

THE TWENTY-TWO MOST FREQUENTLY CITED APL PUBLICATIONS — V

Introductions to and discussions of 21 of the 22 most frequently cited APL publications appeared in issues 2, 3, and 4 of Volume 7 and in issue 1 of Volume 8 of the *Johns Hopkins APL Technical Digest*.

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L. C. Aamodt, J. C. Murphy, and J. G. Parker, "Size Considerations in the Design of Cells for Photoacoustic Spectroscopy," *J. Appl. Phys.* **48**, 927-933 (1977).

Occasionally, the history of science is marked by the rediscovery of forgotten knowledge or techniques. This was the case for photoacoustic spectroscopy, a technique first studied by Alexander Graham Bell in 1881. Although work continued for more than a decade, the nature of the photoacoustic effect was never correctly understood. After this burst of scientific activity, the subject was put aside for more than 50 years until it was revived by work in Germany and at the Johns Hopkins medical facilities to measure the concentration of anesthetic gases in surgery.

Another 20 years passed before photoacoustic spectroscopy was revived as a way to investigate the properties of opaque solids. Independently, John G. Parker at APL¹ and Alan Rosencwaig at Bell Laboratories² rediscovered the effect. At that time, Parker was studying the acoustic properties of gases by means of an acoustic resonance technique. He found that the window of his resonance tube absorbed the intensity-modulated light that he used as a source of acoustic energy. The absorption produced an acoustic signal that contaminated his measurements of the gas properties. Parker offered a theoretical explanation correctly describing the nature of the photoacoustic effect in the glass window.

Rosencwaig's explanation paralleled that of Parker, but he also applied the method to the general absorption spectroscopy of opaque solids and was able to present spectra from such specimens as rose leaves, skin, and a variety of industrially interesting objects including dyes and paints. The key element in his application was the fact that thermal methods directly measured the energy absorbed by a sample material in contrast to conventional spectroscopic methods, which inferred it by measuring the ratio of the incident light to the light transmitted through the sample. This capability of photoacoustic spectroscopy made it possible to obtain the absorption spectra of opaque materials and of materials having properties difficult to handle in optical measurements.

At the time of this rediscovery, Leonard Aamodt and I were working on problems related to the optical and microwave spectroscopy of solids with metastable excited states, a class of material that had become technologically important because it included solid-state phosphors that were the basis of optically pumped solid-state lasers such as ruby and Nd:YAG. The materials were also of scientific interest because they included many organic dyes and other biologically important molecules. In this area of investigation, one missing item was knowledge of the ways that the metastable states lost energy via non-radiative relaxation. Details of the nonradiative processes could be inferred from radiative processes in materials with convenient optical transitions to the metastable states, but the information was often limited. For materials with no convenient optical transitions, little information about the system could be obtained.

It was in this context that we became aware of Rosencwaig's work on photoacoustic spectroscopy and quickly recognized that this method of spectroscopy provided a new diagnostic tool for studying excited state processes in solids since it directly measured nonradiative thermal relaxation.

As we examined the limited amount of photoacoustic literature available and began to assemble an experimental system, it became apparent that both theory and practice were in an extremely rudimentary state. Significant preliminary work would be required. At that time we also became aware of the work of Parker, who was only a floor away from us in the APL Milton S. Eisenhower Research Center. With the benefit of his experimental knowledge of gas-resonance-tube acoustics, we constructed several photoacoustic cells and were able to obtain spectra of a quality comparable to that found in the literature at that time.

Those photoacoustic spectra were marginal at best and inadequate for many important problems. A significant improvement in the performance of photoacoustic systems was needed. We recognized that the improvement depended on replacing the mainly phenomenological description of the photothermal effect then being used with a more critical analysis. Furthermore, we needed to understand better how the performance of the spectrometer

Size considerations in the design of cells for photoacoustic spectroscopy

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The dependence of photoacoustic spectrometer sensitivity on the physical dimensions of the sample cell was investigated for sizes larger than and smaller than the gas thermal diffusion length. The results depend on the thermal properties of the gas and the sample in agreement with an extension of Parker's theory of photoacoustic signal generation.

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Photoacoustic spectroscopy (PAS) is a recently revived tool for the study of solids.¹⁻⁴ It offers special advantages over conventional spectroscopic methods when opaque or highly scattering samples are used. Spectra from powders,^{1,2} from biological materials,² and from liquids have been obtained.³

The basic photoacoustic spectrometer consists of a chopped light source and a sealed sample cell containing a transparent gas. The cell contains a window to admit the light and a sensitive microphone to detect pressure changes in the gas associated with cyclical heating of the sample by absorption of the chopped light. The amplitudes of the pressure fluctuations in the gas depend on the incident light intensity, on the thermal properties of the sample and the gas, and on the details of the thermal diffusion processes responsible^{3,4} for the heat flow to the gas.^{3,4} The amplitudes of the pressure changes for constant light absorption depend on the physical size of the sample cell through the diffusion processes and generally increase with decreasing cell size. This dependence has been widely recognized^{3,5,6} with the result that most published PAS experiments have used small cells. However, no systematic study of this dependence has been made and questions persist concerning the behavior of PAS cells whose physical size is comparable to or less than the thermal diffusion length in the gas. In addition, while there has been experimental confirmation³ of the role thermal diffusion in the absorbing solid plays in PAS spectroscopy, there has not been a corresponding experimental confirmation of the role of diffusion processes in the gas medium.

In this work, the size aspects of PAS cells have been investigated, using a variable size cell whose dimensions could be made larger or smaller than the thermal diffusion length in the gas. The role of gas thermal properties were determined by the use of He and N₂ as working gases. The results are compared with an extension of the theory of photoacoustic signal generation. The extension explicitly includes the size of the PAS cell and finite thermal conductivity in the cell walls. The agreement between experiment and theory is good. The theory has been applied to the design of cells for 77°K operation.⁸

EXPERIMENTAL

The photoacoustic spectrometer was a simplified version of one recently used to study radiationless processes in luminescent solids at 77°K.^{7,8} Both time-

averaged and time-resolved measurements of the PAS signal were made. In the former case, the light source was a 1 mW He-Ne laser (Metrologic 660M). The beam was interrupted by a variable speed chopper (Laser Precision CTX-534) and illuminated the variable length photoacoustic cell. A General Radio electret microphone (GR 1961), preamplifier (GR 1560-P62), and Ithaco (393) lock-in amplifier completed the detection system. In the latter, time-resolved, case, a Spectra-Physics (125A) He-Ne laser (~50 mW output power) was used as a source. The increased laser output power allowed the time-varying PAS signal from the microphone preamplifier to be observed directly on an oscilloscope. The frequency, phase, and size dependence of S_{PAS} so measured agreed with the low-power time-averaged measurements.

A diagram of the PAS cell appears in Fig. 1. The cell was cylindrical. A plunger P, O-ring sealed to the outer cell wall, closed one end of the cylindrical cell. The other end of the cell was closed by a flange F and the electret microphone M. The cell provided for gas substitution through two small-diameter ($D \sim 0.025$ cm) inlets I. A carbon black sample was deposited directly onto the plunger from a smoky flame, uniformly covering the entire face of the plunger. To investigate the role thermal properties of the cell wall play in PAS signal generation, several cells were constructed from 304 stainless steel, aluminum, and Plexiglas. In the first two cases, optical entry to the cell was made through a small quartz window in the cover flange. In the Plexiglas cell, the material itself was used as a window. Flange to plunger separations as small as 0.03 cm could be reproducibly obtained. This value is taken to be the position accuracy of the cell length reported. The frequency dependence of the PAS signal amplitude $|S_{PAS}|$ and the phase ϕ_{PAS} was measured versus cell length for helium and nitrogen gas.

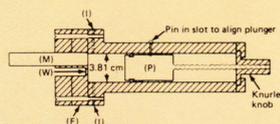


FIG. 1. Cross section of the PAS cell. P is the plunger, M is the microphone, W is the window, F is the cover flange, and I is the inlets for gas exchange. Sample is deposited on P.

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depended on both specimen and experimental parameters.

With this as background, Aamodt and I began a combined experimental/theoretical study of how the sensitivity of photoacoustic systems depended on sample and operational parameters. In the course of the work, we began a collaboration with Parker that led to the cited paper, the first analytical study of photoacoustic cells. The work placed the photoacoustic effect on a firm analytical basis. It pointed to what had to be done to improve photoacoustic instrumentation substantially. A subsequent paper extended the theory to the time domain rather than restricting it to the frequency domain as the original paper had.

This work allowed us to present, soon after the initial photoacoustic publication on solids, the measurement

of the concentration dependence of nonradiative relaxation rates in ruby. In a sense, we had completed a full turn of the circle. Since then, photoacoustic spectroscopy has been developed extensively at APL³ and elsewhere, and many allied photothermal techniques have been introduced into routine use. Thermal-wave imaging, one of those techniques, is still being actively investigated at APL as a tool for nondestructive materials characterization and defect location.

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