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PULSED PHOTOTHERMAL RADIOMETRY FOR NONCONTACT
SPECTROSCOPY MATERIAL TESTING AND INSPECTION
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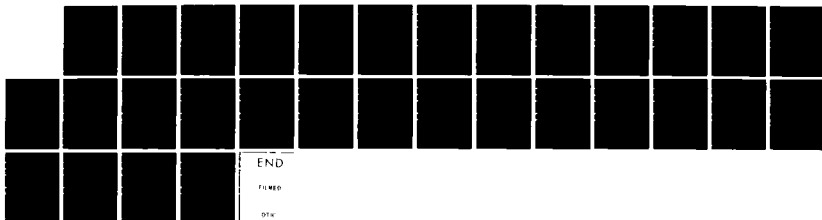
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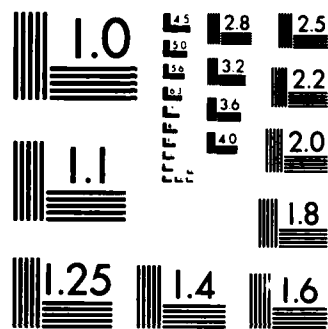
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Pulsed Photothermal Radiometry for Noncontact Spectroscopy,
Material Testing and Inspection Measurements

by

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Research Report

PULSED PHOTOTHERMAL RADIOMETRY FOR NONCONTACT SPECTROSCOPY, MATERIAL TESTING AND INSPECTION MEASUREMENTS

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**PULSED PHOTOTHERMAL RADIOMETRY FOR NONCONTACT SPECTROSCOPY,
MATERIAL TESTING AND INSPECTION MEASUREMENTS**

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ABSTRACT: Photothermal Radiometry (PTR) is a sensitive technique for noncontact spectroscopy and inspection. Its principle is the following: a modulated beam of photons (or other particles) produces temperature transients in a sample; the corresponding transients in the infrared thermal radiation emitted from the sample are analyzed. This can provide absolute absorption coefficients, as well as information on thermal diffusivity, layered structure, and dimensions. Variations of PTR are possible with continuously-modulated or pulsed excitation, and with transmission or back-scattering detection. These variations are reviewed. The recent technique of pulsed PTR with back-scattering detection is described in more detail, and some important single-ended remote sensing applications are discussed.

1. INTRODUCTION

The photo-thermal (PT) effect is the conversion of electro-magnetic energy, in part or in full, into heat energy in a material. PT effect can be detected directly, *e.g.*, by "calorimetry",⁽¹⁻⁴⁾ or indirectly, *e.g.*, by the opto-acoustic effect,⁽⁵⁻⁷⁾ monitoring refractive index variations causing defocusing^(8,9) or deflection of probe beams (10-14), surface distortions,^(15,16) spectroscopy⁽¹⁷⁾ and radiometry. This paper is concerned with the last technique, *i.e.*, photothermal radiometry (PTR). PTR relies on the detection of variations in the infrared (IR) thermal radiation emitted from a sample that is excited by electromagnetic radiation (typically from a laser or from an arc lamp) of varying intensity or wavelength. The advantages of PTR compared to other PT monitoring techniques are the following: (1) It is totally noncontact, so that measurements can be made on "difficult" samples, like those in vacuum, high pressure, high temperature, or other hostile environments. (2) With the use of IR detectors of fast rise time, thermal or mechanical properties of thin film samples can be measured in much shorter times (or even in "real time") compared to conventional methods. (3) Absolute values for absorption coefficients, thermal diffusivity, or thickness of samples can be obtained in a noncontact manner. (4) PTR performed in the back-scattered mode with pulsed laser for excitation appears to be useful for single-ended remote-sensing of samples that may be ~km away, *i.e.*, back-scattering PTR may provide a new PT LIDAR (Light Detection And Ranging).

There are four variations of PTR techniques that have been reported in the literature as indicated in Table I. These variations can be classified according to the excitation mode (continuously modulated or pulsed) and to the detection mode (transmission or back-scattered). In this paper, we first review the various modes of

PTR. Then, we examine in more detail the new back-scattered pulsed PTR (*i.e.*, PPTR), the mathematical basis of this technique, as well as its applications.

2. VARIATIONS OF PTR

The technique of PTR involves a method of modulated heating of the sample and a method of detecting the IR thermal radiation emitted somewhere from the sample. The modulation of the excitation beam (which can be photon, electron, microwave, *etc.*) is usually either a continuous modulation with about 50% duty cycle, or a pulsed modulated with very low duty cycle, but high peak power. The observation spot can in principle be anywhere on the sample; however, the mathematics is simplest for observation of IR emission emitted backwards from the excitation spot (called back-scattering PTR here), or emitted from a spot that is "end-on" through the sample thickness with respect to the excitation spot (called transmission PTR here). Indeed, most workers have used either the back-scattering geometry or the transmission geometry, although Luukkala *et al.*⁽¹⁸⁾ have demonstrated PTR with the observation spot being laterally displaced from the excitation spot. Back-scattering PTR (but not transmission PTR) can be used for thick or bulky materials or for samples with inaccessible back surface.

The principle of all variations of PTR is the following. The modulated excitation beam produces a modulated temperature $\theta(\vec{x}, t)$ in the sample, where $\vec{x}$ is position and t is time. This modulated temperature profile is dependent on the absorption coefficient α of the excitation beam. Thermal diffusion causes a spatial spreading of the temperature profile, depending on the thermal diffusivity D , and on the boundary conditions. In particular, for thin film samples of thickness L , the thermal diffusion in the thickness direction is hindered when the thermal diffusion length is comparable to or larger than L .

The modulated IR radiation emitted from the observation region depends on the temperature at that region as well as the mean absorption coefficient α' of the IR light averaged over the detection bandwidth. The above qualitative discussions indicate that the PTR signal can provide information on the parameters α , D , L , or α' of the sample.

2.1 Continuously Modulated PTR in Transmission

Transmission PTR using an argon ion laser of 1W power modulated at 15-30 Hz has been demonstrated by Busse.⁽¹⁹⁾ This technique was first proposed by Cowan⁽²⁰⁾ in 1961 for thermal diffusivity measurements at high temperatures. In Busse's work, a wedge-shaped piece of aluminum of thickness ranging from 1 to 5 mm is irradiated by the focused laser beam on one surface; the modulated thermal IR emission that is emitted "end-on" from the other surface is detected by a Golay cell. Busse⁽¹⁹⁾ observed that the IR radiometry signal $S(L,t)$ is given by

$$S(L,t) = A \exp(-L/\mu) \exp[i(\omega t - L/\mu)] \quad (1)$$

where L is the aluminum plate thickness at the observation position, A is an amplitude, and μ is the thermal diffusion length for the laser modulation frequency f , with $\omega = 2\pi f$:

$$\mu = [D/\pi f]^{1/2} \quad (2)$$

Busse's⁽¹⁹⁾ experiment indicates that if $S(L,t)$ is measured for a range of modulation frequency f or for a range of thickness L , the thermal diffusivity of the samples can be derived. Further, if a plate with internal voids is scanned across the laser beam, the transmission PTR signal changes whenever the transmitted thermal wave crosses a void. This provides a means of nondestructive subsurface imaging of defects, and Busse found that the monitoring of the phase angle of the PTR signal is more reliable for imaging compared to the monitoring of the amplitude of the PTR signal. This is because the

signal amplitude also depends on the absorption or reflection properties of the sample surface (through the factor A in Eq. (1)), while the phase angle only depend on the thermal diffusivity along the transmission path. Busse and Eyerer⁽²¹⁾ have later applied the technique for remote, nondestructive characterization of structures and properties in polymers, and Busse and Renk⁽²²⁾ have demonstrated a new stereoscopic subsurface imaging technique involving two adjacent modulated PT source for transmission PTR.

2.2 Pulsed PTR in Transmission

The first PTR experiment with pulsed laser excitation was performed by Deem and Wood⁽²³⁾ using transmission monitoring. This method was based on the earlier flash thermometry technique developed by Parker *et al.*,⁽²⁴⁾ who excited the front surface of a metal plate by a flashlamp, and detected the temperature transient at the back surface by a thermocouple. Deem and Wood⁽²³⁾ replaced the contact thermocouple by a noncontact PbS IR detector, and the flashlamp by a 5 Joule ruby laser. They have used their "laser flash thermal diffusivity apparatus" to measure thermal diffusivity D of nuclear reactor fuel materials at high temperatures. For measurements of such types of "hostile" samples, noncontact techniques like PTR is of course preferred to avoid corrosion and aging problems. The value of D (which is related to the quality of the composite fuel material) can be obtained by analyzing the shape of the transmission PTR signal, as already shown in the flash thermometry measurement of Parker *et al.*⁽²⁴⁾ The simplest data analysis method is to measure the "half-time" ($t_{1/2}$) required for the transmitted PTR signal to reach half of the maximum. In this case, D can be shown⁽²⁴⁾ to be

$$D = 1.38 L^2 / (\pi^2 t_{1/2}) \quad (3)$$

where L is the sample thickness.

Deem and Wood's⁽²³⁾ technique, called pulsed PTR in transmission here, is also frequently simply called the "flash diffusivity" or "flash radiometry" technique in the literature. Several authors have taken advantage of this noncontact technique to measure D at high temperatures. For example, Taylor⁽²⁵⁾ has used it to measure D of resin-bonded carbon from 20°C to 1650°C, and observe annealing of the material at 850°C. He also could make measurements under various vacuum or high pressure conditions.

The "shape analysis" in the flash diffusivity technique corresponds to the "phase angle" analysis of Busse.⁽¹⁹⁾ In the flash excitation, the excitation beam is modulated by a broad spectrum of Fourier modulation frequencies. In all cases of subsurface imaging, the authors preferred to use the shape or the phase of the PTR signal rather than the amplitude, because the latter can be affected by surface conditions (like absorptivity or reflectivity) of the sample.

2.3 Continuously Modulated PTR in Back-scattering

Nordal and Kanstad⁽²⁶⁻²⁸⁾ first demonstrated continuously modulated PTR in back-scattering for spectroscopic studies of condensed matter. Earlier, a similar technique was used by Hendler and Hardy⁽²⁹⁾ for the study of heating and temperature sensation in human skin produced by infrared and microwave irradiation. In Nordal and Kanstad's work⁽²⁶⁾ in 1979, they used a continuous CO₂ laser (of power ~50 mW) modulated at 77 Hz at 50% duty cycle as the excitation source, and an InSb photoconductor as the IR radiometric detector. The laser can be tuned from 9.2 to 10.8 μm . They showed that absorption spectra for powdered samples at high temperatures can be obtained by scanning the CO₂ laser and plotting the PTR signal amplitude as a function of laser wavelength. This is quite valuable, since absorption

spectroscopy of an opaque and/or highly light-scattering specimen is traditionally very difficult, especially if the specimen is at high temperature. In subsequent work, Nordal and Kanstad⁽²⁸⁾ has shown that a conventional high pressure Xe lamp/monochromator combination is sufficient for PTR spectroscopy. The excitation power level at the sample is less than 1 mW. A PbSnTe IR detector is used for observing the thermal radiation from the excitation region. By scanning the excitation monochromator, they obtained optical absorption spectra for a broad variety of untreated and strongly light-scattering samples, including Nd_2O_3 powder, blood, and a green leaf. Important applications in photosynthesis studies are also demonstrated.^(30,31) Luukkala⁽³²⁾ has shown that the technique of Nordal and Kanstad⁽²⁶⁻²⁸⁾ is not only good for spectroscopic detection, but also for subsurface imaging applications as well. A very practical application for automated solder joint inspection has been shown by Vanzetti and Traub⁽³³⁾ and an instrument for such a purpose called a "Laser Inspect System" consisting of a modulated continuous Nd:YAG laser and an InSb IR detector is now commercially available.⁽³⁴⁾

2.4 Pulsed PTR in Back-scattering

We have recently developed⁽³⁵⁻³⁷⁾ the new technique of PPTR in back-scattering. The advantages of back-scattering detection have already been noted earlier. The advantage of pulsed excitation is that with the use of a pulsed laser beam, sufficient PT heating can be produced in a distant sample to provide a detectable IR radiometry signal, so that remote sensing of distant samples is possible. Also, with pulsed excitation at low duty cycle (say $\leq 10^{-6}$), a negligible amount of steady-state sample heating is produced, and hence signal interpretation is simplified. Furthermore, the pulse excitation permits the use of "gating" techniques for suppression of noise during the excitation pulse. This is useful because during the excitation pulse, instrumental scattering and electromagnetic

interference effects cause "spurious" signals (*i.e.*, noise); however, the PPTR signal usually has a much broader width compared to the excitation pulse width, and a "detection gate" can be turned on after the excitation pulse. Such a gating advantage for pulsed excitation compared to continuously modulated excitation is already known in other techniques, for example, Tam and Coufal⁽⁷⁾ have discussed such a comparison in connection with opto-acoustic spectroscopy.

The method of PPTR is indicated in Fig. 1. We have used various pulsed excitation sources, for example a short-duration (full width at half maximum=8 nsec) N_2 laser beam with less than 1 mJ energy at 337 nm. Most of our experiments are concerned with the technique of back-scattered PPTR as shown for beam path (a) in Fig. 1, although some of our work is also performed with transmission PPTR as indicated in beam path (b) in Fig. 1. The thermal IR radiation from the sample is refocused onto a HgCdTe detector with a rise time of 0.5 μ sec, and the PPTR signal in back-scattering ($S_B(t)$) or in transmission ($S_T(t)$) is accumulated on a transient recorder (Tektronix 7854 scope with 7D20 plug-in). Maximum sample heating by the laser beam of a spot size being several mm is generally limited to $\sim 10^\circ\text{C}$ to avoid any sample damage or any nonlinear radiometric effects (*i.e.*, the radiometric signal magnitude is proportional to the surface temperature rise ΔT only when ΔT is much smaller than the ambient absolute temperature).

We⁽³⁵⁾ have applied this PPTR in back-scattering for novel absolute absorption spectroscopy of opaque solids and liquids. This is possible because the magnitude of the absorption coefficient α of the excitation beam is related to the "steepness" of the initial temperature profile produced in the sample. Large α corresponds to a steeper temperature profile near the sample surface, causing faster cooling of the surface and

hence faster decay of the back-scattered PPTR signal. By analyzing the shape of the PPTR signal from bulk samples, Tam and Sullivan⁽³⁵⁾ showed that α can be obtained under some conditions if the thermal diffusivity D is known.

Another very important application⁽³⁵⁾ is the remote sensing of the layered structure of a sample by PPTR. To show this, we coat a black rubber substrate with a 45 μm thick polyester film that is transparent in the wavelength of the excitation beam. For this layered structure, the pulsed PTR exhibits two peaks: a prompt peak that decays with the same rate as the bare substrate but with decreased magnitude, and a delayed peak occurring at a time t_d after the firing of the laser. We further found that t_d is related to the thickness ℓ and the thermal diffusivity D_ℓ of the coating by

$$t_d = \ell^2 / 4D_\ell . \quad (4)$$

These observations indicate that the prompt peak is due to IR thermal radiation emitted from the irradiated substrate and attenuated by the coating, and the delayed peak is due to IR thermal radiation emitted from the top coating surface due to heat diffusion from the illuminated substrate surface.

We have also⁽³⁵⁾ demonstrated that PPTR is useful to sense the degree of powder aggregation which affects the "effective" thermal conductivity. The pulsed laser is used to irradiate black carbon-loaded epoxy powders of different degree of compactness. We find that the PPTR signal for the loose powder stops decaying after some time indicating that inter-particle heat transport is very slow. However, the PPTR signal for a compact powder exhibits a continuous decay as in a neat solid.

We have later⁽³⁶⁾ investigated the PPTR signal profile for thin films. For a sample of thickness L , thermal diffusivity D , absorption coefficient being α at the excitation wavelength and being α' at the detection wavelength, the PPTR signal shape (excited by a pulsed laser of duration τ_0) is dependent on different parameters at different delay time periods (see Fig. 2). For simplicity in the present discussion, we assume that τ_0 is short compared to other time scales, and the sample is opaque (*i.e.*, αL and $\alpha' L$ are much larger than 1). Several important time scales are:

$$\tau_\alpha = \alpha^{-2}/4D \approx \text{time required for heat to diffuse a distance } \alpha^{-1}. \quad (5)$$

$$\tau_{\alpha'} = \alpha'^{-2}/4D \approx \text{time required for heat to diffuse a distance } \alpha'^{-1}. \quad (6)$$

$$\tau_L = L^2/\pi^2 D = \text{time required for heat to diffuse through the sample thickness } L. \quad (7)$$

$$\tau_c = \text{characteristic time (assumed long) for the cooling of the sample by radiation and by its modes of thermal contact with its surroundings.} \quad (8)$$

Our theoretical analysis for the simple case of an opaque film with $\tau_\alpha, \tau_{\alpha'} \ll \tau_L \ll \tau_c$ reveals the following: (a) For time $t < \tau_L$, the presence of the back surface is "not felt", the heat diffuses as in the case of a homogeneous semi-infinite solid, and the decay of the signal are characterized by τ_α and $\tau_{\alpha'}$. (b) For $\tau_L < t < \tau_c$, the presence of the back surface is manifested: the signal decays in back-scattering radiometry (or rises in transmission radiometry) approximately exponentially to a steady state value S_1 with time constant τ_L . The thermal diffusivity D or thickness L of the sample can be obtained by fitting this intermediate part of the signal without the necessity of knowing the values of α and α' . The radiometry signal approaches the nonzero "asymptotic" value S_1 (same for back-scattering or transmission monitoring) when t exceeds several times τ_L , because at this time, thermal diffusion has stopped and

temperature is uniform through the sample thickness. (c) For $t > \tau_c$, the "asymptotic" value in (b) decays back to zero as the overall temperature of the sample cools back to room temperature. This cooling time constant τ_c is a very sensitive measure of the degree of thermal contact of the sample with its environment or its substrate. The above discussion indicates that PPTR with back-scattering observation is a useful singled-ended measurement technique for remote sensing of a sample of thickness L . The signal shape provides absolute values of α , α' , and D if L is known; alternatively, it provides absolute values of α , α' , and L if D is known. We have made measurements^(36,37) on metal films and on polymer films of thickness in the range of 10-200 μm to illustrate some of these capabilities of PPTR.

More recently, the application of PPTR for nondestructive evaluation of layered materials like plasma-sprayed coatings and graphite-epoxy laminates has been described by Cielo.⁽³⁸⁾ Also, Imhof *et al.*⁽³⁹⁾ have used PPTR for the very important application of characterizing opaque pigment coatings.

3. THEORY OF PPTR

Detailed theory of the continuously modulated PTR technique has been given by several authors, for example, Santos and Miranda⁽⁴⁰⁾ and Tom *et al.*,⁽⁴¹⁾ and their results will not be described here. We have⁽³⁷⁾ recently derived the theoretical PPTR signal in back-scattering ($S_B(t)$) and in transmission ($S_T(t)$) for a short excitation laser pulse and fast IR detector response time. We show that

$$\begin{aligned} \left[\begin{array}{c} S_B(t) \\ S_T(t) \end{array} \right] &= \frac{AK}{L} \left\{ (1-e^{-\alpha L})(1-e^{-\alpha' L}) \right. \\ &\quad \left. \pm 2 \left[\frac{1}{e^{-\alpha' L}} \right] \sum_{n=1}^{\infty} \left(\frac{1-(-1)^n e^{-\alpha L}}{1 + \frac{n^2 \pi^2}{\alpha^2 L^2}} \right) \left(\frac{1-(-1)^n e^{\mp \alpha' L}}{1 + \frac{n^2 \pi^2}{\alpha'^2 L^2}} \right) e^{-n^2 t / \tau_L} \right\} \end{aligned} \quad (9)$$

where the equation for the upper/lower qualities in the two square brackets correspond to the upper/lower $\pm$ signs. Here, A is a constant depending on the flash pulse energy and the thermal properties of the sample, and K is a constant depending on the emissivity and steady temperature of the sample. Equation (9) is basically the quantitative expression for the qualitative statements in Section 2.4.

Some illustrative numerical results based on Eq. (9) for $S_B(t)$ are shown in Figs. 3 and 4. Figure 3 shows the theoretical shapes of $S_B(t)$ for two samples of identical material (stainless steel) but different thickness: $L=0.005$ cm (dashed line) and $L=\infty$. We see that the two signals totally overlap at early times; however, after $\tau_L=63.3$ μ sec for the $L=0.005$ cm sample, the two signals start to deviate: the thin-film signal stops decaying while the "thick plate" signal continues to decay. These effects have indeed been verified experimentally^(36,37) Figure 4 shows how the theoretical shapes of $S_B(t)$ depend on the absorption coefficients α and α' , with fixed thickness and thermal diffusivity. We see that at early times (*i.e.*, $t < \tau_L$), the stronger absorption coefficients cause a steeper decay of the PTR signal. However, at late times ($t \gg \tau_L$) the decay curves for different values of α and α' are overlapping, showing that the late decay rate is only dependent on L and D, in agreement with the analysis of Parker.⁽²⁴⁾ To sum up, the back-scattered PTR signal $S_B(t)$ is sensitively dependent on α , α' and D for $t < \tau_L$, and sensitively depend on L and D for $t \gg \tau_L$. Theoretical fitting⁽³⁷⁾ of the observed

$S_B(t)$ for a sample can provide values of α , α' , D , and L . Such measurements have the distinct advantages of being single-ended, remote-sensing, and nondestructive.

Equation (9) can be shown⁽³⁷⁾ to approach simple limits when L is large. In this case, $S_T(t) \rightarrow 0$ as $L \rightarrow \infty$, and

$$S_B(t) \xrightarrow{L \rightarrow \infty} \frac{AK\alpha\alpha'}{\alpha'^2 - \alpha^2} \left\{ \alpha' e^{t/4\tau_{\alpha'}} \left(1 - \text{erf} \sqrt{t/4\tau_{\alpha}} \right) - \alpha e^{t/4\tau_{\alpha}} \left(1 - \text{erf} \sqrt{t/4\tau_{\alpha'}} \right) \right\} \quad (10)$$

where $\tau_{\alpha} = (4\alpha^2 D)^{-1}$, $\tau_{\alpha'} = (4\alpha'^2 D)^{-1}$ and erf is the error function.⁽⁴²⁾ Equation (10) is symmetrical with respect to the absorption coefficients α and α' . It further simplifies if one of the absorption coefficient is much larger than another, *e.g.*, $\alpha' \gg \alpha$. In this case:

$$S_B(t) \xrightarrow[\alpha' \gg \alpha]{L \rightarrow \infty} AK\alpha e^{t/4\tau_{\alpha}} \left(1 - \text{erf} \sqrt{t/4\tau_{\alpha}} \right). \quad (11)$$

Equation (11) is precisely the form we have used in our earlier⁽³⁵⁾ PPTR work for obtaining absolute values of α at the excitation wavelength for "semi-infinite" samples.

An excitation spectrum of a distant sample can be obtained with back-scattered PPTR by scanning the wavelength of the excitation laser and monitoring the corresponding peak magnitude of the back-scattered PPTR signal. An example of such an excitation spectrum is shown in Fig. 5. Under certain conditions, such an excitation spectrum truly represents an absorption spectrum of the sample, for example, when sample thickness is large and $\alpha' \gg \alpha$; in this case Eq. (11) indicates that the peak value of $S_B(t)$ occurring at $t=0$ is proportional to $\alpha(\lambda)$ at the excitation wavelength λ .

In Eq. (9), we have neglected the effects due to the finite excitation pulse width and the finite IR detector rise time. Such effects have been incorporated in the work of Leung and Tam,⁽³⁷⁾ where experimental data to support our theoretical $S_B(t)$ and $S_T(t)$ profiles are also presented.

4. CONCLUSIONS

Techniques of PTR rely on the detection of modulated infrared thermal radiation from a sample that is excited by a modulated beam of energy. The two types of detection modes discussed in this paper are back-scattering or transmission, and these are compared in Table II. The two types of modulations commonly used are continuous modulation (duty cycle $\sim 50\%$) or pulsed (duty cycle $\lesssim 10^{-6}$ typically) modulation. The pulsed mode can be regarded as the frequency-multiplexed version of the continuously modulated mode and they are compared in Table III. These variations of PTR are reviewed. The recent technique of pulsed PTR in back-scattering detection is examined in more detail, which is the only variation that is suitable for remote sensing. Its theoretical basis is discussed, and its new applications are indicated, which include absolute absorption spectroscopy, excitation spectroscopy, thickness or thermal diffusivity measurements, monitoring of layered structure, and sensing of degree of contact between materials. These applications should be valuable in science, technology, and medical diagnostics (e.g., fast noncontact monitoring of skin *in-vivo*).

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TABLE I

Examples of Various Modes of Photothermal Radiometry

Source	Detection	
	Transmission	Back-scattering
Continuous modulated	Busse ⁽¹⁹⁾ (1980)	Hendler and Hardy ⁽²⁹⁾ (1961)
	Busse and Eyerer ⁽²¹⁾ (1983)	Nordal and Kanstad ⁽²⁶⁾ (1979)
	Busse and Renk ⁽²²⁾ (1983)	Nordal and Kanstad ⁽²⁸⁾ (1981)
		Luukkala ⁽³²⁾ (1980)
		Vanzetti and Traub ⁽³³⁾ (1983)
Pulsed	Deem and Wood ⁽²³⁾ (1962)	Tam and Sullivan ⁽³⁵⁾ (1983)
	Taylor ⁽²⁵⁾ (1972)	Leung and Tam ⁽³⁶⁾ (1984)
		Cielo ⁽³⁸⁾ (1984)
		Imhof <i>et al.</i> ⁽³⁹⁾ (1984)

TABLE II

Comparison of "Back-scattering" and "Transmission" Detection for PTR

Item	Back-scattered Radiometry	Transmissive Radiometry
Applicability for films with backside being nonaccessible	Yes	No
Time-dependent signal shape	Monotonic decreasing if film is homogeneous; if layered, may have delayed peaks.	Delayed peak and subsequent decay.
Depth-profiling capability	Yes, because smaller depth is sensed by early signal.	No, because the signal is mainly sensitive to an average thermal diffusivity.
Suitability for remote-sensing	Yes, because all measurement equipments are on one side of the sample (<i>i.e.</i> , single-ended).	Not easy, because measurement equipments are needed on both sides of the sample (<i>i.e.</i> , double-ended).

TABLE III

Comparison of Continuous Modulated and Pulsed Excitation for PTR

	Continuous Modulated	Pulsed
Feature	High duty cycle, low peak power	High peak power, low duty cycle
Steady background heating	Usually substantial	Usually small
Suitability for remote sensing of samples (e.g., 1 Km away)	No	Yes (using intense pulsed lasers)
Tight focusing of the excitation laser beam	Usually used	Usually not used
Time-gating of detection signal for noise reduction	Not possible	Possible
Phase sensitive detection for noise reduction	Possible	Not possible
Important parameter to be measured	Phase angle of signal with respect to the excitation	Entire shape of the radiometry transient signal
Fourier components of modulation frequencies	Few (i.e., fundamental and possibly some harmonics)	Many (for short pulsed excitation)

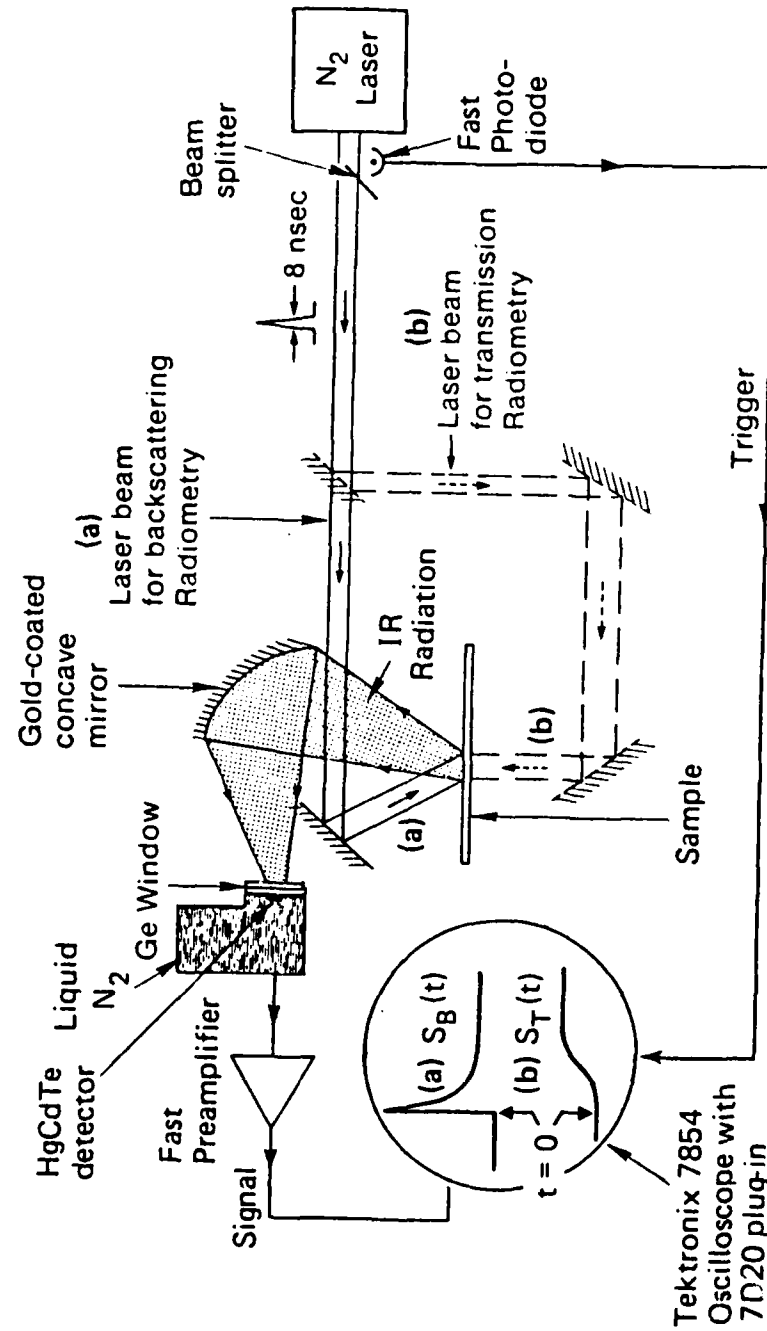


Figure 1. Experimental setup for both single-ended back-scattering (laser beam represented by solid lines) and double-ended transmission (laser beam represented by dash lines) pulsed photothermal radiometry measurements.

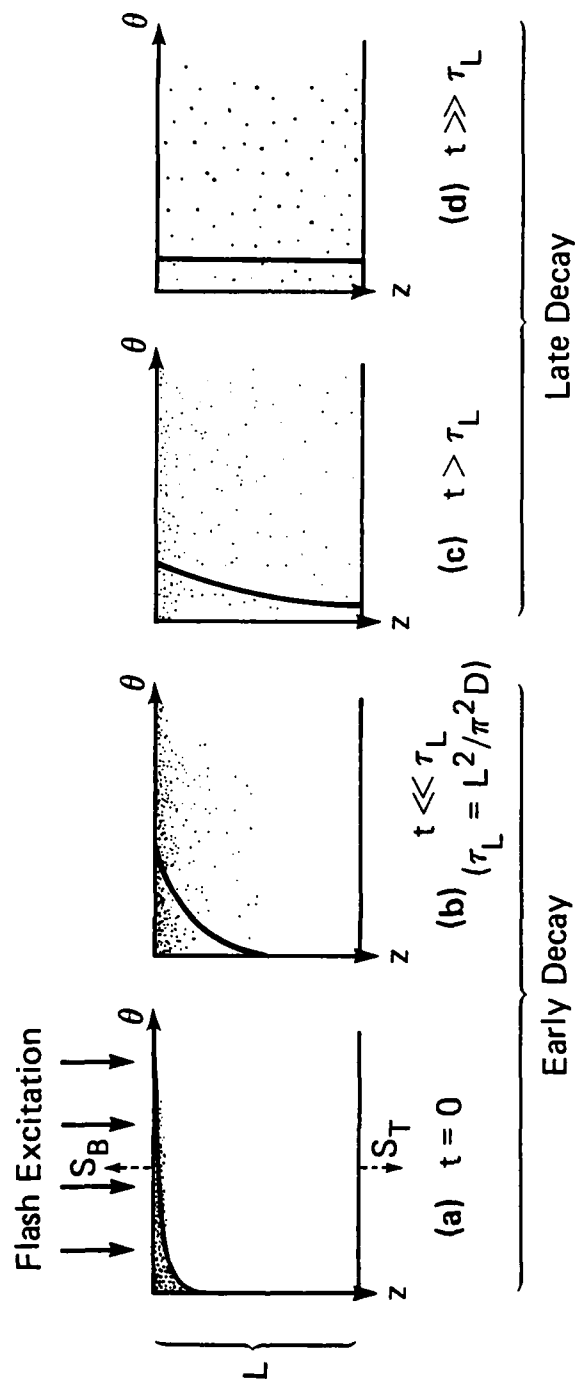


Figure 2. Thermal diffusion in a film of thickness L after a short pulsed heating at the film surface. The local temperature increase above ambient (θ) is plotted at several times (t), and also indicated by the density of the small black dots.

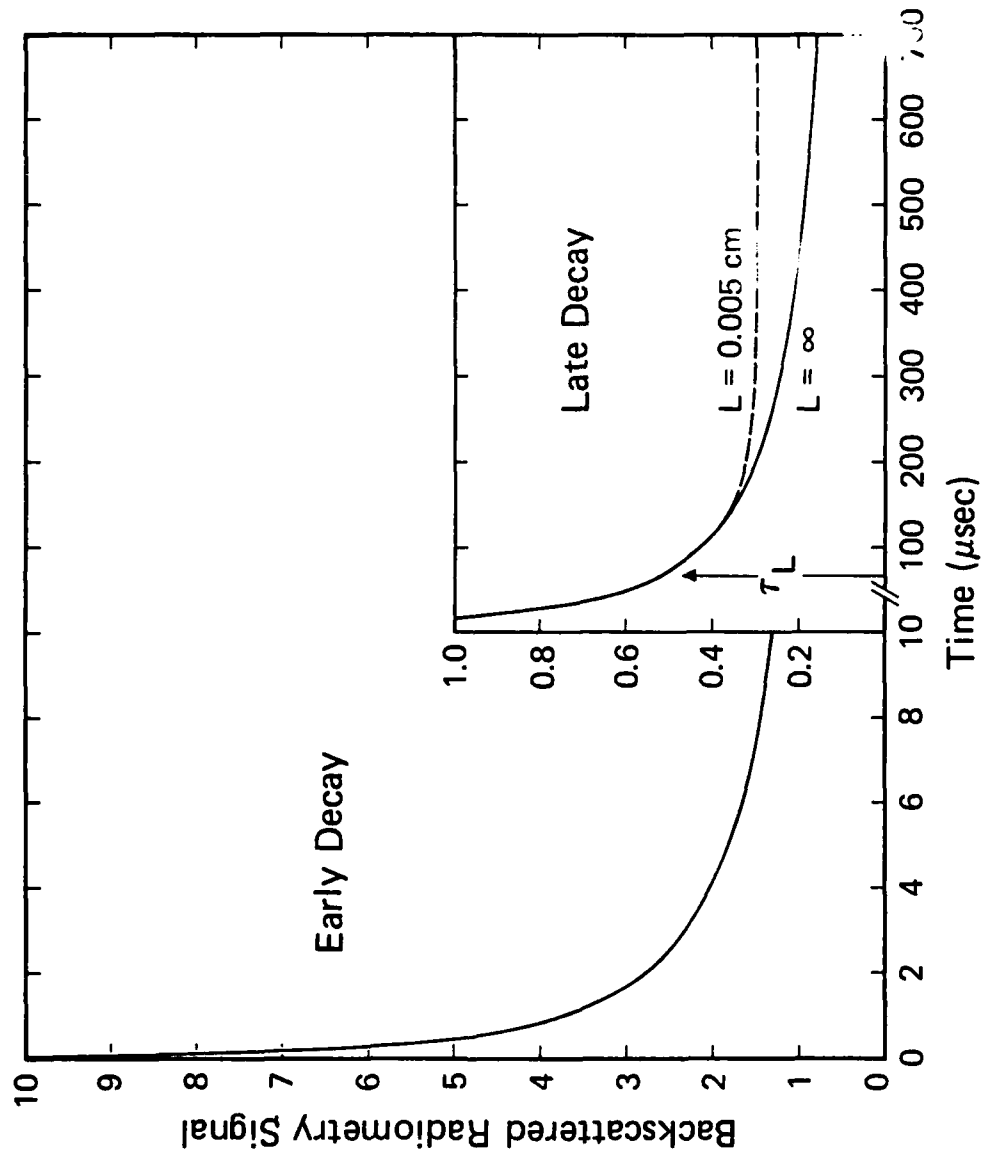


Figure 3. Theoretical profiles of the single ended back-scattered flash radiometry signal showing the effect of sample thickness L . Dash line is for $L=0.005 \text{ cm}$ and solid line is for $L=\infty$. In both curves, α , α' and D are taken as $2 \times 10^4 \text{ cm}^{-1}$, $1 \times 10^4 \text{ cm}^{-1}$ and $0.04 \text{ cm}^2/\text{s}$, respectively, which are typical values for stainless steel. Note that the scale changes for the late decay in the inset.

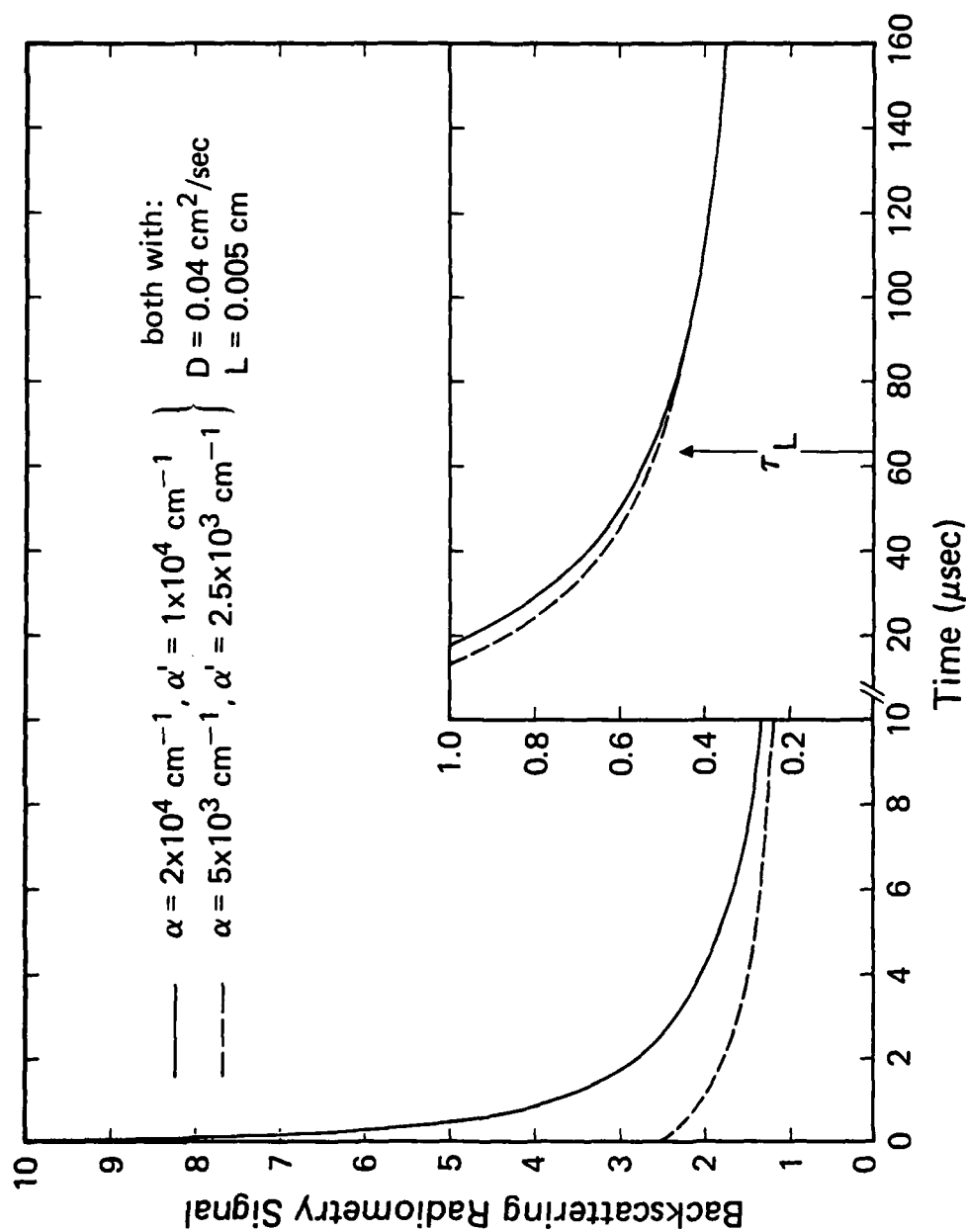


Figure 4. Theoretical profiles of the back-scattered radiometry signal showing the effect of absorption coefficients α and α' . Dash lines is for $\alpha = 5 \times 10^3 \text{ cm}^{-1}$ and $\alpha' = 2.5 \times 10^3 \text{ cm}^{-1}$; solid line is for $\alpha = 2 \times 10^4 \text{ cm}^{-1}$ and $\alpha' = 1 \times 10^4 \text{ cm}^{-1}$. In both curves, L and D are taken as 0.005 cm and $0.04 \text{ cm}^2/\text{s}$, respectively. Note that the scale changes for the late decay in the inset.

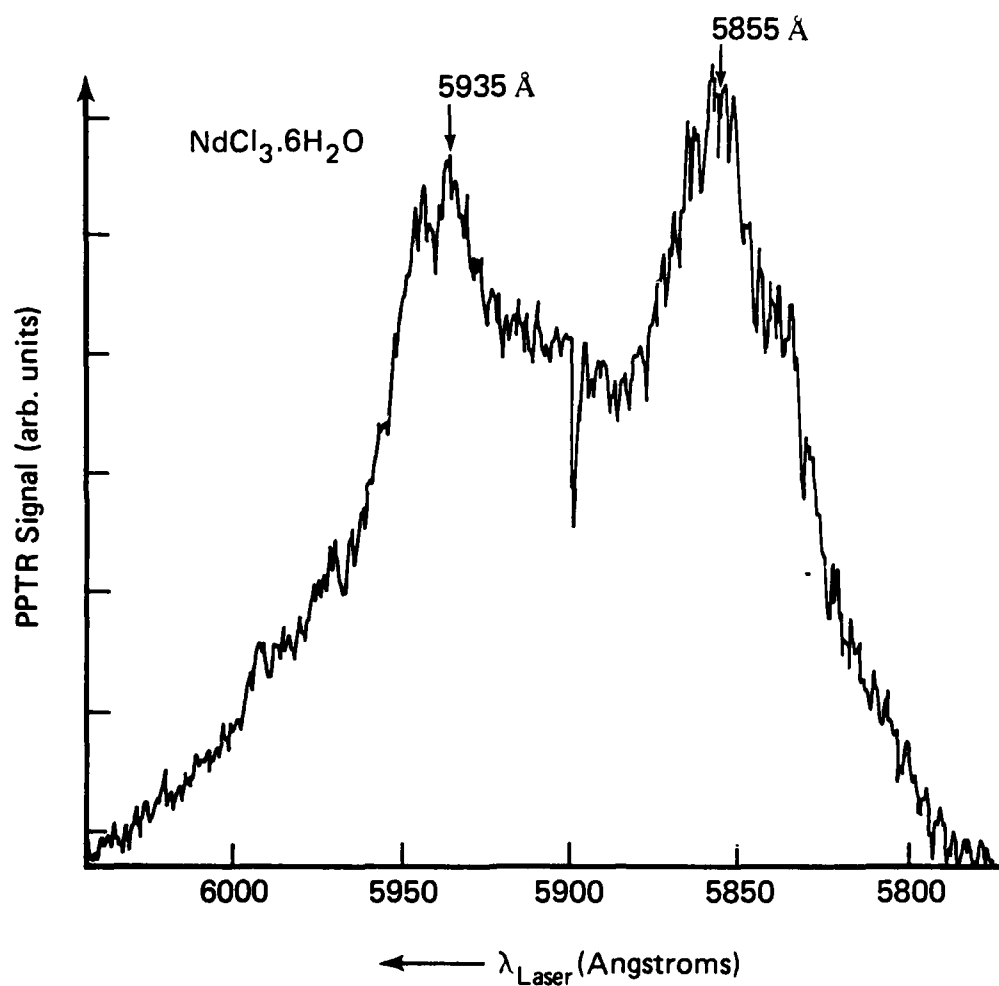


Fig. 5. PPTR excitation spectrum with back-scattering detection for $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$. This is obtained by scanning the excitation pulsed dye laser over the Rhodamine 6G tuning range (5770Å to 6030Å). The numbers marked are in Angstrom units.