Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT
DIVISION

A SENSITIVE PHOTOTHERMAL DEFLECTION TECHNIQUE FOR
MEASURING ABSORPTION IN OPTICALLY THIN MEDIA

A. C. Boccara, D. Fournier, Warren Jackson,
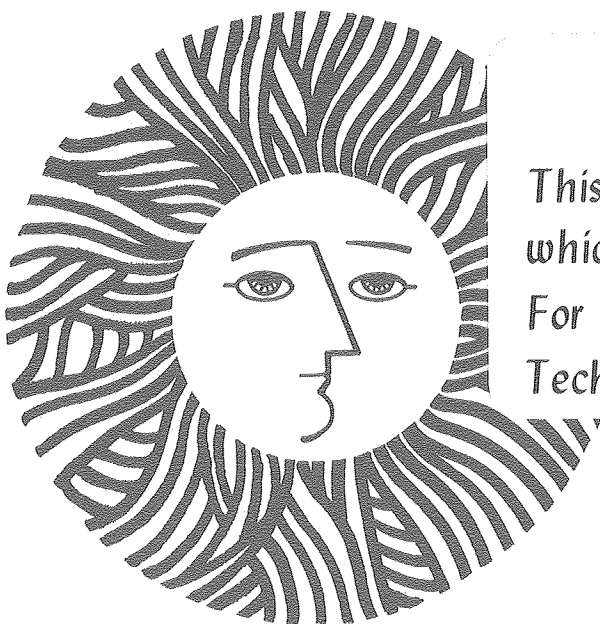and Nabil M. Amer

April 1980

DISCLAIMER

A SENSITIVE PHOTOTHERMAL DEFLECTION TECHNIQUE
FOR MEASURING ABSORPTION IN OPTICALLY
THIN MEDIA

A. C. Boccara and D. Fournier

Laboratoire d'Optique Physique - E. R. 5 du CNRS

École Supérieure de Physique et de Chimie Industrielles

10, rue Vauquelin

75231 Paris Cedex 05, France

and

Warren Jackson and Nabil M. Amer

Applied Physics & Laser Spectroscopy Group

Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720, USA

ABSTRACT

We present a highly sensitive and simple photothermal scheme for determining optical absorptions in condensed matter samples. $\alpha\ell$ values as low as 10^{-7} and 10^{-8} were measured for thin films and coatings and for liquids, respectively. A comparison with thermal lens effect is given, and the experimental factors limiting our sensitivity are discussed.

The evergrowing interest in optical communications and the continuing progress in the development of high power lasers motivate the development of sensitive techniques to measure low absorption losses in highly transparent solids, thin films, and optical coatings. These techniques can also be employed in the investigation of linear and nonlinear optical spectroscopic phenomena. Current state of the art[1] enables the measurement of absorption coefficients of 10^{-5} cm^{-1}.

In this letter, we report on a novel and simple approach, photothermal deflection spectroscopy, for measuring ultralow absorption in condensed matter samples. We have achieved a sensitivity of $\alpha\ell = 10^{-7}$ for thin films and optical coatings, and 10^{-8} for liquids. Our results for gas phase samples are being reported elsewhere[2].

It is well known that when an intensity modulated beam of electromagnetic radiation (pump beam) is incident on an absorbing medium, heating will ensue. Concomitant with this time-dependent change in the medium temperature is a corresponding modulated index of refraction gradient which can be employed to deflect a probe beam intersecting the pump beam <u>within</u> the sample and/or substrate. The deflection can be as small as 10^{-9} - 10^{-10} radians, which is well within the detectivity levels of available position sensors. The amplitude of the deflection is related to the optical absorption in a straightforward manner.

Using diffraction theory, we have recently shown[3] that in the case where the thermal diffusion length of the medium is much smaller than the Gaussian pump beam radius (the case of high frequency modulation and/or low thermal conducting medium), the deflection ϕ is given by

$$\phi = (dn/dT)(P/\omega\rho c\pi^2 a^2)[1-\exp(-\alpha\ell)][-2x_0/a^2)\exp(-x_0^2/a^2)] \tag{1}$$

where dn/dT is the temperature coefficient of the index of refraction of the medium, P is the incident laser power, ω is the angular modulation frequency of the pump beam, ρc is the heat capacity per unit volume, a is the radius of the pump beam at 1/e intensity, x_0 is the separation between the intensity maxima of the pump and probe beams, α is the optical absorption coefficient, and ℓ is the optical path length in the absorbing medium. Thus, for small $\alpha\ell$ ($\lesssim 2$) the deflection amplitude is proportional to the optical absorption and to the power, while inversely proportional to the modulation frequency. Furthermore, ϕ exhibits a maximum near $x_0/a \sim 1$ defining the optimal separation between the pump and probe beams.

On the other hand, in the case where the thermal diffusion length is much larger than the pump beam radius, ϕ is given by

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

where κ is the thermal conductivity of the medium. Note that in this regime, ϕ is independent of ω. Details of our theoretical analysis of photothermal deflection spectroscopy will be reported in Ref. 3.

The experimental arrangement is shown in Fig. (1). A dye laser provided the tunable TEM_∞ pump beam. This intensity modulated beam was carefully focused on a 0.5μ thin film of mixed indium and tin oxides (80% and 20%, respectively) deposited on a glass substrate. The focal spot was $\sim 100\mu$. The associated index of refraction gradient deflected a tightly focused ($\sim 40\mu$ spot) probe beam intersecting the pump beam at the maximum gradient of the index of refraction. The amplitude of the deflection was measured with a position sensor[4]. Under these conditions, maximum deflection and good transverse resolution across the heated region were achieved. It should be noted that in this configuration, the heated

part of the substrate (thermal diffusion length μ_S of 70μ in glass at 100 Hz) is being probed, and to a first approximation one can neglect the deflection in the film itself.

In Fig. (2) we present the amplitude of the deflection as a function of the distance away from the center of the optically heated region. The results are given for low (5 Hz) and high (5 kHz) modulation frequencies. As predicted by Eqs. (1) and (2), at low frequency the optically heated region is much larger than the waist of the probe beam. On the other hand, at high modulation frequency, the probe beam waist and the heated region are of comparable dimensions.

To deduce the minimum detectable absorption coefficient, we compared the wavelength dependence of the photothermal deflection with the absorbance of the film when measured with a Cary 17 spectrophotometer. At the maximum absorption, we find that for an average power of 100 mW and a time constant of 3 seconds, the noise equivalent signal was $\alpha\ell \sim 2 \times 10^{-7}$. This implies a minimum detectable absorbed power of $8 \times 10^{-8}/W.Hz^{1/2}$. Similar sensitivities were achieved with a 2μ film of CdS deposited on a glass substrate.

To demonstrate the applicability of this technique for determining absorption losses in optical coatings, we measured the coating absorption of three, otherwise interchangeable, Coherent Radiation Ar$^+$ laser mirrors at 5950 Å. $\alpha\ell$ values of 0.15×10^{-3}, 0.4×10^{-3}, and 2.7×10^{-3} were obtained indicating a significant variation in absorption losses in supposedly equivalent mirrors.

We have also measured the absorption spectra of bulk liquid samples. In this case, the optically heated medium is directly probed with the He - Ne laser. In Fig. (3) we present the absorption spectrum of the $^3H_4 - {}^5D_1$ transition of a 20 g/liter solution of $PrCl_3.6H_2O$ dissolved in

distilled water. On the same plot we show the absorption spectrum of the 6th harmonic of the C-H stretching excitation of neat benzene[5]. In both cases, the optical path length ℓ was only 1 mm. From these results, we calculate a minimum detectable absorption coefficient of 10^{-7} cm^{-1} for a 100 mW pump beam power and a time constant of 3 seconds. The increased detectivity in the case of liquids is due to their typically larger dn/dT values when compared with those of solids.

To check for saturation of the signal, we measured the absorption of a 0.5 mm didymium glass in the 5900 Å region. We found, as predicted by Jackson et. al.[3], that the deflection amplitude depends linearly on $\alpha\ell$ for $\alpha\ell \simeq 1\text{-exp}(-\alpha\ell)$, beyond which signal saturation sets in.

Factors setting the limits of our sensitivity were:

1. In the case of low frequency modulation, the pointing stability of the probe laser was the limiting factor. This limitation can be allevaited by, for example, the insertion of an intracavity iris to force the laser to oscillate on the fundamental transverse mode. At high frequency modulation, the limits were set by the stability of the probe laser and by the electronic noise of the position sensor.

2. With reasonable isolation, mechanical vibration was not a limiting factor.

A comparison of our technique with the thermal lens effect[6-8] is in order. In the later technique, both the probe and pump beams are colinear and only the curvature of the roughly parabolic heated region is used. In our scheme, we probe the region of maximum index of refraction gradient, thus leading a significantly higher sensitivity. Furthermore, we now have the added degree of freedom of being able to vary the angle between the pump and probe beams, which yields the interesting capability

of differentiating between surface (or coating) and bulk (or substrate) absorptions. This can be accomplished by changing the intersection region of the two beams along the z-direction (see Fig. 1).

In conclusion, we have described in this letter a simple photo-thermally based method for the determination of very small absorption coefficients in thin films and coatings, in highly transparent solids, and in liquids. Extension of this method to the investigation of non-linear absorption phenomena is planned.

REFERENCES

1. A. Hordvik, Appl. Optics 16, 2827 (1977).

2. D. Fournier, A. C. Boccara, N. M. Amer, and R. Gerlach, submitted for publication in Applied Physics Letters.

3. W. Jackson, N. M. Amer, A. C. Boccara, and D. Fournier, in preparation.

4. Silicon Detector Corporation, Newbury Park, California.

5. The background observed in the case of the benzene spectrum (see Fig. 3) is due to scattering from suspended dust particles. Ultra-filtration with $\lesssim 0.2\mu$ filters is necessary for the elimination of such a background. This problem was also reported by the authors of Ref. 7.

6. R. Swofford and J. Morrell, J. Appl. Phys. 49, 3667 (1978).

7. R. Swofford, M. Long, and A. Albrecht, J. Chem. Phys. 65, 179 (1976).

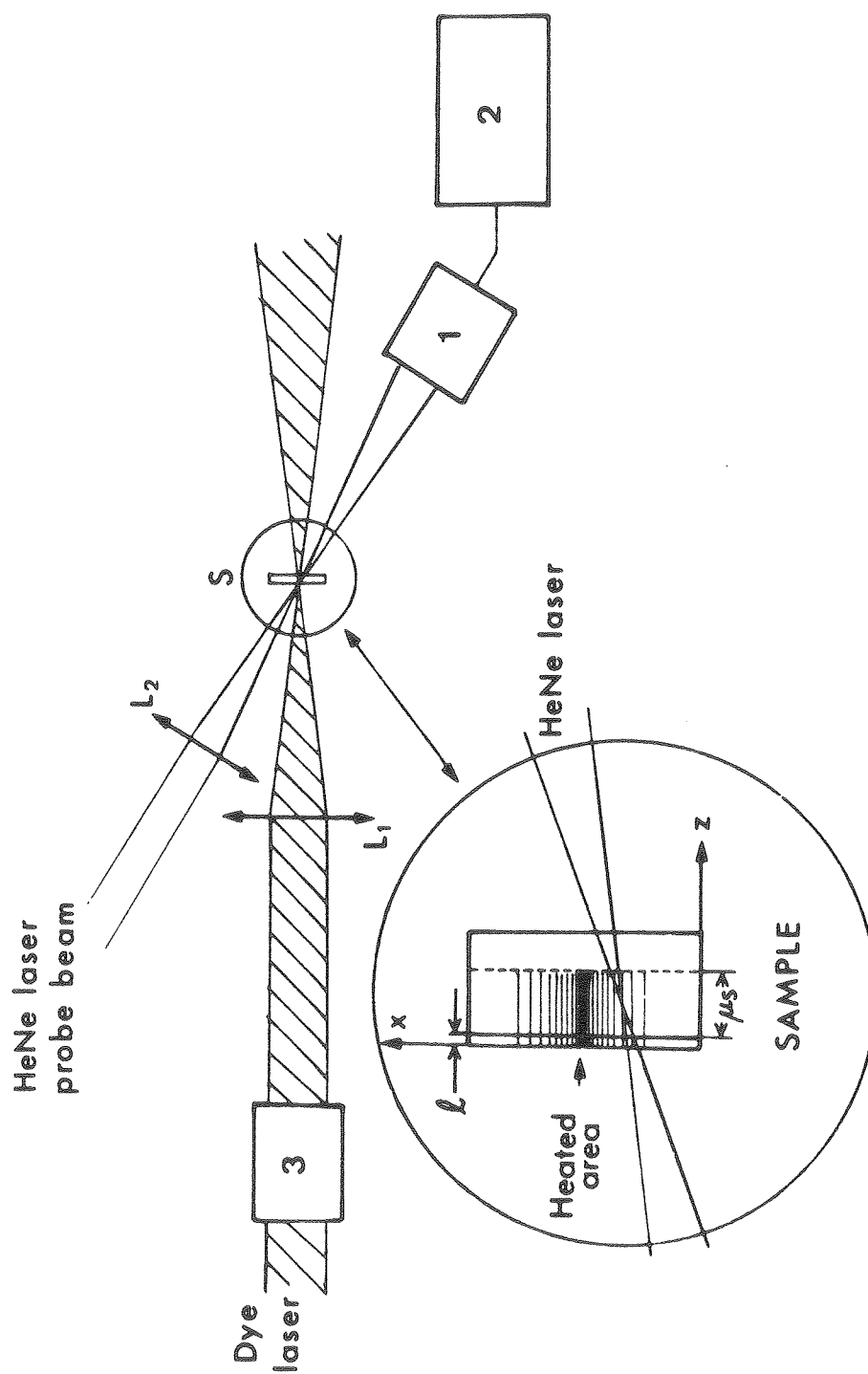8. C. Hu and J. R. Whinnery, Appl. Optics 12, 72 (1973).

FIGURE CAPTIONS

Fig. (1) - Experimental set-up:

      1 - Position sensor

      2 - Lock-in amplifier

      3 - Modulator

      L_1 = 12 cm focal length lens

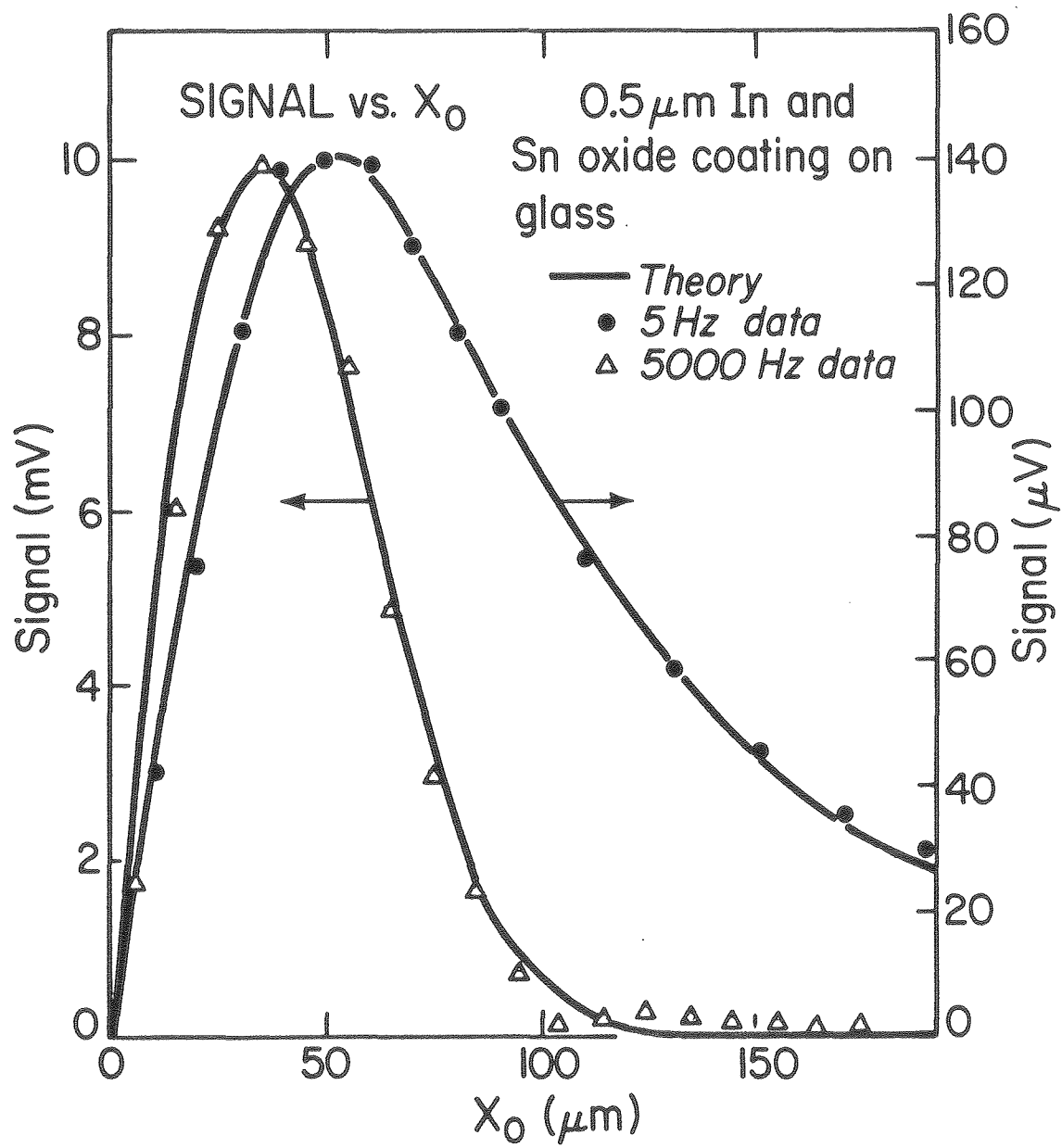 L_2 = 6 cm focal length lens

Fig. (2) - Thermal deflection signal vs. the separation between the pump and probe beams. The solid lines are the results of the theory given in Ref. (3).

Fig. (3) - Thermal deflection signal versus wavelength for:

      X neat benzene[5] (ℓ = 0.1 cm)

      ● $PrCl_3$ in water   (ℓ = 0.1 cm)

      ○ Cary 17 spectrophotometer results for $PrCl_3$ in water (ℓ = 1.0 cm)

(Fig. 1)

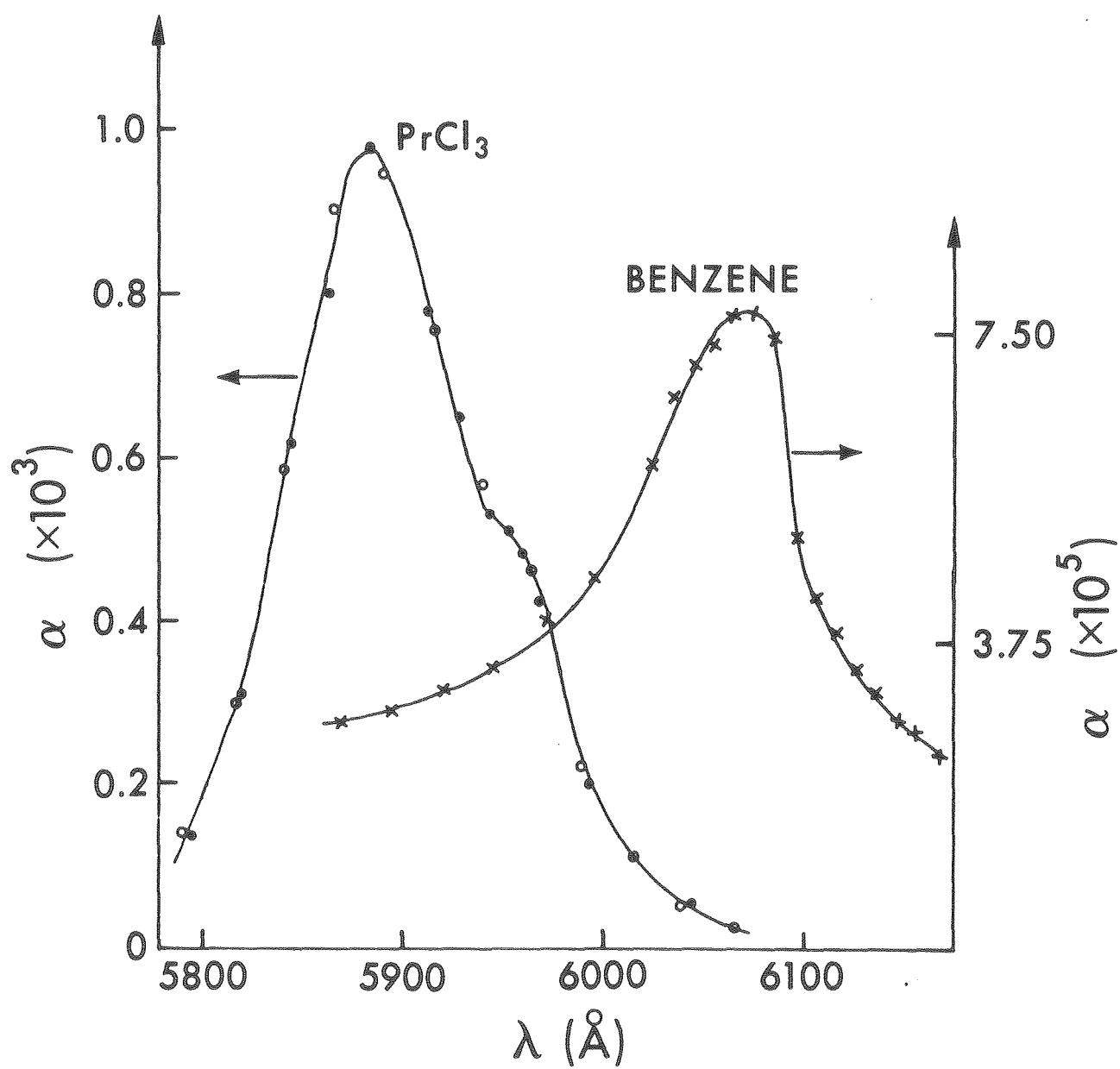SIGNAL vs. X₀ 0.5 μm In and Sn oxide coating on glass
Theory
5 Hz data
5000 Hz data

XBL 804-577

(Fig. 2)

(Fig. 3)