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ABSTRACT

We review the history of photoacoustic, thermal lensing, and photothermal deflection techniques from early experiments to the current time. The paper also describes the main fields of application in chronological order, showing the primary advantages and listing initial technological developments.

I. INTRODUCTION

The ensemble of optical methods currently applied that use the periodic heating of a sample to derive some of its spectroscopic, thermal, or even structural characteristics is based on three different thermally originated phenomena that have received different names: thermal lensing, photoacoustic (or optoacoustic), and photothermal techniques.

Alexander Graham Bell (1847–1922) performed several experiments using sunlight, including one that was a type of telephone that he called *photophone* for which he obtained two patents.[1] During these experiments, he discovered that when a periodically interrupted beam of sunlight shines on a solid in an enclosed cell, an audible sound could be heard by means of a hearing tube attached to the cell.[2] He performed a series of studies[3] of the phenomenon and built an apparatus for the production of sound by light that was called *Spectrophone*.[4] He experimented[5] with a variety of solids, liquids, and gases, attributing the (photoacoustic) effect observed with spongy solids such as carbon black to a cyclic thermal expansion and contraction driving air in and out from the pores of the solid in response to the cyclical heating and cooling of it by chopped light. The first version of the device used as a spectrometer is shown in Fig. 1.

Tyndal[6] (1820–1893) and Roentgen[7] (1845–1923) confirmed that an acoustic signal can be produced when a gas in an enclosed cell is illuminated with chopped light. Rayleigh[8] (1842–1919) published a paper on the *Photophone* explaining the phenomenon as probably due to a mechanical motion of the illuminated solid. However, Preece[9] did not observe any substantial mechanical motion and suggested that the effect was due to an expansion and contraction of the air in the cell. That same year, Mercadier[10] concluded that the sound was due to a vibratory movement determined by the alternate heating and cooling produced by the intermittent radiation.

II. THE EARLY EXPERIMENTS

Tyndall[11] made a series of experiments in which the gas contained in a glass sphere was illuminated by the radiation from a lime-cylinder heated by an oxy-hydrogen flame concentrated by means of a concave mirror and interrupted at audible frequency by a rotating perforated disk. The periodic pressure fluctuations resulting from the selective absorption of the gas was detected by ear through a small tube. He examined many gases and tried to detect methane but failed because of the absence of suitable detectors.

After these first experiments, it seems that there were no further studies until 1938 when, in the Soviet Union at the State Optical Institute, in Leningrad, Veingerov[12] described a method of gas analysis based on the Tyndal–Roentgen *optic-acoustic* effect (Fig. 2).

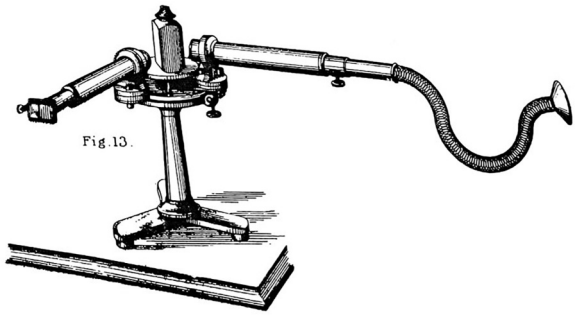

FIG. 1. The first acoustic spectrograph described by Bell. From Bell, Science **2**, 242 (1881). Copyright 1881 American Association for the Advancement of Science. The signal was received through an acoustic horn.

With his apparatus, he was able to detect at atmospheric pressure the presence of 0.2% by volume of carbon dioxide in non-absorbing nitrogen. The accuracy of the measurement was limited by the insensitivity of the detecting microphone and by the background sound produced by the absorption of radiation by the cell's walls. Improvements to this apparatus were later described by the same author.[13]

In 1939, Prud[14] described a similar system in use at the Johns Hopkins Hospital, USA, to detect small concentrations of carbon monoxide and carbon dioxide. He measured directly the temperature changes using a thermopile. In 1943, Luft[15] published the results of over five years' work on an optoacoustic gas analyzer and described a commercial automatically recording instrument, which was subsequently of large use. Luft also gave an account of the use of his apparatus for measuring the infrared absorption spectra of gases and vapors, a method used successfully by Veingerov[16] two years later. The apparatus was still named *spectrophone*. A monochromatic beam of radiation, interrupted at a sonic frequency, was used to irradiate through a rock salt window a volume of the gas under investigation enclosed into a cell. Absorption of radiation in the gas was accompanied by a temperature increase and, owing to the intermittent nature of the irradiating beam, the gas pressure successively rose and fell. These pressure fluctuations were converted into electrical signals by an electro-dynamic microphone placed at the end of the cell and the signal was amplified, rectified, and measured by a galvanometer. The reading of the galvanometer, for a given wavelength, depended on the absorbing power of the gas. Thus, for a fixed gas concentration, the absorption spectrum could be recorded changing the wavelength of the heating radiation.

Veingerov[17] used the system to study the 2.7 μm and 4.3 μm absorption bands of carbon dioxide.

In the Soviet Union, Gorelik[18] seems to have been the first one to propose the use of the optoacoustic effect to investigate the rate of energy transfer between the vibrational and the translational degrees of freedom of gas molecules. The infrared radiation energy is absorbed by the vibrational (rotational) levels of the gas and, after a time delay determined by the rate of energy transfer, appears in the translational modes and causes the gas to heat up. If the modulation frequency is such that the time of irradiation is less than the time required for energy transfer to take place, then the phase of the pressure fluctuations is different from the one of the incident radiation. Thus, a study of the phase of the acoustic pressure oscillations as a function of the modulation frequency should give information about the rate of intermolecular energy transfer. These considerations by Gorelik put the basis of methods of determining molecular vibrational lifetimes, using the optoacoustic effect. Figure 3 shows the apparatus used by Slobodskaya[19] in 1948. Two years later, Stepanov and Girin[20] gave a theoretical account of the temperature changes occurring in the spectrophone. Several works[21–23] have since then improved Slobodskaya's system.

In 1950, Cottrell[24] considered theoretically the possibility of measuring the collision frequency of gas molecules with the spectrophone; however, the effect was too small and was not observed.[25]

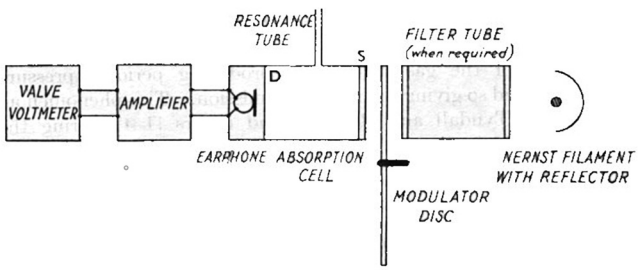

FIG. 2. The Veingerov apparatus. Radiation from a Nerst filament situated at the center of a polished reflector was transmitted through a perforated rotating disk (modulator disk) into an absorption cell, which consisted of a highly polished cylinder closed at one end by a sylvine window s and at the other end by the diaphragm D of a telephone earpiece. The absorption cell had a side tube, which acted as a resonator, the length being chosen to give maximum sound amplitude at the modulation frequency selected, about 100 Hz. The resultant e.m.f. from the earphone was amplified and the output was measured with a valve-voltmeter.

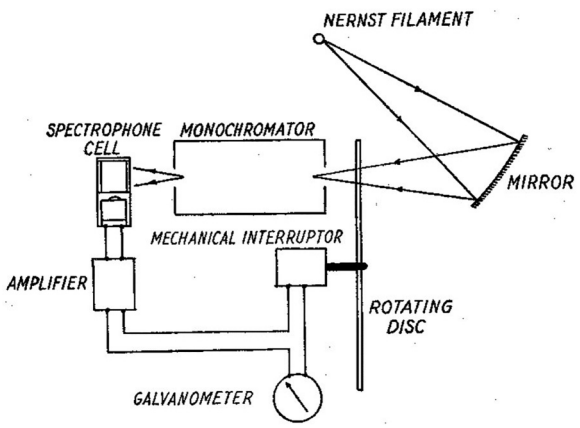

FIG. 3. The apparatus of Slobodskaya for measuring vibrational lifetimes.

These first experiments were described in 1959 by Delaney.[26]

Later, two approaches were used to link the relaxation time to experimentally determined parameters such as the modulation frequency, signal phase, and gas pressure, which ultimately led to the same result. The first approach was a kinetic molecular treatment developed by Delaney[27] and Kaiser,[25] where an equation of balance was set up for the production of vibrationally excited molecules and then solved for various limiting conditions. The second approach was a thermodynamic treatment first used by Gorelik[18] and further developed by Cottrell and McCoubrey.[28]

The first determinations of relaxation times were made on carbon monoxide,[27,29] carbon dioxide, nitrous oxide,[30,31] and other gases.

The early applications of the photoacoustic technique aimed at performing spectroscopy of gases[32–34] and photochemical studies.[35,36] The infrared *spectrophone* was developed and also frequently used to study vibrational–translational relaxation rates using the phase-sensitive detection of the optoacoustic signal.[37]

Later, in 1973, at Bell Labs, Rosencwaig[38] applied it to solids, and a few years later, Fournier *et al.*[39] and Murphy and Aamodt[40] introduced the photodeflection technique that the French researchers called the *mirage effect*.

A modulated optical source to originate a signal is a common feature of all photothermal techniques and phenomena. The produced heat in all cases is non-stationary. This characteristic has led to the discovery of a wealth of phenomena associated with the interaction and propagation of modulated heat in media of all types. The discussion of this type of behavior has led to the introduction of the concept of *thermal waves*, which has largely been used since the early part of 1980. Thermal waves are the damped wave-like temperature fields produced by a periodically modulated heat source, well representing the thermal diffusion dynamics in the media. They exhibit a strong exponential decay and a phase lag with distance from the source, which have been used to determine the thermal diffusivity in bulk and in layered materials as well.[41–46]

We now briefly discuss the first development of the various techniques.

III. PHOTOACOUSTIC TECHNIQUE

The method of using an intermittent light source to excite sound from a gas, solid, or liquid substance has received many names from different authors. Today, to describe this technique, two terms are used: *optoacoustic* or *photoacoustic*. In the first conference on the subject named *Topical meeting on photoacoustic spectroscopy* in Ames, Iowa, USA, in August 1979, the name *photoacoustic* was chosen, but optoacoustic continued to be used and it is used also today.

In photoacoustic spectroscopy, the sample under investigation is excited with a modulated or pulsed light source. Via radiationless decay, part of the absorbed light is released in the sample as heat. With the incident energy being either modulated or pulsed, the heat generation also shows a corresponding time dependence. Thermal waves are, therefore, generated and, due to thermal expansion, acoustic waves are induced as well. These waves can be detected with pyroelectric and piezoelectric transducers, respectively. With a pyroelectric thin film calorimeter, a sensitivity of nanojoules has been obtained at a time resolution of tens of nanoseconds.[47]

Most of the initial experimental work with solids in photoacoustics used a gas/microphone cell in which a portion of the thermal energy produced in the sample by light absorption and subsequent thermalization within the sample was converted to pressure fluctuations in a gas in thermal contact with the sample surface and detected using a microphone. In all cases, the modulated temperature rise in the sample associated with temporally modulated light absorption is directly converted to a spatially varying temperature change in the gas. This temperature change is substantially confined to the region in the gas near the surface of the light absorbing sample. A small fraction of the total thermal energy deposited in the gas by this conduction and diffusion process from the sample is then converted into an acoustic wave that propagated through the cell to the microphone.

The low detection threshold of photoacoustic systems is due to the excellent sensitivity of available microphones.

After the laser was built, photoacoustic spectroscopy had wide applications in optical spectroscopy of gases.[33] The cell containing the gas to be detected was irradiated with a chopped tunable laser beam. When the frequency of the laser coincides with one of the absorption frequencies of the gas, a periodic heating of the gas takes place. The resulting pressure fluctuations are detected by a microphone placed in the cell.

Phase-sensitive detection of an optoacoustic signal was used for some time in infrared spectrophone experiments to measure the vibrational–translational relaxation rates.[31,37]

A strong activity began at Bell Laboratories. Kreuzer[48] developed an optoacoustic cell and used the optoacoustic method to detect NO pollution in air.[32] He detected nitric oxide using a tunable infrared spin flip Raman laser to measure the absorption spectrum of a gas sample in a cell containing only about 1 cc of gas detecting 0.01 ppm of NO with a 4 s integration technique and 15 mW of radiation with wavenumbers in the range 1843–1788 cm^{-1}. Later, Kreuzer[49] was able to detect very low concentrations of contaminants in a gas by tuning an infrared laser to a vibration frequency of the contaminant and recording the microphonic signal resulting from the absorption. De Groot *et al.*[36] reported a study of the photochemistry of aldehydes using the optoacoustic technique.

At Bell Labs, Harshbarger and Robin described the optoacoustic effect considering it as a revival of an old technique for molecular spectroscopy.[35] They discussed the technique applied to gas and investigated solids also. They experimented with spectra of powdered $K_2Cr_2O_7$, flower petals, grass, dried blood smears, ultramarine, and carbon black. The spectra of solids that are otherwise rather intractable can be easily obtained using optoacoustic spectroscopy. After a number of examples, they concluded: "Our experiments show that the technique can give useful information about photochemistry, radiationless relaxation processes, and weakly allowed transitions when ultraviolet and visible light is used as the exciting radiation. We confidently predict that the optoacoustic effect will be used more broadly as a spectroscopic tool in the future than it was in the past 90 years since the discovery of the phenomenon."

They mentioned that Rosencwaig in his laboratory was making optoacoustic spectra of many inorganic solids. The

measurements were published in 1973 by Rosencwaig[50] who started a series of measurements for spectroscopic purposes.

In the same year, Parker and Richte[51] at Johns Hopkins University, USA, studied collisional deactivation of singlet molecular oxygen, stimulating optically the oxygen contained in a high pressure cell and detecting the resulting pressure increase with a condenser microphone (see Fig. 4). Parker[52] also studied the effect of the chopped light entering the high pressure cell that may produce sound even though the gas was not absorbing due to the interaction of the incident light with the cell window and developed a calculation of the temperature.

Rosengren *et al.*[53] in 1974 described a study of laser-acoustic air pollution monitors, and Max and Rosengren[54] studied the characteristics of a resonant optoacoustic gas concentration detector. The year after, Rosengren continued to publish on an optimal optoacoustic detector design to be used with a spectrophone.[55] The introduction of a resonant optoacoustic cell, which increased the sensitivity of the method for two orders of magnitude, was an important step.[56,57]

In 1975, Rosencwaig started to publicize the technique.[58] With Hall, he showed that photoacoustic spectrometry offers a simple and sensitive technique for finding the location and for identifying the separated compounds in thin layer chromatography.[59] Rosencwaig applied the technique to opaque solids;[60] later in 1977, the technique was applied to photochemistry,[61,62] and in 1978 to electrochemistry.[63]

In 1977, Pao published a book on optoacoustic spectroscopy and detection.[64]

The laser optoacoustic technique was used for the measurement of absorption coefficients of a number of pollutants at different IR wavelengths using CO_2 and CO lasers.[65–69] Although the laser spectrophone technique, as it was named, proved to be a very elegant method, it had the disadvantage that the acoustic cell had to be calibrated with a gas of known absorption coefficient.

Even through several descriptions of signal generation in the gas–microphone configuration were published, which differed principally in the level of approximation used to represent the sample-gas coupling,[70–72] the most successful and widely used was the one by Rosencwaig and Gersho,[73] which represented a turning point in the practical application of the photoacoustic technique. They wrote:

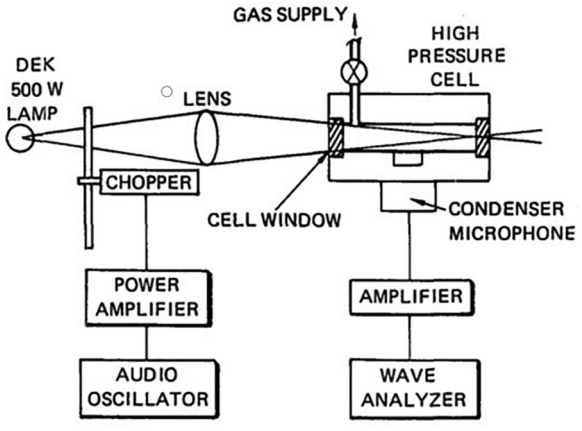

FIG. 4. Parker's setup. Reprinted from J. G. Parker, Appl. Opt. **12**, 2974 (1973). Copyright 1973 Optical Society of America.

"We have found, from experiments in which we first thoroughly evacuated the photoacoustic cell and then refilled it with non-adsorbing noble gas and from experiments with two-dimensional solids and other materials with weak surface adsorption properties, that absorbed gases do not play a significant role in the production of the acoustic signal. Furthermore, it can be readily shown that thermal expansion and contraction of the solid, and any thermally induced mechanical vibration of the solid are generally too small in magnitude to account for the observed acoustic signal. From both experimental and theoretical considerations we feel that the primary source of the acoustic signal in the photoacoustic cell arises from the periodic heat flow from the solid to the surrounding gas as the solid is cyclically heated by the chopped light." Parker had arrived at the same conclusion.[52]

Rosencwaig and Gersho then calculated the temperature distribution in the one-dimensional case of a cylindrical cell. They found that a thin boundary layer responded thermally to the periodic temperature at the surface of the sample. The effective thickness of such a layer is $2\pi\mu$, where $\mu = \sqrt{D/\pi f}$ is the thermal diffusion length of the gas, D is its thermal diffusivity, and f is the modulation frequency. This layer of gas expands and contracts periodically and thus can be thought of as acting as an acoustic piston on the rest of the gas column in the cell, producing an acoustic pressure signal that travels through the entire gas column. They also gave an equation for the magnitude and phase of the signal in terms of the thermal, optical, and geometrical properties of the cell, the sample, and the ambient gas. They then attempted to calculate the resulting pressure variation for various physical situations as optically transparent solids or optically opaque solids. They also justified a change of the name of the effect from optoacoustic to photoacoustic as the need to reduce confusion with the acoustic–optic effect in which a laser beam is deflected by acoustic waves in a crystal.

Rosencwaig later elaborated the matter in a book.[74]

Onward, the photoacoustic technique started to be widely used for a great number of applications. The main reason for its wide spread is that the photoacoustic technique is a powerful tool for determining the optical and thermal properties of solids, liquids, and gases that have very small absorption coefficients. The impetus for such an exploitation has come from the need for a spectroscopic technique, which would provide reliable information about samples, which are difficult to examine by conventional optical transmission or reflectance spectroscopy in the UV-visible and near IR region of the electromagnetic spectrum. The real power of this technique lies in its ability to determine with high sensitivity the periodic component of the surface temperature of a sample, which affords possibilities for non-destructive testing, depth profiling, thickness determination, and thermal transport measurements. The successful application of the technique has also been enabled by the emergence of powerful light sources in general and lasers in particular.

In photoacoustic spectroscopy of solids or liquids, the effect can be observed only when radiation is absorbed by the sample;

therefore, variations of the wavelength of the incident radiation and measurement of the amplitude of the signal at any wavelength provide a measure of the ability of the material to absorb at that wavelength so the absorption spectrum of the sample is obtained. The use of the technique for examining the solid and liquid samples has a number of important advantages over conventional optical spectroscopy, including freedom from light scattering problems, possibility for the use of optically opaque and weakly absorbing materials, etc. The photoacoustic techniques are particularly suitable for weakly absorbing, strongly scattering, or opaque samples. Combined with laser excitation, the detection method offers a unique combination of advantages, such as high sensitivity, high spectral resolution, high time resolution, and instrumental simplicity. It may be used also as a calorimetric method.

The paper by Rosencwaig and Gersho in 1976[73] put the photoacoustic effect in condensed media on a firm theoretical basis. Since then, the field of photoacoustics and the related fields of photothermal phenomena and laser ultrasonics have grown enormously. A multitude of ways of generating the effects has emerged using all types of radiation. Likewise, the diversity in methods for the detection of the generated thermal and acoustic waves has increased dramatically. One of the reasons for the popularity of the photoacoustic and photothermal field is the wide applicability of these techniques for fundamental and applied research.

The combination of thermal and optical investigations of samples has enabled the determination of optical absorption coefficients and thermal properties of opaque or diffusing samples, of thin films or multilayered structures. The photothermal methods have been successfully applied to powder samples, non-polished samples, crystalline, polycrystalline, or amorphous thin films, multilayered structures, and the detection of subsurface defects.

A number of experiments followed the first studies.[75–82] Pulsed optoacoustic spectroscopy of liquids was introduced by Patel and Tam[81] at Bell Labs, Murray Hill.

Fernelius[83] extended the Rosencwaig and Gersho model to the case of an absorbing layer deposited on an absorbing substrate.

The photoacoustic effect had a very significant role in the historical development of photothermal science, and at present, it is still a widely used method of detection.

In Secs. IV and V, we will discuss the origin of two other techniques: the *thermal lens* and the *photothermal deflection*, which both use a laser beam to test the induced thermal field in the material. In fact, the temperature gradients cause the refractive index changes, which may produce the beam focusing/defocusing effects, and the beam deflection as well. These effects can be specifically detected by *photothermal lensing* and *photothermal deflection* techniques, respectively.

IV. THERMAL LENSING EFFECTS

A new method to use thermal effects to study the properties of a material was introduced with the construction of the first gas lasers when the effect of the thermal lens produced by the heating of the active gas medium was recognized.

When a laser beam passes through a lossy material, the absorbed energy produces thermal gradients, which in turn produce gradients of refractive index. There are a number of effects that may be produced including focusing and defocusing (thermal lens) of a light beam trespassing the heated zone that are extremely sensitive to losses.[84]

The effects of the heating produced by a laser beam on a liquid or a solid inserted in the laser cavity was examined after the invention of the laser.

At Bell Labs, Gordon *et al.* in 1964 placed cells of organic liquids inside the resonator of a He–Ne laser to increase the power in his study of Raman spectra of these materials and observed that after a transient behavior lasting a few seconds, a steady state was reached with an expanded beam.[85]

The subsequent year, Leite *et al.*[86] discussed briefly the so-called "thermal lens effect" as an effect observed when a cell containing a transparent liquid or some solids is inserted in the cavity of a gas laser. A diverging lens is formed in the liquid because of the absorption of the laser beam, yielding localized heating and consequent transverse gradient of the index of refraction. They used the technique for the measurement of low absorption materials.

They gave a relation between the absorbance and the focal length of the liquid lens when the beam intensity is Gaussian in the dominant mode and a sufficient time to damp initial transients is allowed.

With that method, which they described in more detail in a following paper,[87] they were able to measure materials with very low absorption coefficients of about $10^4\ \mathrm{cm}^{-1}$, detecting a temperature increase of 75 mK. In the paper, it was shown that the blooming process in liquids is dominated by different mechanisms at different times. Initially, the process involves heating of the medium with consequent beam expansion and heat dissipation by conduction alone. Later, in the process, heat dissipation by convection becomes important. In a horizontal cell, this leads to asymmetry of the bloomed beam. Finally, a steady state is reached in which a convection cell exists and the bloomed beam no longer changes with time. It was calculated that the temperatures needed to obtain appreciable changes were much less than a degree Kelvin.

Other measurements were made.[88,89] Solimini[90] provided a quantitative theory. Dovici and Harris[91] extended the sensitivity of the technique finding a minimum detectable absorbance of 6.3×10^7.

At the Naval Res. Lab, McLean *et al.*[92] observed the induced index changes by means of a Mach–Zender interferometer and an argon laser.

Smith[93] studied the thermal defocusing of a CO_2 laser beam (10.6 μm wavelength) propagating in an absorbing gas. When the radiation passes through the absorbing gas in the cavity, the medium is heated resulting in a temperature gradient transverse to the laser beam. This temperature gradient (and the refractive index gradient) is, in effect, a negative lens that causes the beam to expand in passing through the medium, and Smith studied the steady-state thermal defocusing.

The thermal action of gas lasers resulting in a thermal divergence of the laser beam was studied by several authors.[94–98] Great attention was given to the effect of a refractive index gradient of thermal origin on the laser beams in the laser cavity and to the optical nonlinearities of thermal origin.

In 1976, Swofford *et al.*[99] studied the C–H vibrational states of benzene, naphthalene, and antracene in the visible region by thermal lens spectroscopy.

The change of refractive index resulting from a change in temperature due to light absorption can be seen as a third-order nonlinear optical effect of thermal origin.[100]

Akhmanov paid attention to this nonlinear phenomenon several times and studied both theoretically and experimentally thermal self-defocusing and self-focusing of cw laser beams in liquids and solids giving an analytical theory of thermal self-action.[101]

The thermal lens method was used also by Long *et al.*[102]

V. THE ESTABLISHMENT OF A STABLE STAGE FOR THE PRESENTATION OF THE PHOTOTHERMAL TECHNIQUES AND THEIR APPLICATIONS

In 1978, it seemed that the field of photoacoustic spectroscopy had developed to the point that a dedicated international conference would be appropriate, and John McCleland asked the Optical Society of America if they would be interested to such a meeting. Jarus Quin, the executive director of OSA, was enthusiastic about the idea, so Velmer Fassel, deputy director of the Ames Lab. USDOE of Iowa State University agreed to host the meeting and provided some funding. The National Science Foundation also contributed funding. The conference was held from 1st of August until 5th, 1979, had 151 participants, and was the first of a long series, which had the more recent one in Moscow in July 2019.[103] In this last conference, Fournier and Braslavsky presented an historical overview on the photoacoustic and photothermal development. Since then, the so-called *Photoacoustic and Photothermal Phenomena* international conferences have been held every two years.

VI. PHOTOTHERMAL DEFLECTION TECHNIQUE AND THE MIRAGE EFFECT

In 1979, a new technique was described to measure the temperature rising in the optoacoustic method. The new technique was called *photothermal deflection* or *mirage technique*. This technique instead of using a closed cavity employed a different method to assess the temperature of the heated sample, which was based on the well known mirage effect.

The mirage effect, i.e., the deflection of light beams due to thermal induced gradients of the air refractive index, for example, in a hot desert landscape, was known since the ancient times. It was described in many reports and scientific papers starting from the Greek historian Diodorus Siculus. It was also mentioned in ancient China, Japan, and in Northern's saga. In modern times, a mirage was described in the classic textbook by Wood.[104]

The mirage effect received its first scientific description by the French mathematician Gaspard Monge (1746–1818) the creator of descriptive geometry and the founder of the Ecole Polytechnique. He observed the effect when in Egypt following Napoleon and described it in a paper.[105] He observed that French soldiers during a march from Alexandria to Cairo saw what seemed to be huge lakes at far distance. They could even see distant villages that appeared as if they were on some island surrounded by a lake with an inverted image of the village reflecting off its surface. As they were approaching, the water was retreating until it finally disappeared totally.

He explained the phenomena saying that the light rays were bent by the layer of superheated air just above the sand. Heat radiating from the desert's surface warms the air immediately above it and reduces the air density. There is a boundary layer between the heated and cooler layer, denser air above it acts as a lens, bending or refracting the light rays from the sky back upward toward the cooler layer. The bigger the temperature difference, the bigger the effect of the mirage will be.

He coined the term *se mirer* (look to oneself) on which the translation in English was mirage.

VII. PHOTOTHERMAL DEFLECTION SPECTROSCOPY

The new technique to measure the temperature increase of a sample illuminated with a beam of chopped light using the mirage effect was discussed almost simultaneously by two groups. At the Topical Meeting on Photoacoustic spectroscopy, in Ames, Fournier *et al.* described[39] the principles of the method.

Later, they published an extended version on Applied Physics Letters with a paper received 2 August 1979.[106] On Journal of Applied Physics, Murphy and Aamodt, with a paper received 17 January 1980, described substantially the same method[40] and quoted the Fournier paper.

Boccara *et al.*[107] describe the method in which the absorption coefficient of the sample is deduced from the measurement of the thermal gradient in the gas layer adjacent to the sample surface. In this technique, the periodic heat generated by a chopped pump laser beam on the sample gives rise to a refractive index gradient of the medium over it suitable for periodically deflecting a probe beam propagating along the surface of the solid (mirage effect). The experimental setup is shown in Fig. 5. A light beam of a He–Ne laser is focused near the periodically irradiated sample surface within the thermal diffusion length of the gas where the temperature gradient is noticeable.

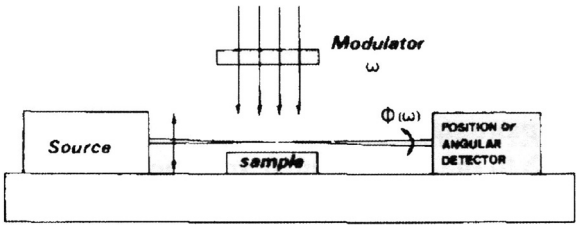

FIG. 5. Experimental setup used by Boccara *et al.* From Boccara *et al.*, Appl. Phys. Lett. **36**, 130 (1980). Copyright 1980 AIP Publishing LLC. The light beam of a He–Ne laser (about 1 mW) is focused near the periodically irradiated sample surface within the thermal diffusion length μ of the gas where the temperature gradient is noticeable. The modulated light source was a Xe arc and a monochromator or a cw dye laser. The periodic deflection of the probe beam was monitored either by use of a position sensor placed at a suitable distance away from the illuminated sample, or with a knife edge, which blocked half of the probe beam diameter, followed by a photocell. The signal was detected with a lock-in amplifier.

The periodic deflection of the probe beam was monitored either by the use of a position sensor placed at a suitable distance away from the illuminated sample surface, or with a knife edge, which blocked half of the probe beam diameter, followed by a photocell. The signal was detected with a lock-in amplifier.

The authors said that the lowest temperature change they could measure was 10^{-4} K. The technique was used to measure absorption of different materials. As an example the spectrum of $Nd_2(MoO_4)$ is shown in Fig. 6.

They also described the measurements made at liquid helium temperature. Later, Boccara *et al.*[107] started to use the photothermal technique in spectroscopy. They used the simple configuration shown in Fig. 5, in which an intensity-modulated beam of electromagnetic radiation (pump beam) is incident upon an absorbing medium, heating it. Concomitant with this time-dependent change in the medium temperature is a corresponding modulated index of refraction gradient, which is employed to deflect a probe beam intersecting the pump beam within the sample and/or the substrate. The deflection, which can be as small as 10^{9}–10^{10} rad, is detected with a position sensor. The amplitude of the deflection was found to be related to the optical absorption in a straightforward manner. In particular the authors gave a formula for the deflection angle of a laser beam by an absorbing medium on a given substrate.

In the following year, Jackson *et al.*[108] presented the theory of the technique considering both collinear photothermal deflection where the gradient of the index of refraction is both created and probed within the sample, and the transverse photothermal deflection where the probing of the gradient of the index of refraction is accomplished in the thin layer adjacent to the sample.

Murphy and Aamodt[109] gave the fundamental equation for the probe beam deflection angle.

A number of papers by the people from the Ecole Superieure de Physique et de Chimie Industrielles, Laboratoire d'Optique Physique, described the effect and its applications[107] and also other researchers used the method.

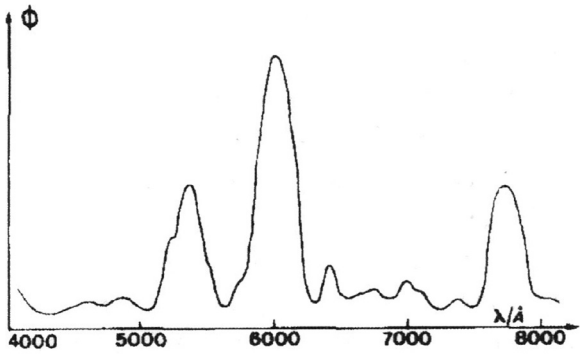

FIG. 6. Thermo-optical absorption spectrum of a $Nd_2(MoO_4)$ crystal with a chopper frequency of 80 Hz. From Boccara *et al.*, Appl. Phys. Lett. **36**, 130 (1980). Copyright 1980 AIP Publishing LLC.

Murphy and Aamodt in their paper extended the calculations of Rosencwaig and Gersho developing the theory of the photothermal effect and made measurements describing the application of the method to the measurement of thermal diffusivity of gases.[40] Later, they proposed a new method of thermal imaging using the deflection technique.[109]

Photothermal deflection spectroscopy of amorphous semiconductors deposited on non-absorbing substrates was proposed by Jackson *et al.*[108] and Fournier *et al.*[110]

VIII. EXPLOSIONS OF APPLICATIONS

The 1980s witnessed an explosion of applications of the photoacoustic and photothermal techniques together to the improvement of a full understanding of their possibilities. In the 1980s, photothermal deflectance,[111,112] photothermal displacement,[113,114] and photopyroelectric spectroscopy[115] techniques were added to the usual photoacoustic and photothermal deflection techniques. Diebold[116] studied the acoustic wave generation in a periodically photodissociated gas.

In 1981, Patel and Tam published a review paper[117] in which they described exhaustively the use of pulsed photoacoustic spectroscopy presenting several experimental results showing the capability of the method to measure absorption coefficients as small as 10^{6} cm^{-1}. They also described the application to two-photon absorption and Raman-gain spectroscopy.

Applications in trace analysis in the gas phase had already demonstrated sub-ppb detection levels[118,119] and in condensed phase spectroscopy, ppt detection limits had been reported for both photoacoustic and thermal lensing measurements.[120,121] Forbidden spectroscopic transitions were examined.[84,89,102,122]

Inverse Raman,[123] two-photon spectroscopy,[124] infrared laser photochemistry,[125] fluorescence quantum yield,[126,127] and Doppler free spectroscopy[128] were also investigated.

Because the photodeflection technique allowed to acquire detailed knowledge on the temperature distribution at the surface of the irradiated sample, it proved to be useful in a greater number of applications other than the spectroscopic ones. One immediate application was the determination of the thermal properties of materials.[120–126]

From this knowledge, a number of applications ensued. We may mention the use of the method for thermal diffusivity determination that was proposed by several groups,[129–139] and the use for coating thickness determination because the technique was able to determine the presence and position of a discontinuity in the thermal properties of the coating and the substrate.[140,141]

It was suggested that with the photoacoustic technique, one can obtain information about the optical and/or thermal characteristics of a sample as a function of depth beneath its surface.[74] Experimentation started[142] and some theoretical analyses were done.[143] The photothermal deflection method proved to be suitable for non-destructive evaluation of materials and layered systems according to the thermal wave interferometry theory, which considers that, when thermal waves at the surface of the sample are produced, they can be reflected by non-homogeneities or defects whose sizes are larger than some critical dimensions.[42,144,145]

Thermal wave imaging of subsurface features was performed with gas–microphone photoacoustics,[146,147] photothermal techniques,[40] and piezoelectric photoacoustics.[148]

Subsurface defect characterization was described by a number of authors.[69,149–152]

An example of the versatility of the methods is given by a work from the Fournier group that showed the ability of the photothermal method to study the quality of welding;[153–155] another application was the use of the method to determine optical losses in optical waveguides[156,157] and the determination of heating on the facets of diode lasers.[158] Similar results were obtained by the Salazar group.[159]

Thermal wave imaging methods applied to many applications of non-destructive recovery of depth dependent information in thin solid media were described.[160–162] Photothermal microscopy,[69] biological[163] and medical,[164] agricultural,[165] food,[166] and environmental[167] applications were described.

Different photothermal techniques were proposed and applied for the study of solids and powders[113,168,169] electric and thermal transport in bulk semiconductors,[170,171] thin films,[172–174] and electronic devices.[158,175,176] The technique showed an uninterrupted growth of new ideas to derive the depth profiling of thermally inhomogeneous materials, by applying several mathematical tools[155,177–184] (i.e., neural networks, genetic algorithms, etc.).[185–187]

A number of review papers or book on the subject of photoacoustic or photothermal techniques were published since 1980.[74,117,188–204] The excellent review paper by Tam[205] synthesized the works in the first years of 1980s. The recent review from Manohar and Razansky[206] traces the first steps of photoacoustic science up to current biomedical applications.

We like to conclude this review article by going back in 1880 when Alexander Graham Bell set up the *photophone* for the first wireless voice communications. He wrote to his father "I have heard articulate speech by sunlight! I have heard a ray of the sun laugh and cough and sing!." He was serious talking about photophone as "the greatest invention [I have] ever made, greater than the telephone," concluding prophetically "Can Imagination picture what the future of this invention is to be!" but could be predictable at that time the ever increasing interest and the great number of applications in the field of the newborn photoacoustic and photothermal science?

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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