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USING A THERMAL WAVE PHASE SHIFTER(U) IBM RESEARCH LAB
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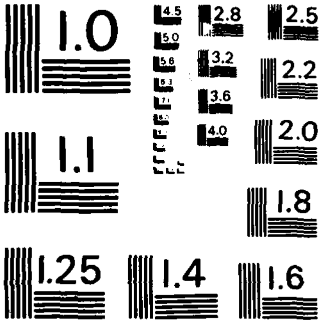

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20. Abstract (Continued)

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Photothermal Spectroscopy of Weakly Absorbing Samples Using a Thermal Wave Phase Shifter

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H. Coufal

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PHOTOTHERMAL SPECTROSCOPY OF WEAKLY ABSORBING SAMPLES USING A THERMAL WAVE PHASE SHIFTER

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ABSTRACT: The concept of a thermal wave phase shifter for photothermal studies of weakly absorbing samples is described. Both sample and reference are excited simultaneously, but their respective photothermal signals reach the detector subsequently. Depending on the phase shift photothermal absorption or transmission spectra can be recorded readily with the same sample. The versatility of this technique is demonstrated by spectroscopic studies of a neodymium oxide doped poly(methyl methacrylate) film. At energy fluences in the order of 10 mJ/cm^2 sensitivities of 10^{14} molecules/cm^2 are achieved with conventional, unstabilized light sources. The quantum yield for nonradiative decay is determined to be 90% throughout the entire visible spectrum.

In photothermal[1] or photoacoustic[2] techniques the sample under study is excited with a modulated or pulsed light source. Subsequent radiationless decay causes local heating, giving rise to thermal wave phenomena. Due to thermal expansion sound waves are generated at the same time. A variety of techniques has been developed for the detection of these waves, applications in spectroscopy or imaging are numerous. The fact that besides optical also thermal and in the case of photoacoustics even acoustic properties are involved in the generation of the signal allows these techniques to address many nonspectroscopic problems. For spectroscopic studies, however, the interpretation of photothermal and photoacoustic spectra is complicated by thermal and acoustic effects. Therefore considerable effort[1,2] went into techniques that compare optical features of otherwise identical samples and into the design of reference samples with well defined and optimized optical and thermal properties.[3] Frequently spectra of samples, recorded *subsequently* and normalized for incident light intensity by using a reference detector, can be compared if the thermal properties of the samples are similar. Simultaneous *parallel* recording of sample and reference spectra, for example in a double beam arrangement, was the method of choice right from the beginning of photoacoustic spectroscopy.[4] This also allows the real time compensation of the signals of two identical samples, thus permitting the detection of minuscule changes in the optical properties of one sample, as caused for example by the deposition of a monolayer of molecules.[5] A third method uses the sample in a time *multiplexed* way as its own reference. This is typically achieved by switching the incident light continuously between two wavelengths[6] or polarizations.[7,8] The use of these techniques has contributed substantially to the advancement of photoacoustic spectroscopy and is essential for applications requiring highest sensitivity, as for example surface vibrational studies of adsorbates.[9]

Besides sequential, parallel and multiplex excitation and detection of sample and reference another approach, particularly suitable for weakly absorbing samples, is possible: sample and reference can be optically in series, the excitation being therefore simultaneous. The detection, however, is sequential due to a thermal delay line or a phase shifter separating sample and reference. Both signals could in principle be deconvoluted. For absorption spectroscopy of weakly absorbing samples, however, the interpretation of the observed spectra will be shown to be straightforward.

In the following discussion of the salient features of this concept a periodic excitation with frequency f and a one-dimensional model with the geometry shown in Fig. 1 and with material parameters summarized in Table 1 is assumed for convenience. The photothermal signal shall be detected at the back side of the reference sample R with a temperature sensitive transducer. The basic findings of this simplified approach can be readily generalized for pulsed excitation or detection from the front side of the sample, other geometries or less idealized material parameters.

The generation of the heat source distribution in the composite sample via optical absorption and subsequent radiationless decay and the heat diffusion afterwards can be treated in the framework of the Rosencwaig-Gersho theory[10] or one of the many techniques developed for the treatment of thermal diffusion problems.[11] For depth profiling purposes of two layered samples with one of the layers being transparent an approximation has been developed[12] that can be easily modified for the trilayered sample of Fig. 1. The materials i are characterized by their respective thickness δ_i, their thermal diffusion length μ_i and their optical absorption coefficient β_i. Radiationless decay is assumed to be instantaneous with the nonradiative quantum efficiency η_i. All other material parameters are assumed to be identical for all three layers.

With these assumptions the amplitude S(x) of the temperature modulation due to absorption in layer 1, as observable at the front side x=0, can be written in the form

$$S(0) = C \times I(\lambda,t,x = 0) \times \eta_1 \beta_1 \delta_1 \ , \tag{1}$$

C being a material constant characterizing the other sample properties and I(λ,t,x=0) the amplitude of the incident, modulated light intensity of wavelength λ. The amplitude R(ℓ) of the temperature modulation due to absorption in layer 3, as observable at the back side x= ℓ can be described accordingly by

$$R(\ell) = C \times I(\lambda,t,x = \ell) \times \eta_3 \beta_3 \delta_3 \ . \tag{2}$$

The amplitude of the total signal contains contributions from both absorbing layers. The diffusive character of thermal propagation can be taken into account by representing layer 2 as an attenuating phase shifting operator P

$$P = e^{-\alpha(1+i)} \ , \tag{3}$$

with the phase shift and attenuation

$$\alpha = \frac{\ell}{\mu_2} \ . \tag{4}$$

The total signal as observed for example at the back side of the sample is a vector sum (Fig. 2) of contributions from both layers

$$T(\ell) = P \times S(0) + R(\ell) \tag{5}$$

or with the use of (1)-(3)

$$T(\ell) = C \times I(\lambda,t,x = 0)[\eta_1 \beta_1 \delta_1 e^{-\alpha(1+i)} + (1-\beta_1\delta_1)\eta_3\beta_3\delta_3] \ . \tag{6}$$

The thermal diffusion length μ is, however, frequency dependent

$$\mu \propto f^{-1/2} . \tag{7}$$

Therefore also the phaseshift α and the observed total signal T are functions of the modulation frequency.

Special cases are discussed in the following. To exemplify the potential of the thermal phase shifter a composite trilayered sample was excited with a conventional photoacoustic spectrometer employing a current modulated xenon high pressure lamp and a scanning monochromator – bandwidth 3 μm, scanning speed 100 nm/min. It should be noted that the resulting light intensity varies by one order of magnitude in the spectral range considered here. The photothermal signal is detected with a pyroelectric transducer and a dual phase lock-in amplifier (EG&G 5206). The sample consists of a 1 μm thick silver film as a reference sample, directly deposited onto the transducer. A 0.1 mm thick poly(methyl methacrylate) (PMMA) layer is cast onto the silver film. On top of this transparent layer a 1 μm thick PMMA film doped with 1% Nd_2O_3 was spin coated on the sample. Instrumental details and sample preparation has been described previously.[5] The fact that most of the light $I(x=\ell)$ is reflected by the silver surface can be accounted for by doubling the intensity $I(x=0)$. The sample contains a number of Nd_2O_3 molecules equivalent to a coverage of one monolayer.

The imaginary part of the signal T

$$\mathrm{Im}\{T\} = C\, I\, \eta_1 \beta_1 \delta_1 e^{a} \sin\alpha \tag{8}$$

represents after suitable normalization the absorption spectrum of the sample. This component has a maximum for $\alpha = \pi/4$. It can be readily recorded by using out-of-phase detection, *i.e.*, observing at a 90° phase shift relative to R. Figure 3 shows the normalized spectrum for the test sample recorded at 2.2 Hz modulation frequency, corresponding to $\alpha=\pi/4$. The much larger background spectrum due to light absorbed in the silver layer is completely suppressed. Spectral features are clearly visible and in excellent agreement with data reported in the literature for much higher concentrations[15] or using sophisticated real time compensation techniques.[5]

For higher modulation frequencies $\alpha>>1$ can be achieved. The signal in this case is

$$T(\ell) = C \times I(\lambda,t,x = 0)[(1-\beta_1\delta_1)\eta_3\beta_3\delta_3] \tag{6b}$$

or

$$T(\ell) = C \times I(\lambda,t,x = \ell)\eta_3\beta_3\delta_3 \ . \tag{6c}$$

No photothermal signal caused by absorption in layer 1 is detectable due to damping of this signal. The transmitted light intensity is detected via the photothermal signal of the reference layer. Such photoacoustic transmission spectrum for $\alpha=5$, after correcting for $I(\lambda,t,x=0)$ with a black reference sample, is shown in Fig. 4. A numerical comparison of this spectrum with the absorption spectrum of Fig. 3 furnishes a cross correlation coefficient of 0.96 indicating that the spectra are almost identical.

All signals have been assumed to be proportional to the incident light intensity. Therefore all vectors in Fig. 2 scale with the incident intensity and angles are not affected by intensity fluctuations I(t). Provided that the photothermal response $\eta_3\beta_3$ of the reference layer is not wavelength dependent, spectral characteristics $I(\lambda)$ of the illuminating light source are automatically accounted for. The phase angle φ of the total signal with respect to the reference signal is

$$\varphi = \tan^{-1}\left\{ \frac{\eta_1\beta_1\delta_1}{\eta_3\beta_3\delta_3} e^{-\alpha} \sin\alpha \right\} ,$$

or for weakly absorbing samples

$$\varphi = \eta_1\beta_1\delta_1 \frac{e^{-\alpha} \sin\alpha}{\eta_3\beta_3\delta_3} . \tag{9}$$

By recording the phase angle φ of the total signal a true photoacoustic absorption spectrum of layer 1 can be recorded. The phase angle spectrum of the test sample is shown in Fig. 5. The out-of-phase component has been maximized by variation of the modulation frequency to ensure $\alpha=\pi/4$. The spectrum shows all the features of the previous spectra, the cross correlation with the spectrum of Fig. 3 is 0.95.

It should be noted that the transmission spectrum shown in Fig. 4 according to formula 6b depends only on the optical absorption length β_1 of the sample layer but not its efficiency η_1 for nonradiative deexcitation. Out-of-phase and phase angle spectra, however, depend on this efficiency, allowing the determination of η_1 by comparison of the transmission spectrum with one of the absorption spectra. From these spectra, using equation (6c) and (8) and taking the reflection from the silver surface into account which essentially doubles the absorbtion signal, the probability for nonradiative decay of Nd^{3+} in this sample is determined to be

$$\eta_1 = 0.9 \pm 0.05$$

throughout the recorded spectrum. In the study reported here pure Nd_2O_3 powder was dispersed in a PMMA matrix. The Nd_2O_3molecules in this sample are therefore subject to concentration quenching, causing a high probability for nonradiative decay. For the $^4I_{15/2}$ energy level of Nd^{3+} diluted in NdP_5O_{14} the quantum yield for nonradiative decay was determined to be 0.55.[14]. Assuming exclusive radiationless decay for the transitions into the $^4F_{3/2}$ state and from the $^4I_{15/2}$ state this would correspond to a total probability for nonradiative decay of 0.92 at an excitation wavelength of 350 nm and 0.83 at 700 nm respectively, in excellent agreement with the data presented here.

In conclusion, it was demonstrated that with a suitable layered structure, composed of a reference layer coated with a transparent material and the sample under study on top of it, submonolayer sensitivity can be achieved readily by recording phase angle spectra; drifts of the incident light intensity or variations with wavelength are automatically compensated. From a comparison of photothermal absorption and transmission spectra, which can be obtained by a simple variation of the modulation frequency using the same sample and detector, quantum yields for nonradiative deexcitation can be determined without effort. For applications like surface analytical studies[7] where the detector frequently has to be coated for UHV compatibility, this technique has numerous applications.

It is a pleasure to acknowledge enlightening discussions with H. Seki and A. Tam. Sample preparation and characterization by L. W. Welsh, Jr. is greatly appreciated. This work was supported in part by the Office of Naval Research.

Table 1

Material Constants and Parameters for the Trilayered Sample of Fig. 1,
f Being the Modulation Frequency of the Incident Light Intensity

Layer Function Property	1 Sample S	2 Phase Shifter P	3 Reference Sample R
Thickness δ_i	$\delta_1<<\ell$	$\delta_2=\ell$	$\delta_3<<\ell$
Absorption coefficient β_i	$\beta_1\delta_1<<1$ $\beta_1(\lambda)$	$\beta_2=0$	$\beta_1\delta_1<<\beta_3\delta_3<<1$ $\frac{d\beta_3}{d\lambda} = 0$
Quantum yield for nonradiative decay η_i	$\eta_1(\lambda)$		$\frac{d\eta_3}{d\lambda} = 0$ $\eta_3>\eta_1$
Thermal diffusion length $\mu_i(f)$	$\mu_1/\delta_1>>1$ for all f	$\pi/4\le\ell/\mu_2\le5$ $f_{min}\le f\le f_{max}$	$\mu_3/\delta_3>>1$ for all f

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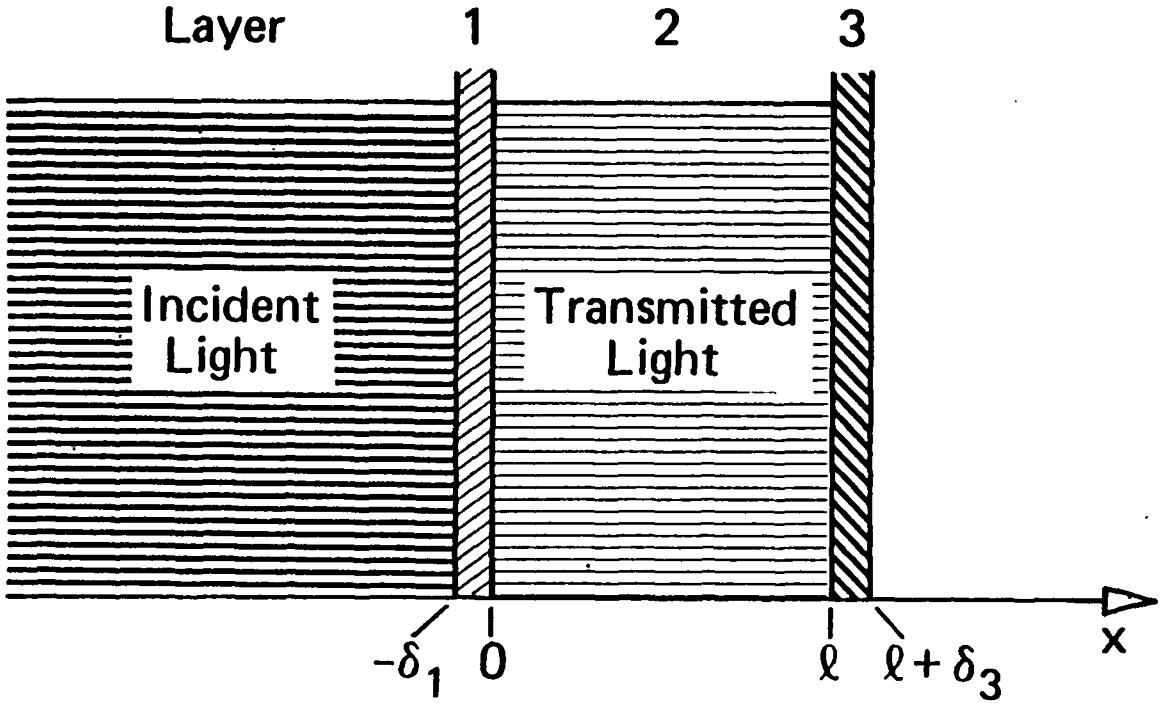

Figure 1. Schematic of composite trilayered sample.

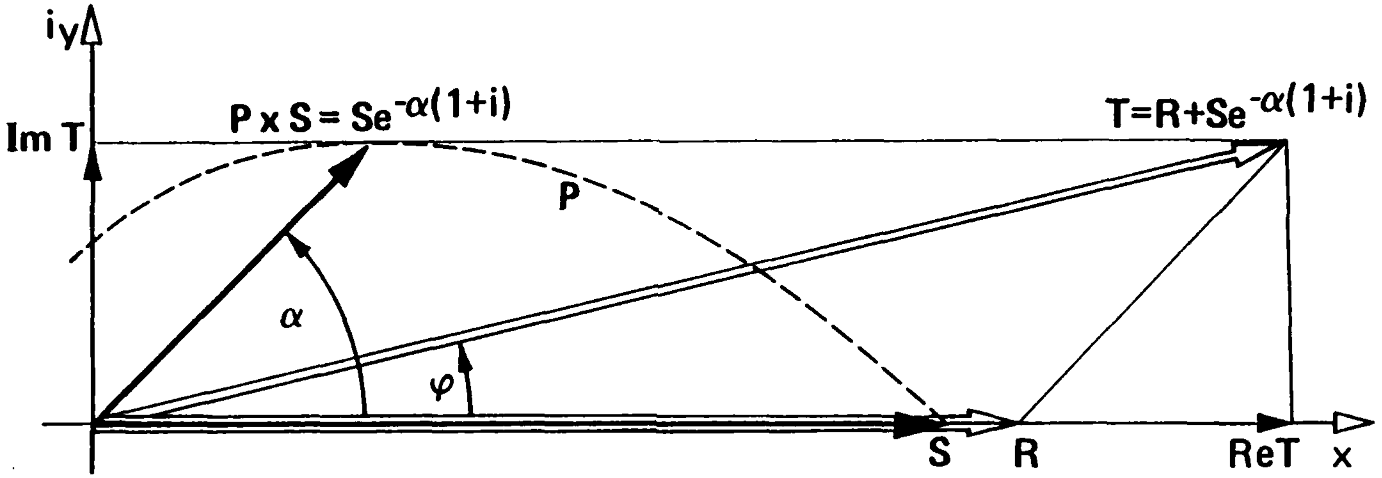

Figure 2. Vector presentation of total signal amplitude T, its components R and S and the effect of the phase shifter P.

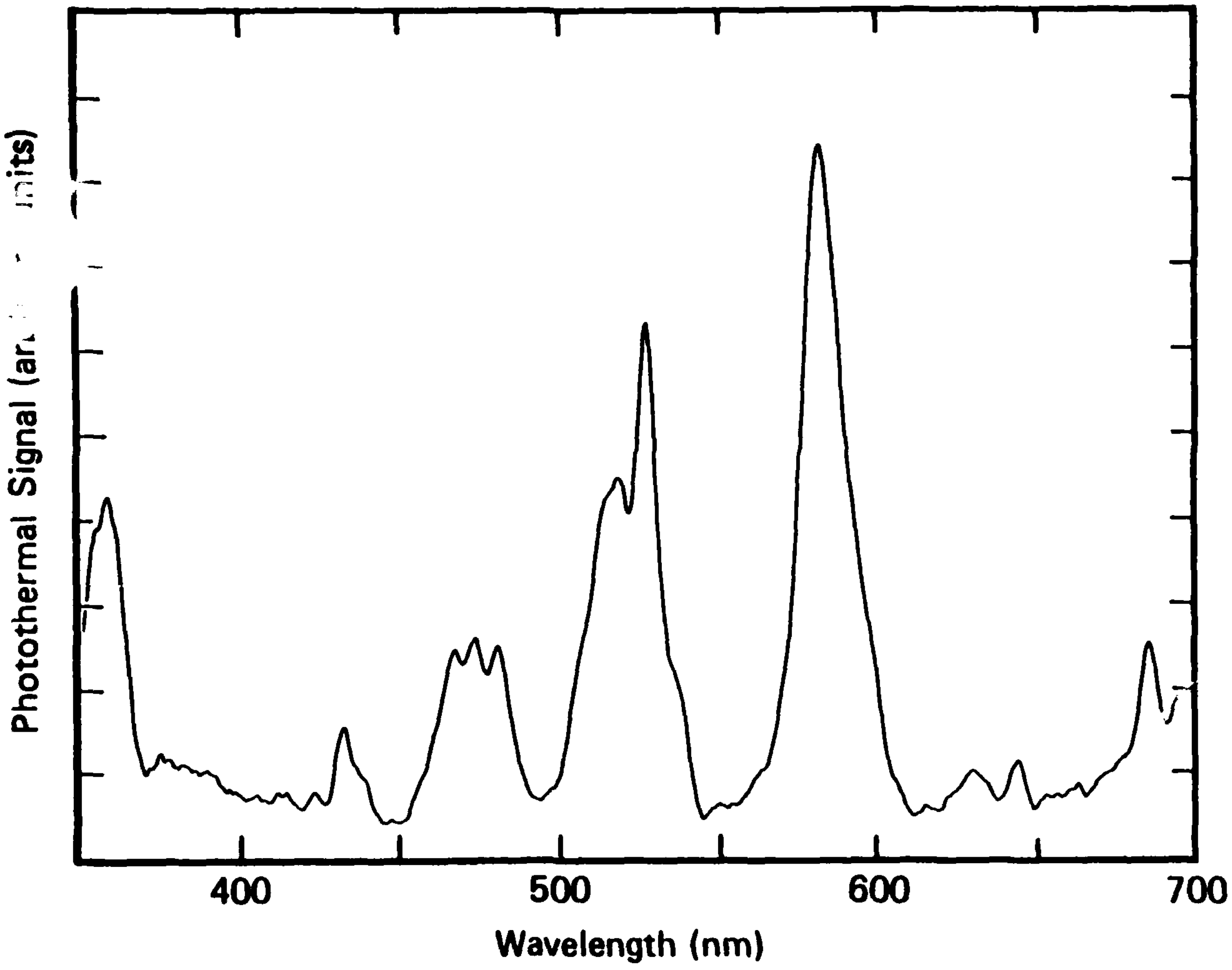

Figure 3. *Normalized* photothermal *absorption* spectrum of 0.8×10^{15} Nd_2O_3 molecules in a 1 μm thick PMMA film coated on top a 0.1 mm undoped PMMA film cast on a silver substrate. Recorded by out-of-phase detection at 2.2 Hz modulation frequency.

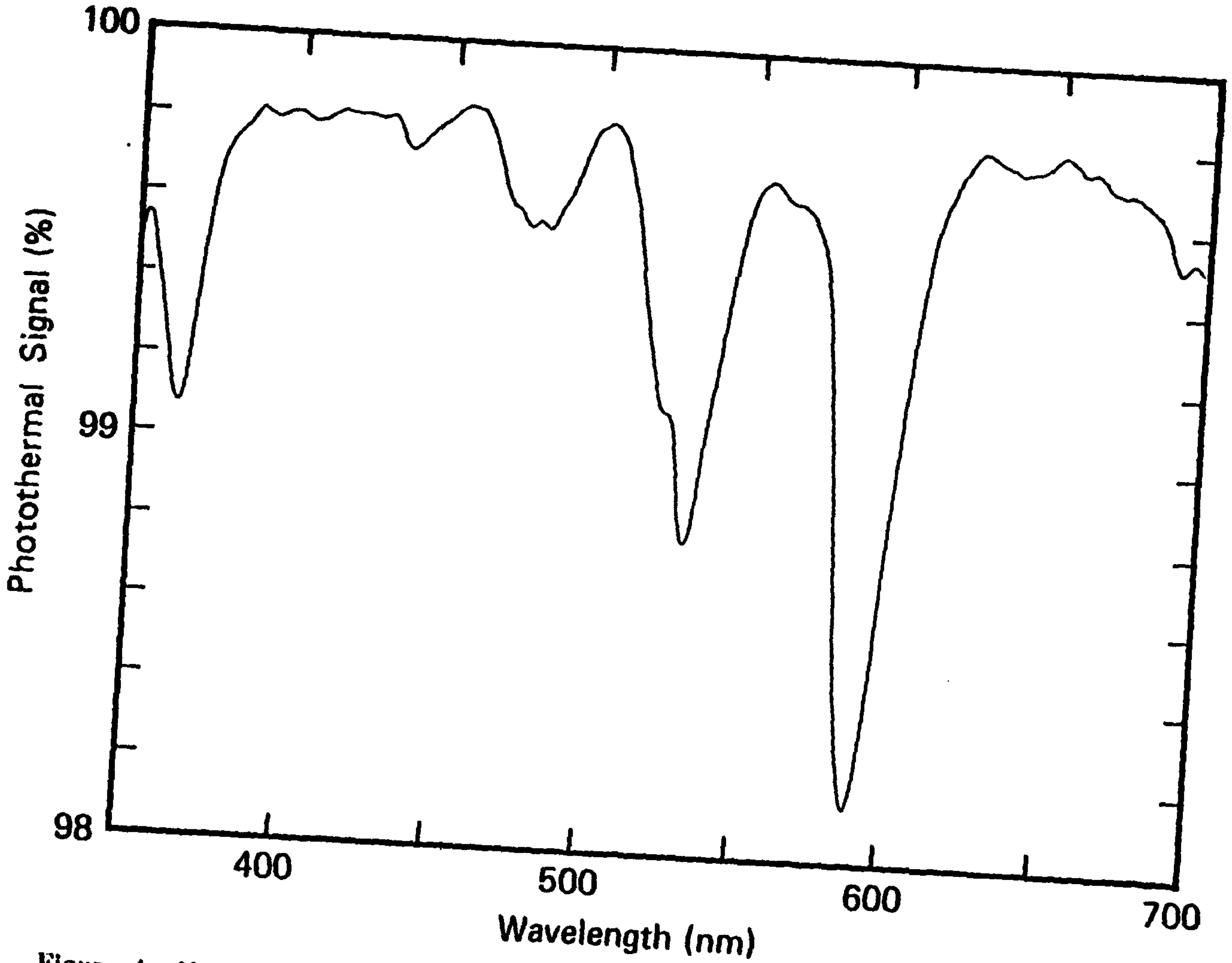

Figure 4. *Normalized* photothermally detected *transmission* spectrum of 0.8×10^{15} Nd_2O_5 molecules in a 1 μm thick PMMA film coated on top of a 0.1 mm thick undoped PMMA film on a silver substrate. Recorded at a modulation frequency of 88 Hz using the silver film as detector for transmitted light.

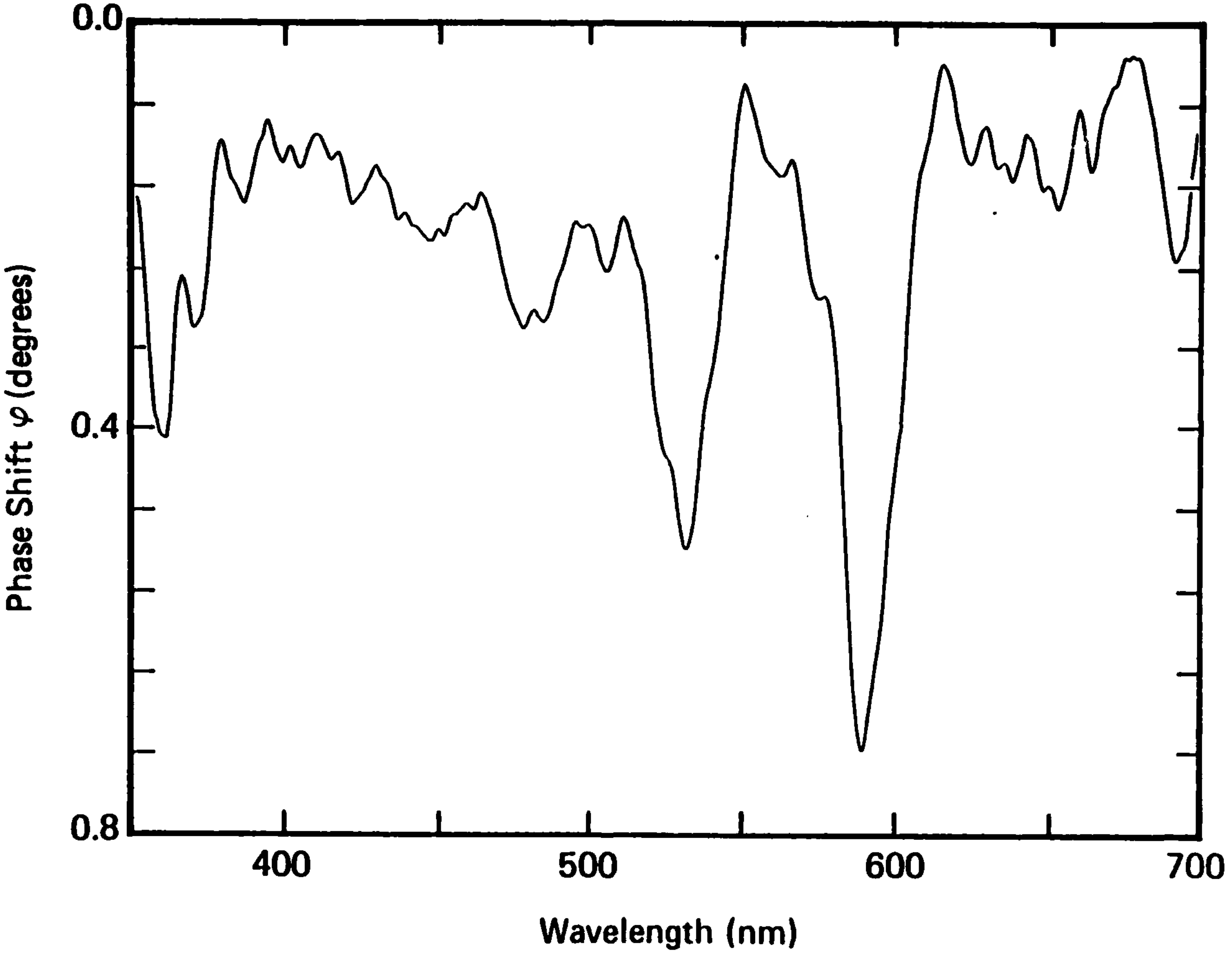

Figure 5. *Unnormalized* phase angle spectrum of 0.8×10^{15} Nd_2O_3 molecules in a 1 μm thick PMMA film coated on top of 0.1 mm thick undoped PMMA film on a silver substrate. Recorded at 2.2 Hz modulation frequency.

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