1

INTRODUCTION

1.1 Photothermal Spectroscopy

Photothermal spectroscopy is a group of high sensitivity methods used to measure optical absorption and thermal characteristics of a sample. The basis of photothermal spectroscopy is a photo-induced change in the thermal state of the sample. Light energy absorbed and not lost by subsequent emission results in sample heating. This heating results in a temperature change as well as changes in thermodynamic parameters of the sample which are related to temperature. Measurements of the temperature, pressure, or density changes that occur due to optical absorption are ultimately the basis for the photothermal spectroscopic methods.

Ingle and Crouch (1988) classify photothermal spectroscopy as one of several indirect methods for optical absorption analysis. Indirect methods do not measure the transmission of light used to excite the sample directly, but rather measure an effect that optical absorption has on the sample. The term indirect applies to the light measurement, not to the optical absorbance. Photothermal spectroscopy is, in a sense, a more direct measure of optical absorption than optical transmission based spectrosopies. Sample heating is a direct consequence of optical absorption and so photothermal spectroscopy signals are directly dependent on light absorption. Scattering and reflection losses do not produce photothermal signals. Subsequently, photothermal spectroscopy more accurately measures optical absorption in scattering solutions, in solids, and at interfaces. This aspect makes it particularly attractive for application to surface and solid absorption studies, and studies in scattering media.

The indirect nature of the measurement also results in photothermal spectroscopy being more sensitive than optical absorption measured by transmission methods. There are two reasons for this. First, photothermal effects can amplify the measured optical signal. This amplification is referred to as the enhancement factor (Dovichi and Harris 1979, Mori, et al. 1982) and is the ratio of the signal obtained using photothermal spectroscopy to that of conventional transmission spectroscopy. Enhancement factors depend on the thermal and optical properties of the sample, the power or energy of the light source used to excite the sample, and on the optical geometry used to excite the sample. Since the optical excitation power or energy, and geometry is variable, the enhancement can be made very large, even for samples with relatively poor thermal and optical properties. In fact, the problem with photothermal spectroscopy is not the absorption detection limit. The problem is the detection of analyte absorbance in the presence of a relatively large (10^5 cm^-1) absorbance of the solvent. The second reason photothermal spectroscopy is more sensitive than transmission is that the precision of the measurement is inherently better than that of the direct transmission method. The fundamental limitation of conventional absorption spectroscopy, namely shot noise, may be partially
circumvented (Bialkowski, et al. 1992). Because of the increased fundamental signal to noise ratios, the problem of being able to detect the analyte in the presence of a relatively large background absorption should be able to be overcome with perseverance.

The high sensitivity of the photothermal spectroscopy methods has led to applications for analysis of low absorbance samples. Dovichi (1987) reviewed the literature regarding the use of photothermal spectroscopy for chemical analysis. The magnitude of the photothermal spectroscopy signal depends on the specific method used to detect the photothermal effect and on the type of sample being analyzed. There are many different reported detection limits and it is difficult to specify an absolute lower limit of detection since the method may be used to measure the background absorption of the solvent itself. But it is safe to say that optical absorbances of less than $10^{-6}$ can be detected with optimized experimental designs. Subsequently, photothermal spectroscopy is often characterized as a trace analysis method. Concentration limit of detection measurements can be impressive. Electronic transitions of strongly absorbing chromophores have molar absorptivities exceeding $10^4 \text{ M}^{-1}\text{cm}^{-1}$. Using photothermal methods, concentrations lower than $10^{-10} \text{ M}$ of these strongly absorbing chromophores may be measured in standard cuvettes. These limits of detection are slightly higher than those obtained using laser excited fluorescence spectroscopy and are 2-3 orders of magnitude better than that obtained using conventional transmission spectroscopy. The low molar absorption detection limits coupled with the fact that the volume being probed can be very small results in extremely small numbers of molecules being detected. The high absorbance sensitivity of these methods has opened up new areas of trace chemical analysis based on optical absorption spectroscopy.

Photothermal signals depend on the thermodynamic and energy transfer properties of the sample. Temperature changes resulting from optical absorption are directly related to heat capacity and thermal conductivity. This makes absolute sample absorption measurements difficult. The thermal and optical properties of the sample must be known to high accuracy, or the instrument response must be calibrated with samples of known composition and absorbance. However, this dependence on thermodynamic and energy transfer properties allows for analysis of the thermal structure of materials. With calibrated apparatuses, the static and dynamic thermal properties of the sample can be measured. Photothermal spectroscopy has been used to measure acoustic velocities, thermal diffusion coefficients, sample temperatures, bulk sample flow rates, specific heats, volume expansion coefficients, and heterogeneous thermal conductivities in solids. In particular, a technique called thermal wave imaging allows nondestructive material inspection by measuring the rate of heat transfer in heterogeneous materials.
Photothermal spectroscopy is usually performed using laser light sources. There are two main reasons for this. The first is the high spectral purity and power. For an excitation of a sample with a given absorption coefficient, the temperature change will be proportional to the optical power, in the case of continuous excitation, or energy, in the case of pulsed excitation. The photothermal spectroscopy signal is generally proportional to the temperature change. Thus the greater the power or energy, the greater the resulting signal. Lasers can deliver high powers or pulse energies over very narrow optical bandwidths thereby enhancing the photothermal signals. The second reason is spatial coherence. The temperature change is not only proportional to the optical power or energy, but also is inversely proportional to the volume over which the light is absorbed since heat capacity scales with the amount of substance. The spatial coherence properties of laser sources allow the light to be focused to small, diffraction limited, volumes. The small volumes used in photothermal spectroscopy enhance signal magnitudes, allows photothermal spectroscopy to be used in small volume sample analysis, and allows for microscopic analysis of heterogeneous materials.

1.2 Basic Processes in Photothermal Spectroscopy

The basic processes responsible for photothermal spectroscopy signal generation are shown in Figure 1.1. Optical radiation, usually from a laser, is used to excite a sample. The sample absorbs some of this radiation resulting in an increase in the internal energy. The internal energy is dispersed in two different modes of hydrodynamic relaxation. The increased internal energy results in a temperature change in the sample or the coupling fluid placed next to the sample. This temperature change results in a change in sample or coupling fluid density.

If the photothermal induced temperature change occurs faster than the time required for the fluid to expand or in a few cases contract, then the rapid temperature change will result in a pressure change. The pressure perturbation will disperse in an acoustic wave. Once the pressure has relaxed to the equilibrium pressure, a density change proportional to the temperature will remain.

In either case there will be a change in temperature induced by the absorption of optical energy. This temperature change will in turn result in a density change in the sample. In combination, temperature and density changes affect other properties of the sample. Photothermal spectroscopy is based on a measurement of these properties. In particular, the sensitive photothermal methods are based on measurement of the refractive index change that occurs with changes in temperature and density of the sample.

There are three main areas that must be considered when attempting to obtain a quantitative description of the photothermal spectroscopy signal. The first is a description of the optical absorption and excited state
relaxation processes. Optical excitation followed by excited state relaxation results in sample heating. The rates and amounts of excited state excitation and relaxation will control the rate and magnitude of heat production. The energy transfer steps that need be accounted for are shown in Figure 1.2. Energy can be transferred to the sample by optical absorption and inelastic scattering process such as Raman. Scattering is inefficient and the amount of energy lost to sample is usually small enough to be neglected. After absorption, the molecules are in an excited state. Excited state relaxation transfers energy to the solvent or sample matrix. Radiative relaxation does not result in complete loss of the absorbed energy to the sample. Some of the energy is lost in the form of the radiated light. Thermal relaxation transfers the energy to the sample matrix and results in sample heating. Excited species may also form long lived metastable states that trap energy and prevent further optical absorption. This will result in a delayed heating of the sample. The excited state species may also participate in photochemical reactions. Photochemical reaction can produce heat but also produce new chemical species which alter the thermal and optical characteristics of the sample.

These relaxation processes may all produce excess energy in the form of heat. The heat increases the internal energy of the sample. The sample will respond to this increased energy. The second area is that of the hydrodynamic relaxation. After optical heating, the sample is not at thermal equilibrium with itself or with the surrounding environment during a measurement. Heat generated by the optical excitation and relaxation processes will result in thermal gradients between the excited sample and the surroundings. The thermal gradients result in heat transport. Heat is transferred within the sample in a fashion such as to move toward thermal equilibrium. Hydrodynamic relaxation produces changes in the temperature, pressure, and density of the sample.

The third area is that of the signal generation process. Photothermal spectroscopy signals are based on changes in sample temperature or related thermodynamic properties of the sample. These are usually monitored through the refractive index of the sample or a thermal coupling fluid placed in contact with the sample. Several properties may affect the refractive index of the medium. The most common is the density. However the refractive index may also change with temperature, population in optically excited states, and with chemical composition if photochemical reaction occurs. There are a variety of instrumental methods used to probe the changes in the sample's refractive index. Other instrumental methods used for photothermal spectroscopy directly probe the temperature or related thermodynamic properties, but the most sensitive methods probe the spatial or temporal gradients of these properties.

<Figure 1.3 - Generic Photothermal Apparatus>
A schematic diagram illustrating the main components to apparatuses used for photothermal spectroscopy is shown in Figure 1.3. Most apparatuses consist of six main components; 1) light used for sample excitation, 2) sample, 3) light used to monitor refractive index perturbations, 4) a mask, aperture, or other form of spatial filter for the probe light, 5) an optical detector used to detect the optically filtered probe light, 6) electronic signal processing equipment. The excitation light heats the sample. The probe light monitors changes in the refractive index of the sample resulting from heating. The spatial and propagation characteristics of the probe light will be altered by the refractive index. The spatial filter selects those components of the altered probe light that change with the samples' refractive index. The optical detector monitors changes in the probe light power past the spatial filter. In some apparatuses, a spatial filter and a single channel detector are combined using an image detector. Signals generated by the photodetector are processed to enhance the signal to noise ratio.

In addition, an apparatus may also be equipped with detectors to monitor the excitation and probe light power, a thermostatic sample holder, and optical spatial filters to control the spatial profiles of the excitation and probe light. This additional equipment is used to control the experiment environment and to measure the optical power required to accurately quantify changes that occur in the sample. These components are necessary when the data must be used to determine absolute absorption of the sample.

In theory, the photothermal spectroscopy signal can be accurately calculated based on knowledge of the experimental apparatus, the parameters that characterize light propagation, and the optical parameters of the sample. The following items must all be accounted for in the calculations; 1) determine the optical absorption resulting in sample heating; 2) determine the rate of heat production; 3) determine the temporal and spatial temperature and density change; 4) relate the refractive index change to the temperature or density change using the thermal-optical parameters of the sample; 5) calculate the strength of the optical element formed from the spatial-dependent refractive index change; 6) calculate the optical and electronic signal resulting from passage of light through apertures or using specialized detectors.
1.3 Photothermal spectroscopy methods

There are a variety of methods used to monitor the thermal state of the analytical sample (Harris 1986, Tam 1986, Dovichi 1987, Tam 1989). Direct calorimetric or thermometric methods use temperature transducers to measure analytical sample temperature. Pressure transducers are used to monitor the pressure wave associated with rapid sample heating. Photothermal interferometry, photothermal deflection spectroscopy, photothermal lensing spectroscopy, also known as thermal lens spectroscopy, photothermal diffraction spectroscopy, and methods based on sample reflection changes are all based on monitoring refractive index changes associated with sample heating. Infrared detectors can be used to monitor changes in the samples infrared emission associated with heating. Each of these methods are based on a measurement of temperature change associated with increasing the energy of the analytical sample.

Photothermal methods have been reported by individuals working in several areas of science and technology. Subsequently, there are several names that the particular methods are known by. The temperature changes resulting from the photothermal effect can be detected using a variety of methods. These methods are summarized in Table 1.1. Temperature can be directly measured using thermocouples, thermistors, or pyroelectric devices in the method of photothermal calorimetry. Temperature changes can

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Table 1.1 Common detection techniques used in photothermal spectroscopy

<table>
<thead>
<tr>
<th>Thermodynamic Parameter</th>
<th>Measured Property</th>
<th>Detection Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Temperature</td>
<td>Calorimetry</td>
</tr>
<tr>
<td></td>
<td>Infrared Emission</td>
<td>Infrared Emission</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photothermal Radiometry</td>
</tr>
<tr>
<td>Pressure</td>
<td>Acoustic Wave</td>
<td>Photoacoustic Spectroscopy</td>
</tr>
<tr>
<td>Density</td>
<td>Refractive Index</td>
<td>Photothermal Lens</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photothermal Interferometry</td>
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<tr>
<td></td>
<td></td>
<td>Photothermal Deflection</td>
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<tr>
<td></td>
<td></td>
<td>Photothermal Refraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photothermal Diffraction</td>
</tr>
<tr>
<td></td>
<td>Surface Deformation</td>
<td>Surface Deflection</td>
</tr>
</tbody>
</table>
also be indirectly measured using methods which monitor infrared emission since the thermal infrared emission is related to sample temperature. The method of thermal emission or photothermal radiometry of infrared radiation can be used to monitor relatively large temperature changes that occur as a consequence of optical absorption. Although not very sensitive, this method has great potential for application in nondestructive materials analysis and testing. Using infrared sensitive cameras, it can be used for imaging the thermal properties of large samples.

Two other temperature dependent thermodynamic parameters that are commonly exploited in photothermal spectroscopy are pressure and density. The pressure changes that occur upon periodic or pulsed sample heating can be detected by using a microphone or other pressure transducer to monitor the acoustic wave. The method of optoacoustic or photoacoustic spectroscopy is based on the measurement of this pressure wave.

Although produced by the same photothermal effects, photoacoustic, infrared radiometry, and photothermal spectroscopies are typically treated as separate methods. Photothermal spectroscopy refers to methods that monitor the temperature dependent refractive index changes, usually with a probe laser. Nonetheless, it is apparent from hydrodynamic relaxation that the photoacoustics cannot be avoided in a treatment of photothermal spectroscopy. The photoacoustic pressure wave generated by the photothermal effect is observed in photothermal spectroscopy and the rate of sample relaxation is controlled by the rate at which the sample can approach isobaric conditions. Moreover, infrared emission is another method of thermal heat transfer that should at least be quantified in terms of the effect that it may have on the photothermal signal magnitude. All of these effects should be considered in a comprehensive treatment of the photothermal effect.

Under steady-state, an isobaric condition, the density is related to the temperature through the volume expansion coefficient. Temperature dependent density changes are difficult to measure directly. But density changes can affect samples in several different ways. In solid samples, the density change alters physical dimensions at sample surfaces. Sample dimension changes give rise to two optical methods for monitoring the temperature change based on surface deformation. A homogeneous deformation (expansion or contraction) displaces the surface of the sample. Interferometry can be used on reflective samples. Since small displacements, on the order of a few parts per million of the wavelength of probe beam light, can be measured using interferometry, this method may be used for sensitive measurement solid sample absorption. Spatially heterogeneous expansion (or contraction) can also cause the surface angle to change. A probe
beam reflected from the surface will change angle when heterogeneous expansion occurs. Measurement of the probe beam angle gives rise to the method of photothermal surface deflection spectroscopy.

The majority of studies addressing the use of photothermal spectroscopy for chemical analysis have been based on refractive index measurements. In transparent samples, the temperature dependent refractive index of the sample itself is probed. For opaque or scattering surfaces, temperature dependent changes in the refractive index of fluid that couples heat out of a solid sample are measured. There are several methods used to detect the resulting refractive index change. Several of these are shown in Figure 1.4. Publications in photothermal spectroscopy come from researchers working in the fields of analytical and physical chemistry, physics, and optical engineering. Subsequently there is a wide range of nomenclature used to describe methods for refractive index change detection in the photothermal spectroscopy literature. But all of these methods rely on a few basic principles of light propagation, namely, optical pathlength changes, diffraction, and refraction. Light refraction can result in a direction change and/or focusing.

<Figure 1.4 - Photothermal Instruments>

The optical pathlength changes that occur due to the photothermal induced refractive index change can be measured with interferometry. Using interferometry, the phase of monochromatic light passing through the heated sample, relative to the phase passing through the reference arm, results in a change in power at a photoelectric detector. There are several different interferometric schemes that can be used to detect changes in the optical pathlength induced by the photothermal effect. These methods may all be classified as being photothermal interferometry.

Spatial gradients in refractive index result in a direction change in the propagation of a ray of light. Thus light will exit a medium with a refractive index gradient at an angle relative to the incident ray. This bending of light path is commonly called photothermal deflection spectroscopy.

Spatial dependent refractive index profiles can also result in focusing or defocusing of light. This occurs when the refractive index profiles are curved. Thus the thermally perturbed sample can act as a lens. Light transmitted through an aperture placed beyond the photothermal lens will vary with the strength of the lens. Photothermal methods based on measurement of the strength of this lens are called photothermal lensing spectroscopy. Some experimental apparatuses measure a signal that is due to the combined effects of deflection and lensing. These may be generally classified as photothermal refraction spectroscopy methods.
Lastly, a periodic spatial refractive index modulation results in a volume phase diffraction grating. The grating will diffract light at an angle that meets requirements from Bragg's Law. The amount of light diffracted is proportional to the refractive index change. The diffracted light is measured with a photoelectric detector. Methods used to measure spectroscopic signals based on volume phase diffraction gratings formed by the photothermal effects are called photothermal diffraction spectroscopy.

The key to the success of sensitive photothermal apparatuses lies in measurement of a thermal change and not the thermal state itself. Although apparatuses could directly or indirectly measure the thermodynamic parameters such as temperature, pressure, density, and energy state, the limiting absorption that could be measured would be imposed by thermodynamic fluctuations. Sensitive photothermal spectroscopy methods circumvent direct measurements by measuring refractive index changes due to a non-equilibrium change in the energy of the sample. The change occurs in both space and time. Photothermal spectroscopy methods measure some effect that the spatially or temporally dependent refractive index change has on the propagation characteristics of light used to monitor the refractive index.

Each of these apparatuses detect the change in refractive index that accompanies optical absorption. Photodetectors are used to monitor probe power changes. These power signals are time dependent. The analytical signal is usually related to the change in detected power relative to the incident power of the probe. There are three main types of time dependence that analytical signals can have. These in turn depend on the temporal character of the excitation source. The main excitation and detection schemes are given in Table 1.2

Table 1.2 Main sample excitation schemes used in photothermal spectroscopy

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Signal</th>
<th>Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed</td>
<td>Short-lived transient, magnitude decreases with time</td>
<td>Peak magnitude estimation and transient waveform analysis</td>
</tr>
<tr>
<td>Continuous</td>
<td>Long-lived transient, magnitude increases with time</td>
<td>Steady-state magnitude estimation and transient waveform analysis</td>
</tr>
<tr>
<td>Modulated</td>
<td>Periodic modulation, magnitude and phase are functions of frequency</td>
<td>Periodic wave magnitude and phase analysis using frequency selective filters or lock-in amplifiers</td>
</tr>
</tbody>
</table>
Pulsed excitation sources produce transient signals. These signals are a maximum immediately following sample excitation and decay as the sample approached equilibrium through thermal diffusion. The transient signals last from a few microseconds in the gas phase to several milliseconds in condensed phases. The time duration is inversely proportional to the thermal conductivity of the media since thermal diffusion or conduction removes energy from the sample and more importantly, distributes the energy throughout the sample. Photothermal lens, deflection, and diffraction apparatuses respond to spatial variations in the refractive index. Thus homogeneous distribution of energy throughout the sample does not result in a signal. Interferometric measurements may be able to detect the refractive index change after thermal diffusion has distributed the energy. However, environmental thermal stability is usually not good enough to allow this. Sensitive interferometric apparatuses rely on the detection of a temporal change in refractive index.

Continuous excitation produces signals that are initially small but increase in magnitude as the irradiation time progresses. Initially, thermal diffusion removes heat slower than the heat produced by optical excitation. The Fourier law of heat diffusion states that the heat flux, \( j_H \), is proportional to the temperature gradient

\[
 j_H = -k \nabla T
\]

The proportionality constant is the thermal conductivity. As the sample absorbs radiation and converts the energy to heat, the temperature gradient increases. When the radiative heating flux equals the energy flux due to thermal conduction, a steady-state spatially-dependent temperature change is attained. Thus the photothermal signals eventually reach a steady-state value. The signals develop over the course of from milliseconds to seconds, the time required to attain the steady-state value being proportional to the thermal conductivity.

For analytical, e.g. concentration, measurements, both pulsed and continuous excitation requires estimation of the signal magnitude. Signal magnitudes are directly proportional to the sample absorbance in a first order approximation. Signal magnitudes can be measured directly, for example using an oscilloscope or ammeter, or the signal transient can be recorded and subsequently processed to enhance measurement precision.

Excitation sources may also be modulated. Chopped or oscillatory excitation produces oscillating signals. The resulting signals can be processed using band pass filters or lock-in amplifiers. The magnitudes of the oscillating signals depend on sample absorbance, the frequency of excitation, and thermal conductivity of the
medium. With modulated excitation, signal magnitudes are proportional to sample absorbance but decrease with increasing frequency. In addition to the signal amplitude information, phase-sensitive lock-in analyzers also produce signal-to-excitation phase-shift information. The frequency dependent phase-shift information is essentially equivalent to that contained in the time-dependent signal transients obtained using pulsed excitation.

1.4 Application of Photothermal Spectroscopy

There have been many applications of photothermal methods for chemical and material analysis. Tam (1983, 1986, and 1989) is perhaps primarily responsible for sorting through the vast amount of literature and characterizing the applications of these methods. Many of these applications are covered in the book edited by Sell (1989). These applications fall under four main categories.

(1) **Photothermal spectroscopy**: the signal magnitude is measured as a function of wavelength in this application. The photothermal signal is proportional to the absorbed light. So the spectrum is technically an excitation spectrum. The resulting excitation spectrum can be an accurate measure of the absorption spectrum if the thermal quantum yield and fraction of light transmitted to the absorber do not change with wavelength. This technique has found widespread use for solid sample analysis where incoherent excitation light sources can be used. Applications to liquid and gas sample analysis has been limited because of the difficulties encountered when attempting to scan the wavelengths of lasers while keeping them focussed at a particular position.

(2) **Photothermal detection**: is similar to photothermal spectroscopy only a single wavelength source is used to excite the sample. The signal magnitude can be related to sample absorbance or analyte concentration. Samples must be prepared and separated so that there is no interference absorption and so that the sample matrix is the same for all measured samples. The main application is for trace analysis. Although not restricted to coherent sources, this application is normally performed using laser excitation sources to enhance the limits of detection. The application is also suited for effluent detection in chromatography. The spatial coherence of lasers allows the use of small volume detection cells or on-column detection.

(3) **Photothermal monitoring of excitation and relaxation process**: in this application the signal magnitude is measured as a function of time or excitation irradiance. The time dependent data is used to deduce photophysical and photochemical parameters such as excited state lifetimes, enthalpies of formation, lifetimes of metastable states, and thermalization times. The excitation irradiance dependent data can be used to calculate multiphoton absorption cross-sections and parameters relating to optical saturation and bleaching.

(4) **Photothermal probing of the physical properties**: many of the physical properties of a sample can be determined using photothermal methods. Photothermal methods have been used to measure temperature,
thermal diffusivities, sound velocity, bulk flow velocities, surface thickness, and specific heats. In homogeneous samples, the full photothermal transient is typically analyzed in order to obtain this information. However, some of these parameters can be determined by measuring signal magnitudes, signal decay times, and signal onset times for carefully designed experiments. Thermal properties of heterogeneous samples can be obtained by raster scanning the optical excitation source over the sample surface. In this case the signal magnitude and phase is measured as a function of spatial coordinate.

1.5 Illustrative history of photothermal spectroscopy

1.5.1 Nature of the photothermal effect

Most of us observe the photothermal effect in our lives. On the beach, sand is too hot to walk on with bare feet in midday summer. This is because the sand absorbs sun's radiation and converts this energy to heat. The added heat results in a temperature increase because of the finite heat capacity of the sand. When heat is generated faster than it can be dissipated by radiative or diffusive mechanisms, the temperature of the sand increases. However, the rate of heat dissipation increases with the temperature difference between the surface sand, and soil below or air above it. Under constant illumination conditions, the sand reaches an equilibrium temperature wherein the rate of heat generated by the photothermal effect is balanced by the rate at which the heat is dissipated. Another way we utilize the photothermal effect is to warm ourselves by the radiation of a campfire. Here, our skin is the absorber and the campfire is the source of the infrared radiation.

A concrete example of the photothermal effect, which is also the basis for a photothermal spectroscopy method, is the shimmering surface or optical mirage effect. This effect is illustrated in Figure 1.5. A hot highway sometimes looks like a reflective surface. It appears as if it were a puddle of water. We come to understand that the apparently shiny surface is not due to reflection. It is just a mirage. In fact, the mirage effect is one of the photothermal effects that have been exploited for chemical and materials analysis. Radiation from the sun is absorbed by the concrete or asphalt resulting in surface heating. The hot surface transfers energy to the air above the surface. A temperature gradient develops between the air near the surface and the bulk air above. Air expands when it is heated. The density of the air at the surface is less than that in the bulk. The decreased density results in a decreased refractive index. Since the speed of light is faster in the low refractive index media, light incident at an acute tangent angle is refracted upward. An observer looking at the surface at an acute tangent angle does not see the surface but rather sees the rays coming from the sky above the surface.

<FIGURE 1.5>
It is likely that our predecessors had a working knowledge of the photothermal effect long before they could apply more abstract concepts such as optical transmission, color, and other factors leading to modern theories of spectroscopy. But although photothermal effects may have been recognized in the prehistoric past, it took an understanding of the photothermal process to apply the photothermal effect for spectrochemical measurements. Much of what is now known about photothermal spectroscopy has been developed over the past century. Many of the advances came about as a result of the developments in laser technology about 25 years ago. Other advances were made simple by the recognition and understanding of what is now called the photothermal effect.

1.5.2 Photoacoustic spectroscopy

The oldest technical application of the photothermal effect is believed to be the communication device, the photophone, invented by Bell (1880, 1881). Bell found that audible sound could be heard coming from a tube filled with various materials when the light shining on the transparent tube was modulated. The sound was loud when the tube was filled with radiation absorbing gases or solids, and weak when filled with a liquid. The operational principles are now well understood. Modulation of the light impinging on an absorbing substance will produce a similar modulation in temperature through the photothermal effect. In a gas of restricted volume, temperature modulation produces a pressure modulation. The periodic pressure modulation is an acoustic signal.

Some time later Viengerov (1938) used the photoacoustic effect to study light absorption in gases and obtained quantitative estimates of concentration in gas mixtures based on signal magnitudes. This may have been the first use of photoacoustic spectroscopy. Sensitive chemical measurement applications followed the work of Kerr and Atwood (1968) who used a laser to excite the samples. More interest in the method was generated when Kreuzer (1971) demonstrated part-per-billion (ppb) detection sensitivities of methane in nitrogen using a 3.39 μm helium-neon laser excitation source, and later (Kreuzer 1972) sub-ppb of ammonia and other gases using infrared CO and CO₂ lasers. These high sensitivity measurements were possible because of the laser source used for excitation. Large photoacoustic spectroscopy signals resulted from the high spectral brightness and the spatial coherence of the lasers used for sample excitation. The photoacoustic measurement methods came at about the same time as the recognition that trace species could have a major impact on the environment.

In the time since the first chemical measurements by Viengerov (1938), the theory and practice has been developed to a high degree. The theories for sound generation, propagation, and interaction with matter were developed though the mid-20th century (Landau and Lifshitz 1959, Herzfeld and Litovitz 1959) and
acoustics were applied to physical chemical analysis. The theories are complex and exact solutions for sample excitation and signal generation are often difficult to interpret and verify. Nonetheless, the principles of photoacoustic spectroscopy are now commonly understood and photoacoustic spectroscopy is being applied to a wide range of analysis problems.

The essential components for an apparatus used for photoacoustic spectroscopy is shown in Figure 1.6. The light source, either pulsed or modulated, periodically heats the sample by the photothermal effect. Periodic sample heating followed by expansion causes a periodic pressure wave which is detected with the pressure transducer. The pressure transducer signal is proportional to the amplitude of the pressure wave. Consider a sample that has a low enough absorption coefficient that the transmission can be approximated by,

$$T(l) = e^{-\alpha l} \approx 1 - \alpha l$$  \hspace{1cm} (2)

where $T(l)$ is the optical pathlength, $l$ (m), dependent transmission, and $\alpha$ (m$^{-1}$) is the absorption coefficient. The amount of energy absorbed from a laser source with an optical energy of $Q$ (J) is $Q(1-T(l)) \approx Q\alpha l$. If the quantum yield for heat production is unity, all the absorbed optical energy is converted into heat. The peak pressure change, $\delta P_{\text{acoustic}}$ (Pa), is proportional to (Lai and Young 1982, Tam 1986)

$$\delta P_{\text{acoustic}} \propto \tau^{3/2} \frac{\alpha Q c}{C_P r} \left( \frac{c}{r} \right)^{1/2}$$  \hspace{1cm} (3)

where $c$ (m s$^{-1}$) is the sound velocity, $\beta$ (K$^{-1}$) is the volume expansion coefficient, $r$ (m) is the radial distance between the transducer and the source, $C_P$ (J kg$^{-1}$ K$^{-1}$) is the specific heat, $Q$ (J) is the pulse energy, and the pressure perturbation time, $\tau$ (s), is the root-mean-square average of the relaxation times and the pulse or modulation width. Relaxation times may include contributions from the excited state relaxation time and the acoustic relaxation time

$$\tau_a^2 = \frac{w^2}{2c^2}$$  \hspace{1cm} (4)

where $\tau_a$ (s) is the acoustic relaxation time, and $w$ (m) is the radius of the beam used for sample excitation. The acoustic relaxation time is that required for the heated sample to expand.

The important points to be deduced from the acoustic pressure equation are 1) the signal scales as the $\alpha Q$ product. 2) The signal falls off as the pressure transducer is moved away from the excited region as $r^{-3/2}$. 3) The signal is inversely proportional to the pressure perturbation time, favoring short pulse excitation and
small beam waists. 4) The signal magnitude is proportional to the thermodynamic properties of the sample through the \((\beta c^3/C_P)\) term. In general, \(\beta\) is much smaller for liquids and solids than it is for gases. Not only does this explain the early observations of Bell (1881) but also explains why direct photoacoustic spectroscopy is most sensitive for gas sample analysis.

*Figure 1.6 - Figure 4 of Tam (1989)*

The spectra of solid or liquid samples can be measured by directly coupling the acoustic wave to a transducer or by coupling the heat generated at the surface to a gas "coupling fluid." This principle was used in Bell's original photophone but wasn't rediscovered until Parker (1973) noticed that optical energy absorbed by the gas sample cell windows would transfer heat to a gas thereby causing a significant photoacoustic signal. This effect was developed by Rosencwaig (1977, 1980) and is now commonly used for obtaining spectra of strongly absorbing solids and liquids. A modern version of a device for photoacoustic spectroscopy of condensed samples is shown in Figure 1.7. A solid or liquid sample is placed in the sealed photoacoustic cell. The excitation source is absorbed at or near the surface. Absorbed radiation is randomized increasing the surface temperature. The heated surface heats the gas causing it to expand. Periodic heating of the surface creates an acoustic wave that is monitored with the sound transducer.

*Figure 1.7 - Figure 5 of Tam (1989)*

There have been scores of publications on the uses of photoacoustic spectroscopy for chemical and material analysis. Absorption detection limits \((\alpha)\) are about \(10^{10}\) cm\(^{-1}\) for gases (Patel, *et al.* 1977) and \(10^6\) cm\(^{-1}\) for liquids (Beitz, *et al.* 1990). These are very close to the theoretical detection limits (Zharov and Letokhov 1985). Many review articles and books have been written on this method. Some of the more recent reviews of general applications are Tam (1983, 1986), Hutchins and Tam (1986). Patel and Tam (1981) reviewed applications of photoacoustic spectroscopy for condensed matter. Betteridge and Meylor (1984) have reviewed the applications of photoacoustic spectroscopy in chemical analysis. Zharov (1986) reviewed photoacoustic applications to chromatography. Meyer and Sigrist (1990) have reviewed applications to gas analysis. General books on photoacoustic spectroscopy include those of Pao (1977), Rosencwaig (1980), and Zharov and Letokhov (1986). Mandelis (1987) has edited a book on application of photoacoustic and photothermal spectroscopy methods for semiconductor analysis. Hess (1989a and 1989b) has edited a books regarding the application of photoacoustic and photothermal spectroscopy methods for gas and surface analysis. Nyquist, *et al.* (1990) and Putzig, *et al.* (1992) have reviewed photoacoustic and photothermal spectroscopies in their *ANALYTICAL CHEMISTRY Fundamental Reviews* of infrared analysis. Kitamori and Sawada (1991) have discussed unconventional applications in their review.
1.5.3 Photothermal lens spectroscopy

The first photothermal spectroscopic method to be applied for sensitive chemical analysis was photothermal lens spectroscopy. The photothermal lens effect was discovered when Gordon, et al. (1964, 1965) observed transient power and beam divergence changes in the output of a helium-neon laser after placing "transparent" samples in the laser cavity. Their apparatus, shown in Figure 1.8, was originally intended to be used as a high irradiance source for Raman spectroscopy. They observed the photothermal lens effect when pure organic liquids and solids, glass and lucite, were placed in the laser cavity. A theory describing the effect was developed to account for their observations. This theory was an accurate description of the physics of thermal lens formation and signal generation, and is essentially the same as that used to this day (Whinnery 1974). The photothermal lens results from optical absorption and heating of the sample in regions localized to the extent of the excitation source. The lens is created through the temperature dependence of the sample refractive index. The lens usually has a negative focal length since most materials expand upon heating and the refractive index is proportional to the density. This negative lens causes beam divergence and the signal is detected as a time dependent decrease in power at the center of the beam.

Laser output power transients for the first apparatus are shown in Figure 1.9. Although the theory was accurate, these transients were difficult to interpret. The transients arose due to the interaction between the intracavity beam propagation altering character of the photothermal lens element and the intracavity apertures. Nonetheless, Solimini (1966) refined the apparatus and measured the absorption coefficients of 27 organic liquids using this method.

The first extracavity sample photothermal lens apparatus was used by Grabiner, et al. (1972) to measure vibrational relaxation rate constants. Hu and Whinnery (1973) recognized that the extracavity sample configuration would be more flexible and could also result in sensitive absorbance measurements. The apparatus and beam analysis, shown in Figure 1.10, is essentially the same as that used for single laser photothermal lens spectroscopy today. The transient signals produced extracavity are less complicated than those of the intracavity configuration and the theory describing the transients is more tractable. The essential components of the apparatus are; 1) the coherent, laser excitation source which can deliver high optical powers over a small cross-section area of the sample, 2) a low-absorbance sample, 3) a spatial filter or pinhole placed in far field, and 4) a photodetector to measure the power past the pinhole.

The extracavity photothermal lens spectroscopy signal can be described in terms of the focal length of the thermal lens formed within the sample. The simplest form of the focal length is found by assuming that
\( \alpha l << 1 \) and unit quantum efficiency for heat production. A sample excited by a laser beam with an irradiance of

\[
E(r) = \frac{2\Phi_0}{\pi w^2} e^{-2r^2/w^2}
\]

where \( E(r) \) (W m\(^{-2}\)) is the radially dependent irradiance, and \( \Phi_0 \) (W) is the incident radiant power, will produce a time-dependent photothermal lens with a focal length, \( f(t) \),

\[
f(t) = f(\infty)(1 + t_c / 2t)
\]

where \( f(\infty) \) (m) is the steady-state focal length formed at infinite time

\[
f(\infty) = \frac{n_0^2 \kappa w^2}{\Phi_0 \alpha l (dn/dT)}
\]

and \( t_c \) (s) is the characteristic thermal time constant

\[
t_c = \frac{w^2 \rho C_p}{4\kappa}
\]

where \( \kappa \) (J cm\(^{-1}\)s\(^{-1}\)K\(^{-1}\)) is the thermal conductivity, \( n_0 \) is the refractive index of the medium where detection takes place (normally air), \( n \) the refractive index of the sample, \( T \) (K) the temperature, \( \rho \) (kg m\(^{-3}\)) the density, and \( C_p \) (J kg\(^{-1}\)K\(^{-1}\)) the specific heat. The lens is formed because the optically heated sample has a different refractive index from that of the bulk of the sample. The differential term \( (dn/dT)_p \) is the temperature dependent refractive index change at constant pressure. The shape of the temperature change produced by a Gaussian excitation source is parabolic near the center. The parabolic refractive index perturbation is equivalent in form to a simple lens.

The photothermal lens signal is obtained by monitoring the laser power that passes through a pinhole placed far from the sample. The photothermal lens will either focus or defocus the laser. When this happens, the power at the center of the beam will either increase or decrease. This change in power is maximized when the sample is placed one confocal distance to either side of the laser's focus. In this case the relative change in power monitored past the pinhole aperture is

\[
\frac{\Phi_d(0) - \Phi_d(t)}{\Phi_d(t)} \approx -\frac{2z_0}{f(t)}
\]
where \( \Phi_d(t) \) is the time-dependent power and the confocal distance is \( z_0 = n_0 \pi w_0^2 / \lambda \), \( w_0 \) being the beam waist radius at the focus and \( \lambda \) (m) is the wavelength of the laser. The + sign applies to samples placed before the focus, the - sign for samples behind the focus. The time dependent signal observed past the pinhole is

\[
\frac{\Phi_d(0) - \Phi_d(t)}{\Phi_d(t)} \approx - \left( \frac{d\Phi_0}{dT} \right) \frac{\lambda \kappa}{1 + t_c / 2t} \tag{10}
\]

The essential components to interpreting the signal are 1) the time dependent signal increases or decreases the power past the pinhole. 2) The time constant for signal evolution, \( t_c \), is proportional to the square of the beam waist radius in the sample. 3) The signal magnitude is proportional to the absorption coefficient, pathlength, and excitation power. 3) The signal magnitude also depends on the thermal, \( \kappa \), and optical, \( (dn/dT) \), properties of the sample. 5) For times much greater than \( t_c \), the steady-state power change is related to absorption coefficient by

\[
\alpha \approx - \frac{\Phi_d(0) - \Phi_d(t)}{\Phi_d(t)} \frac{\lambda \kappa}{\Phi_l(dn/dT)} \tag{11}
\]

The absorption coefficient can be obtained by measuring the power change with knowledge of the temperature dependent refractive index.

\(<Fig \ 1.11 - Fig \ 5 \ Whinnery \ 1973>\>

It is difficult to see from these equations how photothermal lens spectroscopy method can enhance absorbance measurements. Dovichi and Harris (1979) introduced the concept of the enhancement factor. The enhancement factor is the ratio of the photothermal lens signal magnitude to that which would be obtained using conventional transmission spectroscopy. For weakly absorbing samples, the transmission spectroscopy signal can be cast in a form similar to that for the photothermal lens spectroscopy signal

\[
\frac{\Phi_0 - \Phi_l}{\Phi_0} \approx \alpha d \tag{12}
\]

where \( \Phi_l \) is the power after passing through the sample. The ratio of the photothermal lens signal to this signal yields the enhancement factor

\[
E = \left( \frac{dn}{dT} \right)_p \frac{\Phi_0}{\lambda \kappa} \tag{13}
\]

The enhancement is a function of the thermodynamic and optical properties of the solvent, and on the power used to excite the sample. Nonpolar solvents are particularly useful for trace analysis because of their
relatively high \((dn/dT)\) and low \(\kappa\). For example, CCl\(_4\) has temperature dependent refractive index of \(-6.12 \times 10^{-4}\ \text{K}^{-1}\) and a thermal conductivity of 0.103 W m\(^{-1}\)K\(^{-1}\) (Dovichi 1987). The theoretical enhancement factor is 11560 W\(^{-1}\) for the 514 nm line of an argon ion laser. Of course, the higher the power, the greater the enhancement. Even a modest 10 mW laser will yield signals that are over one hundred fold better than those of the conventional transmission spectrophotometer. Absorption coefficient detection limits in 1 cm cuvettes are about \(10^{-7}\ \text{cm}^{-1}\). This detection limit was reported by Dovichi and Harris (1981a) for 514.5 nm excitation of samples in CCl\(_4\) solvent using 160 mW of laser power. The enhancement factor under these conditions is \(~1850\). Based on these, the absorbance detection limits calculated for the equivalent conventional transmission spectrophotometer would be \(2 \times 10^{-4}\) absorbance units. Although it is a matter for discussion, this is about what one might expect from a double dispersing transmission spectrophotometer.

The characteristic time constant, \(t_c\), should also be considered in the experimental design. With a shorter time constant, more measurements can be made in a given time. Since replicate measurements can be used to increase the precision of the estimate, the shorter time constant resulting from smaller focus spot sizes, are favored. For example, CCl\(_4\) has a thermal diffusivity of \(7.5 \times 10^{-8}\ \text{m}^2\ \text{s}^{-1}\). A laser with a beam waist radius of 1 mm in the sample cell will produce a signal with a characteristic thermal time constant of 3.3 second whereas using a 10 \(\mu\)m beam waist radius, \(t_c=0.33\) msec. The 10 \(\mu\)m beam would allow \(10^4\) replicate measurements in the same time required to obtain one measurement with a 1 mm beam waist. The measurement precision would increase by 100 using the smaller beam waist and equivalent measurement times.

The first analytical application of photothermal spectroscopy was the trace level determination of Cu(II) with an EDTA complex reported by Dovichi and Harris (1979). They used the single laser extracavity photothermal lens apparatus. This method is perhaps the most well-known and used of all the photothermal spectroscopy methods. The relative simplicity of the apparatus coupled with the low solution absorption detection limits, \(10^{-7}\ \text{cm}^{-1}\) (Dovichi and Harris 1981), make it highly attractive for trace analysis applications.
1.5.4 Photothermal interferometry

Shortly after the discovery of the photothermal lens effect, researchers found that the photothermal induced refractive index change could be measured by more direct means. McLean, Sica, and Glass (1968), and Longaker and Litvak (1969) recognized that optical absorption resulting in sample heating and subsequent changes in refractive index would cause a phase shift in light passing through the heated region. The optical phase shift can be detected with an interferometer. The method of using optical interferometry to measure refractive index changes was not in itself new, but using an excitation laser to heat the sample while monitoring the refractive index change was. Most photothermal interferometry apparatuses are based on laser excitation sources. Stone (1972, 1973) showed that both coherent and wide-band incoherent sources could be used. Stone used the modified Jamin interferometer apparatus shown in Figure 1.12 to obtain the absorption spectrum of chlorobenzene shown in Figure 1.13. Using this apparatus, 2-3 mW of excitation source power could be used to measure absorption coefficient of about 2×10^{-5} cm^{-1}.

<Figure 1.12 - Figure 7 of Whinnery 1974>
<Figure 1.13 - Figure 8 of Whinnery 1974>

The conventional approach to measuring small absorption coefficients is to increase the optical pathlength. The data in Figure 1.13 compares results obtained using long pathlength transmission spectrophotometry to those of the photothermal interferometer. Transmission losses may be due to reflection, scattering, and absorption. The finite transmission losses seen in the bromobenzene spectrum are not necessarily due to optical absorption. On the other hand, the photothermal interferometer responds only to absorption. The resulting spectrum is technically an excitation spectrum since the heat is generated by optical absorption of the excitation light.

An almost astonishing feature of the interferometric method is its sensitivity. Davis and Petuchowski (1981) have measured absorption coefficient detection limits as low as 10^{-10} cm^{-1} for gaseous samples in windowless absorption cells using chopped infrared excitation lasers at irradiances of 2.5 MW m^{-2}. Other sensitive interferometric methods for measuring the photothermal effect are discussed by Friedrich (1983), and Dovichi (1987) has reviewed the applications to chemical analysis.

The interferometric studies of Longaker and Litvak (1969) used cameras to obtain images of phase shift patterns resulting from the refractive index perturbation produced by pulsed Nd glass laser sample excitation. This classic and innovative work revealed a wealth of information regarding photothermal effects. The apparatus used for these studies is shown in Figure 1.14. The photographic camera was used to obtain pictures of the fringe patterns for visual analysis and the vidicon camera was used to obtain quantitative...
information for critical evaluation of the data. Photographic images shown in Figure 1.15 reveals some of
effects they observed. For absorbing samples, the refractive index perturbation had two components with
different space and time behaviors. A long-lived transient was observed near the region excited by the
pulsed laser. This component was the thermal perturbation produced by the photothermal effect.

\[ \delta \phi (\text{rad}) \]

The phase shift, \( \delta \phi \) (rad), produced from the thermal component is related to the density change through

\[ \delta \phi = \frac{2\pi l}{\lambda} \left( \frac{dn}{d\rho} \right) \delta \rho \]  \hspace{1cm} (14)

were \( \lambda \) is the wavelength of the laser used to measure the refractive index change. The theory developed by
Longaker and Litvak predicts that for weakly absorbing samples with rapid excitation and excited state
relaxation times, the on-axis time dependent density change for pulsed radiation is

\[ \delta \rho(t) \propto \frac{2\beta a Q}{\pi \omega^2 C_p} \left( e^{-t/\tau} - 1 \right) \]  \hspace{1cm} (15)

for times much shorter than \( \tau \). Thus the signal rise-time is limited by the same acoustic relaxation time that
limits the signal magnitude in photoacoustic spectroscopy. The spatial density change could be
quantitatively determined by counting interference fringes. Videocon camera data were analyzed in terms of
the thermal-induced phase shifts and the focal length of the photothermal lens resulting from the thermal
perturbation. This later data was found to agree with the theory developed by Gordon, et al., to describe the
photothermal lens.

In addition to the thermal component, a short-lived transient component was found. This component
propagated away from the heated region as a wave. This was identified as an acoustic pressure wave.
Referring to the ammonia gas data in Figure 1.15, the thermal perturbation can be seen at the center and the
dark ring around the central perturbation is due to the propagating pressure or acoustic wave. The acoustic
wave is produced by the rapidly expanding sample heated by the pulsed laser. The ammonia gas absorbs
energy from the pulsed excitation source. Excited state ammonia rapidly relaxes hereby increasing the
temperature of the sample. The heated sample then expands to produce an acoustic compression wave. The
compression wave propagates out away from the excited region. The compression increases the density of
the gas thereby causing an increase in the refractive index. Thus the acoustic wave also results in a
photothermal signal. Although the acoustic wave carries away some of the energy, most of the thermal
energy remains in the region local to the excitation laser irradiation (Bialkowski 1988). Although Longaker and Litvak were not the first to observe this effect, their pictorial observations clearly demonstrate the principles of photothermal and photoacoustic spectroscopies and showed the connection between the two.

Photoacoustic wave generation by the photothermal effect is only one of several mechanisms for acoustic wave generation. Figure 1.15 also shows data obtained for CS₂, a non-absorbing, highly polarizable liquid. The CS₂ data illustrates acoustic waves created without a photothermal perturbation. The acoustic waves are generated by an effect called electrostriction wherein polarizable media are compressed by the electric field of the optical radiation. Electrostriction has not, to date, been observed using photothermal spectroscopy methods.

### 1.5.5 Two-laser photothermal lens spectroscopy

The two-laser photothermal lens apparatus was used before the extracavity single laser method was found. Grabiner, et al. (1972) used a helium-neon laser to probe the photothermal lens produced by a pulsed, infrared laser. They used this two-laser photothermal lens apparatus to determine the vibrational relaxation rate constants for methyl chloride and methyl fluoride gases. Later, Siebert, et al. (1974) used the technique to study relaxation of vibrationally excited CD₄, SO₂, and OCS. Of interest was the rise-time of the photothermal lens signal. The rise-times were measured as a function of added gas pressure and the vibrational relaxation rate constants were deduced from these measurements. The technique was found to be quite satisfactory for relaxation times that were greater than the acoustic limited rise-times. The vibrational relaxation rate constants compared well to those obtained using other methods. Although not exploited in this work, Grabiner, et al. and Siebert, et al. showed that by using this photothermal lens method, infrared absorption could be measured using visible detectors. This would later be used to the advantage of short pathlength infrared absorption studies.

Long, et al. (1976) used the two-laser photothermal lens apparatus shown in Figure 1.16 to measure absorption spectra due to vibrational overtones in pure solvents. A repetitively chopped continuous dye laser was used to form the photothermal lens in the sample and a continuous helium-neon laser probed the resulting lens element. The equations that describe the temperature change and focal length of the photothermal lens are the sample as those given above. However, several advantages to using separate excitation and probe light sources in photothermal lens spectroscopy can be realized in this configuration. 1) The dye laser can be scanned to produce excitation spectra of the sample without having to account for photodetector wavelength response. 2) The excitation source can be focused directly into the sample. This increases the irradiance and the resulting photothermal lens signal by decreasing the beam waist radius in the
sample. 3) A lock-in amplifier can be used to decrease the bandwidth of the measurement thereby enhancing
the signal to noise ratio.

<Figure 1.16 Figure 6 from Fang and Swofford (1984)>

Twarowski and Kliger (1977a) developed a quantitative theory to describe the pulsed laser excited
photothermal lens spectroscopy signals and applied this theory to study the two-photon absorption of
benzene (1977b). This was the first derivation of the time dependent thermal lens given for pulsed laser
excitation. Basically, a pulsed laser with an integrated irradiance $H(r,t)\ (J\ m^{-2})$ of

$$H(r,t) = \frac{2Q}{\pi w^2} e^{2r^2/w^2} \tag{16}$$

will produce a temperature change of

$$\delta T(r,t) = \frac{2\alpha Q}{\pi w^2 \rho C_p} \frac{e^{2r^2/w^2(1+2t/t_c)}}{1 + 2t/t_c} \tag{17}$$

for a single-photon absorption process and for times greater than required for acoustic relaxation. The
inverse focal length was found to be

$$\frac{1}{f(t)} = \frac{1}{n_0} \frac{dn}{dT} \frac{8\alpha dQ}{\pi w^4 \rho C_p} \left( \frac{1}{1 + 2t/t_c} \right)^2 \tag{18}$$

The main characteristics of the pulsed laser photothermal lens spectroscopy signal are 1) the signal
magnitude is greatest at zero time, just after acoustic relaxation of the sample. This allows the pulsed laser
technique to be used to study excited state relaxation kinetics. 2) The signal is inversely proportional to $w^4$
favoring tighter focused beams. 3) The signal decays in a time that is inversely proportional to $t^2$. 4) As
with the chopped continuous excitation laser method, the pulsed laser method can use dye lasers to obtain
excitation spectra and the excitation laser can be focused into the sample cell resulting in greater signal
magnitudes. 5) The high irradiance at the focus can be high enough to induce nonlinear absorption effects.
The multiphoton absorption signal is essentially the same but with the caveat that the absorbed energy is
proportional to the integrated irradiance raised to the power of the number of photons absorbed. Thus the
effective squared beam waist radius is decrease by a factor inversely proportional to the number of photons
absorbed per transition, $w^2/p \to w^2$. This further enhances the signal magnitude and has led to the belief that
photothermal lens spectroscopy is very useful for multiphoton spectroscopy.
Barker and Rothem (1982) pointed out that the simple theoretical description of the photothermal lens shown above does not yield quantitative results in the early times of the signal. They point out an apparent dilemma wherein Grabiner, et al. (1972) use an acoustic wave equation to model results while Twarowski and Kliger (1977a) use a thermal diffusion equation. Barker and Rothem developed a quantitative theory for predicting the photothermal lens signal that takes into account several hydrodynamic relaxation effects. This theory predicts that all but the first of the five points given above hold, but that the signal rise-time is limited by the rate at which the density can change. The latter is related to the sound velocity and the radius of the excitation source (Barker and Toselli 1989).

Fang and Swofford (1983) have written an excellent overview of the theory and developments in photothermal lensing spectroscopy. Dovichi (1987) has reviewed the literature and has commented on analytical applications of the technique. Absorbance detection limits of about $10^{-7}$-$10^{-8}$ cm$^{-1}$ for liquids and gases using 10-200 mW continuous sources. Sell (1989) has collected together a number of chapters addressing many important applications of photothermal spectroscopy. Morris and Fotiou (1989) have reviewed applications to chromatography detection. Dovichi (1990) has included this technique in his review of laser-based micro-analysis.

1.5.6 Photothermal deflection, refraction, and diffraction

The mirage is a common and well understood example of the photothermal effect. However, the analytical method based on this principle, photothermal deflection spectroscopy, was somehow overlooked until Boccara, et al. demonstrated probe laser beam deflection in 1979. The method was applied to surface analysis. A typical experimental set up for photothermal deflection analysis of surfaces is shown in Figure 1.17c. Like the indirect photoacoustic spectroscopy method, this method may be used to examine optical absorptions at or near the surface of solid samples. The sample absorbs optical radiation and heats the gas or liquid above the surface. The heated gas acts like a prism and deflects the probe laser incident tangent to the surface. Probe laser beam deflection is monitored with a position sensing detector. The apparatus is very easy to set up and can produce very sensitive measurements of surface absorption.

The theory for describing the photothermal deflection signal has been worked out for both chopped and pulsed excitation sources. This theory is more complicated than those describing homogeneous fluids because the thermal conduction in the solid and the fluid must both be accounted for. The temperature change that occurs upon pulsed irradiation of a surface with an adsorbed absorbing species is
\[ \delta T_f(x,t) = \frac{\kappa_s H}{\rho_s C_{P,s} D_{T,s}^{1/2} + \rho_f C_{P,f} D_{T,f}^{1/2}} \frac{1}{(4\pi t)^{1/2}} e^{-x^2/(4D_{T,f} t)} \]  

where the \( x \) direction is normal to the surface, \( \kappa_s \) is the unitless surface absorption coefficient, and \( D_T \) and \( \rho C_P \) are the thermal diffusivities and heat capacities of the solid (\( s \)) and fluid coupling medium (\( f \)) respectively. The deflection angle of a probe being refracted by the temperature gradient produced by the heated surface is

\[ \phi(x,t) = -\left( \frac{dn}{dT} \right) \frac{\kappa_s H}{\rho_s C_{P,s} D_{T,s}^{1/2} + \rho_f C_{P,f} D_{T,f}^{1/2}} \frac{x}{4D_{T,f} \sqrt{\pi t}^{3/2}} e^{-x^2/(4D_{T,f} t)} \]

The deflection angle is monitored using a position sensing detector which is placed a short distance from the surface. A change in angle at the sample results in a displacement of the probe laser spot on the detector. For small angles, the linear displacement of the probe laser beam spot is directly proportional to the deflection angle. The above equation shows that the magnitude of the signal will be a function of the offset, \( x \), of the probe laser beam from the surface. There is an optimum offset for maximum signal. This optimum offset is a function of time. The time is that required for the temperature change to diffuse to the region probed by the laser. The temperature diffusion process is often called the thermal wave. This equation also shows that at a particular offset, the time-dependent deflection signal will rise and then fall with time. The time to the maximum is \( t_{max} = x^2/(6D_{T,f}) \). So the time to the maximum signal and the magnitude of the maximum signal are both functions of the displacement of the probe laser beam relative to the surface. This distance is difficult to measure and so photothermal deflection cannot be used to measure absolute absorption coefficients.

One application of this technique caught on rapidly. It was apparent that photothermal deflection could be used for topographic and thermal characterization of samples. The signal magnitude depends on the surface topography, surface absorption coefficient, the thermal properties of the fluid, and the thermal properties of the solid. All other parameters being equal, the signal dependence on the surface to probe laser beam offset allows the surface topography to be measured. For relatively flat surfaces, signal dependence on the solid's thermodynamic parameters allows a thermal image of the solid to be obtained (Murphy and Aamodt 1980, 1981). A solid with a constant surface absorption or an optically dense solid will result in a signal that is inversely proportional to the solid's thermal conductivity. An example of a thermal imaging apparatus is
shown in Figure 1.18. When the solid sample is raster scanned under a focusedexcitation laser source, the
photothermal deflection signal magnitude will be inversely proportional to the solid's thermal parameters.
This thermal imaging technique has been used to determine sample thickness, inclusions in metals
(McDonald 1986), inspect coatings (Busse 1989), and imaging boundaries at crystal domains (Murphy, et al.
1986). The thermal image shown in Figure 1.19 is of aluminum metal. The lighter regions are thought to be
due to subsurface inclusions in the metal. Several applications of photothermal deflection spectroscopy have
been discussed in the recent chapter by Fournier and Boccara (1988).

An useful extension of this technique is to irradiate the entire surface with a series of patterns instead of
scanning the excitation and probe lasers across the surface. Fotiou and Morris (1986) use a moving
Hadamard encoded mask to analyze the spatial distribution of absorption on stationary thin-layer-chromatography plates. This method is more fully described in Morris and Fotiou (1989). A typical
apparatus is shown in Figure 1.20. This apparatus was used to measure band positions and absorptions on
dyed plates. Imaging thus far has been one dimensional but there is no apparent reason why two-
dimensional images could not be obtained.

Jackson, et al. (1980, 1981) extended the photothermal deflection method to include optically transmitting
gas and liquid analysis. In these experiments the excitation and probe lasers propagate collinearly through
the sample cell. In this case the pulsed laser induced temperature change results in the deflection of a
collinear probe beam

$$\phi(r,t) = -\frac{dn}{dT} \frac{8r \alpha dQ}{\pi w^4 \rho C_p} e^{-2r^2 / w^2 (1+2t / t_c)^2}$$  \hspace{1cm} (21)

There is a subtle distinction between the photothermal methods used for surface and transparent sample
analysis. For surface analysis, the probe laser is used to detect a refractive index gradient formed in the
media above the surface. In transparent samples, the refractive index is changed within the sample itself.
Thus the deflection angle signal is essentially the same as the pulsed laser photothermal lens inverse focal
length. In fact, the signal strengths observed are about the same (Jackson, et al., 1981). This method is very
similar to photothermal lens spectroscopy. The similarity between the photothermal lens method and the
beam deflection technique has been noticed by many authors, for example see Tam (1983, 1986, 1989) and
Dovichi (1987). Photothermal lens and photothermal deflection methods both rely on the generation of a
refractive index gradient in the sample itself. Collectively, they have become known as refractive index
gradient detection or photothermal refraction spectroscopy methods (Zharov and Letokhov 1986, Tam 1986). The different geometries for sample excitation and monitoring of the photothermal response are shown in Figure 1.17.

The main advantage of photothermal deflection spectroscopy is in the versatility. The same method can be used for solid, surface, liquid, and gas phase analysis. Excitation sources can be either pulsed or chopped continuous. The absorption coefficient detection limits for these methods are about the same as those of the two-laser photothermal lens method. Fournier, et al. (1980) demonstrated absorption coefficient detection limits of $10^{-7}$ cm$^{-1}$ for gas phase samples in a windowless flow cell using a 1 W modulated infrared carbon dioxide excitation laser. Long and Bialkowski (1985) used a 10 mJ pulsed infrared laser to obtain gas phase absorption coefficient detection limits equivalent to $10^{-8}$ cm$^{-1}$. Bialkowski and He (1988) later used an etalon to amplify the deflection angle signal and found a 100 fold signal-to-noise ratio improvement, or $\sim 10^{-10}$ cm$^{-1}$ detection limit for a 10 mJ pulse. Jackson, et al. (1981) demonstrated $10^{-6}$ cm$^{-1}$ absorption coefficient detection of benzene in CCl$_4$ using a 1 mJ pulsed dye laser. The solvent itself had an absorption coefficient of $10^{-6}$ cm$^{-1}$ and absorption due to the benzene analyte was found by scanning the wavelength of the pulsed pump laser. The estimated limit of absorption coefficient detection was $10^{-7}$ cm$^{-1}$. Dovichi (1987) pointed out that the photothermal refraction methods are advantageous when there is a significant signal due to sample cell window absorbance. Since the excitation and probe lasers do not have to pass into the sample at the same spot, photothermal perturbations due to the window can be ignored. There has been several reviews on probe beam deflection techniques. These reviews are often compiled along with those for photoacoustic spectroscopy. The reviews by Tam (1983, 1986, 1988), Murphy, et al. (1986), Dovichi (1987), Fournier and Boccara (1988) all cover aspects of this method. The books edited by Mandelis (1987) and Hess (1989a, 1989b) have chapters devoted to this method.

Another method based on the generation of refractive index changes within the sample is photothermal diffraction spectroscopy. Laser-induced gratings have been known for quite some time (Eichler, et al. 1986) and are the basis of optical holography (Collier, et al. 1971). However, the first analytical application was by Pelletier, et al. (1982), who demonstrated that a refractive index grating could be formed in a weakly absorbing sample by interfering two beams from a single excitation laser within the sample. The apparatus is shown in Figure 1.21. The grating diffracts a probe laser beam at a specific angle that satisfies the Bragg condition.

<Figure 1.21 Figure 2 of Pelletier, et al 1982>

For pulsed laser excitation, the diffracted probe beam power is (Pelletier and Harris 1983)
Here $\Phi_+$ is the diffracted and $\Phi_0$ is the incident probe laser power, $Q$ is the total (combined) pulse energy, $\lambda$ is the wavelength of the probe laser, and $2\theta$ is the angle between the two pulsed pump laser beams. The diffraction signal is proportional to $(\alpha Q)^2$, thus apparently limiting the sensitivity at low concentrations.

However, unlike infrared emission, the background is very small. The background noise limitation is essentially the same as those of laser excited fluorescence spectroscopy. Current absorbance detection limits are about $\sim 10^{-6}$ cm$^{-1}$. Although not exploited to any great extent, this method has potential for trace analysis.

The main advantage of this technique is apparently in the relatively simple data that result when the sample undergoes nonlinear absorption. In this case the distorted grating formed by nonlinear absorption can be decomposed by Fourier analysis into a series of orthogonal gratings, each with a different spatial period. Each grating then produces a different diffraction angle. The type of nonlinear absorption can be determined by analysis of the magnitude and irradiance dependence of the probe laser at each diffraction angle. The connection between photothermal lens, photothermal refraction, and photothermal diffraction spectroscopies has recently been given by Harris (1986) and the principles and applications of the photothermal diffraction method have recently been reviewed by Zhu, McGraw, and Harris (1992).

1.5.7 Photothermal radiometry

Another photothermal method is photothermal radiometry. In photothermal radiometry, the sample is excited with an optical source and the infrared emission is monitored. The infrared emission is related to the sample temperature by the black-body radiation law (Ingle and Crouch 1988)

$$B(\lambda, T) = \varepsilon(\lambda) \alpha(\lambda) \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

where $B(\lambda, T)$ (W sr$^{-1}$m$^{-2}$) is the radiant emissivity, $h$ (J s) is Planck's constant, $k$ (J K$^{-1}$) is Boltzmann's constant, and $\varepsilon(\lambda)$ is the sample emissivity. For samples at thermal equilibrium, $\alpha(\lambda) = \varepsilon(\lambda)$. The relative change in spectral radiance with respect to temperature is

$$\frac{\delta B(\lambda, T)}{B(\lambda, T)} = ch \frac{\alpha(\lambda)}{\lambda kT^2} \frac{\alpha(\lambda)}{1 - e^{hc/\lambda kT}} \delta T$$

In the mid-infrared region, $hc/\lambda kT < 1$ and for pulsed laser excitation

$$\frac{\delta B(\lambda_{em}, T)}{B(\lambda_{em}, T)} \approx \frac{ch\alpha(\lambda_{em})}{\lambda_{em} k T^2} \frac{2\alpha(\lambda_{em})Q}{\pi w^2 \rho C_p}$$
where $\lambda_{em}$ is the emission wavelength and $\lambda_{ex}$ is the excitation wavelength. The important features of this equation are 1) the relative radiance increases with excitation laser energy and absorption coefficient, 2) decreases with equilibrium temperature, 3) decreases with increasing wavelength, 4) since $\alpha(\lambda_{em})$ and $\alpha(\lambda_{ex})$ are both proportional to number density or concentration, the relative emission signal decreases as the square of the number density. The later suggests that this method will not be as sensitive as other photothermal techniques since the sensitivity decreases with decreasing $\alpha$.

This method of analysis has a long and somewhat obscured history. The advent of lasers and cryogenic infrared detectors resulted in several studies of infrared emission from excited gas samples. The method used to study gas samples is called laser-induced fluorescence (Hocker, et al. 1966, Yardley and Moore 1966, Stephenson, Wood, and Moore 1968, to name a few). These pioneering studies used pulsed infrared lasers to excite specific vibrational modes while monitoring infrared fluorescence at wavelengths different from that used for excitation. Time resolved fluorescence emission studies were performed to reveal the excited state vibrational lifetimes of the low pressure gas species. These lifetimes are a direct measure of the thermalization time of the sample. With the notable exception of the work by Belz, et al. (1987) infrared emission methods have been neglected for gas analysis although the utility is apparent.

Photothermal radiometry has been recognized as an important tool for surface studies and material analysis (Nordal and Kanstad 1979). The solid being analyzed is treated as a black-body emitter. The total surface emission will follow the Stefan-Boltzmann law. The relative temperature dependent change in surface emittance, e.g., integrating over wavelength, is simply,

$$\frac{\partial M(T)}{M(T)} = 4 \frac{\Delta T}{T}$$

where $M(T)$ (W m$^{-2}$) is the temperature dependent emittance of the surface and $\Delta T$ is induced by the photothermal effect. The temperature change can be produced by either pulsed or chopped excitation sources. This method is not very sensitive and rather large temperature changes have to be induced in the samples to obtain good thermal images. The thermal images are not a function of surface topography (unless three-dimensional imaging optics are used). The images will only depend on the optical absorption coefficient and the heat capacity of the sample. Time or phase dependent analysis of the emittance yields information regarding the thermal conductivity. If the integrated emission data is not processed as indicated in the above equation, the thermal image will also be a function of the topographical emissivity of the material. Tam (1985) has examined the use of photothermal radiometry for solid sample analysis and has

**Table 1.3 Major developments in the early history of photothermal spectroscopy**

<table>
<thead>
<tr>
<th>Year</th>
<th>Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>1880</td>
<td>Photoacoustic effect used for photophone by Bell</td>
</tr>
<tr>
<td>1938</td>
<td>Viengerov uses photoacoustic effect for gas phase chemical analysis</td>
</tr>
<tr>
<td>1964</td>
<td>Photothermal lens used to measure optical absorptions by Leite, <em>et al.</em></td>
</tr>
<tr>
<td>1968</td>
<td>McLean, <em>et al.</em> use interferometry to monitor photothermal effect</td>
</tr>
<tr>
<td>1969</td>
<td>Longaker and Litvak find thermal and acoustic components in photothermal effect. Use of pulsed excitation laser</td>
</tr>
<tr>
<td>1971</td>
<td>Kreuzer demonstrates sensitive gas phase detection with photoacoustic spectroscopy</td>
</tr>
<tr>
<td>1973</td>
<td>Hu and Whinnery develop extracavity single-laser photothermal lens spectroscopy</td>
</tr>
<tr>
<td>1979</td>
<td>Dovichi and Harris use single-laser photothermal lens for chemical analysis and introduce the enhancement factor Boccara, <em>et al.</em> report photothermal deflection</td>
</tr>
<tr>
<td>1981</td>
<td>Murphy and Aamodt report thermal images using photothermal deflection Davis and Petuchowski report 10^{-10} cm^{-1} detection limits for gas phase photothermal interferometry measurements Dovichi and Harris report 10^{-7} cm^{-1} detection limits with single-laser solution phase photothermal lens</td>
</tr>
</tbody>
</table>
1.5.8 Historic summary
The important discoveries in the history of photothermal spectroscopy are given in Table 1.3. Many of these discoveries were made possible by using lasers. Although lasers do not have to be used to excite samples, the signals thereby obtained are much greater than those obtained using incoherent light sources. Historically, the birth of high sensitivity photoacoustic and photothermal spectroscopies can be traced back to the laser. The first application of the photoacoustic effect was that of A. G. Bell (1880) while chemical analysis applications of photoacoustic spectroscopy can be traced back to Viengerov (1938). The first photothermal method was discovered by Leite, et al. (1964) when they found an intracavity sample, laser based apparatus gave rise to photothermal blooming, the photothermal lens. Some time later Kreuzer (1971) showed that photoacoustic spectroscopy could be used for sensitive analysis when laser light sources were utilized.

The reasons why lasers have made such an impact on high sensitivity spectroscopy are because they posses a high spectral brightness and they have outputs which are coherent. The high spectral brightness allows high powers or energies to be imparted to the sample. The coherence, in particular the spatial coherence, allows this power or energy to be delivered to small volumes. The signals in both photoacoustic and photothermal spectroscopies are enhanced with smaller excitation volumes.

1.6 Some important features of photothermal spectroscopy
We have now come to regard photothermal spectroscopy as a group of high sensitivity techniques that can be used for chemical and materials analysis. Photothermal signals arise from optical absorption in a sample. However, photothermal spectroscopy techniques have sensitivities far exceeding those of conventional absorption spectrophotometry. The reason for the high sensitivity of photothermal spectroscopy is that it is an indirect technique for measuring optic absorption. For an analyte with less than unit fluorescence quantum yield, electromagnetic energy absorbed and not lost by subsequent emission results in an increase in the energy of the sample. Energy absorbed and not subsequently lost by emission is usually randomized resulting in sample heating. The photothermal spectroscopy signal is derived from this heating.

There are a variety of methods used to monitor sample heating. Calorimetric or thermometric methods use temperature transducers to measure sample temperature. The method of photoacoustic spectroscopy uses a pressure transducer to monitor the pressure wave associated with rapid sample heating. Photothermal emission radiometry uses photometric transducers to monitor changes in the samples infrared emission associated with heating. Photothermal interferometry, photothermal deflection, photothermal lensing, and
photothermal diffraction spectrometry are all photothermal techniques that are based on monitoring refractive index changes associated with sample heating.

The distinctions between all but the calorimetric and photothermal radiometry techniques are lessening. The connection between photothermal and photoacoustic spectroscopies is apparent. Signals attributable to the photoacoustic effect are seen in photothermal spectroscopy experiments though the converse is not true. A pressure transducer placed far from the photothermal spectroscopy experiments will not respond to the thermal perturbation. Photoacoustic spectroscopy apparatuses may use probe lasers to detect the acoustic wave. This eliminates the use of pressure transducers that may have low response times. However, photoacoustic deflection spectroscopy is orders of magnitude less sensitive than photothermal lensing or deflection.

Accurate theories for describing photothermal spectroscopy signals have been developed. In most cases, these theories take into account the thermodynamics, hydrodynamics, and optics of the experimental apparatuses. In some cases, for example in the single laser photothermal lens apparatus, the absorption coefficient may be obtained directly from the signal if the thermodynamic and optical parameters are known well enough. In most other cases the signal magnitude has an instrumental factor that must be determined using samples of known absorbance in sample matrices that are identical to those of the unknown sample.

Table 1.4 Absorption coefficient detection limits using photothermal and photoacoustic methods for pulsed $\alpha$ (J$^{-1}$ cm$^{-1}$) and chopped $\alpha$ (W$^{-1}$ cm$^{-1}$Hz$^{-1/2}$) sources

<table>
<thead>
<tr>
<th></th>
<th>Photothermal Spectroscopy$^1$</th>
<th>Photoacoustic Spectroscopy$^2$</th>
<th>Theoretical Photoacoustic$^3$</th>
<th>Typical Background$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pulsed</td>
<td>CW</td>
<td>Pulsed</td>
<td>CW</td>
</tr>
<tr>
<td>Gas</td>
<td>$10^{-12}$</td>
<td>$10^{-10}$</td>
<td>$10^{-10}$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>$10^{-10}$</td>
<td>$10^{-8}$</td>
<td>$10^{-9}$</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>Solid</td>
<td>-</td>
<td>-</td>
<td>$10^{-7}$</td>
<td>$10^{-5}$</td>
</tr>
</tbody>
</table>

1) Section 1.5 of this book and Dovichi (1987) $\alpha$ detection limits scaled to W$^{-1}$ or J$^{-1}$
2) Tam (1983), and Zharov and Letokhov (1986)
3) Theoretical absorption detections limits summarized by Zharov and Letokhov (1986)
4) Background absorptions typical of water vapor at 10 $\mu$m, solvent overtones in liquids, and impurities in fused silica in the visible
A summary of the best absorption coefficient detection limits for photothermal and photoacoustic methods are given in Table 1.4. The detection limits are given in inverse energy or power units since all photothermal methods scale proportional to the excitation. For continuous excitation, lock-in amplifier signal processing is generally used to recover the oscillatory signal. The noise power is proportional to the bandwidth of the measurement; these detection limits are inversely proportional to the square root measurement bandwidth. The theoretical detection limits are based on thermodynamic fluctuations in sample pressure (Slatkine 1981).

The noise equivalent power, NEP (W Hz\(^{-1/2}\)), is

\[
NEP \approx \left(4 k_B T^2 \delta f \frac{2\pi r l k}{\sqrt{4 D_T / f}} \right)^{1/2}
\]  \hspace{1cm} (27)

where \(k_B\) is the Boltzmann constant, \(f\) is the frequency, \(\delta f\) is the measurement bandwidth, \(r\) and \(l\) are the radius and length of the sample cell, \(k\) is thermal conductivity, and \(D_T\) is the thermal diffusivity.

The fluctuations that ultimately limit photoacoustic spectroscopy should also place a lower bound on photothermal spectroscopy since pressure and density are related

\[
\delta \rho = \left(\frac{\partial P}{\partial \rho}\right)_T \delta P = \rho_0 K_T \delta T
\]  \hspace{1cm} (28)

where \(K_T\) (Pa\(^{-1}\)) is the isothermal compressibility.

For gas and solution phase analysis, photothermal and photoacoustic spectroscopy apparatuses have been developed which yield signals that are close (1-2 orders of magnitude) to the theoretical limits of absorbance detection. Quantitative work in solid analysis is nearly impossible because of the difficulty in preparing standard samples. These detection limits are lower than the background absorbance of water and other trace gases in the atmosphere, and of solvents used to host the analyte. The lower detection limits are obtained for gas samples because of reduced matrix absorptions and favorable thermodynamic parameters. The problem with the sensitive absorbance measurement methods is not so much the measurement of low absorption coefficients, but rather in discriminating the low analyte from that of the solvent or other species in the sample.
From these and other examples it is clear that photothermal spectroscopy is a valuable tool which can be used to solve a variety of chemical and materials analysis problems. Some salient features are;

1. The sensitivity of photothermal spectroscopy is theoretically enhanced over that of conventional absorption spectrophotometry. This theoretical enhancement has been realized and absorbance detection limits of $\sim 10^{-7}$ in liquids and $\sim 10^{-10}$ in gases are possible. High sensitivity has allowed the measurement of weak optical absorbances in pure samples and trace analysis, and in volume restricted samples.

2. Photothermal spectroscopy signal contains both magnitude and dynamic (time-dependent) components. The magnitude component is most important for quantitative absorption studies, spectroscopy, trace analysis, chromatography, etc. The dynamic component is important in qualitative analysis, material composition, chemical kinetics, etc.

3. Photothermal signals are inversely proportional to the excitation volume. This arises not only because of the higher temperature changes that can be induced with a given power or energy, but also because photothermal signals are usually derived from a spatial gradient in the resulting refractive index change. The small volume character of photothermal spectroscopy has lead to its use for micro-analysis and effluent detection in chromatography.
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Chapter 1 Figure Captions

Figure 1.1 Processes involved in photothermal spectroscopy. Absorption of radiation from the excitation source followed by non-radiative excited state relaxation results in changes in the sample temperature, pressure, and density. The density change is primarily responsible for the refractive index change which can be probed by a variety of methods.

Figure 1.2 Several of the mechanisms for excited state relaxation are illustrated. The main steps are optical interaction, energy transfer, sample heating, and thermal effects. Radiative relaxation, metastable state production, and photochemical reaction may result in some sample heating. Energy transfer step may result in fast or slow kinetic energy production.

Figure 1.3 A generic photothermal spectrometer showing essential features.

Figure 1.4 Four methods used for photothermal spectroscopy. Interferometry directly measures the refractive index. Deflection measures the gradient. Photothermal lens spectroscopy is based on beam focusing or defocusing. Diffraction methods measure the power of a beam diffracted by the periodic index.

Figure 1.5 An early photothermal deflection apparatus for measuring absorbance of the Earth's surface. Since the signal depends on meteorological and solar conditions, this measurement is difficult to obtain accurate numbers using the human detector.

Figure 1.6 Schematic of a photoacoustic spectrometer based on direct acoustic wave detection. Chopped (a) or pulsed (b) sample excitation results in acoustic pressure wave generation. The signal is detected with a piezoelectric pressure transducer and processed with either a lock-in or sampling (boxcar) amplifier.

Figure 1.7 Schematic of an indirect photoacoustic spectrometer based on chopped excitation. The thermal perturbation generated in the sample is coupled to the fluid, usually a gas, sensed with the microphone pressure transducer. The microphone signal is then processed with a lock-in amplifier to enhance the signal.

Figure 1.8 First photothermal lens apparatus. The sample was placed in the cavity of the laser. Irises were used to restrict the laser to single, TEM$_{00}$, mode operation. Detectors were used to measure the laser power, and the laser output both with and without an external pinhole. (Figure 1 from Gordon, et al. 1985)

Figure 1.9 Transient signals observed using the intracavity photothermal lens apparatus. The top trace was obtained with an extra-cavity pinhole and the bottom trace was obtained without the pinhole. This data was used to confirm the premise that the laser was operating in single mode and that the signal was generated by the internal apertures. These signals were difficult to analyze because of the interrelationships between laser power and cavity losses. (Figure 2 from Gordon, et al. 1985)

Figure 1.10 A schematic of the extra-cavity photothermal lens spectrometer used by Hu and Whinnery (1974) to measure the optical absorbances in transparent fluids. The lens focuses the laser beam one
confocal distance in front of the sample cell. The pinhole and detector are placed in far field of the focus. (Figure 3 from Whinnery 1974)

**Figure 1.11** Illustration of the beam geometry and definitions used for extra-cavity photothermal lens spectroscopy. (Figure 4 from Whinnery 1974)

**Figure 1.12** Modified Jamin interferometer apparatus used by Stone (1973). Incoherent light from a xenon arc is collimated and filtered by a series of band-pass filters before passage through the center of the sample cell along (c). Helium-neon laser light detects the optical phase shift. The laser light is split by the optical flat and passes through a reference path (a) and a probe path (b). The two laser beams are combined at the second optical flat. One detector monitors the power of the reference beam and the other the power in the interfering beams (a+b). A phase shift in the two interfering beams results in a power change at the signal detector. Phase shifts are found from the ratio of the signal to reference powers. (From Whinnery 1974, Figure 7)

**Figure 1.13** Data obtained for chlorobenzene using the photothermal interferometer of Figure 1.12 (solid), and that of bromobenzene in a glass capillary (broken line) obtained with a transmission spectrophotometer. The structured absorption features are C-H stretch vibrational overtones.

**Figure 1.14** Interferometer used by Longaker and Litvak (1969) to obtain images of the density perturbation in gas and liquid samples. The pulsed Nd laser is used to excite the sample and the continuous Ar+ laser is used to probe the refractive index changes. The camera records the fringe shift of the Ar+ laser beam.

**Figure 1.15** Image data obtained with the apparatus illustrated in Figure 1.14. The picture on the left is that of a 5 cm sample of non-absorbing liquid CS2. No thermal perturbation is observed and the fringe shift is due only to the acoustic wave generated by electrostriction. The image on the right is for a weakly absorbing sample and has both a thermal perturbation (in the center) and an acoustic wave component (the dark ring). (Figure 11 from Longaker and Litvak, 1969)

**Figure 1.16** A dual-beam photothermal lens spectrometer. The dye laser excites the sample and the probe source monitors the resulting refractive index change through the photothermal lens effect. The diverging probe beam passes through a pinhole spatial filter to develop the signal. The wavelength filter rejects the excitation wavelength. The chopped signal is processed with a lock-in amplifier to improve the signal to noise ratio. The dye laser can be scanned to obtain photothermal excitation spectra. (From Fang and Swofford 1987, Figure 6)

**Figure 1.17** Various excitation and probe beam geometries used in photothermal spectroscopy. (Figure 3 from Tam 1986)
**Figure 1.18** Photothermal deflection apparatus used to measure the photothermal image of a surface. The magnitude and phase of the photothermal deflection signal is measured at each position of sample excitation. The sample is raster scanned using the x-y translational stage. The microcomputer records the data and performs image analysis. (Figure 4 from Murphy, et al. 1986)

**Figure 1.19** A photothermal deflection image of an aluminum surface. (Figure 7 from McDonald 1986)

**Figure 1.20** One dimensional imaging apparatus developed for plate chromatography based on a time-multiplexed Hadamard encoded mask. Each position of the mask results in a unique surface excitation pattern. A photothermal deflection signal is recorded for each position of the mask and the resulting data set is transformed. The transformed data yields the absorption image of the thin layer chromatography plate. (Figure 11 of Morris and Fotiou 1989)

**Figure 1.21** A schematic of an apparatus used for photothermal diffraction. The two excitation beams are mutually coherent, arising from the same laser excitation source. Interference of the two beams produced a periodic irradiance and subsequently a periodic refractive index perturbation, or phase grating, in a weakly absorbing sample. The phase grating is probed with a second probe laser. (Figure 2 of Pelletier, et. al 1982)