Title
IN SITU ULTRATRACE GAS DETECTION BY PHOTOTHERMAL SPECTROSCOPY: AN OVERVIEW

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Publication Date
1982-02-01

LBL-14051

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UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

Invited Talk presented at the International Workshop on Laser and Optical Remote Sensing, Monterey, CA, February 9-11, 1982; and to be published in the Proceedings

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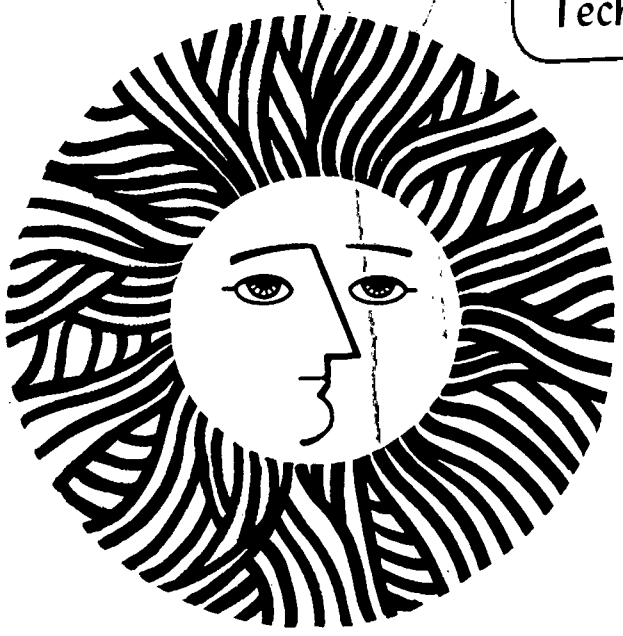

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

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This work was supported by the Director, Office of Energy Research, Pollutant Characterization and Measurements Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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Two photothermal detection schemes, photoacoustic and photothermal deflection, are reviewed in the context of *in situ* ultrace detection of atomspheric constituents.

OVERVIEW

In recent years, optical heating has been employed in novel ways to measure minute absorption coefficients of gases, liquids, and solids. The physical principle underlying these measurements is that when a beam of electromagnetic radiation is absorbed by a given medium, heating will ensue. The conversion of light into heat is what is used to measure optical absorption coefficients as low as approximately 10^{-9} - 10^{-10} cm^{-1}.

In the case of gases, photothermal detection can be accomplished in one of two ways:

a. The optical heating, when modulated, will cause a time-dependent pressure fluctuation which can be detected with a suitable transducer, typically a microphone. This type of detection is known as photoacoustics[1-8], and can be performed in either acoustically resonant or acoustically non-resonant regimes.

b. The modulated optically-induced heating will cause a corresponding modulation of the index of refraction of the absorbing material. The gradient of the modulated index of refraction is used to

periodically deflect a weak laser probe beam propagating through the material [9,10]. The deflection, which can be as small as 10^{-10} radian, is readily detected with a position sensor.

In both approaches, the amplitude and the phase of the output signal are related quantitatively to the absorption coefficient.

IN SITU DETECTION SCHEMES

The following two schemes illustrate the high sensitivity and the *in situ* capability of photothermal detection.

a. Windowless Resonant Spectrophone [2]

In conventional acoustically resonant photoacoustic detection[11], the optically exciting beam passes through the windows at normal incidence to the cylindrical cavity. This implies that the beam enters and leaves the spectrophone at points of high pressure amplitude; thus window absorption will contribute an unwanted background signal.

This problem can be alleviated altogether by placing the windows at nodes of the mode being excited. Since the amplitude $A_j(\omega)$ of the j'th acoustical mode excited at frequency ω by the absorption of light by the gas is given by:

$$A_j(\omega) = f(\omega)(\alpha/V_c) \int P_j^*(\vec{r})\, I(\vec{r})\, d\,V$$

here $f(\omega)$ is the resonance lineshape, α is the absorption coefficient, V_c is the call volume, $I(\vec{r})$ is the laser intensity, and $p_j^*(\vec{r})$ is the j'th mode normalized eigenfunction. Hence, for most efficient excitation of the j'th mode, it is desirable that the integrand have the same sign throughout the rather small region of the cell volume in which $I(\vec{r})$ differs significantly from zero.

A significant consequence of placing the windows at pressure nodes is that one can then eliminate such windows completely, i.e., have uncovered openings in the structure of the spectrophone where the windows would have been mounted. Since these openings are located at pressure nodes, one would expect that the quality factor Q of the resonant cavity should not be degraded significantly. Such a spectrophone is shown in Fig. (1).

We have demonstrated that this windowless spectrophone has a high Q of 509 (as opposed to 560 when operated with windows), and achieved a detection sensitivity of about 20 parts per trillion for ethylene in

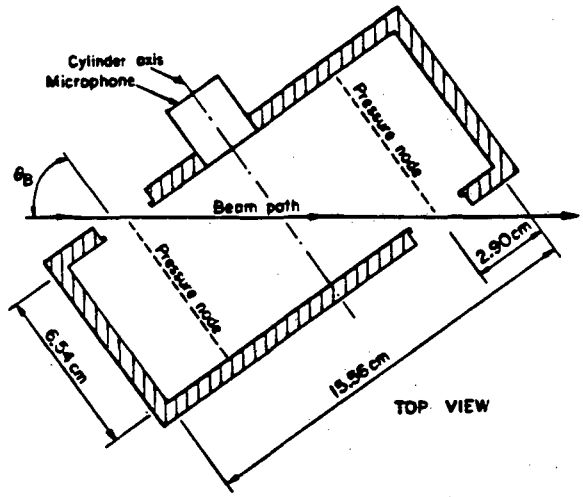

Fig. (1) Cross Section of Windowless Spectrophone

nitrogen.

Clearly then, windowless operation permits the *in situ* continuous monitoring of atmospheric constituents in the field; thus obviating the need for sampling.

b. Photothermal Deflection Detection [9,10]

For low modulation frequency, we have shown that the amplitude of the deflection ϕ of the probe beam is given by

$$\phi \sim (dn/dT)\ (P/\kappa\ \pi^2\ x_o)\ [1 - \exp(1-\alpha\ell)]\ [1 - \exp\ (-x_o^2/a^2)]$$

where dn/dT is the temperature coefficient of the refractive index, P is the incident-laser power, κ is the gas thermal conductivity, x_o is the distance between the intensity maxima of the pump and probe beams, α is the optical absorption coefficient, ℓ is the interaction length of the pump and probe beams, and a is the pump beam radius at the 1/e intensity. Thus, for small $\alpha\ell$ ($\lesssim 2$), the amplitude of the deflection is proportional to $\alpha\ell$ and to the power. Furthemore, ϕ exhibits a maximum near

$x_o/a \sim 1$; this then defines the optimal separation between pump and probe beams.

A typical photothermal deflection detection scheme is shown in Fig. (2).

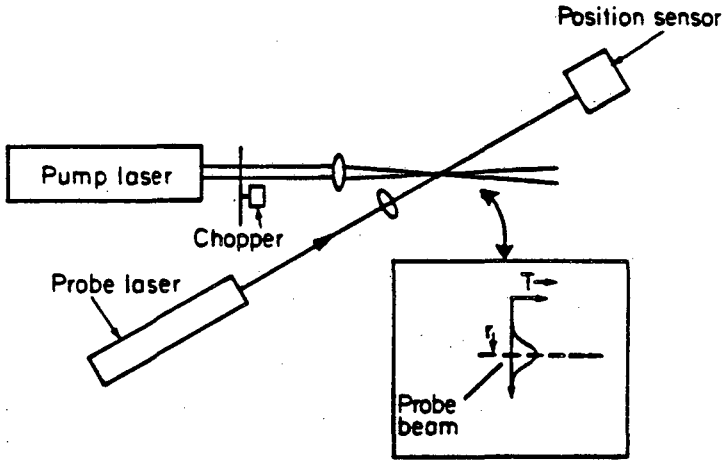

Fig. (2) Detection Scheme

To maximize the signal, the angle between the pump and probe beams can be minimized. However, it should be noted that collinearity is not required.

We have demonstrated the feasibility of this scheme for performing *in situ* measurements in the absence of sample cells or containers, hence eliminating the drawbacks associated with sampling. Typical minimum detectivity is $\sim 10^{-9} - 10^{-10}$.

CONCLUSION

Photothermal deflection and photoacoustic detections have been shown to be highly sensitive, relatively simple, and readily amenable for *in situ* detection and measurements. This is primarily due to the well developed theoretical understanding of the physics of signal generation in both techniques.

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Pollutant Characterization and Measurements Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

REFERENCES

(1) For an overview of photoacoustics, see Optoacoustic Spectroscopy and Detection, Y.-H. Pao, Ed. (Academic press, New York, 1977).

(2) R. Gerlach and N.M. Amer, Appl. Phys. 23, 319 (1980).

(3) R. Gerlach and N.M. Amer, Appl. Phys. Lett. 32, 228 (1978).

(4) D.R. Wake and N.M. Amer, Appl. Phys. Lett. 34, 379 (1979).

(5) L.J. Thomas, M.J. Kelly and N.M. Amer, Appl. Phys. Lett. 32, 736 (1978).

(6) C.K.N. Patel and R.J. Kerl, Appl. Phys. Lett. 30, 578 (1977).

(7) L.B. Kreuzer and C.K.N. Patel, Science 173, 45 (1971).

(8) C.K.N. Patel, E.G. Burkhardt, C.A. Lambert, Science 184, (1974).

(9) D. Fournier, A.C. Boccara, N.M. Amer, R. Gerlach, Appl. Phys. Lett. 37, 519 (1980).

(10) W.B. Jackson, N.M. Amer, A.C. Boccara, and D. Fournier, Appl. Opt. 20, 1333 (1981).

(11) C.F. Dewey, R.D. Kamm, and C.E. Hackett, Appl. Phys. Lett. 23, 633 (1973).

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