Laser Photoacoustic Spectroscopy

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Photoacoustic spectroscopy (PAS), also known as optoacoustic spectroscopy, was pioneered by Alexander Graham Bell more than a century ago. The advent of the laser strongly stimulated research and applications of this technique and the interest is such that international topical meetings on photoacoustic and photothermal phenomena are now held biennially.

The photoacoustic (PA) effect is essentially an energy-conversion process. When a sample (solid, liquid or gas) is irradiated by a laser beam or some other radiation source, part of the absorbed energy is converted into translation energy of the molecules by radiationless transitions. It is this de-excitation channel which is responsible for heat production within the sample although secondary reactions may also play a role (see Fig. 1). If either the incident radiation or the absorption by the sample is modulated, the periodic heating finally results in a pressure modulation. The PA signal thus originates from the thermal response of the sample to the absorbed energy detected as pressure fluctuations acoustically. Owing to thermal diffusion processes the magnitude of this signal depends not only on the thermal and optical characteristics of the sample but also on the nature of the coupling mechanism between sample and detector. Consequently the coupling medium plays an important role and one can differentiate between the light-to-heat conversion and the heat-to-sound conversion efficiencies.

Experimental Arrangement

Since the time of Bell who used the Sun as radiation source, a foot-operated chopper for modulation and an earphone as acoustic detector, numerous experimental arrangements have been developed which mainly differ in the radiation sources employed and the system of both modulation and detection. Since the PA signal amplitude is proportional to the radiation power, the high spectral brightness offered by lasers is advantageous for the measurement of small absorptions, i.e., for weakly absorbing media or trace detection.

Two types of modulation should be distinguished: modulation of the incident radiation and modulation of the sample absorption. Schemes for the first include the widely-used amplitude modulation by mechanical choppers, electro-optic and acousto-optic modulators and the direct modulation of the radiation source including notably pulsed sources as well as frequency- or wavelength-modulation. These last offer the advantage of eliminating the continuum background PA signal resulting from a wavelength-independent absorption, e.g., of the entrance window of the PA cell containing the sample. On the other hand, modulation of the absorption characteristics of the sample can be achieved on the basis of the Zeeman or Stark effect, by applying modulated magnetic or electric fields to the sample. Thereby the absorption wavelength is varied corresponding to a wavelength modulation and the continuum background is again suppressed.

While the design of the PA cell is not critical for solid or liquid samples, it may represent a crucial point for studies on weakly absorbing gases. In these cases acoustically resonant cells are often used. The modulation frequency is then tuned to a resonance frequency of the cell preferably with pressure nodes at the cell windows to reduce the background originating from window absorption.

Finally, various different schemes exist for the detection of the thermal or acoustic disturbances caused by the absorbed radiation. The choice depends on the sample, the sensitivity to be achieved, ease of operation, ruggedness, and any requirement for non-contact detection, e.g., in aggressive media. The methods which have been developed for solid samples are summarized in Fig. 2; they include 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 above the sample with a microphone (photoacoustics). Induced changes of the refractive index can be sensed by monitoring the deflection of a probe beam, e.g., from a HeNe laser, either within the (transparent) sample or directly above the (plane) sample surface (photothermal deflection, mirage effect). Changes of the sur-

Fig. 1 — Principle of the photoacoustic effect.

Fig. 2 — Photoacoustic and photothermal detection schemes.
Fig. 3 — Experimental set-up for photoacoustic studies on gases.

Studies on Liquids

Studies on Solids

A main advantage of PAS applied to solids is the fact that no elaborate sample preparation is required and unpolished sample surfaces pose no problems. Since the PA signal is proportional to the absorbed energy, even spectra of strongly scattering samples, like e.g., powders, can easily be measured. Another advantage is the high sensitivity that can be achieved because the PA detection is a null method for measuring absorption. To date, PAS performed with pulsed lasers and direct piezoelectric detection of the generated acoustic waves permit the detection of absorbances below \( 10^{-7} \). In the pulsed regime noise is easily rejected by time gating. Furthermore, the high laser intensities enable the use of non-linear optical techniques to generate intense tunable infrared and ultraviolet radiation for spectroscopy.

Recent work has been aimed at studying adsorbates on the surfaces of solids. PAS is expected to be rather sensitive to surface adsorption, especially if the substrate is transparent or highly reflective in the wavelength region in which the adsorbate absorbs. Both sinusoidal modulation of the incident laser beam and pulsed lasers have been used for this purpose. For example, ammonia (\( \text{NH}_3 \)) adsorbed on a silver substrate, cooled to 90 K in ultrahigh vacuum, has been detected with sub-monolayer sensitivity.

In another PAS study the thermal disordering of Langmuir-Blodgett (LB) monolayers of cadmium stearate on sapphire has been investigated. A pulsed laser with piezoelectric detection followed by boxcar integration gave a detection limit of \( 5 \times 10^{-10} \) J absorbed per laser pulse for an average of 100 pulses. The technique has also been applied to photochemical studies of adsorbed organometallics as well as to \( \text{in situ} \) diagnostics of laser chemical vapour deposition (CVD).

Studies on Liquids

In principle there are five important interaction mechanisms which can be responsible for the excitation of acoustic waves in liquids by the impact of pulsed laser radiation: dielectric breakdown, vaporization, thermoelasticity, electrostriction and radiation pressure. Their contributions depend on the parameters of the incident laser beam as well as on the optical and thermal properties of the medium. PAS studies on liquids are essentially based on the pure thermoelastic effect where the thermal expansion of the laser-heated volume generates the acoustic wave. Experimental and theoretical studies have been performed for a wide absorption range including "transparent" and opaque liquids.

In the first case, minimum absorption coefficients of \( 10^{-6} \) cm\(^{-1} \) have been detected corresponding to absorbed laser pulse energies of only \( 10^{-9} \) J. Owing to the high sensitivity, the method has been successfully applied e.g., to the measurement of the 8th harmonic of the C-H fundamental stretching vibration of benzene and to the detection of impurities in transparent liquids.

Depending on the penetration depth and the actual laser beam diameter, plane or hemispherical sound waves are excited in opaque liquids for most media within the IR wavelength range. In this case, different boundaries, i.e., surface conditions as e.g., free and confined surfaces or optically thin and thick surface films, can be investigated. PAS allows us to analyze and monitor surface films on liquids \( \text{in situ} \) in a non-contact and rather simple manner.

A recent example concerns the monitoring of polymerization in a surface film. The sample consisted of an optically thick layer (100 µm) of octadecyl methacrylate (ODMA, C\(_{22}\)H\(_{42}\)O\(_2\)) floating on a water surface. This layer can be polymerized in a nitrogen atmosphere by UV irradiation at room temperature. During the polymerization process the absorption band of ODMA centred at 940 cm\(^{-1} \) diminishes and finally vanishes completely. We used this fact for PA monitoring of the polymerization by measuring the PA signals which are excited by the impact of CO\(_2\) laser pulses at different wavelengths as a function of the UV irradiation time \( t_{\text{irr}} \). An example is shown in Fig. 4 where the time dependence is plotted for the 10P(28) laser transition located at the centre of the ODMA absorption band and the 10P(20) transition situated on the edge of the band. At the time \( t_{\text{irr}} = 0 \), i.e., before polymerization...
with respect to concentration. The method is thus suitable for both immission and emission studies.

(v) Detection of numerous components with one single apparatus, equipped e.g. with a tunable IR laser, is possible.

(vi) Only a short absorption path is required, i.e. wavelengths beyond atmospheric windows can be applied.

(vii) Continuous in situ measurements on flowing air with suitable PA cells are possible.

Since most molecules exhibit characteristic absorption features within the mid IR range, the so-called fingerprint region, tunable lasers emitting in this wavelength range are most appropriate for trace gas detection. In the course of our own studies in this field we have built two computer-controlled PA systems: a stationary apparatus with a CO laser and a mobile system with a CO₂ laser. Both lasers are only line-tunable, not continuous, which poses special requirements on the analysis of measured PA spectra of multicomponent gas mixtures with interfering absorptions. The analysis is performed on the basis of calibration spectra of single trace components by using a new iterative formalism. This procedure permits the determination of individual concentrations as well as the evaluation of the best laser transitions for the detection of specific components, yielding a minimum of interference with other components at optimum sensitivity.

A specific application concerns the analysis of motor vehicle exhaust gas samples performed with our CO laser PA system. Since water vapour exhibits a considerable absorption in the wavelength range between 5.15 µm and 6.35 µm of the CO laser, we have used a dual-beam arrangement with specially designed sample and reference PA cells. In spite of the water-vapour interference we have been able to derive the concentrations of 12 of the most important components like nitric oxide, ethylene, propylene, aromatic hydrocarbons and aldehydes at ppmV and sub-ppmV concentrations. It should be emphasized that even the isomers of xylene can be determined separately. This separation is difficult, if not impossible, to achieve with conventional methods, e.g. with gas chromatography.

Our second PA apparatus is equipped with a sealed-off CO₂ laser, line-tunable between 9.2 µm and 10.8 µm. A special design of the acoustically resonant PA chamber permits continuous measurements on air samples with a flow rate of ca 1 l/min without loss in sensitivity. The minimum detectable absorption coefficient is 10⁻⁶ cm⁻¹ which corresponds to trace gas concentrations of ppbV (µg/m³) under interference-free conditions. For the in situ monitoring of air pollutants, the entire PA apparatus is installed in a mobile air-conditioned trailer of 4 m length.

Hitherto, our mobile system has been applied at various locations for the in situ recording of specific pollutants like ethylene (C₂H₄) in outdoor air. Since today considerable amounts of C₂H₄ are emitted in the atmosphere by road traffic and various industries, the enhanced C₂H₄ concentrations are a continual source of stress for plant growth in urban areas. Furthermore, C₂H₄ acts as a precursor substance for photochemical smog. The 10P(14) CO₂ laser transition at 949.49 cm⁻¹ is ideally suited for detecting C₂H₄ because of the proximity of the C₂H₄ vibrational band νₓ located at 948.77 cm⁻¹. With the resulting large absorption cross section of 1.3 x 10⁻¹⁸ cm² we achieve a detection limit for C₂H₄ in ambient air of below 5 ppbV if attention is paid to the interfering absorption by CO₂. Diurnal concentration profiles are correlated with the strength of traffic, wind data and, on sunny days, with the local ozone production.

Recent studies which demonstrate the versatility of PAS concern in situ measurements on industrial exhaust air which represents a mixture of numerous components with concentrations varying in time. The continuous record-
yielding ethanol and methanol volatile organic compounds. The PA production plant besides numerous other great importance. As an example Fig. 5 showing of the main constituents is thus of good agreement between the photo-acoustically derived concentrations and independent gaschromatographic (GC) measurements (represented by x in Fig. 5) is obtained under steady state conditions. The PA data are not systematically higher than the GC data as could be supposed from the results in Fig. 5, but the time resolution offered by PAS is better and can be exploited for the monitoring of even short-term concentration fluctuations.

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EQEC: 2nd European Quantum Electronics Conference
Dresden, 28 August - 1 September 1989

Following EQEC-1, the first Divisional Conference of the Quantum Electronics Division held in Hannover in 1988, EQEC-2 took place in Dresden's Town Hall under the auspices of the GDR Academy of Sciences, the Friedrich Schiller University, Jena, and the Physical Society of the GDR.

The four plenary papers highlighted present mainstreams in quantum electronics. Akhmanov (Moscow) reported on non-linear optics in 2-dimensional systems, discussing non-linear wave dynamics, large scale transverse wave interaction, optical turbulence and spatial squeezing. These abstract concepts were beautifully illustrated by experimental results shown in an impressive movie. Wellin (Hannover) reviewed the many routes towards very-short-wavelength lasers and their potential applications. Glauber (Cambridge) discussed the theory of radiating atoms in resonant cavities, while Paul (Berlin) addressed a basic issue in quantum optics, namely interference between independent single photons, touching upon basic issues in quantum measurement theory.

An important contribution in the area of laser physics was made by Birnborg (W. Berlin) who reported on gain switching of semiconductor lasers where picosecond pulses can be produced by driving the laser with a much longer electrical pulse in such a way that only the first relaxation oscillation spike occurs. Dunn (St. Andrews) discussed the use of excimer lasers to pump optical parametric oscillators (OPO's) in the visible. Generally speaking OPO's have been of marginal importance during the past 25 years but they are now rapidly gaining popularity owing to new non-linear materials and new pump sources becoming available. Prior (Rehovot) addressed current models used to describe laser fluctuations, namely phase diffusion, random phase jumps and telegraph noise, generalizing these into a non-Markovian stochastic jump model. Distributed feedback gas lasers were analysed in their own right, and as a model system for DFB solid state lasers, by Kneubühl (Zurich). DFB gas lasers allow easy tests of theory since their parameters are much better controlled than in the case of a DFB semiconductor laser. Lasers were also addressed by Ovchinnikov (Moscow) in the context of the intriguing analogy between lasing action and superconductivity that can be made by comparing Cooper pairs with photons.

Regarding non-linear optical materials, Kobayashi (Tokyo) considered the problems which arise when one has to assess the many new materials (particularly polymers) which are presently being developed for fast optical switches and optical logic. He introduced a simple method based on measuring the transmission spectrum of a polymer layer sandwiched between two transparent electrodes. Stockman (Novosibirsk) gave a very interesting presentation of the giant optical non-linearities of fractal clusters such as aggregates of colloidal gold.

Walther (Max-Planck-Institut, Garching) reported on recent single-atom experiments which allow many early "Gedanken" experiments to be performed in the laboratory. Such experiments may resolve some basic issues in quantum physics since ensemble averaging is no longer present. Another significant contribution in a related area included the report by Chebotayev (Novosibirsk) on synchronisation in quantum transitions, making connections with Ramsey fringes, photon echoes and free induction decay. Possible applications would be super high resolution spectroscopy and high-speed atomic memory systems. In a theoretical paper Stenholm (Helsinki) touched upon the issue of Landau-Zener crossing during a laser assisted collision. For reasons not yet understood the range of validity of the "classical" Landau-Zener result is apparently much larger than expected.

Finally, Noordam (Amsterdam) reported recent results obtained in producing electronic wave packets in Rydberg atoms using picosecond laser excitation. A full set of abstracts of all invited and contributed papers has been published in Volume 13D of the Europhysics Conference Abstracts series which is available from the EPS Secretariat.

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