.

1.9 Recent applications

1.9.1 Differential TLS in the infrared region

Latest progress in TL technique is the construction of TL signal spectrometers, which operate in the IR region [76,77]. Franko constructed differential IR TLS spectrometer [35], which enables better cancellation of the blank signal when two identical sample cells, containing the solvent in which the analyte is dissolved, are placed symmetrically with respect to the probe beam waist. With this setup they determined organophosphate and carbamate pesticides extracted into organic solvents and they determined pesticides at the ng ml−1. However, working in the IR spectral region imposes certain limitations in the instrumental design.
1.9.2 Microscopic TLS

The possibility of focusing laser beam to points smaller than 1 μm in diameter opens an area of new applications of TLS. This includes the measurements of absorbance on the microscopic level and eventually inside a single living cell. Application and development of microscopic TLS represents an important contribution to general trends towards miniaturization of analytical instrumentation [78,79]. Use of microscopic TLS demonstrated the measurements of pigments and colour distribution in a 5 μm-thick slice of human hair measuring 125 μm in diameter.

1.9.3 Foodstuff analysis

Applications of TLS to foodstuff analysis were governed by the need for new analytical tools to control the quality of foodstuffs and eventual adulteration. Franko [35] using IR TL spectrometer detected the adulteration of fruit juices and low quality of olive oils. With this setup they identified trans unsaturated fatty acids, free fatty acids, etc.

1.9.4 Analysis of environmental samples

TLS is best suited for the analysis of liquid samples. Various organic pollutants, heavy metals and biologically active compounds can be detected with high sensitivity. Further more the high sensitivity of TLS technique has been successfully combined with separation techniques such as HPLC and ion chromatography or bio-recognition methods such as biosensors. Philip et al
[80] studied the effect of phosphorus in saline solution and Power and Langford [81] studied the brown colouration of fresh water due to the dissolved organic matters, which are detrimental to the environment.

1.9.5 Trace detection

The high absorbance sensitivity of these methods has opened up new areas of trace chemical analysis based on optical absorption spectroscopy. The first study of the application of TL technique to trace determination in solution was done by Dovichi and Harris [13] in 1979. They developed a low power (cw) thermal lens spectrometer to study the determination of Cu\(^{2+}\) having a molar absorption coefficient of 47 mol\(^{-1}\) dm\(^3\) cm\(^{-1}\). Grabiner et al [17] designed a collinear dual beam arrangement using Q-switched CO\(_2\) laser - and they suggested that excellent sensitivity of TL technique could prove to be valuable for the detection of trace concentration of absorbing species in atmospheric samples. Mori et al [81] using similar setup carried out the trace determination of NO\(_2\) and Long and Bialkowski [82] conducted a quantitative determination of CF\(_2\)Cl\(_2\). Using this setup they evaluated the TL signal in flowing gas samples. Nakanishi et al [84] constructed a compact TL spectrometer using a near- infrared semiconductor laser and applied it to the trace analysis of phosphorus at sub-micromolar levels.

1.9.6 Measurements of absolute absorption coefficients

The high sensitivity of thermo-optic spectroscopy methods has led to applications for analysis of low absorbance samples. Using this method, concentrations lower than 10\(^{-7}\) M of these strongly absorbing chromophores may be measured in standard cuvettes. These limits of detection are slightly higher than those obtained using laser excited fluorescence spectroscopy and are 2-3 orders of magnitude better than that obtained using conventional transmission
Thermal lens spectroscopy. The low molar absorption detection limits coupled with the fact that the volume being probed can be very small, results in extremely small numbers of molecules being detected.

1.9.7 Measurement of Fluorescence Quantum yield

Hu and Whinnery [11] were the first to demonstrate that thermal lens spectrometer could be used to measure the fluorescence quantum yield of organic dyes using a reference standard. More details of these measurements are discussed in chapter 3 of this thesis. Terazima and Azumi [85-88] carried out a series of investigations for the measurements of quantum yield of triplet formation and triplet lifetime of different species in the liquid and solid phase using time resolved TL technique. The photodissociation of iodine has been studied by Lebedkin and Klmov [89].

1.9.8 Chemical kinetics of solution

Dual beam thermal lens technique has been successfully employed for the study of the reaction kinetics in solutions. Haushalter and Moris [90] monitored the reaction of the enzyme-catalysed oxidation of dopamine by polyphenyloxidase. The details of this application are given in chapter 7. TL spectroscopy has been used to measure thermal diffusion coefficients, sample temperatures, bulk sample flow rates, specific heats, volume expansion coefficients, and heterogeneous thermal conductivities in solids. Detailed experimental techniques, analysis of results and conclusions drawn there from are given in subsequent chapters.
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