Chapter 1

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It can truthfully be said that much of science is concerned with spectroscopy in one form or another, that is with the experimental and theoretical investigation of how energy and matter interact as a function of the frequency and/or intensity of the energy. The interaction of matter with photons ranging from high-energy γ-rays to very low-energy far-infrared photons is an immense field and one of the most important in elucidating of the properties of solid matter. The two most common spectroscopic techniques are *transmission spectroscopy* in which one measures as a function of photon wavelength the amount of light transmitted through the material under investigation, and *reflection spectroscopy* in which one measures the light reflected from the surface of the material. The absorption spectroscopy was normally carried out indirectly through a measurement of the incident, reflected and/or transmitted intensity, from which one can determine the absorbed intensity. The principle techniques to measure absorption directly in either though photothermal or photoacoustic (PA) spectroscopy. Both spectroscopies measure the heat deposited in the material due to absorption of photon, either optically in the case of (photothermal) or acoustically in the case of (PA).

It is well known that upon the absorption of electromagnetic radiation by a given medium, a fraction, or all the excitation energy will be converted into thermal energy through the de-excitation processes. This de-excitation mechanism has provided the physical basis for the highly sensitive photothermal spectroscopies [1]. Among the better known examples of these spectroscopies are:

1- Interferometric (IF) spectroscopy

The Interferometric (IF) spectroscopy was introduced by Stone [2] in 1972. He used a thermo-optical technique to measure the attenuation of light in liquids due to the absorption. Since an interferometer was used in the measurement in this experiment, the sample to be studied was placed in an interferometer in which two beams traversed the sample. However, the two beams were of unequal intensity when traversing the sample so that the energy absorbed in the sample from the two beams was different. A differential thermal transient was thus introduced between the two beams, and since the index of refraction is temperature dependent, a transient difference was introduced in the optical path of the two beams resulting in a transient change in the interferometer output. This transient could be interpreted to give absorptivity of the sample [3], see Fig.(1-1).

2- Thermal Lensing (TL) spectroscopy

This method is based on the temperature rise in an illuminated liquid induced by the absorption of small amount of energy from Cw laser beam passing through the liquid. The localized temperature change brings a transverse gradient in the index of refraction which can be probed optically as a "thermal lens". In the early work R. Swofford et al. [4] used a single beam thermo-optical spectrometer proposed by Hu and Whinnery [5]. In that technique the laser beam was allowed to shine on the sample until an equilibrium was established when the heat deposited in the liquid by the laser was just balanced by radial thermal conduction out of the illuminated region. Using the earlier calculations of Gordon et al. [6], Hu and Whinnery demonstrated how one could accurately determine the absorptivity of the liquid from the fractional change of the laser beam size in the far field. In a later work [7], they employed a dual-beam instrument. In this technique, a pulsating thermal lens is created by a chopped heating beam. A second much weaker "probe" laser beam directed along the same path through the liquid can sense this pulsating thermal lens and the intensity in the central portion of the probe beam is synchronously detected. The relation between the thermal length F and the temperature gradient (dT/dr) was given by [7]

$$F = - [\, l \, \frac{dn}{dT} \frac{\partial^2 T}{\partial r^2}]^{-1} \qquad (1\text{-}1)$$

where l is heating length and dn/dT is the change of refractive index with temperature, see Fig.(1-2).