Chapter 1

General Introduction

This thesis describes the application of laser induced photothermal phenomena for the study of nonlinear phenomena in certain organic compounds. We attempted photothermal studies in laser dyes and fullerenes for a better understanding of the different nonlinear processes taking place in these molecules. Thermal lens and photoacoustic techniques were employed. First two sections of this chapter presents a brief introduction into different photothermal techniques like thermal lensing and photoacoustics. In the preceding sections a brief description of the photophysical properties of laser dyes and different nonlinear absorption mechanisms are given.
Photothermal Phenomena

The warming effect of sunlight on a cool morning is perhaps one of most pleasurable experiences offered by nature. Observation of the thermal effects of electromagnetic radiation has played an important role in the discovery and understanding of many natural processes. In modern times, interest in the thermal effects of radiation developed with the invention of the laser. This is because of the special properties which laser beams possesses in contrast with ordinary light beams.

Lasers can provide highly directed, highly monochromatic radiations with high power densities. Following the invention of the laser, many of its striking applications to analytical measurements have been reported [1]. Improvements over conventional light sources have been possible when one takes advantage of special properties of laser light. High power levels can lead to larger signals in laser-excited fluorescence [2] and thermo-optical effects [3], as well as in new types of signals in, e.g., two photon excited fluorescence [4]. Coherence can enhance interferometric measurements [5]. High resolution can provide unique and accurate information in atomic spectroscopy [6]. Good collimation and polarization properties can improve polarimetric measurements [7]. Short pulse durations allow temporal resolution of events. In recent times ultrafast events have been successfully studied with femtosecond laser pulses.

During the past few years an optical technique, called photothermal technique has been developed to investigate the optical properties of materials that are unsuitable with the traditional spectrophotometry. In photothermal spectroscopy, the energy absorbed by the material as a result of its interaction with incident radiation is measured directly and the heat produced by nonradiative decay of excited species acts to modify the optical properties of the sample [8]. Photothermal effects are caused by the heating of a sample after the absorption of optical energy (or in general, the absorption of an energetic beam). After optical absorption, other deexcitation channels besides heating can also occur, as indicated in fig.1.1. These other deexcitation branches complement the heating branch in the sense that all branching ratios must add up to one. Photothermal heating of a sample is produced with the use of laser beams, xenon arcs or other intense light sources [9-14].

All photothermal techniques have a common origin in the use of electromagnetic radiation in the UV to IR region of the spectrum as probing radiation and in this respect are similar to conventional UV/VIS spectroscopies. Unlike these, however, the sample is not quantified by transmission or luminescence but rather by the nonradiative de-excitation of excited states,
Thermal deexcitation

Optical Absorption Heat

Figure 1.1: Possible consequences of optical absorption.

Table 1.1 Detection techniques for photothermal spectrometries

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<th>Technique</th>
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<td>Pressure wave in a closed cell containing the sample, contacting gas and microphone. Attached sensor detects the thermal wave in the sample by deformation or temperature rise.</td>
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<td>(a) Microphone</td>
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which results in a change in temperature of the substrate or contacting medium. Often these techniques employ a laser to provide a modulated or pulsed excitation beam which is tuned to the absorption maximum of a chromophore and focused into the sample. Subsequent non-radiative relaxation generates a thermal wave which can be detected in the sample or in the
contacting medium using any of several different detection schemes summarised in Table 1.1.

The advantages of photothermal techniques are: 1) photothermal heating can provide convenient and sensitive methods for detecting optical absorption in matter 2) information concerning deexcitation mechanisms can be obtained. 3) very delocalized or very rapid photothermal heating can be achieved to provide novel measurements or produce new effects.

1.1 Thermal Lens Spectroscopy

The thermal lens (TL) effect or thermal blooming was discovered by Gordon and co-workers [15] only a few years after the invention of the continuous wave (cw) laser. While carrying out an intracavity excitation of a liquid sample for Raman spectroscopy, the authors observed time-dependent changes in the laser intensity which they could attribute to localized heating of the sample. They derived a theory for the thermal defocusing of the beam, which predicted the magnitude and time constant of the response.

The TL effect may be described as a change in the optical path of the sample induced by absorption of a laser beam. Fig.1.2 represents schematic of the TL effect. A laser beam passes from left to right through the sample having an optical length bounded by the vertical lines. The initial unheated sample and far-field beam profile are shown in fig.1.2 (a). A steady state TL and the beam profile are shown in fig.1.2 (b). In a typical TL experiment, the sample is illuminated with a laser beam having gaussian intensity distribution. Some of the incident energy is absorbed by the sample or by the chromophore within the sample. Excited states formed in this way may either lose energy radiatively e.g., fluorescence or phosphorescence or by nonradiative routes e.g., internal conversion or by interaction with other molecules in the sample which results in the generation of heat. The flow of heat from the region illuminated by the laser results in a thermal gradient that is proportional to the beam intensity profile in the sample. Heating is stronger at the centre of the beam profile than in the wings. The temperature gradient creates a refractive index gradient. The greater heat produced at the beam center raises the temperature and, for most liquids that expand upon heating, lowers the refractive index, n. This creates a shorter optical path, nl, along the center of the beam path, where l is the physical length of the sample. The resulting thermo-optical element has the shape of a negative lens which causes the laser beam to diverge. As the beam passes through the solution, it progressively diverges. The degree of divergence depends upon the power of the laser beam and the absorption coefficient of the sample. The increased divergence of the beam may be observed some distance beyond the sample as a larger spot size or a lower
1.1.1 Thermal Lens Theory

In this section the theory of the TL effect is described, and this enables one to determine the absorbance of a sample by this technique. This theory also identifies the optical and sample-dependent factors that affect the measurement sensitivity. The TL effect has been theoretically treated under a variety of experimental conditions [16-30]. The existing theoretical models range from relatively simple formulations to complex and sophisticated derivations. These models cover TL effects which are generated under different excitation conditions (pulsed and cw excitation), different pump-probe geometries (single beam, dual beam, collinear and crossed beam configuration, pump and probe beam displacements) and different sample conditions (stationary and flowing samples).

Generation of temperature gradient inside the irradiated sample is common to all photothermal techniques. The first step in the derivation of a theoretical TL model is, therefore, the solution of the appropriate nonsteady thermal diffusion equation [30],

$$\frac{\partial T(r,t)}{\partial t} = D \nabla^2 T(r,t) - v_x \frac{\partial T(r,t)}{\partial x} + \frac{1}{\rho C_p} Q(r,t) \quad (1.1)$$

where $T(r,t)$ is temperature, $D$ is the thermal diffusivity, $\rho$ is the density and $C_p$ is the specific heat at the constant pressure of the medium of the uniform velocity $v_x$ in the $x$ direction. $Q(r,t)$ is the source term which represents the heat produced per second per unit volume of the sample due to the absorption of pump beam light and the subsequent radiationless deexcitation of excited atoms or molecules in the sample. The source term depends mainly on the mode of excitation and other experimental parameters. These dependencies can be
written in simplified forms if the sample is optically thin (transmittance \( z \approx 1 \)), which is usually in the case of TL measurements.

For pulsed excitation case, \( Q(r,t) \) during excitation \((0 \leq t \leq t_0)\) is given as

\[
Q(r,t) = \frac{2 \ln(10) \alpha E_0}{\pi \alpha^2 t_0} \exp \left( -\frac{2(\omega^2 + \gamma^2)}{\alpha^2} \right)
\]  

(1.2)

where \( E_0 \) is the energy of the laser pulse, which is propagating in the \( z \)-direction, \( \alpha \) is the decadic absorption of the medium per unit length, and \( \gamma \) is the \( 1/e^2 \) radius of the pump beam with Gaussian profile. After the excitation \((t > t_0)\), \( Q(r,t) \) equals zero.

For the case of cw excitation \( Q(r,t) \) is given as

\[
Q(r, t) = \frac{2 \ln(10) \alpha P_{av}}{\pi \alpha^2} \exp \left( -\frac{2(\omega^2 + \gamma^2)}{\alpha^2} \right) (1 + \cos \omega t)
\]  

(1.3)

where \( P_{av} \) is the average power of the beam, which is sinusoidally modulated at a frequency \( F = \omega/2\pi \). As a result the power \( P \) of the beam oscillates between \( P=0 \) to \( P=2P_{av} \).

When the source term is known, one can obtain time dependent temperature distribution inside the sample \((T(r,t))\). This can be evaluated for any particular case of excitation by substituting the appropriate expression for \( Q(r,t) \) into eqn. (1.1).

In pulse mode excitation case temperature distribution in the sample cell \( T(x,y,t) \) may be written as

\[
T(x, y, t) = \frac{2 \ln(10) \alpha E_0}{
\pi t_0 \rho C_p} \int_0^{t_0} \frac{1}{8D(t - \tau) + a^2} \times \exp \left( -\frac{2[(x - u_x(t - \tau))^2 + y^2]}{8D(t - \tau) + a^2} \right) \, d\tau
\]  

(1.4)

when \( t > t_0 \). Similarly, the solution of equation for cw excitation mode is given by

\[
T(x, y, t) = \frac{\ln(10) \alpha P_{av}}{
\pi \rho C_p} \int_0^t \frac{1 + \cos \omega t}{8D(t - \tau) + a^2} \exp \left( -\frac{2[(x - u_x(t - \tau))^2 + y^2]}{8D(t - \tau) + a^2} \right) \, d\tau
\]  

(1.5)

Due to nonuniform radial temperature distribution, time dependent refractive index gradient is formed inside the sample and can be described as

\[
n(x, y, t) = n_0 + \left( \frac{\partial n}{\partial T} \right)_{T_A} T(x, y, t)
\]  

(1.6)

where \( n_0 \) is the unperturbed refractive index at ambient temperature \( T_A \).

The irradiated sample acts like a lens, which affects the laser beam intensity profile by altering its radius \( w \). Relative changes in the beam intensity which are proportional to the relative changes in the power of the beam reaching the detector are, therefore, a direct
measure of the TL strength. Since the change in beam radius is usually small (weak TL approximation), the TL signal \( s(t) \) for a laser beam with a Gaussian profile is given as

\[
s(t) = \frac{w_2^2(t) - w_2^2(0)}{w_2^2(0)}
\]

where \( w_2(0) \) is the radius of the unperturbed beam at the detector site and \( w_2(t) \) is the time dependent radius of a beam perturbed by a TL. \( w_2(t) \) may be found by using an appropriate ray transformation matrix according to the so-called ABCD law [16, 31], which gives

\[
w_2^2(t) = w_0^2 \left[ \left( 1 - \frac{z_2}{f(t)} \right)^2 + \frac{1}{z_0^2} \left( z_1 + z_2 - \frac{z_1 z_2}{f(t)} \right)^2 \right]
\]

where \( z_2 \) is the distance between the sample and the detector, \( z_1 \) is the distance between the probe beam waist and the sample and \( w_0 \) is the radius of the probe beam at its waist, \( z_0 = \pi w_0^2/\lambda \) is the confocal distance of the probe beam with a wavelength \( \lambda \) and \( f(t) \) is the focal distance of the TL.

Substituting eqn. (1.8), eqn. (1.7) can be simplified for weak TL case \( (f(t) \gg z_1 \) and \( z_0) \). Knowing that at \( t=0, f(0) = \infty \), \( s(t) \) for the far field approximation \( (z_2 \gg z_1 \) and \( z_2 \gg z_0) \) can be written as

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

When calculating the focal distance of the TL, which is needed to evaluate the TL strength, it is necessary to consider different possible geometrical configurations of pump and probe beams. Most frequently collinear configuration is used, even though geometries of transverse [32] as well as obliquely crossed [33] TL were also utilized and treated theoretically.

The steady state focal length of the induced lens given in the parabolic approximation of the lens is given by [34]

\[
f = \frac{\pi k w^2}{2.303 P(\text{dn/dT}) A}
\]

where \( k \) is the thermal conductivity of the sample, \( P \) is the laser excitation power and \( A \) is the absorbance of the sample. Thus as \( P, \text{dn/dT} \) and \( A \) get larger then the focal length of the lens gets shorter and the beam divergence increases.

By combining eqns. (1.9) and (1.10) and by taking adequate derivatives of eqns. (1.4) and (1.5), expressions for TL signal under pulsed or cw excitation conditions can be obtained. It is however, much more convenient to use somewhat less complex expressions to illustrate the differences in the dependency of the TL signals on experimental parameters. The focus will placed on nonflowing samples \( (v_z=0) \) and on cases where displacement between the probe and
the pump beam beam is negligible. Since the TL signal is usually measured as the relative change in the probe beam center intensity, \( x = y = 0 \) can also be assumed.

For excitation with a very short laser pulse \((t_0 \rightarrow 0; \text{ impulse approximation})\) the assumptions mentioned above yield the following expression for the TL signal \([30]\]

\[
s_p(t) = -\frac{4\ln(10)AE_0x_1}{\pi ka^2t_c}\frac{\partial n}{\partial T}(1 + 2t/t_c)^2 \tag{1.11}
\]

where \( s_p(t) \) is the TL signal with pulsed mode excitation, \( A = \alpha l \) is the absorbance of the sample, \( t_c = a^2\rho C_p/4k = a^24D \) is the characteristic time constant of the TL experiment, and \( k \) is the thermal conductivity of the sample.

Similarly TL signal \( s_c \) corresponding to cw excitation is given by

\[
s_c(t) = -\frac{2\ln(10)APz_1}{\pi ka^2}\frac{\partial n}{\partial T}(1 + t_c/2t) \tag{1.12}
\]

It must be noted that eqns. (1.11) and (1.12) are subject to certain limitations, which originates from the approximations used during their derivations. From these equations it is found that the TL signal strength is strongly dependent on the energy of the pulsed laser or the power of a cw laser used for excitation. Eqns. (1.11) and (1.12) indicate that the TL signal also dependent on the size of the pump beam. Since \( t_c \) is related to the inverse square of the pump beam radius the pulsed excitation is advantageous, particularly in the case of small volume samples.

### 1.1.2 Sensitivity and Temporal Characteristics

The sensitivity of a pump-and-probe method depends on the relative positions of the two beams in the sample. If the pumping laser is much smaller than the probe, the fraction of the probe beam which is affected by the refractive index gradient would be small, resulting in a minimal effect on the probe beam divergence. If the spot size of the source beam is much larger than the probe, the entire probe beam is affected, but by a weaker refractive index gradient. As a result, the maximum effect on the probe beam divergence occurs when the pump laser beam within the sample is approximately the same size as the probe beam.

The relative change in the intensity induced by the TL reaches a steady state value after several time constants. The relative change in the beam centre intensity can be related to the absorbance through the relation \([34]\)

\[
\frac{\Delta I_{bc}}{I_{bc}} = 2.303EA + \frac{(2.303EA)^2}{2} \tag{1.13}
\]
where $E = -P(dn/dT)\lambda k$ is the enhancement in sensitivity over transmission measurement that would produce a relative intensity change

$$\frac{I_0 - I}{I_0} = 1 - 10^{-A} \approx 2.303A$$  (1.14)

for small absorbances.

The sensitivity of a TL measurement, therefore, depends linearly on laser power. The choice of solvent can greatly influence the enhancement one observes for the laser power available [16]. Nonpolar solvents like carbon tetrachloride are particularly advantageous since they exhibit a large $dn/dT$ and small thermal conductivity. The sensitivity of TL measurement made in water under similar conditions would be 30 times smaller. The time constant of the TL effect also varies with solvent to a lesser extent. The time constant depends quadratically on the beam spot size while the sensitivity is independent of spot size. This is somewhat surprising since the strength of the TL increases with decreasing spot size as shown by eqn. (1.10). This can be explained as follows. For a laser beam having gaussian intensity profile, in the far-field region of the beam at large distances from the waist, the spot size, $\omega$ increases linearly with propagation, or equivalently, the divergence angle $\phi$ becomes constant [16]

$$\phi = \tan^{-1} \frac{\omega}{Z} \approx \frac{\omega}{Z} = \frac{\lambda}{\pi \omega_0}$$  (1.15)

where $\omega_0$ is the spot size at the beam waist. Hence, the concomitant increase in the divergence angle of the beam, $\phi$, with decreasing spot size, shown in eqn. (1.15), exactly cancels the effect of the stronger TL.

It is instructive to examine the refractive index and temperature sensitivity of the TL effect. Assuming a 1% change in the beam center intensity can be detected, the corresponding induced phase shift is $\theta = 0.01 = -2\pi \Delta n b/n\lambda_0$, where $b$ is the sample path length and $\Delta n$ is the refractive index change at the beam center compared with the edges. For a 1-cm path length and $\lambda_0 = 632.8$ nm, the relative change in the refractive index is only $\Delta n/n = -1.0 \times 10^{-7}$. For a solvent having a large $dn/dT$ such as carbon tetrachloride, this refractive index change corresponds to a temperature difference of $\Delta T = 2.5 \times 10^{-4}$ K. The sensitivity of a spatially coherent laser beam to such small refractive index gradients is the basis of the detection capabilities of the TL effect.
1.1.3 Measurement Approaches

1.1.3.1 Single - Beam Measurements

Single-beam TL spectrometers are unique among the TL instruments because the same laser beam is used to excite the sample and simultaneously probe the TL formed. Single beam setup was used in the early stages of TL technique. Initially, they were applied to study the dependence of the TL effect on parameters such as laser power, beam divergence, sample length, concentration and flow [35-37]. Application of TL in the chemical analysis has not been realized until 1979 when Dovichi and Harris [38] used the technique to detect CuII at ppm levels. Authors still used the single beam configuration, despite the availability of dual beam instruments, which should provide better sensitivity. The reason for this, and for the relatively frequent use of single beam instruments is probably due to relative simplicity of such instrument and ease of operation compared to dual beam instruments i.e., only one laser is used to generate and detect TL.

In single beam TL instrument, the laser beam is focused with a lens and modulated with a chopper or shutter. After passing through 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 gives the transient change in the beam center intensity.

The single beam method of TL measurements can be used to produce a differential response by optical means [39]. Reference and unknown samples are located on opposite sides of the beam waist so that the TL strengths of the two samples are subtracted by their opposite effect on the far-field beam spot size. This differential configuration was found to exhibit immunity from laser power fluctuations, but is limited to sufficiently weak TL, so that the divergence of the beam responds linearly to the absorbance in each cell.

The positioning of the sample with respect to probe beam waist is essential to obtain high sensitivity of the TL measurements. As can be inferred from eqn. (1.12) the sample should be positioned as far as from the probe beam waist as possible in order to observe the largest effect of the TL on the beam. However, because the same beam is probing the TL, one must take into account the decrease in power density due to the increase in beam radius with distance. The TL signal should be maximum when the sample is positioned at one confocal distance from the beam waist \( z_1 = z_0 \). For such a case eqn. (1.12) can be written as

\[
s_c(t) = -\frac{\ln(10)AP\partial n}{\pi k} \frac{1}{\partial T(1 + t_c/2t)}
\]

(1.16)
This expression was obtained under the assumption that the TL is a perfect thin lens (parabolic refractive index distribution) with no aberrations. Such an approximation gives a good qualitative description of the TL but is quantitatively inaccurate. Sheldon and co-workers [42] derived a more accurate theoretical model which takes into account the true aberrant nature of the TL. According to the aberrant TL model the sample should be placed at a distance $z_0/\sqrt{3}$ from the beam waist to obtain maximum TL signal which is given by

$$s_c(t) = -\frac{\ln(10)AP\partial n}{\pi k} \tan^{-1}\left(\frac{1}{(1 + t_c/t)\sqrt{3}}\right)$$

(1.17)

Nevertheless, the optimal position for the sample cell is most frequently found experimentally and not by calculation, which requires accurate data on beam radius that is difficult to obtain.

1.1.3.2 Dual-Beam Configurations

In dual-beam TL method, the generation and detection of the TL was achieved separately by a modulated pump beam and nonmodulated probe beam respectively. A high power cw or pulsed laser usually serves as the source of the pump beam, while the probe is derived from relatively weaker cw laser. By using separate lenses to focus the excitation beam directly onto the sample and to mismatch the beam waists of the pump and probe beam, the highest TL signal strength can be achieved. Good spatial overlapping of both beams inside the sample is necessary for optimal sensitivity. The alignment and combining of the two beams is facilitated by a beam splitter or dichroic mirror. The generated TL produces fluctuations in the intensity of the probe beam that can be sensitively monitored by signal averaging devices such as lock-in amplifiers and boxcars, provided that the excitation beam is filtered out before reaching the detector. Signal intensities in a dual beam TL experiment usually obtained from the differences $(I(t) - I(0))$ between the probe beam center intensities at the beginning $(I(0))$ and at the end $(I(t))$ of pump laser excitation.

The first report of dual beam TL measurements were the work of Grabiner et. al. [40]. They used a He-Ne probe laser beam to measure the time resolved formation of the TL as monitor of energy transfer in gas phase molecules pumped by a pulsed CO$_2$ laser. The first application of the dual beam TL technique to spectroscopic absorption measurements was the work of Long et. al [41]. Swofford and Morrel [27] have presented the mathematical analysis of the cw dual beam TL technique by extending the model of Gordon et. al [15] to account for the cumulative effect of the chopped heating beam. Fang and Swofford [43] have discussed in detail the various experimental requirements that are to be met in carrying out TL experiments in particular.
Modeling the response of a dual-beam TL experiment is more complicated than the single-beam theory presented since one must take into account the confocal parameters and spot sizes of both pumping and probing laser beams [43]. Using the simplifying assumption that the spot sizes of the two beams in the sample are approximately equal, which probably produces less than optimum sensitivity [44, 45], a numerical model for the dual beam experiment was developed [46]. An analytical solution to the frequency response was also published [47] and the results, expressed in terms of a reduced frequency, \( \nu_0 = \pi \nu t_c \), where \( \nu \) is the chopping frequency and \( t_c \) is the TL time constant. While the response is found to decrease markedly for chopping at frequencies, \( \nu > 0.1t_c^{-1} \), the signal-to-noise ratio over a similar range of \( \nu_0 \) was found to be nearly constant [47].

### 1.1.3.3 Comparison of Single and Dual Beam Configurations

In single beam TL experiment, one uses a single laser source to provide both the sample excitation and the means for probing the heat produced by the absorption process. In many cases however, the use of separate laser sources for the pump and probe beams can provide significant benefits in performance. For example in absorption spectroscopy, where the pump laser is to be tuned over a wavelength range, the point by point measurement scheme of the single beam technique becomes very time consuming and cumbersome. In such cases the use of separate lasers to pump and to probe the TL will be more advantageous. Since only a single wavelength is always detected, the detection optics and detectors need to be optimized only for a single probe wavelength, one need not take into account the spectral response of the optical elements and the detector.

The principal advantage of single beam configuration over pump - and - probe is optical simplicity. No matching of beam spot sizes, coaxial alignment of beams, or careful overlap within the sample is required. The beam needs only to be focused through the sample and centred on the detector in the far field and the sample translated to find the position of maximum response. This greatly reduces the likelihood of spurious results due to drift in alignment as well as the cost of the experimental set up in optical mounts and alignment effort.

An experimental comparison of the dual-and single-beam TL methods was published [48]. Under the constraint of equal spot sizes at the sample, the ratio of the sensitivities was found to agree with the theoretical prediction:

\[
\frac{E_p}{E_s} = \frac{(dn/dT)_p \lambda_s}{(dn/dT)_s \lambda_p}
\]  

(1.18)
where s and p subscripts correspond to the single beam and probe beams, respectively. This result indicates a potential sensitivity advantage for probing with a shorter wavelength laser beam, which would be significant for improving the sensitivity of infrared absorption measurements made with a TL [49]. The reproducibilities and limits of detection for the single- and dual-beam configurations were found to be equivalent, probably affected by a common source of noise. Since the intensity noise of the two lasers was quite different, the sample must be contributing to the uncertainty in the two measurements, either from convection [50] and/or small particles [51].

1.1.4 Important Applications of Thermal lens

TL technique finds many applications in different fields of science and technology. An excellent review by Snook and Lowe [52] gives a detailed account of the applications of TL spectroscopy. Only a few important applications will be discussed in the preceding sections.

1.1.4.1 Trace detection

The TL effect has begun to be developed as a new tool for trace-level determinations [53-57]. Grabiner and co-workers [58] suggested that the excellent sensitivity of the TL technique could prove to be valuable for the detection of trace concentrations of absorbing species in atmospheric samples. This work and that of Nieman and Colson [59], where TL spectroscopy was used in a study of the electronic states of trans-butadiene and SO₂, implies that TL spectroscopy is useful in the determination of characteristics of molecules in the gaseous phase. The change in refractive index with temperature of a typical gas at 1 atm pressure, nitrogen for example, is only 0.9×10⁻⁶ K⁻¹, which is a factor of 600 smaller than liquid CCl₄ [60]. Due to the small density and heat capacity, time constants for the TL effect in gases are very short. The short time constants in gases point to a significant sensitivity advantage for pulsed excitation, since the breakeven pulse energy, \( E_b = P \cdot t_c \), is proportional to \( t_c \) [16]. The above concepts were described in detail in the first analytical paper on gas-phase thermal measurements [54].

The first study of the application of the TL technique to trace solute determination was by Dovichi and Harris [38]. TL measurements have also been carried out for the determination of iron [61-66]. Spectrophotometric determination of nonmetals has also been accomplished using the TL. Nitrite [44] was detected at a 0.2 nM concentration using a single-beam TL experiment. Hu and Whinnery [65] first observed the anti-symmetric dependence of the TL
lens effect on the position of the induced TL relative to a waist in a Gaussian beam. Dovichi and Harris [39] constructed a differential TL spectrometer. If the value of for the sample is negative, then a diverging lens will ensue if the sample is placed beyond the waist in the beam. If the same sample is positioned an equal distance before the waist, a converging lens will result. Therefore, when two cells, filled with identical weakly absorbing samples, are placed symmetrically about a beam waist, a cancellation of ~ 99% of the TL signal is observed. In this manner, the signal due to the sample matrix or the solvent, can be optically subtracted from that of the sample automatically, if one cell filled with a blank sample, is placed \(3/2Z_c\) before the beam waist, and the sample cell is placed \(3/2Z_c\) beyond the beam waist. Using this experimental arrangement, an improvement in the detection limits of more than an order of magnitude was reported [39]. Theoretical and experimental details of the use of TL on the kinetic determination of chemical reactions have been reported by various authors [44].

1.1.4.2 Measurement of Absolute Absorption Coefficients

The assumption that the signal generated by a TL spectrometric experiment is proportional to the absolute absorption coefficient was made in most of the initial publications on this technique [66-68]. Whinnery [68] assumed that the thermal energy absorbed from a laser beam passing through a nearly transparent material allowed the measurement of the absorption coefficient with sensitivities of \(< 10^{-5}\) cm\(^{-1}\). Twarowski and Kliger [69] measured the two photon absorption spectrum of benzene with a pulsed nitrogen laser pumped dye head in the range 360-530 nm using a series of laser dyes. Carter and Harris [70] showed that the detection limits for the smaller sample volume (pathlength = 0.1 cm) reflect greater precision and a larger sensitivity compared with the greater sample volume (1cm).

1.1.4.3. Chromatographic Detection and Flow Injection Analysis

The sensitivity of the TL technique, the small volume characteristics of a focused laser beam, and the more general applicability of thermal rather than fluorescence detection have made this method an attractive detector for liquid chromatography and flow injection analysis [71, 72]. Given the need for selectivity in TL measurements, combining these methods would appear to be mutually beneficial. To use a TL as a detector of a flowing process, the effect of flow on the measurement needed to be considered [73].

The first application of TL detection to liquid chromatography employed a single-beam experiment [74]. A dual-beam instrument was tested with conventional [47] and microbore
HPLC [75]. The combination of TL detection and flow injection analysis is also mutually
beneficial. Flow injection analysis has been advocated as a means of reducing contamination
and carry over in ultra trace analysis with laser-based detectors [54].

1.1.4.4. Quantum Yields

Hu and Whinnery [65] were the first to point out that TL technique could be used to measure
the fluorescence quantum yield of organic dyes. The total power absorbed by the dye solution
can be measured spectrophotometrically, and then the power that is converted into heat is
measured by TLS. More details about the fluorescence quantum yield measurements using
TLS are discussed in Chapter 5 of this thesis. Terazima and Azumi [76-78] carried out a series
of investigations to measure the quantum yield of triplet formation and the triplet lifetime of
several different species in the liquid and solid phase, using time - resolved TL method. The
quantum yield of photodissociation of iodine has been studied by Lebedkin and Klimov [79].

1.1.4.5 Heats of Reaction, Energetics and Kinetic Studies

Time resolved TL has been successfully employed to study heats of reaction and energetics
[80] which highlights the potential for TL in fundamental studies of reaction kinetics and
energetics. Since the time-resolved method detects time-dependent heat emitted through
radiationless transitions metastable and excited state information can be obtained which is
not obtainable by other techniques such as flash photolysis.

1.1.4.6 Thermal Lensing in Glass and Other Solid Laser Materials

The characterization of the transmission properties of laser beams through optical glasses,
ruby, sapphire and lithium niobate crystals has been extensively studied for more than two
decades. The existence of undesirable thermal effects associated with the generation of laser
light is a basic problem in the design, and operation of any efficient solid-state laser device.
In 1968, Dabby and Whinnery first termed these thermo-optical effects seen in solid samples,
TL [81]. They observed that TLs were formed in common lead glasses, which decreased
the natural laser beam divergence, demonstrating a positive value for dn/dT. They observed
strong thermal self-focusing of an argon ion laser beam, when it was passed through a 15
cm length of lead glass. Baesso et al [82] measured the absolute thermal diffusivity of soda-
lime glass using a time-resolved TL method and was in agreement with that found using
photoacoustic spectroscopy [83] on an identical sample.
1.2 Photoacoustic Spectroscopy

The photoacoustic (PA) or optoacoustic (OA) effect is the generation of acoustic waves in a sample resulting from the absorption of photons. This process was first invented by Bell [84], Tyndall [85] and Rontgen [86] in 1881. Sunlight was focused onto a sample contained in a cell that was connected to a listening tube. When the sunlight was repeatedly blocked and unblocked, sound could be heard through the listening tube at the sunlight chopping frequency. Although the effect has been known for over 100 years, there has been a recent increased interest in the phenomenon, both in theoretical and experimental studies. This renewed interest stems from several possible reasons. Two of them are the availability of intense light sources such as lasers and development of high sensitivity detection tools for measuring acoustic waves. It has been used to study a variety of chemical and physical phenomena in a number of fields. PA techniques have been shown to be capable of detecting weak absorption features in gases as well as in condensed matter. Furthermore, PA methods are finding many unique applications, such as in spectroscopic studies of opaque or powdered materials, studies of energy conversion processes, and nondestructive evaluation or imaging of invisible subsurface defects in solids [87-91].

The essential feature of photoacoustic spectroscopy (PAS) is that the heat deposited in the sample by the absorption of a modulated light beam is detected. Thus PAS has the following advantages: (a) it can be used for strongly light scattering materials and (b) the PA signal is dependent on the excited state decay pathways resulting in acoustic generation. These features distinguish PAS from other spectroscopic methods.

This section is meant for describing the PA generation processes, the acoustic detection methods and a brief account of the applications of PA, but not to be an extensive review. Detailed reviews of the PA theory and applications have been discussed by various authors [92-99].

1.2.1 Principle of Operation

The basic theory behind PA detection is quite simple. Light absorbed by a sample will excite a fraction of the ground-state molecular population into higher energy levels. In general, following electronic excitation, a molecule has three channels open to it: (i) it may luminesce, leaving little or no heat in the sample; (ii) it may undergo photochemistry, again leaving little or no heat in the sample; or (iii) it may do nothing, i.e., cascade through the manifold of electronic-vibrational-rotational levels to finally reach its ground state with the surrounding
molecules concomitantly being heated. It is this part of the excitation energy, which is conventionally called the radiationless pathway. The nonradiative component will ultimately generate heat in the localized region of the excitation light beam. If the incident radiation is modulated, the absorption of energy is interrupted at the frequency of modulation and consequently the heat produced in the sample after energy conversion also appears at this frequency. This temperature rise in a closed system of constant volume produces a periodic increase in pressure which follows the modulation frequency of the incident radiation. The pressure wave is then detected with a suitable sensor such as microphone transducer used for a gaseous sample. PA detection is unique in that it is a direct monitor of the nonradiative relaxation channel and, hence, it complements absorption and fluorescence spectroscopic techniques. It is also an extremely sensitive technique, with the ability to detect highly forbidden optical transitions and trace components in a mixture.

Indeed in the original work of Bell [84], using the sun as the source, distinctly audible signals were detected for various samples using only the unaided ear as the detector. It is apparent, even with the simple apparatus for the demonstration of the PA effect, that the amplitude of the signal is directly proportional to the intensity of the source. In addition, the amplitude of the signal is inversely proportional to the modulation frequency, since at high frequencies the radiant energy supplied to the sample per pulse decreases and thus results in less heat energy per pulse being available to cause the pressure change. It is also observed that the amplitude of the PA signal is greatest with samples of large surface area, e.g., fine powders [100], where the most efficient absorption of radiation by the solid and effective heat transfer to the surrounding gaseous atmosphere is possible.

1.2.2 Generation of Acoustic Waves

PA generation is generally due to photothermal heating effects. The mechanism of sound excitation by the interaction of laser radiation with matter are diverse. In principle there are five important interaction mechanisms which can be responsible for the generation of acoustic waves: dielectric breakdown, vapourization or material ablation, thermoelastic process, electrostriction, and the radiation pressure. Their contribution depends on the parameters of the incident laser beam as well as on the optical and thermal parameters of the medium.

The dielectric breakdown only occurs at laser intensities above \( \sim 10 \text{ GWcm}^{-2} \) which is easily obtainable from a pulsed laser in the focus of lens. This effect has been investigated experimentally and theoretically in detail for gases, liquids and solids [101-104]. The plasma
production related to the dielectric breakdown produces a shock wave which propagates initially at supersonic speed in the medium. The dielectric breakdown is the most efficient process for converting optical energy into acoustic energy. The conversion efficiency can reach up to 30% in liquids [105]. The dielectric breakdown dominates the interaction at high laser intensities, especially in transparent media where sound generation due to ordinary absorption does not occur [106].

The second interaction mechanism, i.e., explosive vaporization in the case of liquids [103] or material ablation on solids [107], is responsible for the acoustic wave generation if the laser energy density within the absorbing volume of the sample exceeds a certain threshold determined by the thermal properties of the medium. The material ablation on solids is usually accompanied by plasma formation. The ejection of material from the surface involves a recoil momentum which propagates into the bulk as an acoustic transient. For liquids the conversion efficiency in this case can reach 1 [108].

For absorbing media the thermoelastic process is important for the sound generation. This process is based on the transient heating of a restricted volume by the absorbed laser energy. The induced temperature gradient produces as a result of thermal expansion, a strain in the body. This causes an acoustic wave which propagates away from the heated zone. The thermoelastic process, i.e., heating without phase change, dominates the excitation of sound in absorbing matter at laser energies below the vapourization threshold. The conversion efficiency in this case is rather low, typically < 10^{-4} for liquids [109].

The electrostriction as the fourth interaction mechanism is always present due to the electric polarizability of molecules in the sample which causes them to move into or out of regions of higher light intensity depending on positive or negative polarizability. These motions produce a density gradient and, consequently, a sound wave similar to that caused by the thermoelastic process [110]. Electrostriction as a sound generation mechanism is only important in very weakly absorbing media where it may limit the PA detection sensitivity. However, it has been demonstrated theoretically [111] and experimentally [95] that by using suitable time-gated detection of the acoustic signal, strong suppression of the electrostrictive component is possible.

In comparison to other sound generating mechanisms the radiation pressure itself is negligible for acoustic wave generation. For the case of total absorption of the laser radiation at the sample surface the amplitude of the radiation pressure is given by $P_{\text{rad}} = I/c$, where $I$ is the laser intensity and $c$ the light velocity in vacuum. For a laser intensity of 1 MW cm$^{-2}$ one obtained $P_{\text{rad}} = 0.3$ mbar compared, for example, to a few bars in the case of thermoelastic
Figure 1.3: some common mechanisms of PA generation. The technique of PA spectroscopy always uses the thermal expansion mechanism.

There are three further mechanisms that play a role only under specific circumstances. These are (a) photochemical effects where molecules AB are formed from the initial species A and B under the action of laser radiation (A+B+hν → AB); (b) molecular dissociation where the opposite takes place (i.e., AB + hν → A+B); and (c) bubble formation [103, 112].

1.2.3 PA Generation

PA generation can be classified as either direct or indirect. Some of the possible PA generation mechanism are given in fig. 1.3. In the direct PA generation, the acoustic wave is produced in the sample where the excitation beam is absorbed [113-116]. In indirect PA generation [117-121], the excitation beam produces a modulated temperature at the surface of a solid or liquid sample. The sample is kept in contact with a transparent coupling medium and time dependent expansion of the coupling fluid is produced. This pressure wave can be sensed by a microphone. Here, the coupling medium is typically a gas or a liquid, and the sample is a solid or a liquid. Both direct and indirect PA generation are widely used for spectroscopic purposes.
PA generation can also be classified according to the two excitation modes: the continuous wave (cw) modulation mode and the pulsed mode. In the cw case, the signal is typically analyzed in the frequency domain; amplitude and phase of one or several Fourier components are measured and narrow-band filters can be used to suppress the noise. In cw modulated PA measurements, the modulation frequency is typically in the 1-1000 Hz regime and the acoustic propagation distance during a period is typically much larger than the sample cell. In such cases, we must first determine the acoustic eigen modes of the sample cell, and the excitation beam will excite an eigen mode to an amplitude depending on the magnitude of the overlap integral of the thermal source with the eigen mode [95]. When systematic noise (like noise to window, PA cell wall, or substrate absorption) dominates in the experimental system pulsed PA detection is usually preferred.

In the pulsed PA technique, the signal is acquired and analyzed in the time domain, making simple gating techniques for noise suppression possible. In pulsed PA measurements, the excitation pulse is typically short (< μs) and the acoustic propagation distance during the excitation pulse is typically much smaller than the dimension of the sample; hence in most cases, the PA pulse shape is independent of boundary reflections, and the sample can often be treated as infinite in extent.

The factors that affect and limit the ultimate sensitivity of PPA technique include (a) Optical absorption signals from windows, (b) scattering of light from the bulk of the liquid being absorbed by the transducer and (c) electrostriction. The signals arising from the first two can be minimized by the choice of low-loss windows, reduction of scattering impurities in the liquid and an appropriate time gating of the acoustic signals. Time gating is very important since scattered light travels at the velocity of light in the medium while the acoustic signal generated in the bulk travels at the acoustic velocity in the medium. Thus the bulk acoustic signal will be delayed as compared to the acoustic signals generated from scattered light. On the other hand for the case of acoustic signals resulting from optical absorption by the windows, the acoustic pulse arrives after that originating from the sample.

The acoustic pulse generated due to electrostriction processes in the laser-irradiated region is of similar to that arising from the bulk absorption, and hence there is no reasonable way to distinguish between the two. The use of short laser pulse durations (giving rise to high optical intensities and correspondingly high electric fields) will increase the effects of electrostriction. It can be shown that the absorption coefficient $\alpha_1$ at which the PA signal and the acoustic signal due to the electrostrictive effect become equal is inversely proportional to the diameter of the laser spot size [121]. For a laser pulse duration of 70 ns and beam spot size ~3 mm
the estimated value of \( \alpha_1 \approx 6 \times 10^{-8} \text{cm}^{-1} \), and if the pulse width is longer, say 1 \( \mu \text{s} \), then \( \alpha_1 \) becomes \( \approx 4 \times 10^{-9} \text{cm}^{-1} \). Further there is negligible dependence of the electrostriction effect on laser wavelength. Hence, even the \( 4 \times 10^{-9} \text{cm}^{-1} \) level does not represent a limitation on the smallest absorption coefficient that can be measured using pulse PA, if the material being studied has a wavelength dependent absorption. The detailed general theories of PA generation tend to be rather involved: to show the important parameters, we consider a simple case of direct and indirect PA generation.

1.2.4 Simple Theory for Direct PA Generation

The simplest case of direct thermal PA generation is indicated in fig. 1.4 for the case of an infinite weakly absorbing medium excited by a narrow pulsed beam producing PA source of radius \( R_s \). It is assumed that the laser pulse width \( \tau \) is sufficiently short so that the thermal diffusion effects can be neglected. The initial expansion \( \Delta R_s \) of the source radius \( R_s \) immediately after the laser pulse is given by [98]

\[
\pi (R_s + \Delta R_s)^2 l - \pi R_s^2 l = \beta V \Delta T
\]  \hspace{1cm} (1.19)

with the initial temperature rise

\[
\Delta T = \frac{E \alpha l}{\rho V C_p}
\]  \hspace{1cm} (1.20)

where \( l \) is the length of the PA cell (assumed long), \( \beta \) is the expansion coefficient, \( V = \pi R_s^2 l \) is the source volume, \( E \) is the laser pulse energy, \( \alpha \) is the absorption length (with \( \alpha l << 1 \)), \( \rho \) is the density and \( C_p \) is the specific heat at constant pressure. Combining eqns.(1.19) and
\[ \Delta R_s = \frac{\beta E \alpha}{2\pi R_s \rho C_p} \]  

The peak displacement \( U(r) \) at the observation point at distance \( r \) from the PA source (for \( r << 1 \)) varies as \( r^{1/2} \) because of conservation of acoustic energy, as described by Landau and Lifshitz for a cylindrical acoustic wave [122]

\[ U(r) = \Delta R_s \left( \frac{R_s}{r} \right)^{1/2} = \frac{\beta E \alpha}{2\pi R_s^{1/2} \rho C_p r^{1/2}} \]  

The peak acoustic pressure \( P(r) \) at position \( r \) is related to the acoustic displacement \( U(r) \) and sound velocity \( c \) by

\[ P(r) \approx \frac{c \rho U(r)}{r} \]  

Substituting eqn.(1.22) in eqn.(1.23), we obtain the peak PA pressure observed at \( r \) for small source radius as

\[ P(r) = \frac{\beta c E \alpha}{2\pi R_s^{1/2} C_p r^{1/2}} \]  

Eqn.(1.24) shows the basis of PA spectroscopy based on direct PA generation. It indicates that the normalized PA signal, defined as the detected acoustic pressure amplitude \( P \) divided by the laser pulse energy \( E \) is proportional to the absorption coefficient \( \alpha \) with a proportionality constant \( K \) that depends on geometry and thermo-elastic properties. Thus, if the laser beam is tunable, the normalized PA spectrum provides an uncalibrated absorption spectrum if \( K \) is unknown. Absolute calibration is possible by calculating \( K = \beta c / (2\pi R_s^{1/2} C_p r) \sqrt{r} \), or more practically, by measuring the normalized PA signal for a known absorber at one wavelength and thus empirically finding \( K \). Eqn.(1.24) also indicates clearly the advantages and features of the PA spectroscopy of weak absorption by direct PA generation. For detecting small \( \alpha \), the signal magnitude \( P \) is increased by using intense laser pulses.

### 1.2.5 Simple Theory for Indirect PA Generation

A simple case of indirect PA generation is indicated in fig. 1.5. In general, indirect PA generation does not provide high sensitivity as the direct PA generation for detecting weak absorptions, basically because it is only a thin layer of a thermal diffusion length at the surface of the solid sample that is thermally coupled to the gas, producing the detected acoustic wave. However, PA generation is very valuable for the case opposite to weak absorption, that is, when the optical absorption is so strong that no light passes through the sample and hence
conventional transmission monitoring fails. A detailed mathematical treatment of the indirect PA generation in solids has been given by Rosencwaig and Gersho, now commonly referred to as R-G theory [94]. R-G theory has been found to be very successful in interpreting most of the experimental results. This theory shows that in a gas-microphone PA cell, the acoustic wave generation depends on the pressure disturbance produced at the sample-coupling gas interface and the transport of this disturbance to the microphone. The generation of the acoustic pressure disturbance depends upon the temperature distribution at the sample surface. Thus the R-G theory could exactly predict the temperature distribution in the gas which directly depends on the absorption of light by the sample. A brief outline of the R-G theory is presented here. The detailed account of the theory is given elsewhere [94].

Let the incident laser beam of radius $r$ and modulated at frequency $f$ be incident on the sample of thickness $l_s$ in a cylindrical cell of radius $R$ and coupling gas thickness $l_g$. Let the sample optical attenuation coefficient be $\alpha$ at the excitation wavelength, and the optical absorption length be $\mu_\alpha = 1/\alpha$. The modulated component of the laser-induced heating is distributed over a diffusion length $\mu_s$ given by [98]

$$ \mu_s = \left( \frac{D_s}{\pi f} \right)^{1/2} \quad (1.25) $$

where $D_s$ is the thermal diffusivity of the sample. We assume that the optical wavelength and the modulation frequency are chosen so that the length $l_s$, $\mu_\alpha$ and $\mu_s$ are in decreasing magnitudes. This represent one of the most interesting cases for PA spectroscopy. Let the
The modulated heat produced within the diffusion length \( \mu_z \), which is the depth in communication with the coupling gas, is only a fraction \( \mu_z/\mu_\alpha \) of the power input \( I_0 \) that is absorbed over a depth \( \mu_\alpha \). The heat conduction in the geometry of fig.1.5 can be described as follows:

Thermal conductivity \( \times \) thermal gradient = thermal power within the diffusion length, which means

\[
k_t \frac{\theta_0}{\mu_\alpha} \approx I_0 \frac{\mu_z}{\mu_\alpha}
\]  

(1.27)

where \( k_t \) is the sample conductivity and \( \theta_0 \) is the amplitude of the temperature variation on the sample surface, which is thermally coupled to an active volume \( V_{\text{act}} \) of the gas, given by (for \( l_g > \mu_g \)),

\[
V_{\text{act}} \approx \pi \mu_\alpha^2 l_g
\]  

(1.28)

where \( \mu_g \) is the gas thermal diffusion length. Using the ideal-gas law, the amplitude \( \delta V \) of the volume change of \( V_{\text{act}} \) is

\[
\delta V = \frac{V_{\text{act}} \theta_0}{T}
\]  

(1.29)

where \( T \) is the absolute temperature. Now the volume fluctuation \( \delta V \) causes a pressure fluctuation \( \delta P \) at the microphone. Assuming the adiabatic pressure-volume relation, we have

\[
\delta P = \frac{\gamma P \delta V}{V}
\]  

(1.30)

where \( \gamma \) is the ratio of the specific heats and \( V \) is the total cell volume, given by

\[
V = \pi R^2 l_g
\]  

(1.31)

Combining eqns. (1.27) to (1.31), we obtain the PA amplitude \( \delta P \) as

\[
\delta P = \frac{\gamma P \mu_g^2 I_0 l_g^2}{\mu_\alpha k_t l_g^2 T R^2}
\]  

(1.32)

Eqn.(1.32) which agrees with the more detailed work of Rosencwaig and Gersho [94], indicates that the PA magnitude is proportional to the sample absorption coefficient \( \alpha = 1/\mu_\alpha \), and the normalized PA signal \( \delta P/I_0 \) measured for a range of excitation wavelength \( \lambda \) can provide the absorption spectrum \( \alpha(\lambda) \) as in the direct PA generation case. The unusual advantage here is that spectra of totally opaque or highly light-scattering materials can now be measured.
1.2.6 PA Detection

PA generation is caused by a modulated absorption which can be due to a modulated light beam. Modulation methods for the light source include Q-switching, mode locking, flashlamp pumping, wavelength switching, mechanical chopping, electro-optic or acousto-optic modulating, wavelength modulating etc.

The PA cell is a container for the sample and for the microphone or transducer, such that the incident excitation beam is absorbed by the sample to produce an acoustic signal. Many designs of PA cells have been described in the literature [94, 95, 98, 123, 124], aiming at various aspects of signal improvement, noise reduction, and ease of use. PA cells can be classified into two general kinds: cells designed for gaseous samples [125], and those designed for condensed matter samples [123]. The former generally utilizes a microphone (with a relatively soft deflecting diaphragm) to sense the gaseous pressure fluctuations produced by the optical absorption. Besides microphone detection, fibre-optic detection [126] and optical probe-beam-deflection detection can also be used for gaseous samples [121]. In the second type of cells, for condensed matter, both microphones and piezoelectric transducers are in common use for detection. At low modulation frequencies or long enough pulse durations of the excitation beam, the exact geometry of the PA cell is important, since the acoustic wave can be reflected from the cell walls to produce interference and resonances. Hess [127] has reviewed the effects of acoustic resonance upon PA detection sensitivity. Noise can be reduced by locating the excitation beam entrance and exit positions at acoustic nodes in a resonant cell. On the other hand, at very high modulation frequency or very short pulse duration of the excitation beam, effects of reflections from cell walls are unimportant, and so is the geometry of the PA cell. Piezo-electric transducers are preferred over microphones for pulsed PA detection in condensed matter because of their much faster rise times and better acoustic impedance matching [128].

1.2.7 Applications of PA Effect

There exist several excellent reviews on applications of PA technique in various fields of physics chemistry, biology, engineering and medicine in the literature [92-95,97,105,121,129]. Only a brief account of the PA applications will be described here.

There are four general classes of applications of PA methods:

(1) PA spectroscopy: In this class of application, the PA signal amplitude is measured for a range of optical excitation wavelength, producing a PA spectrum; other factors (e.g., efficiency
in thermal deexcitation and in acoustic wave generation) are usually kept or assumed fixed while the PA spectrum is obtained. This is actually an excitation spectrum based on acoustic detection [124].

(2) PA monitoring of deexcitation processes: Here, the thermal decay branch is monitored to provide information on a competing decay branch. After optical excitation, four decay branches are generally possible: luminescence, photochemistry, photoelectricity, and heat that may be generated directly or through energy-transfer processes. For example, if luminescence and heat are the only two competing branching, PA monitoring of the heat branch can provide the quantum efficiency of luminescence under suitable circumstances [128, 129].

(3) PA probing of thermoelastic and other physical properties of materials: various information can be obtained conveniently with the help of the optical generation of thermal waves or acoustic waves. Such information includes sound velocity, elasticity, temperature, flow velocity, specific heat, thermal diffusivity, thickness of thin film, substrate defects and so on [87, 88, 130].

(4) PA generation of mechanical motions: PA effects can produce motions like liquid droplet ejection or structural vibrations.

PA detection techniques have been applied to a wide range of problems including many forms of spectroscopy in gases, liquids, and solids. A main attribute of acoustic detection is its high detection sensitivity. In addition, the energy deposited in the sample is measured directly. Several advantages result from this feature and PA spectroscopy often complements normal absorption and fluorescence spectroscopy. In the past two decades, PA effect has found many applications in spectroscopy of solids, liquids and gases, in medicine and biology, trace analysis, pollution monitoring, remote sensing, physics of semiconductors and amorphous materials, in thin films and so on. The application of PA effect has been so widely accepted that PA microscopy (PAM), Fourier transform PAS, PA trace analysis, PA magnetic resonance etc. are, by themselves areas of very strong research activity.

PA spectroscopic applications naturally divide into two categories, those utilizing chopped cw excitation sources and those using pulsed light sources. Considering only lasers, attributes of chopped cw sources are their inherent spectral purity (narrow frequency bandwidth) and high average power. Applications include high-resolution spectroscopy, thermal diffusivity measurements, the detection of 'forbidden' transitions such as singlet to triplet electronic transitions or vibrational overtone absorptions. Trace analysis and detection also falls into the category of weak absorption spectroscopy [131].

Pulsed excitation sources have a high peak light intensity or power which is advanta
geous for enhancing nonlinear photoprocesses. Nonlinear photoprocesses which have been
detected acoustically include two photon visible/UV absorption spectroscopy, stimulated Ra-
man spectroscopy and infrared multiphoton absorption. Pulsed PA also provide time domain
discrimination allowing real time monitoring of photoinduced relaxation processes [132].

The PA effect can be observed only when the incident radiation is absorbed by the sample. Thus, if the wavelength of the ultraviolet, visible or near infrared radiation incident upon the sample is varied, the amplitude of the PA signal observed at a given wavelength will provide a measure of the ability of the sample to absorb the incident radiation, i.e., the absorption spectrum of the sample will be obtained. The PA power spectrum obtained by measurement of the signal amplitude vs wavelength of the incident radiation should therefore resemble the electronic absorption spectrum of the sample and be complementary in this way for the examination of solid samples should have a number of advantages over conventional optical absorption or diffuse reflectance spectroscopy.

Due to its high sensitivity, PA detection is ideally suited for measuring weak vibrational overtone absorptions. Vibrational overtone spectroscopy promises to provide much greater insight into the processes which control the photophysics of highly excited vibrational levels. Overtone absorption in liquids was detected by many PA researchers, the first reported in benzene [133, 134]. These studies have been extended to water and D$_2$O to study the weak absorption in water in the visible region, which is important for underwater laser communication studies [135]. The fluorescence quantum yield of laser dyes also has been determined using PA technique [136, 137]. PA studies have been extensively applied to the study of biological and medical processes [138, 139]. Recently, the technique of Pulsed PA was used to investigate the diffusion of chromophores in human skin [140]. The photochemical reactions, which necessarily occurs in all plants, can be studied by PA technique due to the fact that if a fraction of the absorbed energy is consumed by the photochemical process, then the PA spectra differs from the absorption spectra. These measurements can be performed by comparing the PA spectra obtained for a calibrated PA cell for the sample before and after the photochemical process has taken place. Extensive studies were performed on chloroplasts using this technique.

PA technique has been widely applied to gas phase studies, especially in the areas of spec-
troscopy, trace analysis and pollution monitoring [141]. In gases, the absorption measurement capacity of $\sim 10^{-10}$ cm$^{-1}$ with a cell length of $\sim 10$ cm, using a continuously modulated laser for excitation, has been reported [142].
1.3 Photophysical Properties of Laser dyes

Fluorescence is the result of the rapid emission of light energy from a molecule which has become excited by light absorption. Fluorescence occurs following the radiative transition of the excited molecules from the first excited singlet state to the ground state. Such transitions are quantum mechanically 'allowed' and the emissive rates are typically $10^8 \text{ sec}^{-1}$. These high emissive rates result in fluorescence lifetimes $\sim$ ns. The lifetime is the average period of time a fluorophore remains in the excited state. Substances which emit significant fluorescence possess delocalized electrons formally present in conjugated double bonds. Laser dyes contain an extended system of conjugate bonds, i.e., alternating single and double bonds. Laser dyes are characterized by a strong absorption band in the visible region of the electromagnetic spectrum. Dyes are large molecules (with molecular weight ranging from about 175 to 1000) that can absorb light from a wide spectral region and fluoresce at longer wavelengths. This section describes some fundamental aspects of fluorescence emission from laser dyes. In addition the section is intended to give an insight into the different optical processes taking place in a dye after light absorption along with the lasing characteristics of organic dyes.

1.3.1 Origin of Fluorescence

At room temperature most molecules are in the lowest vibrational level of the ground electronic state and from here transitions take place upwards on absorption of light. A dye molecule raised to an upper vibrational level of higher excited state rapidly loses its energy by collisions with surrounding molecules. This process indicated by the wavy lines in the fig.1.6, is known as internal conversion. It is found that a dye molecule when raised to higher electronic excited states, undergo internal conversion whereby it decays nonradiatively from a low vibrational level of the upper state to a high vibrational level of the lower state having the same total energy. Once internal conversion has occurred, the molecule again rapidly loses its excess vibrational energy by collision with solvent molecules. The net result of all these processes is that molecules raised to levels higher than the lowest vibrational level of the first excited state (i.e. level 0 of $S_1$) rapidly fall to the latter. Some substances may undergo photochemical reaction when raised to upper excited states but the processes leading to such reaction (e.g. dissociation) must take place rapidly to compete with the internal conversion and loss of vibrational energy by collisions. Similarly for light emission from these upper states to be appreciable, it also would have to a much more rapid process than it normally is, and consequently in solution the observation of light emission due to transitions from upper
excited states is very rare.

From level 0 of \( S_1 \), the molecule can return to any one of the vibration-rotation levels of the ground state with the emission of fluorescence. If all the molecules that absorb light return to the ground state in this way, the solution will fluoresce with a quantum yield of unity. A fraction of the excited molecules may return to the ground state by other mechanisms, for example by intersystem crossing to the triplet manifold. The lowest vibrational level of the lowest triplet state is generally situated some way below that of the lowest excited state. Intersystem crossing occurs by the molecule crossing over to one of the upper vibrational levels of the lowest triplet state. From here the molecule rapidly loses its excess vibrational energy and falls to near the lowest vibrational level of the triplet state. The quantum efficiency of fluorescence then will be less than unity.

There are two possible ways, at least in principle, of using the dye solution as an active medium in dye laser: one might utilize either the fluorescence or the phosphorescence emission. At first sight the long lifetime of the triplet state makes phosphorescence look more attractive. On the other hand, due to strongly forbidden transition, a very high concentration of the active species is required to obtain an amplification factor large enough to overcome the inevitable cavity losses [143]. In fact, for many dyes this concentration would be higher than
the solubility of the dyes in any solvent. A further unfavourable property of these systems is that there will almost certainly be losses due to triplet-triplet absorption. It must be remembered that triplet-triplet absorption bands are generally very broad and diffuse and the probability that they would overlap the phosphorescence bands is high. Because of these difficulties no laser using the phosphorescence of a dye has been reported. The possibility cannot be ruled out because further study of phosphorescence and triplet-triplet absorption in molecules of different types of chemical constitution might eventually lead to a laser operating, for example, at the temperature of liquid nitrogen.

The fact that at room temperature absorption takes place almost exclusively from the lowest vibrational level of the ground state, while the emission takes place exclusively from the lowest vibrational level of the first excited state explains why only one transition, namely the 0-0 transition, is common to both the absorption and emission spectra. Frequently the emission spectrum is an approximate mirror-image of the first absorption band because the distribution of vibrational levels in the first excited state, which determines the shape of the first absorption band, is often similar to the distribution of vibrational levels in the ground state, which determines the shape of the fluorescence emission spectrum.

Energy losses between excitation and emission are observed universally for fluorescing molecules, except in the vapour phase. This phenomenon was first observed by Stokes in 1952 [144] and Stokes law states that the wavelength of the fluorescence is always longer than that of the exciting light. One common cause of Stokes shift is the rapid decay to the lowest vibrational level of $S_1$. Furthermore, fluorophores generally decay to excited vibrational levels of $S_0$, resulting in loss of vibrational energy. In addition to these effects, fluorophores can display further Stokes' shifts due to solvent effects and excited state reactions. In the gas phase, atoms and molecules do not always show Stokes' shifts. An unshifted emission is observed when the gas concentrations are sufficiently small so that the excited molecule does not collide with any other molecules prior to emission. Such encounters are a source of relaxation. In the fluid phase such collisions are continuous.

The fluorescence spectrum is generally observed irrespective of the excitation wavelength. Upon excitation into higher electronic and vibrational levels, the excess energy is quickly dissipated, leaving the fluorophore in the lowest vibrational level of $S_1$. This relaxation occurs in about $10^{-12}$ sec, and is presumably a result of a strong overlap among numerous states of nearly equal energy. Because of this rapid relaxation, emission spectra are usually independent of the excitation wavelength. Exceptions exist, such as azulene [145] which may emit both from $S_2$ and $S_1$. 30
1.3.2 Quantitative Aspects of Light Absorption and Emission

Consider a parallel beam of light of intensity $I_0$ directed on a parallel sided specimen. Then,

$$I_0 = I_R + I_R + I_S + I_A + I_T \quad (1.33)$$

where $I_R$ and $I_R$ are the intensity of light reflected at each interface; $I_S$, the scattered part; $I_A$, the intensity of absorbed light and $I_T$, the part that is transmitted.

At some point within the medium bounded by the infinitely thin layer $dl$, let the light intensity be $I$. The intensity of light absorbed, $dI_A$, in traversing the thin layer is thus equal to the product of the incident intensity, $I$, on the layer, and the total effective cross-section of the molecules per cm$^2$ of the beam in the layer, i.e.

$$dI_A = -dI = Ikc'dl \quad (1.34)$$

where $c$ is the number of molecules/cc and $k$ is the effective cross-section of one molecule in cm$^2$. On integration between 0 and $l'$, the above equation gives the Beer-Lambert law.

$$I_T = I_0e^{-kc'l} \quad (1.35)$$

A more practical form of the above equation is as follows:

$$\log_{10} \frac{I_0}{I} = \epsilon c l \quad (1.36)$$

in which $c$ is now measured in moles/litre and $\epsilon$ is known as the molecular extinction coefficient.

The quantity $\log_{10} \frac{I_0}{I}$ is known as the optical density or absorbance of the solution and is proportional to the concentration of the absorbing species. If more than one absorbing species is present the optical density of the mixture is equal to the sum of the optical densities of the separate components.

Absorption spectra consist simply of a plot of $\epsilon$, or of $\log \epsilon$, against the wavelength or frequency of the light being absorbed. Fluorescence emission spectra are normally plotted in one of three ways. In the first method the number of quanta emitted per second within a unit wavelength interval at the wavelength concerned is plotted against the wavelength $\lambda$. In the second method the number of quanta emitted per second within a unit frequency interval is plotted against frequency. A third method is to plot energy emitted per second within unit wavelength interval against wavelength. The fluorescence is emitted from the specimen in all directions, but it is rarely necessary to plot the intensity scale in absolute units, relative values are all that are usually needed.
Because emission almost takes place exclusively from the lowest vibrational level of the first excited state, the fluorescence emission spectrum is always the same, no matter what the wavelength of the exciting radiation. This is a most useful rule in practical spectrofluorimetry because if it is found that the shape of the emission spectrum of a solution does change when the wavelength of the exciting light is varied, the presence of more than one fluorescence species should be suspected.

The relationship between the intensity of fluorescence and the extinction coefficient can be derived from the Beer-Lambert law. The rate of fluorescence emission, $Q$ is equal to the product of the rate of light absorption (measured in quanta per sec) and the fluorescence quantum efficiency, $Q_f$ [146]

$$Q = I_A Q_f$$  \hspace{1cm} (1.37)

and from eqn.(1.35) therefore

$$Q = I_0 (1 - e^{-kcl}) Q_f$$  \hspace{1cm} (1.38)

$$Q = I_0 \left( kcl - \frac{(kcl)^2}{2} + \frac{(kcl)^3}{6} - \ldots \right) Q_f$$  \hspace{1cm} (1.39)

Taking the concentration in moles/litre, and changing into molecular extinction coefficient, we have:

$$Q = I_0 (2.3 ecl) \left( 1 - \frac{2.3 ecl}{2} + \frac{(2.3 ecl)^2}{6} - \ldots \right) Q_f$$  \hspace{1cm} (1.40)

For weakly absorbing solutions for which the optical density, $ecl$ is small, and the equation simplifies to

$$Q = I_0 (2.3 ecl) Q_f$$  \hspace{1cm} (1.41)

The above equation indicate that for a given substance in dilute solution contained in a particular cuvette, the intensity of the fluorescence observed is proportional to the product of concentration and the intensity of the exciting light.

1.3.3 An Overview of Dye Lasers

The first report of dye laser action was that of Sorokin and Lankard [147] who observed laser emission from a solution of chloroaluminium pthalocyanine. Independently, Schafer, Schmidt and Volze [148] obtained laser action in the infrared from a number of cyanine-type dyes. The uniqueness of these contributions was that they were the first reports of laser action from broad, diffuse energy bands rather a set of discrete energy levels, typical of gas and rare earth lasers. The tunability of the dye laser is a consequence of the broadened electronic levels characteristic of organic dyes.
Dye lasers are perhaps the most versatile and one of the most successful lasers available today. The most important attribute of the dye laser is its tunability, which gives the user access to essentially any wavelength. In the dye laser's region of operation, only a few lasers are competitive and those are only in limited parts of the dye laser’s spectral region. A few new tunable lasers are beginning to threaten some of the traditional domains of the dye laser [149]. These include semiconductor, color-center, Ti-sapphire, alexandrite, and a few optically pumped solid state lasers. Other nontunable lasers exist that oscillate in the visible and near-visible region of the spectrum; for example, the Kr-ion and Ar-ion lasers have many useful lasing lines, and the optically pumped dimer lasers (sodium, lithium, iodine, etc.) have hundreds of lines, but the lines are relatively narrow and, even when combining all of these lasers, the actual fractional coverage of the available spectrum is small.

Dye lasers offer to researchers both pulsed and continuous wave (cw) operation that is tunable from the near-UV to the near-IR. A number of photophysical properties such as absorptivity, fluorescence yield, Stokes' shift, triplet population formation influence threshold determine the laser characteristics. The influence of solvent medium on laser-dye photophysics also plays significant role in determining the laser qualities [150, 151]. The cw dye laser is a well-established tool of optical science. This laser has a unique set of capabilities that include broad tunability, high power, and the ability for extremely high resolution. No other optical source can provide a comparable combination of tunability, resolution and power. The power levels available from cw dye lasers are generally more than adequate for spectroscopic applications. The output power of cw dye lasers varies with dye. Special high power cw dye lasers systems have been developed that can produce tens of watts of tunable visible radiation. With broad tuning ranges and narrow line widths, single-mode cw dye lasers can provide impressively large resolution. Continued improvements in the pump lasers, the dyes, and the nonlinear optical materials will undoubtedly provide higher output powers and extended spectral coverage. The spectral characteristics of cw dye lasers are both good and bad: good with respect to their line widths, and hence, spectral resolving capabilities, but generally poor with respect to their amplitude noise properties. Because of necessity, techniques have been developed to reduce the problems associated with this amplitude noise.

1.3.4 Requirements for a Dye to Act as a Laser Dye

The fact that out of thousands of commercially available dyes, only a few are good laser dyes, indicates that these must meet some special requirements to qualify as laser dyes. As
discussed in earlier sections, radiative process (i.e. fluorescence) is responsible for stimulated emission in the case of these dyes. Nonradiative processes always compete with fluorescence pathway and these can diminish the laser output and sometimes they may be prominent that the laser action may be completely diminished. Hence a good laser dye should have the following features.

1. As the fluorescence is responsible for stimulated emission, a laser dye should have very high fluorescence yield. Also it should have a wide fluorescence band so as to tunable over a broad spectral range.

2. As non-radiative processes deactivate the excited state and thus reduce the fluorescence quantum yield, the dye structure should be such that these processes are not favoured.

3. Because of the relatively long lifetime of the triplet molecules (in the order of microseconds) the dye accumulates during the pumping process in the triplet state T1, which often has considerable absorption for the laser light. Thus some of the molecules are taken away from the lasing process. Moreover, due to triplet-triplet absorption, they cause an additional loss in the laser.

4. An efficient laser dye in its first excited singlet state should have negligible absorption at the excitation and lasing wavelength. Otherwise, losses would occur, as in triplet-triplet absorption, because the decay to the first excited singlet or triplet level is nonradiative.

5. The absorption spectrum of the dye should match with the spectral distribution of the pump source in order to take full advantage of the pump source.

6. During the lasing process a certain amount of thermal energy is released, giving rise to temperature gradients in the solution that may cause optical inhomogeneities. Hence the dye should be soluble in solvents having good thermal properties such as water, methanol etc..

7. An ideal laser should possess very good photochemical stability, otherwise not only the dye is depleted but sometimes the photo-products can quench the laser output.

Of the thousands of organic dyes available, only a few classes of dyes meet the stringent criteria for becoming useful laser dyes. The various classes of dyes and the region of the spectrum they cover are illustrated in elsewhere [152].

Many of these dyes may be viewed as having a benzene ring as the base chromophore, substituted with a number of electron donating groups - such structures generally increases the transition moment for optical absorption and also fluorescence emission. The light absorption of dyes on a semi quantitative basis has been explained by Kuhn [153, 154]. Factors increasing the fluorescence efficiency will increase the efficiency of dye lasers. It is known that a rigid planar molecular structure favours high fluorescence efficiency [155]. Generally,
a freely rotating group attached to the molecule reduces the fluorescence efficiency. In rhodamine B having two freely rotating diethylamino groups, the fluorescence efficiency is highly sensitive to change in temperature. But rhodamine 101 in which rigidization of the latter diethylamino group increases fluorescence substantially, is independent of temperatures [155].

Electron donating substituents on the aromatic ring generally increase the fluorescence efficiency as they increase the \( \pi \) electron density on the ring and hence the oscillator strength is increased. Also a dye substituted with heavy atoms shows reduced fluorescence efficiency as heavy atoms introduce increased spin-orbit coupling and increase the intersystem crossing efficiency [145, 156].

1.3.5 Effect of solvent

The photophysical and chemical properties of dyes are influenced to a great extent by the solvent environment. Hence solvent plays a very important role in dye lasers. During the dye laser operation the solution is subjected to a very high intense field of radiation. Nonuniform heating of the solvent takes place which in turn generates temperature gradient that may cause optical inhomogeneities in the solution. Hence the solvent used in a dye laser should possess good thermo-optical properties like water and heavy water. The solvent should not help dimerization and other photochemical processes in the laser dyes. The solvent should be transparent to the pump and lasing wavelength.

There are many solvent introduced effects which lead to changes in fluorescence efficiency. There are no generalized effects on solvents for all these dyes, but they vary from dye to dye. It has been observed in many cases that there is a considerable shift in the absorption and emission wavelengths of the dyes. Hence change of solvent can be used as a method for tuning the laser dyes. The energy difference between the 0-0 transitions should be greatest for those molecules showing a large change in the dipole moment on excitation to the first excited state. For a given substance it should also be greater in more polar solvents [146]. There is a relationship connecting the 0-0 band shift, the polarity of the solvent and the change in the dipole moment of the solute on excitation. By measuring the 0-0 band shift in a series of solvents, the dipole moment in the excited state can be calculated [157].

The selection of solvent can affect the performance of laser dyes in terms of alteration of fluorescence yield and lifetime as well as fluorescence wavelength. This phenomenon is also related to the long-held observation that dyes perform better when rigidly fixed in planar geometries. This restriction of allowed constraints imposed by assembly of dye substituents
in rings. These findings can now be understood in terms of a confluence of effects associated with the creation of dye dipoles, the conformational mobility of substituent groups, and solvent stabilization of charged species. The effects of selected solvents on the fluorescence yield and lifetime parameters for coumarin XI have been reported by Jones and co-workers [150, 158]. Studies by Jones et. al [150] revealed the principal influence of increased solvent polarity on nonradiative rate constant, \( k_\alpha \). More over, this undesirable reduction of emission yield and lifetime can be reversed (1) on adoption of very viscous solvents like glycerol, (2) with operation at low temperatures (ideally below room temperature).

Acidity of the solvent is another important property that influences the dye laser emission especially when the \( pK_a \) of the ground and excited states are different. Thus by changing the \( pH \) of the solution it is possible to get large tuning range [155].

Formation of donor-acceptor charge transfer complexes between excited dye molecules and solvent also plays a major role. If such an exciplex is non-fluorescent, its formation may quench the fluorescence [159]

### 1.3.6 Dye Aggregation

Aggregation that can occur for higher concentrations of dye in water or alcohol solutions is well known. Potential driving forces for this phenomenon include the freeing the solvent molecules from solvation (hydration) spheres surrounding individual dye structures. Weak intermolecular bonding involving dipole-dipole and other forces is also important. The results of dimerization, which can be suppressed at higher temperatures, include subtle shifts in absorption due to exciton interaction (the coupling of the electronic states of individual molecules - splitting of energy levels - due to mutual overlap of orbitals). Fluorescence in dimers or higher aggregates is completely suppressed. This unwelcome alteration in dye dynamics is connected to the reduced lifetime of aggregated forms of organic dyes. For example, using fast time resolved fluorescence and absorption methods, Smirli et al [160] have shown that rhodamine B monomer and dimer in water display excited state lifetimes of 1.6 ns and 100 psec, respectively, signaling a high rate of nonradiative decay for the dye dimer. Aggregation is not an important deterrent where very low concentrations can be accommodated ([dye] generally < 10\(^{-4}\) M) or where dye molecules are isolated in microdomains such as those provided by detergents.
1.4 Nonlinear Absorption

The intense monochromatic radiation from a laser can induce profound changes in the optical properties of a material. Nonlinear absorption refers to the change in transmittance of a material absorbing more than one photon before relaxing to the ground state can be greatly enhanced. As early as 1931, Goppert-Mayer derived the two photon transition probability in a system using second order quantum perturbation theory [161]. Since the invention of the laser, not only has this phenomenon of the simultaneous absorption of two photons been observed in a wide variety of materials, multiphoton (> 2) absorption has also been widely studied. In addition, population redistribution induced by intense laser fields leads to interesting counter plays of stimulated emission and absorption, complicated energy transitions in complex molecular systems, and the generation of free carriers in solids. These phenomena are manifested optically in a reduced (saturable) or increased (reverse saturable) absorption.

All optical nonlinearities can be broadly classified into two groups: instantaneous and accumulative nonlinearities. For the former, the polarization density resulting from an applied electric field occurs essentially instantaneously. For such interactions, the polarization density amplitude is usually expanded in a Taylor series in the electric field amplitude, E, or:

\[ P = e_0 \chi^{(1)} E + \chi^{(2)} E E + \chi^{(3)} E E E + \ldots \]

\( \chi^{(n)} \) is the complex susceptibility tensor of order \( n \). The first term \( \chi^{(1)} \) is responsible for linear absorption and refraction, while the remaining terms are associated with light-induced nonlinear effects. The \( \chi^{(2)} \) term is present only in noncentrosymmetric materials, and it gives rise to sum and difference frequency mixing, optical rectification, and the electro-optic effect. The term most widely applied to optical limiting is that involving \( \chi^{(3)} \). The most important \( \chi^{(3)} \) processes for optical limiting are two photon absorption, which is associated with the imaginary part of \( \chi^{(3)} \), and the electronic Kerr effect, which is associated with the real part of \( \chi^{(3)} \).

In contrast with the instantaneous nonlinearities, accumulative nonlinearities arise from interactions with memory, i.e., the polarization density generated by an applied field either develops or decays on a time scale comparable to or longer than the period of the exciting radiation. Such interactions are dissipative, i.e., they require energy transfer from the field to the medium, and the nonlinearity is initiated by this energy transfer. In contrast with the instantaneous nonlinearities which depend on the instantaneous intensity in the medium, accumulative nonlinearities depend on the energy density deposited in the medium. Examples
of such accumulative nonlinearities include nonlinear absorptive processes such as excited state absorption and free carrier absorption, and nonlinear refractive processes associated with free carrier generation or optically induced heating. These nonlinearities can also be nonlocal, i.e., the polarisation density induced at position \( r \) may depend on the optical intensity at position \( r' \). An important example of such a process is the photorefractive effect.

The many different effects produced by nonlinear absorption in the frequency dependent transmittance of a material have led to several applications in science and technology. These include such diverse areas as nonlinear spectroscopy and optical limiting. In the subsections that follow, several of the formulas and phenomenon pertinent to an understanding of simultaneous multiphoton absorption, cumulative multistep absorption and absorption effects associated with population redistributions are discussed.

### 1.4.1 Two Photon Absorption

Two photon absorption (TPA) involves a transition from the ground state of a system to a higher-lying state by the simultaneous absorption of two photons from an incident radiation field. This process involves different selection rules than those of single photon absorption. Hence TPA spectroscopy complements linear absorption spectroscopy in studying the excited states of systems.

Two possible situations are illustrated in fig.1.7. In the first, two photons from the same optical field oscillating at frequency \( \omega \) are absorbed to make the transition, which is approximately resonant at \( 2\omega \). In the second situation, two optical fields at frequencies \( \omega_e \) and \( \omega_p \) are present, and one photon from each field is absorbed for the transition, which is approximately resonant at \( \omega_e + \omega_p \). The first field in this case (\( \omega_e \)) can be thought of as the pump or excitation beam, while the second (\( \omega_p \)) can be thought of as the probe beam. In both cases, the intermediate (or virtual) state is not real (i.e., does not involve a real stationary state of the system). Hence the system must absorb the two photons simultaneously. This makes the process sensitive to the instantaneous optical intensity.

Although the transition does not involve a real intermediate state, often there are impurities present that will produce a small amount of linear absorption. It should be understood that this absorption does not contribute to the transition to the final state of the process but only serves as an additional loss mechanism. Two-step absorption involving a single photon pumped intermediate state is described as Excited State Absorption (ESA).
1.4.1.1 Single beam TPA

The nonlinear absorption in this case is proportional to the square of the instantaneous intensity. The differential equation describing the optical loss is given by [162]

\[
\frac{dI}{dx} = -\alpha I - \beta I^2
\]  

(1.43)

where \( \alpha \) is the linear absorption coefficient due to the presence of impurities and \( \beta \) is the TPA coefficient.

The TPA coefficient \( \beta \) is a macroscopic parameter characterizing the material. Often, there is interest in the individual molecular TPA property that is described by the TPA cross-section \( \sigma_2 \). The relation between \( \beta \) and \( \sigma_2 \) is given by

\[
\sigma_2 = \frac{\hbar \omega \beta}{N}
\]  

(1.44)

where \( N \) is the number density of molecules in the system, and \( \hbar \omega \) is the energy of photons in the incident optical field. The TPA coefficient is also related to the third order susceptibility. This relation is [161]

\[
\beta = \frac{3\pi}{\varepsilon_0 n^2 c \lambda} \text{Im}\left[ \chi^{(3)}_{xxxx}(-\omega, \omega, \omega, -\omega) \right]
\]  

(1.45)

Note that it is the imaginary part of \( \chi^{(3)} \) that determines the strength of nonlinear absorption.

1.4.1.2 Two-beam Two-photon Absorption

This process, depicted in fig.1.7(b), involves the simultaneous absorption of two photons of different frequencies. These are designated as the pump or excitation frequency \( \omega_e \) and the
The intensity in each of these beams can be comparable, but more often $I_p << I_e$.

The TPA coefficients involved in this process are again related to the third order susceptibility. The fact that the excitation and probe fields can have orthogonal polarization implies that this nonlinear process can lead to an induced dichroism in the material.

The differential equations describing the attenuation of the beams are [163, 164]

$$\frac{dI_e}{dz} = -\alpha_e I_e - 2 \left( \frac{\omega_e}{\omega_p} \right)^{1/2} \beta_{ep} I_e I_p - \beta_{ee} I_e^2$$ \hspace{1cm} (1.46)

$$\frac{dI_p}{dz} = -\alpha_p I_p - 2 \left( \frac{\omega_p}{\omega_e} \right)^{1/2} \beta_{pe} I_p I_e - \beta_{pp} I_p^2$$ \hspace{1cm} (1.47)

The first and last terms in these equations describe the linear and self-induced two-photon absorption, respectively, while the middle terms are what give rise to induced dichroism.

Two situations are considered. First, the excitation photon energy is less than half the energy of the first two-photon allowed transition. Thus the term involving $\beta_{ee}$ can be ignored. Also, the self-induced absorption term involving $\beta_{pp}$ is ignored since the probe is assumed to be weak relative to the excitation beam. In the second situation, self-induced TPA by the excitation beam is allowed, and the induced dichroism by the probe on the pump is assumed to be negligible. This implies that the excitation beam can pump allowed two-photon states both by itself (at $2\omega_e$) and in conjunction with the probe (at $\omega_e + \omega_p$). This is possible when there is a large density of two-photon allowed states, such as occurs in the conduction band of semiconductors and in the excited state spectrum of polyatomic molecules.

### 1.4.2 Three Photon Absorption

The phenomenon of resonant three photon absorption (3PA) is illustrated in fig.1.8. Three cases are shown involving one, two and three fields. Only the single field is treated here. Assuming that impurities introduce some background linear absorption, the equation describing the attenuation of a beam experiencing 3PA is given by

$$\frac{dI}{dz} = -\alpha I - \gamma I^3$$ \hspace{1cm} (1.48)

where $\gamma$ is the 3PA coefficient. 3PA is a fifth order nonlinear process and $\gamma$ is related to the fifth order susceptibility [163, 164]

$$\gamma = \frac{5\pi}{\varepsilon_0^3 n_0^3 c^3 \lambda} \text{Im} \chi^{(5)} (\omega; \omega, \omega, -\omega, -\omega)$$ \hspace{1cm} (1.49)

Again the beam is assumed to be linearly polarized and the medium is centrosymmetric.
1.4.3 Multiphoton Absorption

Multiphoton absorption (MPA) refers to the simultaneous absorption of photons from a single beam or multiple beams. The analogous to equations (1.43) and (1.48) for the absorption of \( n+1 \) photons from a single optical beam is [163]

\[
\frac{dI}{dz} = -(\alpha + \gamma^{n+1} I^n)I
\]  

(1.50)

where \( \gamma^{(n+1)} \) is the \( (n+1) \) photon absorption coefficient and has units of \( m^{2n-1}/W^n \).

Nonresonant MPA is usually very weak for \( n \geq 3 \). It can, however, be significant in semiconductors, especially narrow band gap materials.

Shen gives the transition probability rate per molecule for a nonresonant \( n \)-photon transition as [1]

\[
W^{(n)} = \frac{\sigma^{(n)} I_1(\omega_1) I_2(\omega_2) \ldots I_n(\omega_n)}{\hbar^n \omega_1 \omega_2}
\]  

(1.51)

where \( \sigma^{(n)} \) (assumed a scalar quantity) is the \( n \)-photon absorption cross-section.

For nonresonant transitions, \( \sigma^{(n+1)}/\sigma^{(n)} \approx 10^{-34} \) [163]. Therefore, \( \sigma^{(n+1)} I/\hbar \omega \approx 10^{-6} \sigma^{(n)} \) for \( I \sim 1 \text{ GW/cm}^2 \). Thus very high intensities are required to excite MPA. This is usually accompanied by avalanche ionization and breakdown in condensed matter.

1.4.4 Excited State Absorption

When the incident intensity is well above the saturation intensity, then the excited state can become significantly populated. In systems such as polyatomic molecules and semiconductors, there is a high density of states near the state involved in the excitation. The excited electron
can rapidly make a transition to one of these states before it eventually returns back to the ground state. There are also a number of higher-lying states that may be radiatively coupled to these intermediate states, and for which the energy differences are in near-resonance with the incident photon energy. Therefore before the electron completely relaxes to the ground state, it may experience absorption that promotes it to a higher-lying state. This process is called excited state absorption (ESA). It is observable when the incident intensity is sufficient to deplete the ground state significantly.

When the absorption cross-section of the ESA is smaller than that of the ground state, the transmission of the system will be increased when the system is highly excited. This process is called Saturable Absorption (SA). When the absorption cross-section of the excited state is larger than that of the ground state, then the system will be less transmissive when excited. This gives the opposite result as saturable absorption (SA) and is thus called Reverse Saturable Absorption (RSA).

In semiconductors, the absorption of a photon with energy greater than the band gap will promote an electron to the conduction band, where it is a free carrier and can contribute to current flow when a field is applied. The excited electron will rapidly thermalize and relax to the bottom of the conduction band. From there it will recombine with an excited hole in the valence band after a characteristic recombination time. However, at sufficiently high intensities, it can with high probability absorb another photon while it is still in the conduction band. This process is called free carrier absorption. It has similar qualitative characteristics to RSA.

1.4.5 Two-photon Assisted Excited State Absorption

When two-photon absorption is particularly strong in a material, it can lead to significant population of a two-photon allowed state. Often there are allowed radiative transitions from this state to higher-lying states of the system, i.e., excited state absorption can ensue from the two-photon pumped state. This occurs both in polyatomic molecules and in semiconductors.

The attenuation and excited state population equations are given by

\[ \frac{\partial I}{\partial z} = -\alpha I - \beta I^2 - \sigma NI \]  
(1.52)

and

\[ \frac{\partial N}{\partial t} = \frac{\beta I^2}{2\hbar \omega} - \frac{N}{\tau_1} \]  
(1.53)

where \(\alpha\) is the linear absorption coefficient for impurity absorbers, and \(\tau_1\) represents the
lifetime of two-photon excited states. By solving these equation, the nonlinear transmittance of the system can be determined.

1.5 References


[84] A. G. Bell, Philos. Mag., 11, 510 (1881)

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