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PHOTOTHERMAL DEFLECTION SPECTROSCOPY

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SENSITIVE IN SITU TRACE GAS DETECTION BY
PHOTOTHERMAL DEFLECTION SPECTROSCOPY

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ABSTRACT

We present a sensitive (5 ppb for ethylene, 10^{-7} cm^{-1}) and simple photothermal scheme for the detection of trace gases and for measuring weak absorptions in gas phase samples. We also demonstrate the feasibility of this scheme for performing in situ measurements in the absence of sample cells or containers, thus eliminating the drawbacks of sampling and sampling techniques. Factors limiting our detectivity are discussed, and a comparison to the thermal lens effect is made.

Recently Boccara et al.¹ reported on a new technique for the measurement of optical absorption coefficients of strongly absorbing solids and of samples of poor optical quality. This technique is based on the "mirage effect", i.e., when an absorbing medium is irradiated with intensity modulated electromagnetic radiation, its surface will exhibit periodic temperature fluctuations which in turn will induce a modulated refractive index gradient in a layer of gas (of thickness on the order of the thermal diffusion length) adjacent to the sample surface. This time-dependent gradient is then employed to periodically deflect a probe beam propagating parallel to and near the sample surface. The deflection amplitude can be related to the strength of the absorption in a straightforward manner.

In this letter we present a different approach to photothermal deflection spectroscopy where the refractive index gradient is both created and optically detected within the medium of interest (in this case a gas). Such an approach proved to be sensitive and suited for the in situ detection of trace gases since it obviates enclosing the sample in some container in order to perform the detection. The applicability of this technique for the determination of optical absorption of weakly absorbing condensed matter samples and of thin films and optical coatings will be reported elsewhere.²

Using diffraction theory, Jackson et al.³ have recently shown that for modulation of the pump beam at low frequency, the amplitude ϕ of the probe beam deflection is given by

$$\phi = (dn/dT)(P/\kappa\pi^2x_0) [1-\exp(-\alpha\ell)] [1-\exp(-x_0^2/a^2)] \quad (1)$$

where dn/dT is the temperature coefficient of refractive index, P is the amplitude of the incident laser power modulation, κ is the thermal conductivity of the gas, x_0 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 radius of the pump beam at $1/e$ intensity. Thus, for small $\alpha\ell$ ($\ll 2$) the amplitude of the deflection is proportional to $\alpha\ell$ and to the power. Furthermore, ϕ exhibits a maximum near $x_0/a \sim 1$ defining the optimal separation between the pump and probe beams.

To investigate the sensitivity of photothermal deflection spectroscopy for the detection of small absorption in gases, we chose to determine the minimal detectable concentration of ethylene at a signal to noise ratio (S/N) of unity. We also tested the in situ capability of this detection scheme by measuring the absorption spectrum of laboratory air (without any sample cell or enclosure) in the 9-11 μm region of the infrared.

The experimental arrangement is shown in Figure 1. A CO_2 laser, intensity modulated by current modulation at 16 Hz, operating on the P(14) transition of the 10.4 μm band provided the pump beam source. The typical average power was 1 W, with 100% modulation depth, and the beam was focussed on the interaction region with a 100 cm focal length mirror. A 0.5 mW He-Ne laser was used as the probe beam and was set slightly off the axis of the pump beam to allow for probing the region of maximum gradient (see insert in Figure 1). By this geometry, the use of beam splitters was avoided. The interaction region between the pump and probe beams was ~ 10 cm. The periodic deflection of the He-Ne beam was monitored by a silicon photodiode located 100 cm away from the interaction region. A razor blade edge, blocking half the diameter of the probe beam, was placed directly in front of the photodiode. In order to determine the sensitivity and obtain a calibration of the apparatus we initially employed a calibrated mixture of ethylene⁴ in nitrogen, and other lower-concentration mixtures

obtained by dilution of the calibration mixture, in a 20 cm long cell. In Figure 2 we plot signal from the photodiode as a function of ethylene concentration. As can be seen, the detected signal is a linear function of the concentration over four orders of magnitude. No coherent background signal was detected when the cell was filled with nitrogen only. From these results we compute a minimum detectivity ($S/N=1$) of 5 ppb, i.e., a minimum absorption coefficient detection of $\sim 10^{-7} \text{ cm}^{-1}$.

We also measured, in situ, the absorption spectrum of laboratory air using the various lines of the R branches of the 9.4 μm and 10.4 μm bands of CO_2 lasers. In Tables I & II we present our results and compare them with published data.⁵ While the dominant contribution to the absorption in the 9.4 μm region can be interpreted as due to water vapor, in the 10 μm region other unidentified gases appear to contribute significant absorption.

Our detection limits were set by the following factors:

- 1) Fluctuations in the pointing stability of the probe beam, which were estimated to be two orders of magnitude above the photon noise. This limitation can be alleviated by, for example, the inclusion of an intra-cavity iris to force the laser to oscillate on the fundamental transverse mode.
- 2) In the case of experiments requiring long probe beam paths, air turbulence can be a limiting factor when the pump beam is modulated at low frequencies. Introduction of a Fabry-Perot interferometer¹ as close as possible to the interaction region should overcome this problem. Another simple solution is to have the two laser beams intercept each other inside an open ended tube.
- 3) Electronic noise was a limiting factor only when a position-sensing detector¹ was used.

- 4) With adequate isolation, mechanical vibrations do not set the detection limit.

Finally, we compare this technique to the thermal lens effect. Hu and Whinnery⁶ reported that for a 4.78 cm sample a 10^{-8} change of the index of refraction was detectable. In terms of optical path length difference this corresponds to $5 \text{ \AA}$. In the case of photothermal detection, the corresponding value for the optical path length is $10^{-2} \text{ \AA}$. Furthermore, our technique eliminates the need for using beam splitters and filters.⁷

In conclusion, we have shown that photothermal deflection spectroscopy provides a simple means for the measurement of very weak absorptions in gas phase samples. We have also demonstrated its feasibility for in situ measurements, i.e., in the absence of a sample container, thus eliminating the problems associated with sampling techniques. This technique also eliminates the background signal associated with the heating of sample cell windows which one encounters in photoacoustic spectroscopy.

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TABLE I
OBSERVED SIGNAL FOR LABORATORY AIR IN THE
9.4 μm BAND OF THE $\text{C}^{12}\text{O}_2^{16}$ LASER

Laser line	Frequency (cm^{-1})	Experimental absorption ^a coefficient (10^{-6} cm^{-1})	Abs. coeff. of water vapor of ref. 5 (10^{-6} cm^{-1})
R(10)	1071.884	2.9	0.35
R(12)	1073.278	1.5	0.44
R(14)	1074.646	2.3	1.48
R(16)	1075.988	1.45	0.57
R(18)	1077.303	1.35	0.43
R(20)	1078.591	1.2	0.40
R(22)	1079.852	1.51	0.40
R(24)	1081.087	1.65	0.39
R(26)	1082.296	1.2	0.36
R(28)	1083.479	1.3	0.38
R(30)	1084.635	2.6	1.40
R(32)	1085.765	3	0.58

(a) Our data were normalized to the measurements of Ref. 5 for the
R (20) line of the 10.4 μm band.

TABLE II
OBSERVED SIGNAL FOR LABORATORY AIR IN THE
10.4 μm BAND OF THE $\text{C}^{12}\text{O}_2^{16}$ LASER

Laser line	Frequency (cm^{-1})	Experimental absorption ^a coefficient (10^{-6} cm^{-1})	Abs. coefficient of water vapor of ref. 5 (10^{-6} cm^{-1})
R(8)	967.707	0.55	0.41
R(10)	969.139	0.65	0.34
R(12)	970.547	1.5	0.97
R(14)	971.930	1	0.92
R(16)	973.289	1.1	0.78
R(18)	974.622	0.75	0.61
R(20)	975.930	5.5	5.49
R(22)	977.214	0.85	0.84
R(24)	978.472	0.65	0.50
R(26)	979.705	0.68	0.49
R(28)	980.913	0.68	0.40
R(30)	982.096	1	0.46
R(32)	982.252	0.95	0.40

(a) Our data were normalized to the measurements of Ref. 5 for the
R (20) line of the 10.4 μm band.

FIGURE CAPTIONS

Figure 1 - Experimental set-up

Figure 2 - Thermal deflection signal versus ethylene concentration in nitrogen (molar fraction).

Fig. (1)

Fig. (2)