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RECENT PROGRESS IN PHOTOTHERMALLY-BASED SPECTROSCOPIES

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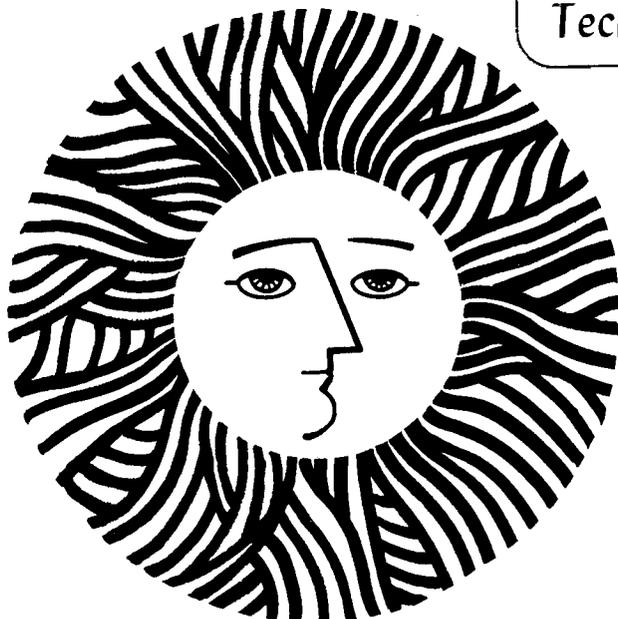
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Nabil M. Amer

September 1981

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Recent Progress in  
Photothermally-Based Spectroscopies

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Recent Progress in  
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The major objective of our research effort is to exploit novel optical heating schemes for the ultrasensitive (e.g., parts per trillion), unambiguous, and relatively simple characterization of effluents produced during energy production and utilization.

The physical principle underlying our detection schemes is that when a beam of electromagnetic radiation is absorbed by a given medium (gas, liquid, solid, or aerosol), heating will ensue. The heat is what we employ to measure very low optical absorption coefficients ( $\sim 10^{-10} \text{ cm}^{-1}$ ). This is accomplished in one of three ways: a) optical heating will cause a rise in pressure which can be detected with a suitable transducer, e.g., a microphone. This type of spectroscopy is known as photoacoustic;<sup>(1)</sup> b) optical heating causes a corresponding modulation of the index of refraction of the absorbing material which can be used to deflect a weak laser probe beam propagating through the material. The amplitude and phase of the deflection is quantitatively related to the absorption coefficient<sup>(2)</sup>; or c) in the case of solids, heating will cause deformation of the sample which can be detected, for example, interferometrically and related to the optical absorption coefficients.<sup>(3)</sup>

A brief summary of our recent results in photothermal spectroscopies is given below.

I. Photoacoustic Spectroscopy and Detection:

A. The Investigation of Loss Mechanisms in Acoustically Resonant Spectrophones <sup>(\*)</sup>

We have measured the pressure dependence of quality factors  $Q$  and resonant frequencies of a resonant spectrophone for various buffer gases (noble, diatomic, and polyatomic). The results agree very well with the theoretical predictions which took into account classical surface and volumetric losses as well as molecular relaxation.

An interesting observation was a shift in the resonant frequencies of the spectrophone as a function of pressure. This shift is fully

explained by relaxational dispersion, non-ideal gas behavior, and classical boundary layer effects.

#### B. The Scattering Contribution to Photoacoustic Signal (5)

Insensitivity of scattering has been generally assumed to be an inherent characteristic of photoacoustic detection. The physical reasoning underlying this assumption has been that the photoacoustic signal arises from the heat generated following optical absorption, and thereby it is a measure of the absorption cross section. However, the generated thermal energy is a function of the intensity distribution of the light within the sample, which is a strong function of its scattering characteristics. Consequently, deviation from Beer's Law should affect the thermal signal.

Using radiation transfer theory, we show that for highly scattering media, the photoacoustic signal is strongly dependent on the scattering parameters. On the other hand, for optically thin solids and liquids, the photoacoustic signal is insensitive to light scattering up to a scattering coefficient  $\lambda\alpha$  of  $\sim 1/\ell$  where  $\ell$  is the sample thickness,  $\lambda$  is the fraction of scattered light, and  $\alpha$  is the total attenuation coefficient of the coherent beam.

Consequently, whereas under certain conditions photoacoustic spectroscopy is indeed insensitive to scattering, under others it can significantly affect the photoacoustic spectra.

#### II. Photothermal Deflection Spectroscopy and Detection (2)

We have developed, and experimentally verified, a theoretical framework for this highly sensitive spectroscopic scheme. We considered cw and pulsed cases for transverse and collinear photothermal deflection detection for solids, liquids, gases, and thin films. The implications for imaging and microscopy will be given, and the sources of noise will be analyzed.

#### III. Detection by Deformation Due to Optical Heating (3)

Very recently we have succeeded in employing the deformation of an absorbing sample due to optical heating to measure optical absorption. Preliminary results, using interferometry, indicate the high sensitivity and versatility of this approach.

#### References:

- 1) See, for example, R. Gerlach and N. M. Amer, Appl. Phys. 23, 319 (1980); W. Jackson and N. M. Amer, J. Appl. Phys. 51, 3343 (1980); Z. Yasa, N. M. Amer, H. Rosen, T. Novakov, Appl. Opt. 18, 2528 (1979); R. Gerlach and N. M. Amer, Appl. Phys. Lett. 32, 228 (1978).

- 2) W. B. Jackson, N. M. Amer, A. C. Boccara, D. Fournier, Appl. Opt. 20, 1333 (1981)
- 3) M. Olmstead, S. E. Kohn, N. M. Amer, D. Fournier, and A. C. Boccara, Submitted to Opt. Lett.
- 4) R. H. Johnson, R. Gerlach, and N. M. Amer, accepted for publication in Appl. Opt.
- 5) Z. A. Yasa, W. B. Jackson, and N. M. Amer, accepted for publication in Appl. Opt.

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