

Theoretical Aspects of Photoacoustic Effect with Solids: A Review

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Abstract- Photo acoustic effect uses both light and sound and is based on the absorption of electromagnetic radiation by analyte molecule. Photo acoustic effect offers a minimal or no sample preparation, the ability to look at opaque and scattering sample and the capability to perform depth profiling experiment. These features mean that Photo acoustic can be used for on-line monitoring of various gases and also in depth-resolved characterization of materials. The absorbed energy can be measured by detecting pressure fluctuations in the form of sound waves or shock pulses. A photo acoustic spectrum consists of a plot of the intensity of the acoustic signal detected by a microphone or a piezoelectric detector, against the excitation wavelength or another quantity related to the photon energy of the modulated excitation. A brief review of the Photoacoustic effect with solids is presented in this paper.

Keywords- Photo acoustic effect, Photo acoustic absorption spectrum, piezoelectric detector, electromagnetic radiation, excitation wavelength, modulated excitation

I. INTRODUCTION

In 1880–1881, Alexander Graham Bell [1] found that when a thin disk was exposed to mechanically chopped sunlight, sound was emitted. In addition, he noted a similar effect when infrared or ultraviolet light was used. This effect is called as Photoacoustic effect. A plot of the loudness of the sound versus the wavelength of the light used, is called a photoacoustic spectrum. According to Haisch and Niessner [2], this effect essentially was forgotten until researchers led by Allen Rosencwaig (ironically) at Bell Labs rediscovered the phenomenon.[3]

II. PHOTOACOUSTIC EFFECT

A. Principle :

Photoacoustic effect is based on the absorption of electromagnetic radiation by analyte molecules. Non-radiative relaxation processes, such as collisions with other molecules, lead to local warming of the sample matrix. Pressure

fluctuations are then generated by thermal expansion, which can be detected in the form of acoustic or ultrasonic waves. In other words, the transformation of an optical event to an acoustic one takes place in photoacoustic effect [4]. A fraction of the radiation falling upon the sample is absorbed and results in excitation, the type of which being dependent upon the energy of the incident radiation.

Non-radiative de-excitation processes which normally occur, give rise to the generation of thermal energy within the sample. If the incident radiation is modulated then the generation of thermal energy within the sample will also be periodic and a thermal wave or a pressure wave will be produced having the same frequency as this modulation. Energy is transferred by the thermal wave or the pressure wave towards the sample boundary, where a periodic temperature change is generated. The periodic variation in the temperature at the surface of the sample results in the generation of an acoustic wave in the gas immediately adjacent and this wave propagates through the volume of the gas to the detector (microphone, piezoelectric transducers or optical method) where a signal is produced. This detector or microphone signal, when plotted as a function of wavelength, will give a spectrum proportional to the absorption spectrum of the sample.

This Principle of photoacoustic effect can be schematically represented as follows.

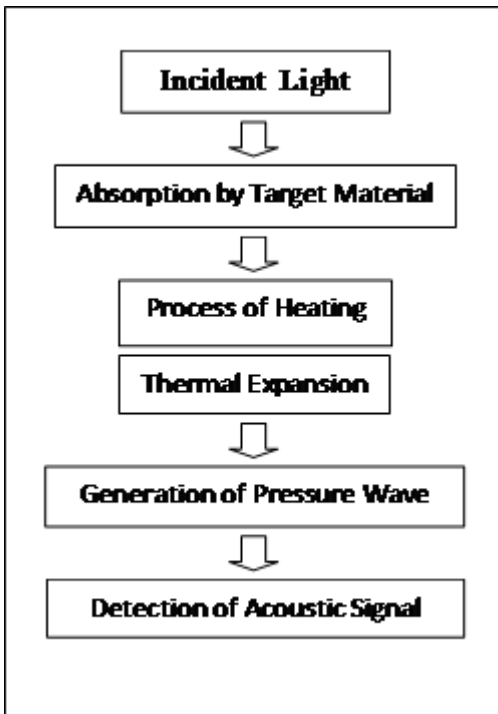


Figure 1 : Processes in Photoacoustic effect

Pressure fluctuations are then generated by thermal expansion, which can be detected in the form of acoustic waves.[5] In solids, the commonly accepted mechanism is that the main source of the acoustic wave is the repetitive heat flow from the absorbing condensed, phase sample to the surrounding gas, followed by propagation of the acoustic wave through the gas column to microphone based detector. This theory is called Rosencwaig - Gersho (RG) theory.

B. Photoacoustic cell

The photoacoustic cell is a small gas-tight enclosure with a sensitive microphone built into one wall. The periodic variations in the temperature at the surface of the sample results in the generation of an acoustic wave in the gas immediately adjacent and this wave propagates through the volume of the gas to the microphone which converts it into electrical signals. Hence the photoacoustic signal is the result of two types of processes occurring in the sample, namely the absorption of electromagnetic radiation specified by the absorption coefficient B and the thermal propagation in the sample specified by the thermal diffusivity.

For absorbing samples the optical absorption length is an important parameter and may be taken as the depth into the sample at which essentially all of the incident radiation has been absorbed. The thermal wave produced in the sample is heavily damped and may be considered to be fully damped out within a distance $2\pi\mu_s$ where μ_s is the thermal diffusion length. It is normally assumed that only those thermal waves

originating from a depth less than or equal to us will make an appreciable contribution to the photoacoustic signal measured. The thermal diffusion length is a function of thermal diffusivity and the modulation frequency to of the incident radiation. These are connected through the relation

$$\mu_s = \sqrt{\frac{\alpha}{\omega}} \quad \dots \quad \dots \quad \dots \quad (1)$$

This important relationship means that for a sample of given thermal diffusivity, the depth examined us may be varied by adjusting the modulation frequency ω .

The observed photoacoustic signal is a complex quantity having a magnitude and phase relative to the modulation of incident radiation. Being a function of the absorption coefficient, modulation frequency and thermal characteristics of the sample as well, the photoacoustic signal is directly proportional to the incident power of the radiation and also depends upon the characteristics of the gas in contact with the sample surface and the properties of the backing material upon which the sample is positioned.

C. Excitation

As mentioned earlier, the Photoacoustic effect is based on the sample heating produced by optical absorption. [6] In order to generate acoustic waves, which can be detected by pressure sensitive transducers, periodic heating and cooling of the sample is necessary to generate pressure fluctuations.

D[1]. Modulated excitation

In modulated excitation schemes, radiation sources are employed whose intensity fluctuates periodically in the form of a square or a sine wave, resulting in a 50% duty cycle. This can be realized for example by the mechanical chopping of a light source. A way to overcome the 50% duty cycle is to modulate the phase instead of the amplitude of the emitted radiation. Whereas chopped or modulated lamps or IR sources from commercial spectrometers are used for the determination of UV or IR absorption spectra of opaque solids. Modulated continuous wave lasers are the most common sources for Photoacoustic gas phase analysis. Photoacoustic cell play an important role in photoacoustic effect. This fact can be utilized for signal enhancement by acoustic resonance. Thus, acoustic resonance curves must be considered in PA cell design.

In pulsed PAS, laser pulses with durations in the nanosecond range are usually employed for excitation. Since the repetition rates are in the range of a few Hz, the result is a short illumination followed by a much longer dark period, i.e.

a low duty cycle. This leads to a fast and adiabatic thermal expansion of the sample medium resulting in a short shock pulse. [7] Transformation of the signal pulse into the frequency domain results in a wide spectrum of acoustic frequencies up to the ultrasonic range.

D[2]. Pulsed excitation

In pulsed PAS, laser pulses with durations in the nanosecond range are usually employed for excitation. Since the repetition rates are in the range of a few Hz, the result is a short illumination followed by a much longer dark period: a low duty cycle. This leads to a fast and adiabatic thermal expansion of the sample medium resulting in a short shock pulse. Data analysis in this case is performed in the time domain. Therefore, the signal is recorded by oscilloscopes, boxcar systems, or fast A to D converters. Transformation of the signal pulse into the frequency domain results in a wide spectrum of acoustic frequencies up to the ultrasonic range. Thus, laser beams modulated in the form of a sine wave excite one single acoustic frequency, whereas short laser pulses are broadband acoustic sources.

E. Signal generation

Induction of an acoustic wave by modulated or pulsed irradiation inside a gaseous, liquid or solid sample is termed as direct Photoacoustic generation. Here, detection takes place inside or at an interface of the sample. [8] In indirect Photoacoustic generation modulated warming of the sample is induced by modulated excitation. Subsequently, the heat deposited in the sample is transported to the interface of the sample with the adjacent gas phase.

F[1] : Direct PA Signal generation in solids

In condensed matter, short laser pulses are used for direct photoacoustic generation. The short illumination with relatively high peak power leads to an instantaneous adiabatic expansion of the medium, generating pressure pulses that propagate through the sample at the speed of sound. These ultrasonic pulses can be detected directly at a boundary of the sample by piezoelectric transducers or optical methods. Depth resolution of pulsed photoacoustic effect depends mainly on the time resolution of the ultrasonic detector. The depth resolution can be calculated as the product of the temporal resolution of the detector and the speed of sound in the sample. If fast piezoelectric detectors and data recording with temporal resolutions in the nanosecond range are used, depth resolutions in the lower micrometer range can be realised. The maximum sampling depth can reach a few centimeters in weak absorbing and scattering samples. If piezoelectric detector

arrays, scanning PA sensors or suitable optical methods for detection are employed, two dimensional and three dimensional imaging are feasible by pulsed photoacoustic effect.[9]

F[2] Indirect PA Signal generation

Analysis of condensed matter by modulated photoacoustic excitation and subsequent detection of the directly generated acoustic wave by a microphone is not suitable due to strong acoustic impedance mismatches between solid and gas phase. Thus, an indirect scheme for photoacoustic generation is employed. Modulated warming of the sample is induced by modulated excitation.[10] Subsequently, the heat deposited in the sample is transported to the interface of the sample with the adjacent gas phase. This heat transport can be described as thermal wave.

G. Production of photoacoustic signal

Having worked out the properties of our cell, we now look to the signal which it will amplify. Production of photoacoustic signal can be understood as a series of energy transfer mechanisms. First there is absorption of light (optical energy), then production of sound waves (thermal energy), and finally detection by the microphone (electric energy). In the following sections we assume a two-level (energy) system. Our goal is to derive expressions for energy at each of the three steps in the production and detection of photoacoustic signal. It is possible to conceive of each optical transition we are looking for as a transition between two discrete energy levels of the molecule. In doing so we neglect possible transitions to energy levels other than the two considered. This simplifies the following derivation.

H. Absorption of Light

In the absorption of light by a two level system, radiative and nonradiative (collision-induced) energy transfers between the two states i and j are important parameters. Let us consider the coefficients r_{ij} and c_{ij} . The radiative transition rate r_{ij} is a sum of the Einstein coefficients for stimulated and spontaneous emission, B_{ij} and A_{ij} are of the form,

$$r_{ij} = \rho\omega B_{ij} + A_{ij} \dots \dots \dots (2)$$

where $\rho\omega$ is the spectral energy density at the frequency of the transition between E_0 and E_6 . The quantity $\rho\omega$ measures the radiant energy per volume per unit frequency and thus has units JS.

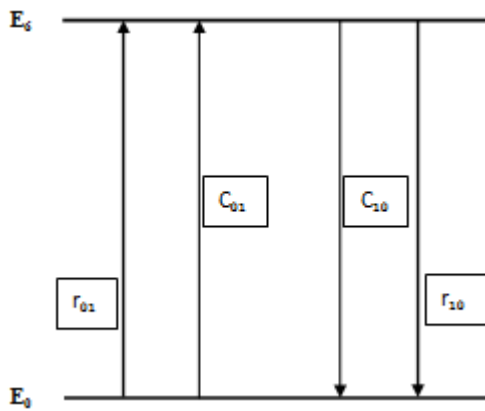


Figure 2 : A schematic representation of a two level system.

Note that $B_{ij} = B_{ji}$ so that $B_{06} = B_{60}$. But $A_{06} = 0$ since spontaneous emission from a state of lower energy to one of higher energy does not occur. Hence $r_{06} = \rho\omega B_{06}$. Similarly, we reason that the probability of a collisional excitation from E_0 to E_6 is very low, approximately zero, so $c_{06} \sim 0$.

In order to determine the rate of transition, let us distinguish the population densities of absorbing molecules in the ground and excited states (with energies E_0 and E_6) as n_0 and n_6 , respectively. To examine the rate of change of upper state population, consider the difference between the number of molecules entering and leaving the excited state as

$$\begin{aligned} n_6 &= (r_{06} + c_{06})n_0 - (r_{60} + c_{60})n_6 \\ &= \rho\omega B_{06}n_0 - (\rho\omega B_{06} + A_{60} + c_{60})n_6 \\ &= \rho\omega B_{06}(n_0 - n_6) - (A_{60} + c_{60})n_6 \dots\dots\dots (3) \end{aligned}$$

Let us define the radiative and collisional time constants be $\tau_r = 1/A_{60}$ and $\tau_c = 1/c_{60}$ respectively.

The total time constant is, then

$$\begin{aligned} \tau &= \tau_r + \tau_c \\ \text{Now, } n_6 &= \rho\omega B_{06}(n_0 - n_6) - (\tau^{-1} + \tau_c^{-1})n_6 \\ n_6 &= \rho\omega B_{06}(n_0 - n_6) - \tau^{-1}n_6 \dots\dots\dots (4) \end{aligned}$$

Let us repeat a similar process to find n_0 as

$$\begin{aligned} n_0 &= (r_{60} + c_{60})n_6 - (r_{06} + c_{06})n_0 \\ n_0 &= \rho\omega B_{06}(n_6 - n_0) + (\tau^{-1} + \tau_c^{-1})n_6 \\ n_0 &= \rho\omega B_{06}(n_6 - n_0) + 2(\tau^{-1})n_6 \dots\dots\dots (5) \end{aligned}$$

Hence,

$$n_6 - n_0 = -2\rho\omega B_{06}(n_6 - n_0) - (2\tau^{-1})n_6 \dots\dots\dots (6)$$

In steady-state, intensity I must vary slowly enough for us to consider upper- and lower- population an adiabatic interchange, then we can say $n_6 - n_0 = 0$.

Recalling the total molecular density

$N = n_0 + n_6$, we can simplify it as
 $0 = -2\rho\omega B_{06}(N - n_0 - n_0) - 2\tau^{-1}(N - n_0)$
 $0 = 4\rho\omega B_{06}n_0 - 2N(\rho\omega B_{06} + \tau^{-1}) + 2\tau^{-1}N(\rho\omega B_{06} + \tau^{-1})$
 In steady-state, intensity I must vary slowly enough for us to consider upper- and lower- population an adiabatic interchange and we can say $n_6 - n_0 = 0$. Recalling the total molecular density $N = n_0 + n_6$

Thus the spectral radiant energy density is directly proportional to the intensity of the light source I [11].

I. Depth Profiling

One main advantage of PAS is the ability to get information about the depth in the sample of the absorption. The amount of the sample contributing to the PA signal is proportional to the thermal diffusion depth. This thermal diffusion depth μ , is inversely proportional to the modulation frequency f . Model sample that has a thermally thin surface layer (thickness $\ll \mu$) on a bulk substrate. After the light has been absorbed, the heat has to diffuse from the point of absorption to the surface of the sample to be detected. Since this thermal diffusion is a slow process relative to the light absorption and non- radiative decay, an absorption in the bulk will have a phase lag between the time of absorption and the thermal signal. However, a surface absorption should not have a phase lag since the heat doesn't have far to travel to generate the detected pressure change in the transfer gas.

J. Signal detection

Sound waves generated directly or indirectly in the gas phase are detected usually by condenser or electric microphones. Detection of sound waves by microphones in condensed matter is typically not suitable. Due to high acoustic impedance mismatches, less than 10^{-4} of the acoustic energy is transferred from a solid sample to the adjacent gas phase. In pulsed excitation of condensed matter, the application of microphones is additionally hampered due to their restricted bandwidth. Therefore, piezoelectric transducers are employed in many cases for the detection of ultrasonic pulses in liquid and solid samples. Quartz crystals, piezoelectric ceramics such as lead zirconate titanate (PZT), lead metaniobate, and lithium niobate as well as piezoelectric polymer films can be applied to the detection of laser-induced shock pulses.

K. Pressure - Temperature Relation

It is evident that the temperature of the gas is related to the pressure by an equation of state. In the region of audio frequencies, ~ 105 Hz, the wave length of the sound wave is

much greater than the length l_g of the gas column. Therefore, the pressure of the gas does not depend on x , Fig. 1. The problem is to determine the pressure that corresponds to a spatial temperature distribution in the gas in the form of Eq. (9), if the pressure is assumed to be constant all over the volume.

Rosencwaig and Gersho have solved this problem by introducing a spatially averaged temperature. They define an average temperature variation $\langle \delta T \rangle$ in a gas column with the length of a temperature wave length $2\pi\mu_g$ equation in the form of

$$\langle \delta T \rangle = \frac{1}{2\pi\mu_g} \int_0^{2\pi\mu_g} V_g e^{-\sigma g x + j\omega t} dx = \frac{\sqrt{2}}{4\pi} V_g e^{j(\omega t - \frac{\pi}{4})} \dots\dots\dots (7)$$

where V_g is the complex amplitude. This average temperature is one of the mean features of the RG model. The relation between $\langle \delta T \rangle$ and the pressure variation δP is obtained from the assumption that the thermodynamic process is performed in two steps.

In the first step, the temperature variation $\langle \delta T \rangle$ varies isobarically, the volume of the gas column with the initial length $2\pi\mu_g$ by the amount

$$\delta V = V \beta_T \langle \delta T \rangle = 2\pi\mu_g A \beta_T \langle \delta T \rangle \dots\dots\dots (8)$$

and,

$$\left(\frac{\partial V}{\partial P}\right)_P = V\beta_T \dots\dots\dots (9)$$

Here, β_T is the thermal cubic expansion coefficient of the gas and A the cross section of the gas column.

In the second step, the displacement δV , is considered as a "piston" acting on the remaining gas column and leading to an adiabatic variation of pressure (Fig. 2),

$$\delta P = \frac{\delta V}{X_s A l_g} \dots\dots\dots (10)$$

It is obtained from the relation

$$\left(\frac{\delta V}{\delta P}\right)_S = X_s V \dots\dots\dots (11)$$

where X_s is the adiabatic compressibility and $V A l_g$ is the volume of the gas column with the assumption $l_g \gg 2\pi\mu_g$.

The pressure temperature relation become

$$\delta P = 2\pi\mu_g \beta_T \langle \delta T \rangle \frac{\delta T}{X_s l_g} \dots\dots\dots (12)$$

The pressure variation decreases with increasing volume, pressure and temperature of the gas. From Eq. (12) it

is obvious that in an experiment the length of the gas column should be made as small as possible.

One problem of the RG model is that the limiting lower frequency of its applicability cannot be defined. From hand waving arguments it can be estimated to be in the order of a thermal diffusion length. This has been shown experimentally by Aamodt et al.[13] and by Tam and Wong [14]. For length of the gas columns smaller than a diffusion length, the PA-amplitude decreases with decreasing l_g . Tam and Wong have explained this signal behavior at small gas lengths with a "residual volume". It is essentially the volume in the tube or channel connecting the gas region in front of the sample with the microphone.

Another point of the RG model one should think about is the idea of the "piston". It is based on the assumption that a sub-volume of the gas expands isobarically, while the pressure of the remaining volume changes. Therefore, the pressure should vary over the volume. But as long as the wave length of the pressure wave is large compared to l_g , the pressure is constant. Starting from the basic ideas of Rosencwaig and Gersho, it should be possible to take into account all phenomena mentioned above in a proper way and develop a modified RG model even for $l_g \rightarrow 0$.

III. CONCLUSION

The photoacoustic effect has the capability of characterizing surface and subsurface structures in solids. This technique also shows excellent properties for nondestructive evaluation applications to solids.

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