Characterization of Photonic Materials Using Thermal Lens Technique

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Characterization of Photonic Materials Using Thermal Lens Technique.

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Front Cover:

Thermal lens effects showing the blooming of the laser beam cross section- a schematic representation.

Back Cover:

Photograph showing the experimental set up to record thermal lens signal.

To my husband Dr. Mathew Varughese

and my children Shon and Shema,

whom are such an important part of my life.

Certificate

Certified that the research work presented in the thesis entitled, ***"Characterization of Photonic Materials Using Thermal Lens Technique"*** *is* based on the original work done by Mrs. Achamma Kurian under my guidance in the International School of Photonics, Cochin University of Science and Technology, Kochi 682 022 and has not been included in any other thesis submitted previously for the award of any degree.

Kochi
12 July, 2002

Dr. V. P. N. Nampoori

Declaration

Certified that the work presented in the thesis entitled, "***Characterization of Photonic Materials Using Thermal Lens Technique***" is based on the original work done by me under the guidance of Prof. V. P. N. Nampoori in the International School of Photonics, Cochin University of Science and Technology, Kochi 682 022, and has not been included in any other thesis submitted previously for the award of any degree.

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Achamma Kurian

Preface

One of the major achievements in the field of science and technology during the second half of the twentieth century was the invention of lasers in 1960. Laser, which generates coherent, monochromatic, intense and directional light beam, is the dream source of spectroscopists and optical scientists. Initial phase of laser research, known as the period of solution in search of a problem, has triggered a number of advancements in almost all fields of human knowledge and activities – Physics, Chemistry, Biology, Archeology, Geology, Medicine, Entertainment and Consumer devices and the list expands day by day.

Laser resolution gave birth to another revolution in the field of Communication and Information Technology. Capabilities of photons to compute, to transmit information and to get guided through optical fibre have opened up a new branch of technology called Photonics. The capabilities of optics based computers in high speed parallel processing and in ultrahigh dense connectivity have made Photonics an integral part of the fifth level computers, which fuses IT with logical processing.

Breakthrough in optical computing was possible due to the development of Non Linear Optics (NLO) that made laser a wonder source of light. Hence, synthesis and characterization of NLO materials form an integral part of Photonics based research. There exist a number of techniques to characterize optical and thermal properties of materials of which Thermo-Optic method is one of the prominent one.

The work described in the present thesis deals with the use of one of the thermo-optic phenomena called Thermal Lens (TL) effect, to investigate optical and thermal properties of a class of photonic materials namely laser dyes in solution as well as in solid matrices. When the energy of radiation matches with that of a transition between the ground state and an excited state of the molecule a photon is absorbed. The excited molecule can eventually return to the ground state by radiative or non-radiative transition. The nonradiative de-excitation causes local heating in the sample along the beam path. The heating results in the creation of a refractive index gradient, which causes the effect of thermal blooming, or thermal lensing in the medium. This thermal lens causes a significant deviation of the probe beam path. Measurements of a change in the divergence of a laser beam after the blooming of the thermal lens allows determination of absorbance in the range $10^{-7}-10^{-6}$.

There are different configurations for the thermal lens setup. In single beam experiment, the same laser is used as both the excitation source and probe beam. In dual beam configuration, separate lasers are used as the pump and probe beams. Dual beam TL technique is more advantageous since only a single wavelength (probe) is always detected and there need be no correction for the spectral response of the optical elements and detector. Moreover one can record TL spectra only by dual beam setup. The important feature of thermo optical spectroscopy is its non-destructivity nature of analysis that provides the studies of fluorescent materials, the analysis of biological objects, the remote analysis and on-line determination in the flow. TL effect has been exploited for a number of measurements such as evaluation of triplet and fluorescence quantum yield in solid and liquid phases, study of the multiphoton processes, determination of thermal diffusivity of various samples and calorimetric trace analysis. Thermal lens spectrometry is 100-1000 times more sensitive than conventional spectrophotometry.

The eight chapters of the thesis describe the details of the work carried out and the results obtained therein.

Chapter 1 reviews the history and development of the TL effect, outlines different theoretical models along with the theory of TL spectroscopy. Applications of TL effect have been specially emphasized in this chapter.

Chapter 2 gives a detailed account of the experimental setup used for the present studies. For the study of TL effect, both pulsed and continuous wave (CW) lasers are used. Pulsed laser such as Optical Parametric Oscillator (OPO) and continuous lasers such as diode pumped solid-state laser and Argon ion laser are used as the excitation beam. He-Ne laser is used as the probe beam in the TL setup. The details of the detectors such as Digital storage oscilloscope, Lock-in amplifier, Monochromator-PMT assembly, Photodetectors, etc., used in different studies are detailed in this chapter.

Chapter 3 describes the use of dual beam thermal lens technique for the evaluation of fluorescence quantum yield of dye-doped polymers. Solid-state lasers provide an alternative to conventional liquid lasers because of their various technical and economical advantages. Luminescence quantum efficiency is one of the most important optical properties of fluorescent materials. The TL method, for evaluating quantum yield, offers significant advantages over conventional methods because the absolute values of quantum yield can be measured and no standard sample is required. TL method can be effectively used to study the variation of fluorescence quantum yield of Rhodamine 6G doped PMMA for a range of concentrations. The photodegradation of the dye molecules under cw and pulsed laser excitation are also studied using the present method details of which are included in this chapter.

Chapter 4 deals with intermolecular transfer of electronic energy, which has become a powerful tool for obtaining information about molecular excited states not obtainable by ordinary spectroscopic methods. Without electronic energy transfer, the photosynthetic process in plants could not be as efficient as it is or might not operate at all. Excitation energy transfer processes are important controlling factors in fields ranging from radiation physics to biology.

Energy transfer from a donor molecule to an acceptor molecule in a dye mixture affects the operation and spectral output of the dye laser. The energy transfer rate and the distance between molecules like

Rhodamine6G- Rhodamine B and Fluorescein – Rhodamine B are evaluated using this method. The variation of quantum yield with pH of Fluorescein and Rhodamine B are discussed in detail in this chapter.

Chapter 5 gives a detailed account of the nonlinear absorption process occurring in organic liquid like aniline. Two photon induced thermal lens spectra of aniline are recorded using Optical Parametric Oscillator (OPO). The overtone frequencies are also determined using this technique. The thermal lens spectra of Rhodamine B and Crystal Violet are also discussed in this chapter.

Chapter 6 describes a method of implementing AND, OR and NAND optical logic gates using dual beam thermal lens technique. The rapid growth of the Internet demands faster speeds and larger bandwidths than electronic circuits can provide. The speed of computers has now become a pressing problem as electronic circuits reach their miniaturization limit. This can be overcome by using optical data processing. Logic gates are the building blocks of any digital system. An optical logic gate is a switch that controls one light beam with another. Optical media used in this experiments are chemically stabilized Rhodamine 6G doped PMMA.

Chapter 7 presents the use of TL technique as a tool to study the rate of inorganic chemical reactions like that of potassium iodide – potassium persulphate. The reaction is monitored using lock-in amplifier and from the reaction curve we can calculate the reaction rate. Argon ion laser is used as the pump source for this study.

Chapter 8 gives a general conclusion and future prospects of the work carried out in the present thesis.

Publications in Journals

1) Study of energy transfer in organic dye pairs using thermal lens technique
Achamma Kurian, K P Unnikrishnan, Pramod Gopinath, V P N Nampoori and C P G Vallabhan, *J. of Nonlinear Optical Physics & Materials*, 10, 415-421 (2001).

2) Thermal lens spectrum of organic dyes using Optical Parametric Oscillator
Achamma Kurian, K P Unnikrishnan, D. Sajan George, Pramod Gopinath, V P N Nampoori and C P G Vallabhan, Spectrochimica Acta *Part A* (in press).

3) Effect of pH on quantum yield of fluorescein using thermal lens technique
Achamma Kurian, Nibu A George, D. Sajan George, K P Unnikrishnan, Binoy Paul, Pramod Gopinath, V P N Nampoori and C P G Vallabhan, *J. Opt. Soc. India*, (in press)

4) Realization of logic gates using thermal lens technique
Achamma Kurian, Nibu A George, Thomas Lee S, D. Sajan George, K P. Unnikrishnan, V P N Nampoori and C P G Vallabhan, *Laser Chemistry*, (in press)

5) Application of laser beam deflection technique to study the diffusion process in electrolyte solutions
Achamma Kurian, C.V. Bindhu. S. S. Harilal, Riju C Issac, V P N Nampoori and C. P. G. Vallabhan, *Pramana J. of Physics*, 43, 401-406 (1994).

6) Realization of NAND & XOR logic gates using Thermal lens effect
Achamma Kurian, K P Unnikrishnan, Pramod Gopinath, Binoy Paul, V P N Nampoori and C P G Vallabhan, Photonic systems & Applications, 27-30, Nov. 2001, Singapore, *Proccedings of SPIE*, PP 100-106.

7) Nonlinear absorption and optical limiting in solutions of some rare earth substituted phtahlocyanines
K P Unnikrishnan, Jayan Thomas, Binoy Paul, **Achamma Kurian**, Pramod Gopinath, V P N Nampoori and C P G Vallabhan, *J. of Nonlinear Optical Physics & Materials*,10, 113, (2001).

8) Two and three photon absorption in rhodamine 6G methanol solutions using pulsed thermal lens technique
C.V.Bindhu, S.S.Harilal, **Achamma Kurian**, V P N Nampoori and C P G Vallabhan, *J. of Nonlinear Optical Physics& Materials,*10, 113 , (1998).

9) Studies on two photon absorption of aniline using thermal lens effect,
Achamma Kurian, K P Unnikrishnan, Thomas Lee S, D. Sajan George, , V P N Nampoori and C P G Vallabhan (communicated to *J. of Nonlinear Optical Physics & Materials*).

10) Studies on fluorescence efficiency and photodegradation of Rhodamine 6G doped PMMA using thermal lens technique,
Achamma Kurian, Nibu A George, Binoy Paul, V P N Nampoori and C P G Vallabhan, (communicated to *Laser Chemistry*).

CONTENTS

1

Thermal lens spectroscopy - An overview

This chapter introduces different photophysical processes taking plare 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.

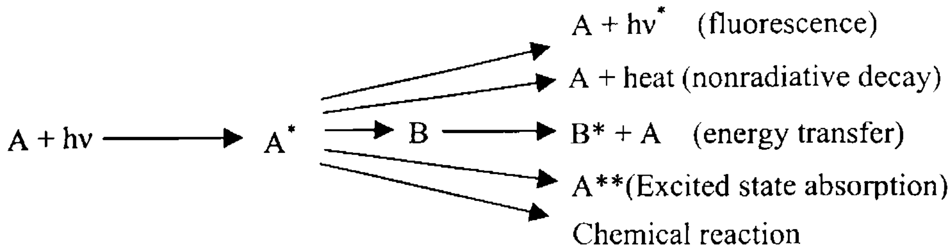
1.1 Introduction

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

$$\text{Stokes' shift} = 10^7\left(\frac{1}{\lambda_{ex}} - \frac{1}{\lambda_{em}}\right) \text{ nm}^{-1} \qquad (1.1)$$

where λ_{ex} and λ_{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.

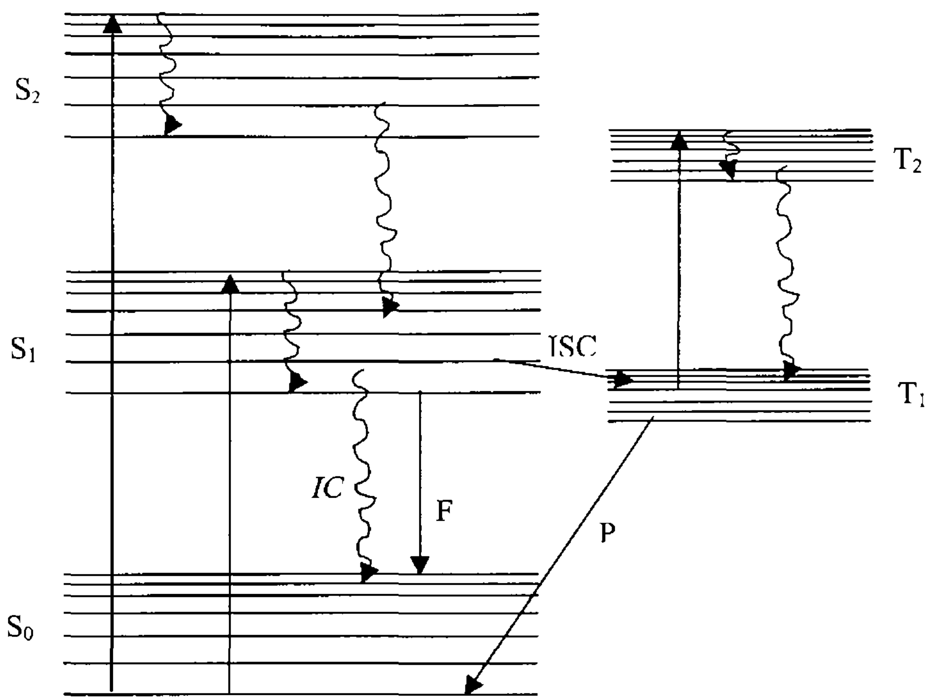


Figure 1.1 Energy level diagram of typical dye molecule illustrating several optical and kinetic processes (A-absorption, IC-internal conversion, F-fluorescence, P-phosphorescence and ISC-intersystem crossing)

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.

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

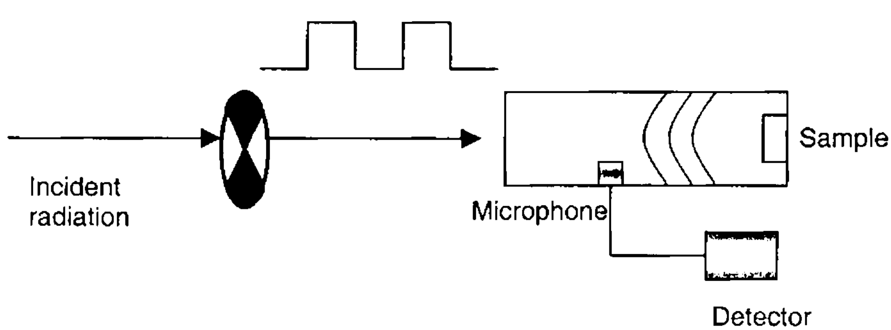


Figure 1.2 Photoacoustic effect

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.

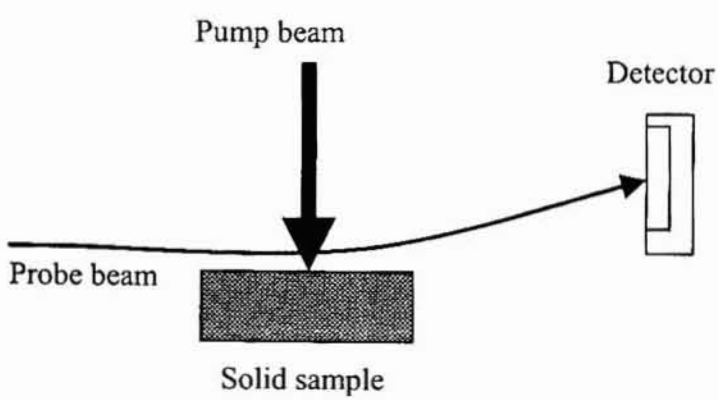


Figure 1.3 Photothermal deflection

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

$$I_r = I_0 e^{-2r^2/\omega^2} \tag{1.1}$$

where ω 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