A Review on Photoacoustic Spectroscopy

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On the basis of photo acoustic effect, photo acoustic spectroscopy is an unusual form of spectroscopy which 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.

**Keyword:** Photo acoustic effect, piezoelectric detector, electromagnetic radiation, excitation wavelength, modulated excitation

**INTRODUCTION**

In 1880–1881, Alexander Graham Bell 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. A plot of the loudness of the sound versus, for example, the wavelength of the light used, is called a *photoacoustic spectrum*. According to Haisch and Niessner, this effect essentially was forgotten until researchers led by Allen Rosencwaig (ironically) at Bell Labs rediscovered the behavior and provided a theoretical basis. To indicate the growth of the field, Figure 1 shows the Chemical Abstracts Service under the subject "photoacoustic spectroscopy".

Photoacoustic spectroscopy (PAS) 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 spectroscopy. 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.

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Non-radiative de-excitation (relaxation) 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/pressure wave will be produced having the same frequency as this modulation. Energy is transferred by the thermal wave/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 methods) 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. Therefore, the photoacoustic signal is a function of two types of processes occurring in the sample: the absorption of electromagnetic radiation specified by the absorption coefficient $\beta$ and the thermal propagation in the sample specified by the thermal diffusivity $\gamma$.

**Theory of PAS**

Photoacoustic spectroscopy 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.

**Fig. 1: Number of articles published using the key phrase**

**Fig. 2: Principle of photoacoustics experiment**
Pressure fluctuations are then generated by thermal expansion, which can be detected in the form of acoustic waves. In gases similar mechanism is followed but in solids the commonly accepted mechanism is called RG theory - 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.

**Techniques**

In this section, various schemes for the excitation, generation, and detection of Photoacoustic signals are presented.

1. **Excitation**

   As mentioned earlier, the Photoacoustic effect is based on the sample heating produced by optical absorption. 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.

   **1[a] 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/Vis or IR absorption spectra of opaque solids, modulated continuous wave (cw) lasers are the most common sources for Photoacoustic gas phase analysis. PA cell play an important role. This fact can be utilized for signal enhancement by acoustic resonance. Thus, acoustic resonance curves must be considered in PA cell design. In solid samples, tuning of the modulation frequency allows depthre solved investigations. 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. Transformation of the signal pulse into the frequency domain results in a wide spectrum of acoustic frequencies up to the ultrasonic range.

   **1[b] 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
Photoacoustic spectroscopy techniques

Modulated Excitation

Direct generation
Gaseous samples

Indirect generation
Solid and liquid samples

Pulsed Excitation

Direct generation
Solid and liquid samples

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/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.

1. **Signal generation**\textsuperscript{11,12,20-25}

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. In indirect Photoacoustic generation, heat is generated by modulated illumination inside a solid or liquid sample and transported to an interface. Subsequently, sound waves are generated and detected in the gas phase adjacent to the sample.

![Fig. 3 Indirect generation of photoacoustic waves for the analysis of solid and liquid samples](image)

2[a] **Direct PA generation in gases**

Chopped continuous wave lasers or modulated laser diodes are employed for the modulated excitation of PA signals in gases. The modulated laser beam irradiates the gaseous sample inside a (usually cylindrical) PA cell, and sound waves with an acoustic frequency defined by the modulation frequency of the laser can be detected using microphones. The signal amplitude can be described by

\[ p = F \nu \omega_\mu_0 \]
Where,
\[ W_0 = \text{Incident radiation power} \]
\[ a = \text{Absorption coefficient of the sample}. \]
\[ F = \text{The proportionality factor} \]

The cell constant \( F \) is,
\[ F = G (\gamma-1) \frac{L}{\gamma V} \]

Where,
\( G = \text{Geometric factor of the order of one}, \)
\( \gamma = \text{Adiabatic coefficient of the gas}, \)
\( L = \text{Length of the cell} \)
\( V = \text{Volume of the cell} \)
\( \omega = 2\pi \nu \text{ the modulation frequency.} \)

The photoacoustic signal is indirectly proportional to the modulation frequency and the cross section \( V/L \) of the cell. Thus, the signal increases with decreasing cell dimensions and modulation frequency. As the noise increases with a decrease in these parameters, there is a maximum in the S/N ratio for a certain combination of cell size and modulation frequency.

Photoacoustic spectroscopy is that it can be performed on all phases of matter. Figure 2 shows a general setup for the photoacoustic spectroscopy of a gas sample. When a species absorbs some of the incoming light, one of several mechanisms of de-excitation is intermolecular colliding, which ultimately leads to increases in translation energy of the gas particles that is, heating. According to the various gas laws, an increase in the temperature of the gas leads to an increase in the pressure of an isochoric (constant-volume) sample. If the incoming light is modulated modulation frequencies can vary from single to several thousand hertz the gas pressure increases and decreases accordingly, creating sound.

**Fig 4. Photoacoustic spectroscopy on a gas**

2[b]Direct PA generation in liquids and solids

In condensed matter, short laser pulses are used for direct PA 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 both pulsed PAS and LIU 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 realized. The maximum sampling depth can reach a few centimetres 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 PAS.

2(c) Indirect PA generation
Analysis of condensed matter by modulated PA 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 PA generation is employed. 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. This heat transport can be described as thermal wave.

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 $\mu$, 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.

3 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.

Instrumentation

a. Radiation source

Radiation source can be output from a laser, a monochromator furnishing radiations in UV, IR, or a FT-IR spectrometer (tungsten lamp, carbon arc lamp, high pressure xenon lamp, Nernst glower and lasers.) All radiation must be pulsed at an acoustical frequency 50-1200Hz. PA cell is filled with transparent gas often air or helium and cell volume is kept small, less than 1cm³ in order to preserve the strength of the acoustical signal. In commercial photoacoustic spectrometers, incoherent sources such as lamps are employed in combinations with filters or interferometers. Devices equipped with a small light bulb, with either a chopper or direct current modulation as modulated source and appropriate filters to avoid absorption interferences with other species, are used as compact gas sensors, e.g. for indoor CO₂ monitoring. However, since the generated photoacoustic signal is proportional to the absorbed (and thus to the incident) radiation power, powerful radiation sources, particularly lasers offering high spectral brightness, are advantageous for achieving high detection sensitivity and selectivity in spectroscopic applications.

Modulation Schemes

Modulation schemes can be classified into the modulation of the incident radiation and modulation of the sample absorption itself. The first technique includes the most widely used amplitude modulation (AM) of continuous radiation by mechanical choppers, electro-optic or acousto-optic modulators as well the modulation of the source emission itself by current modulation or pulsed excitation. In comparison to amplitude modulation (AM), frequency modulation (FM) or wavelength modulation (WM) of the radiation may improve the detection sensitivity by eliminating the continuum background caused by a wavelength independent absorption, e.g. absorption by cell windows, known as window heating. This type of modulation is obviously most effective for absorbers with narrow line width and most easily performed with radiation sources whose wavelength can
Fig. 6: Instrumentation

rapidly be tuned with a few wave numbers.\textsuperscript{11-13}

\begin{itemize}
  \item Photoacoustic cell
  
  The Photoacoustic cell serves as a container for the sample under study and for the microphone or other device for the detection of the generated acoustic wave. An optimum design of the Photoacoustic cell represents a crucial point when background noise ultimately limits the detection sensitivity. In particular, for trace gas application many cell configurations have been presented including acoustically resonant and non-resonant cells, single and multipass cells, as well as cell placed intracavity. Nonresonant cells of small volume are mostly employed for solids samples with modulated excitation or for liquids and gaseous samples with pulsed laser excitation. As a unique example, a small volume cell equipped with a ‘tubular’ acoustic sensor consisting of up to 80 signal miniature microphone has been developed. These microphones are arranged in eight linear rows with ten microphones in each row. The row are mounted in a cylindrical geometry parallel to the exciting laser beam axis and located on a circumference around the axis.\textsuperscript{26-27}

  \item Detection Sensors
  
  As mentioned earlier the acoustic disturbances generated in the sample are detected by some kind of pressure sensor. In contact with liquid or solid samples these are piezoelectric devices such as lead zirconate titanate (PZT), \text{LiNbO}_3 or quartz crystals. These sensors offer fast response times and are thus ideally adapted for pulsed photoacoustics.\textsuperscript{22}

  \item Experimental Arrangement\textsuperscript{11, 14-22}
  
  As the photoacoustic and related photothermal phenomena comprise a large diversity of facets, there exist a various detection technique which rely on the acoustic or thermal disturbances caused by the absorbed radiation, the selection of the most appropriate scheme for a given application depends on the sample, the sensitivity to be achieved, ease of operation,
ruggedness, and any requirement and any require for non-contact detection, e.g. in aggressive media or at a high temperature and/or pressure.

Experimental schemes for photoacoustic studies on solid sample includes the measurement of the generated pressure wave either directly in the sample with a piezoelectric sensor for the pulsed regime, or indirectly in the gas which is in contact with the sample by a microphone. The typical experimental arrangement for the absorption spectroscopy is weakly absorbing liquids. The beam of a pulsed tuneable laser is directed through the PA cell that contains the sample under study. The generated acoustic waves are detected by a piezoelectric transducer with fast
response time. Usually, only the first peak of the ringing acoustic signal is taken and further processed. Pulse-to-pulse variations of the laser power are accounted for by normalizing the piezoelectric signal with the laser power measured with the power meter after the cell.

The typical setup for gas phase measurement is shown in Fig.6. A tunable laser with narrow line width or a conventional (broadband) radiation source followed by optical filters is used. In general, amplitude-modulated (or sometimes pulsed) radiation is directed through the PA cell. The acoustic sensor is usually a commercial electret microphone or a condenser microphone. These devices are easy to use and sensitive enough for trace gas studies with very low absorption.

Often, the detection threshold is neither determined by the microphone responsivity ($R_{\text{mic}}$) itself nor by the electrical noise but rather by other sources (absorption by desorbing molecules from the cell walls, window heating, ambient noise, etc.). However, if this latter background is known from reference measurements, the ultimate detection sensitivity is determined solely by fluctuations of the radiation intensity, and by microphone and amplifier noise. The frequency dependence of $R_{\text{mic}}$ is usually rather small and the temperature dependence may have to be taken into account in special cases only. If modulated radiation is employed the microphone signal is fed to a locking amplifier locked to the modulation frequency.

Fig 9. Photoacoustic detection in liquids

Double-Beam Photoacoustic Spectroscopic

Two types of PA cells, a standard-type cell and a gas exchangeable cell equipped with two valves for gas flow, were used. Each cell was composed of an aluminum body and a Pyrex glass window, being transparent over the range of measurements, 300-600 nm. These cells were suspended with rubber bands to minimize vibrational noise during the measurement. A powder sample was placed in the cell. The atmosphere was ambient air or controlled by a gas flow of argon (Ar), nitrogen (N$_2$), oxygen (O$_2$), and artificial air. The difference between ambient-air and artificial-air is the content...
of water vapor; the former contains a large amount of water vapor, whereas the amount in the latter is negligible. In addition to this ordinary single-beam measurement, measurements with simultaneous continuous photo-irradiation, i.e., DB measurement, were also carried out. A more intense light beam from another Xe lamp passing through a UV-D33S optical filter (transmitting radiation of ca. 300-400 nm) was used as a continuous UV-light source (8.2 mw cm$^{-2}$). The PA signal was normalized using carbon black powder as a reference to compensate wavelength-dependent light intensity.

**Advantages of PAS$^{9-10}$**

- The sample does not have to be dissolved in some solvent or embedded in a solid matrix, it is to be used as its
- Conventional absorption spectroscopy is based on excitation by electromagnetic radiation with intensity $I$ and the measurement of reflected or transmitted light intensity $I$. Thus, the absorbencies derived indirectly from transmittance or reflectance, whereas in PAS pressure waves are detected which are generated directly by the absorbed energy.
- PA signal is not influenced by the scattering particles.

**Fig 11. Double beam Instrumentation**

- PAS allows the determination of absorption coefficients over several orders of magnitude. This analytical technique can be applied to the measurement of weak absorption using PA cells with relatively small path lengths, allowing compact and mobile set-ups.
- PA signal depends on the incident radiation power hence the sensitivity can be tuned to desired range by choosing an
appropriate radiation source (for example, a lamp versus a laser)

- PAS is useful for sample that are powered, amorphous or otherwise not conductive to reflective or transmission form of optical spectroscopy

**APPLICATION**

- **Depth Profiling of Mammalian Cells for Localization of Ligands**

Phase-resolved monitoring of photoacoustic signals can provide information about the depth profile of a sample. The principle of photoacoustic spectroscopy has been used to determine the depth profiles of ligands and antitumor agents in mammalian cells.

- **Photoacoustic spectroscopy as a key technique in the investigation of nanosized magnetic particles for drug delivery systems**

The study includes how cubic ferrite nanoparticles, suspended as ionic or biocompatible magnetic fluids, can be used as a platform to built complex nanosized magnetic materials, more specifically magnetic drug delivery systems. The study shows the use of the photoacoustic spectroscopy as an important technique in the investigation of key aspects related to the properties of the hosted nanosized magnetic particle.

- **Analysis of Biological Material**

Conventional spectroscopy does not yield satisfactory spectra because of the string light scattering properties of the blood cells, protein and lipid molecules present. PAS permits spectroscopic studies of blood without the necessity of a preliminary separation of these large molecules.

- **Other biological application**

PAS include identification of bacteria states, study of animal and human tissues including teeth, bone, skin, muscle etc., analysis of drug in tissues, investigating of the photo-oxidative decay in human eye lenses etc.

- **Quantitative analysis of drug content in semisolid formulation using step scan FTIR Photoacoustic spectroscopy**

Step-scan FT-IR photoacoustic spectroscopy in conjunction with a phase modulation technique (modulation frequency of 25 Hz) and digital signal processing was applied in order to quantify the content of brivudin and dithranol in vaseline/drug ointment. The PA spectra of the mixtures exhibit an excellent signal to noise ratio and bands belonging to the drugs are clearly observable down to an 0.5 wt% concentration of the drug.

- **Gas Phase Analysis**

In recent years, the development of new PA setups for on-line gas monitoring has been achieved through new developments in diode lasers. Atmospheric pollutants that can be detected by PA measurement
techniques includes sulfur oxides (such as SO₂), nitrogen oxides (NO₂), carbon oxides (CO and CO₂), hydrogen sulfide, ammonia, methane, and aerosol particles (such as soot).

➢ **Analysis of highly concentrated textile dyes using photoacoustic spectroscopy**

The concentrations of textiles dyes are in the range of more than 5 g L⁻¹, resulting in absorption coefficients of 10³ cm⁻¹. The combination of extremely high absorption and scattering particles in the dye solution makes a classical transmission spectroscopic analysis impossible. PA spectroscopy is a viable approach to overcome the problems.

➢ **The malaria parasite monitored by photoacoustic spectroscopy**

Noninvasive photoacoustic spectroscopy was used to study the malarial parasites Plasmodium chabaudi and Plasmodium berghei, their pigment and ferriprotoporphyrin IX which is a byproduct of the hemoglobin that the parasite ingest. The result indicate that the pigment consits of ferriprotoporphyrin self aggregates and a noncovalent complex of ferriprotoporphyrin and protein.

**Conclusion**

Photoacoustic spectroscopy (PAS) is based on optical absorption and subsequent detection of pressure fluctuations. Wide dynamic range (several orders of magnitude), highly sensitive trace gas analysis with short path lengths, measurement of high absorption coefficients, even in opaque samples, without sample dilution, determination of absorption spectra of solid samples, even in the form of powder, chips, or large objects, less influence from light scattering compared to conventional measurement technique, depth profiling of layered samples.

In the characterization of industrial products, additional benefits include the potential to determine absorption spectra of opaque solids and depth profiles of layered materials. The most common PA techniques are; Modulated excitation and direct generation of sound waves in gaseous samples, modulated excitation of liquid and solid samples with subsequent indirect generation of sound waves in the adjacent gas phase and pulsed excitation and direct generation of pressure pulses in liquid and solid samples.

**REFERENCE**

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