Time-resolved, photothermal-deflection spectrometry with step optical excitation

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A theoretical model of a novel time-resolved, photothermal-deflection spectrometry with step optical excitation (a rectangular pulse of a finite duration) is presented. To make the theory practicable, i.e., able to be used to determine the values of optical and thermal properties of the sample by fitting experimental data to the theory, approximations are introduced. The numerical simulations show that when the value of the thermal conductivity of the deflecting medium (e.g., air) is small, the adiabatic approximation for the heat conduction at both front and rear surfaces of a sample is effective for both transparent and opaque samples, while the adiabatic and isothermal approximations for the heat conduction at the front and rear surfaces, respectively, are valid only for an opaque sample. With these approximations, the optical and thermal properties—such as optical absorption coefficient and thermal diffusivity—of solid materials (optically transparent or opaque) can be directly measured by this novel method.

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1. INTRODUCTION

Since 1970, photothermal techniques have been developed for nondestructive material characterization, such as measuring optical and thermophysical properties of different materials and depth profiling, that are important because of their high sensitivity and versatility. These techniques can be classified into two main categories by the criterion whether the samples contact or do not contact the detection system. Photothermal and photopyroelectric methods are examples of the contact techniques. Remote (noncontact) techniques, such as photothermal deflection (namely, optical beam deflection) and thermal lens methods, are suitable for studying samples in a severe environment.

In transverse photothermal-deflection (PD) (or mirage effect) spectrometry, a probe beam senses the gradient of the optical refractive index in the ambient medium adjacent to a sample surface, resulting in deflection of the probe beam. The gradient of the optical refractive index is induced by the temperature gradient from the sample surface to the medium, and the temperature rise in the sample is the result of conversion of the absorbed electromagnetic excitation radiation into heat. The optical and thermophysical properties of the sample, therefore, can be measured by monitoring the frequency dependence (for frequency-modulated excitation) or the time dependence (for impulse excitation) of the PD signal. The theory, and applications of PD spectrometry can be found in Refs. 1–7, and the reported thermophysical property measurement with the PD technique were achieved mainly by use of frequency-modulated excitation. One may measure thermal diffusivity in a frequency-modulated experiment by using the linear relationship between two measurable parameters whose slope can be used to retrieve the thermal diffusivity value. However, a careful management of the linear relations is necessary since some of them are strictly valid only under ideal conditions that are very difficult to achieve in practice.

With no requirement to find any linear relations, time-resolved, thermal-lens spectrometry by means of step optical excitation (i.e., the rectangular-pulse optical excitation) has enjoyed great success in the determination of the thermal diffusivities of transparent samples. The results are absolute measurements, and the thermal diffusivity values can be obtained directly by a convenient procedure of fitting experimental data to a theoretical model. In this paper, we propose theoretically a novel time-resolved, photothermal-deflection spectrometry with step optical excitation. Similar to the thermal-lens technique, this PD technique can be used not only for measuring optical properties of materials, but can be employed for determining thermophysical properties. Furthermore, this technique can be employed to study both transparent and opaque samples, while thermal-lens spectrometry can be applied only to transparent samples.

In this work, we start with the calculation of the one-dimensional temperature rise due to the absorbed energy of step optical excitation in a thin, solid slab sample of finite thickness with boundary conditions. Then we work out the temperature-rise distribution in the deflecting medium owing to the heat conduction from the front surface of the sample to the medium.
the time-resolved PD signal based on the temperature gradient in the deflecting medium.

To calculate the temperature rise in the sample and its surrounding medium after the absorption of the step optical excitation by the sample, scientists have used Laplace transforms, such as in the theoretical work in Ref. 13. Only in some special cases could the temperature rise (in the time domain, not in s space) in the gas medium adjacent to the sample’s front surface be obtained with an analytical expression. Green’s functions have also been employed to solve the equation of heat conduction and find the temperature rise in the sample; one may find an example in the theoretical work of Ref. 14. Although the Green’s function method might be an approach to calculate the temperature increases after the step optical excitation in both the sample and the surrounding media, as a complete treatment (not just for special cases), to the best of our knowledge, there is little work reported in which this approach was used.

In using Green’s functions to solve the heat conduction equations, we present here a complete theoretical treatment of photothermal-deflection spectrometry with step optical excitation, aiming to obtain a practicable theory, i.e., one that can be used to determine the values of optical and thermal properties of the sample by fitting experimental data to the theory. However, there is an obstacle to the theory’s being practicable: To use this theory practically to measure optical and thermal properties, one needs to know the thermal property to be measured to solve a transcendental equation. To remove this obstacle, we introduce approximations. Numerical simulations show that when the thermal conductivity of the deflecting medium is small (e.g., air), the adiabatic approximation for the heat conduction at both front and rear surfaces of the sample is effective for both transparent and opaque samples, while the adiabatic and isothermal approximations for heat conduction at the front and rear surfaces, respectively, are valid only for an opaque sample. Consequently, these approximations make this novel time-resolved, photothermal-deflection spectrometry practicable.

2. THEORETICAL MODEL

In a PD experiment as shown in Fig. 1 an isotropic, homogenous, thin slab sample is placed in a transparent and homogeneous deflecting medium. The thickness of the sample is \( l_s \), and the optical absorption coefficient of the sample is \( \beta \). The distance between the probe beam and the sample surface is \( a \). A heating beam of spot size \( d \) is uniformly incident on the sample surface at \( x = 0 \) with intensity \( I_0 \) and a pulse duration \( \tau_p \) (step heating):

\[
I(t) = \begin{cases} 
I_0, & (t \leq \tau_p, \text{ active heating interval}) \\
0, & (t > \tau_p, \text{ relaxation interval}) 
\end{cases}
\]

(1)

For the convenience of later discussion, all variables with subscript \( i \) are for the active heating interval \((t \leq \tau_p)\), while those with subscript \( r \) are for the relaxation interval \((t > \tau_p)\). If we assume the absorbed optical energy is converted into heat through a nonradiative process completely and instantaneously, the heat due to the optical absorption per unit volume per unit time at \( x \) in the sample is

\[
Q(x, t) = \beta I(t) \exp(-\beta x).
\]

(2)

The differential equations of heat conduction in the sample and the deflecting medium are given by

\[
\frac{\partial^2 T_s(x, t)}{\partial x^2} - \frac{1}{\alpha_s} \frac{\partial T_s(x, t)}{\partial t} = \frac{Q(x, t)}{k_s},
\]

(3)

\[
\frac{\partial T_g(x, t)}{\partial x^2} - \frac{1}{\alpha_g} \frac{\partial T_g(x, t)}{\partial t} = 0.
\]

(4)

Here, we define \( T_s(x, t) \) as the temperature rise for both the active interval and relaxation interval; the actual temperature is the sum of the temperature rise \( T_s(x, t) \) and the ambient temperature \( T_a \). \( k_i \) is the thermal conductivity, \( \alpha_i = k_i / \rho_i c_i \) is the thermal diffusivity, and \( \rho_i \) and \( c_i \) are the density and the specific heat, respectively; \( i = s \) or \( g \) stands for the sample or the deflecting medium, respectively. The initial condition is

\[
T_s(x, 0) = 0.
\]

(5)

The boundary conditions are the continuities of the temperature and heat fluxes at the boundaries of \( x = 0 \) and \( x = l_s^g \):

\[
T_s(0, t) = T_g(0, t),
\]

(6a)

\[
T_s(l_s^g, t) = T_g(l_s^g, t),
\]

(6b)

\[
\left. k_s \frac{\partial T_s(x, t)}{\partial x} \right|_{x=0} = k_g \left. \frac{\partial T_g(x, t)}{\partial x} \right|_{x=0},
\]

(6c)

\[
\left. k_s \frac{\partial T_s(x, t)}{\partial x} \right|_{x=l_s^g} = k_g \left. \frac{\partial T_g(x, t)}{\partial x} \right|_{x=l_s^g}.
\]

(6d)

These conditions assume that the heat transfer from the sample to the deflecting medium adjacent to the sample surfaces is dominated by heat conduction. The heat conduction from the sample surface to a location \( x = -l_s^g \) in Fig. 1 in the deflecting medium takes time \( \tau_g \approx l_s^g / 4 \alpha_g \) (Ref. 2, p. 106). We may call this thin layer of medium in contact with a sample surface with thickness \( l_s^g \) a thin-skin layer (Ref. 15, p. 20). When \( t \ll \tau_g \), the
temperature increases \( T_g(-l_g, t) \) and \( T_g(l_s + l_g, t) \) are zero, i.e., the actual temperature at \( x \leq -l_g \) and \( x \geq l_s + l_g \) is the ambient temperature \( T_a \). By neglecting the heat capacities of this thin skin layer on the front sample surface \( x = 0 \) and following Refs. 9 and 16, as a first approximation we have

\[
\frac{\partial T_g(x, t)}{\partial x} \bigg|_{x=0} = \frac{k_g}{l_g} (T_g(0, t) - T_g(-l_g, t)) = \frac{k_g}{l_g} T_g(0, t).
\]

Relation (7) is the rate of heat flow through the thin-skin layer (Ref. 15, p. 20) when \( t \ll \tau_a \), and at that time \( T_g(-l_g, t) = 0 \). By substituting the boundary condition Eq. (6a) of the temperature continuity at the boundary \( x = 0 \) into Eq. (7), the heat flux continuity of Eq. (6c) can then be replaced by the boundary condition for the linear heat transfer through the thin-skin layer into a medium at zero temperature rise \( T_g(0, t) \).

\[
k_x \frac{\partial T_s(x, t)}{\partial x} \bigg|_{x=0} = h_s T_s(0, t) = 0. \tag{6c'}
\]

Similarly, one can find the boundary condition at \( x = l_s \)

\[
k_x \frac{\partial T_s(x, t)}{\partial x} \bigg|_{x=l_s} + h_s T_s(l_s, t) = 0. \tag{6d'}
\]

Here, \( h_1 = h_2 = k_g/l_g \) are the heat transfer coefficients for the boundary condition of the third kind. One can find a similar expression in Ref. 15, p. 20. When \( t \ll \tau_a \), Eqs. (6a), (6b), (6c'), and (6d') are the boundary conditions of the differential Eqs. (3) and (4) of heat conduction in the sample and the deflecting medium.

The Green’s function for the heat conduction Eq. (3) with the initial condition of Eq. (5) and the boundary conditions of Eqs. (6c') and (6d') is given by

\[
G(x, x', t, \tau) = \sum_{m=1}^{\infty} A_m Z(x, x') \exp[-\alpha_m \delta_m^2 (t - \tau)], \tag{8}
\]

(not valid for both \( h_1 = 0 \) and \( h_2 = 0 \); Ref. 15, p. 360), where

\[
A_m = \frac{2(k_s^2 \delta_m^2 + h_s^2)}{(k_s^2 \delta_m^2 + h_s^2)(k_s^2 \delta_m^2 + h_s^2) + (h_1 h_2 + k_s h_1 (k_s^2 \delta_m^2 + h_s^2))}, \tag{9}
\]

\[
Z(x, x') = (k_s \delta_m \cos \delta_m x + h_1 \sin \delta_m x)(k_s \delta_m \cos \delta_m x' + h_1 \sin \delta_m x'). \tag{10}
\]

\( \delta_m \) is the root of the following transcendental equation:

\[
\tan \delta_m l_s = \frac{\delta_m k_s (h_1 + h_2)}{k_s^2 \delta_m^2 - h_1 h_2} \tag{11}
\]

The temperature rise in the sample due to the absorption of the step optical excitation is then given by

\[
T_{s,\alpha}(x, t) = \int_{0}^{t} \int_{0}^{\tau} Q(x', \tau) \rho_s c_s G(x, x', t, \tau) dx' d\tau,
\]

\( t \leq \tau_p \). \tag{12a}

\[
T_{s,\varphi}(x, t) = \int_{0}^{t} \int_{0}^{\tau} Q(x', \tau) \rho_s c_s G(x, x', t, \tau) dx' d\tau,
\]

\( t > \tau_p \). \tag{12b}

\( T_{s,\varphi}(x, t) \) stands for the temperature rise in the active heating interval and \( T_{s,\alpha}(x, t) \) the temperature rise in the relaxation interval. Let \( u_m = \delta_m l_s \). By substituting Eqs. (2) and (8) into Eqs. (12), we have

\[
T_{s,\alpha}(x, t) = \sum_{m=1}^{\infty} B_m \left[ \frac{k_s u_m}{l_s} \cos \frac{u_m x}{l_s} + h_s \sin \frac{u_m x}{l_s} \right]
\times \left[ 1 - \exp \left[ -\frac{(u_m \tau_p)^2}{\tau_a} \right] \right], \quad t \leq \tau_p,
\tag{13}
\]

\[
T_{s,\varphi}(x, t) = \sum_{m=1}^{\infty} B_m \left[ \frac{k_s u_m}{l_s} \cos \frac{u_m x}{l_s} + h_s \sin \frac{u_m x}{l_s} \right]
\times \left[ \exp \left[ \frac{(u_m \tau_p)^2}{\tau_a} \right] - 1 \right] \exp \left[ -\frac{(u_m \tau_p)^2}{\tau_a} \right],
\]

\( t > \tau_p \). \tag{14}

where

\[
B_m = \frac{\beta l_s A_m l_s^2}{k_s u_m^2 (u_m^2 + \beta l_s^2)} \left\{ k_s u_m \right.
\times \left[ \exp(-\beta l_1) \sin u_m - \beta l_s \cos u_m + \beta l_s \right]
\left. - h_1 l_s \left[ \exp(-\beta l_1) \left( \cos u_m \sin u_m + \beta l_s \sin u_m \right) - u_m \right] \right\}. \tag{15}
\]

In Eqs. (13) and (14), \( \tau_a = l_s^2/\pi^2 \alpha_s \) is the characteristic diffusion time constant of the sample. The physical meaning of \( \tau_a \) is that for a semi-infinite solid of thermal diffusivity \( \alpha_s \) heated by a Dirac delta heating impulse on its surface plane \( x = 0 \) at \( t = 0 \), the temperature rise at \( x = l_s \) in the sample due to heat conduction is less than

10% of the surface magnitude when \( t = \tau_a \).

From Eqs. (13) and (14), we have the temperature rise on the sample surface \( x = 0 \) as

\[
T_{s,\alpha}(0, t) = \sum_{m=1}^{\infty} B_m \frac{k_s u_m}{l_s} \left[ 1 - \exp \left[ -\frac{(u_m \tau_p)^2}{\tau_a} \right] \right], \quad t \leq \tau_p, \tag{16}
\]
\[ T_{s,r}(0, t) = \sum_{m=1}^{\infty} \frac{B_m k_s u_m}{l_s} \left\{ \exp\left[ \frac{u_m}{\pi} \frac{t}{\tau_s} \right] - 1 \right\} \exp\left[ -\frac{u_m}{\pi} \frac{t}{\tau_s} \right], \quad t > \tau_p. \]

Equations (16) and (17) will be used as the boundary conditions in calculating the temperature rise in the deflecting medium.

The deflecting medium can be regarded as semi-infinite, so the temperature rise with the above initial and boundary conditions Eqs. (5) and (6a) is given by

\[ T_g(x, t) = \frac{1}{\sqrt{\pi}} \int_{x/2 / a_g t}^{\infty} \phi \left( \frac{t - \xi^2}{4 a_g \xi^2} \right) \exp(-\xi^2) d\xi \]

\[ (\text{Ref. 15, p. 63}), \text{where } \phi(t) = T_{s,r}(0, t) \text{ in the active heating interval and } \phi(t) = T_{s,r}(0, t) \text{ in the relaxation interval. By substituting Eqs. (16) and (17) into Eq. (18), we can obtain the temperature rise in the deflecting medium as} \]

\[ T_{g,a}(x, t) = \sum_{m=1}^{\infty} \frac{B_m k_s u_m}{2l_s} \left\{ 2 \text{erfc}\left( \frac{x}{2 \sqrt{a_g} t} \right) - \exp\left[ -\frac{u_m}{\pi} \frac{t}{\tau_s} \right] \times \exp\left( j \frac{\alpha_s u_m x}{a_g l_s} \right) \text{erfc}\left( \frac{x}{2 \sqrt{a_g} t} \right) \right. \]

\[ \left. - j \frac{u_m}{\pi} \sqrt{\frac{t}{\tau_s}} \right) \times \exp\left(-j \frac{\alpha_s u_m x}{a_g l_s} \right) \text{erfc}\left( \frac{x}{2 \sqrt{a_g} t} \right) \]

\[ \left. + \frac{j}{\pi} \frac{u_m}{\sqrt{\frac{t}{\tau_s}}} \right) \times \text{erfc}\left( \frac{x}{2 \sqrt{a_g} t} \right), \quad t \leq \tau_p, \quad (19) \]

\[ T_{g,r}(x, t) = T_{g,a}(x, t) - T_{g,a}(x, t - \tau_p), \quad t > \tau_p. \]

Here \( \text{erfc}(z) \) is the complementary error function.

From the geometric optics theory of photothermal-deflection spectroscopy, the probe beam deflection angle in one dimension can be written as

\[ \varphi(x, t) = \frac{1}{n} \frac{\partial T(x, t)}{\partial x} d, \quad (21) \]

where \( n \) is the optical refractive index of the deflecting medium. \( \partial n / \partial T \) is the temperature coefficient of the refractive index of the medium, which can be regarded as constant (usually negative) when the temperature rise is small. With Eqs. (19) to (21), the deflection angle can be expressed as

\[ \varphi(x, t) = \frac{1}{n} \frac{\partial T(x, t)}{\partial x} d, \quad (22) \]

3. DISCUSSION

To use the above theory to measure the optical and thermal properties of the sample, one needs to solve transcendental Eq. (11) that is associated with the thermal conductivity \( k_s \) of the sample. This in turn means that one needs to know the thermal conductivity to be measured to apply the theory for measuring the thermal properties of the sample, which renders the theory impracticable for experimental measurements. It is, therefore, necessary to find an approach to simplify Eq. (11) so it can be easily solved without knowledge of the sample’s thermal properties. Furthermore, with the real boundary conditions Eqs. (6c)’ and (6d)’, the mathematical expressions of the temperature rise in the sample and the deflecting medium, as well as the probe-beam deflection angle (PD signal), are complicated. It will be helpful for processing the experimental data if the mathematical expressions can be simplified. In the discussion below, we will try to develop an approach and determine its validity and the conditions for the approach and simplification based on some reasonable approximations.

A. Boundary Conditions

For optically opaque samples, the temperature rise is produced mainly at the front surface \( x = 0 \) in Fig. 1. With the physical meaning of \( \tau_s \), one can infer that when \( t < \tau_s \), the heat has not reached the rear surface of the sample, i.e., the temperature rise at the rear surface \( x = l_s \) is then zero; that is, the actual temperature is the ambient temperature, which is equivalent to isothermal contact with the deflecting medium, i.e., \( h_2 \to \infty \). At the front surface of the sample \( x = 0 \), if the thermal conductivity value of the deflecting medium is low, the heat flow crossing the boundary at \( x = 0 \) will be insignificant. So the boundary condition at the front surface of the sample may be approximated by adiabatic insulation \( h_1 \to 0 \) when \( t \) is short and the thickness \( l_s \approx \sqrt{4 k_s / \alpha_s} \) of the thin-skin layer in the deflecting medium adjacent to the sample front surface is thin enough that the thermal ca-
Table 1. Optical and Thermal Properties of Glassy Carbon and Lime Glass

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (kg/m³)</th>
<th>Specific Heat (J/kg K)</th>
<th>Thermal Conductivity (W/m K)</th>
<th>Absorption Coefficient (m⁻¹)</th>
<th>Thermal Diffusivity (m²/s)</th>
<th>Thermal Effusivity (W/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy Carbon</td>
<td>1.45 x 10³</td>
<td>1.1 x 10³</td>
<td>8</td>
<td>10⁶</td>
<td>5.02 x 10⁻⁶</td>
<td>3.57 x 10³</td>
</tr>
<tr>
<td>Lime Glass</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
<td>49</td>
<td>4.6 x 10⁻⁷</td>
<td>1.5 x 10³</td>
</tr>
</tbody>
</table>

*See Ref. 19.
*See Ref. 10; pc = 2.2 x 10⁶ J/m³ K.
*At 647.1 nm.

pacity of the thin-layer medium is negligible and the approximation of Eq. (7) is applicable.

For optically transparent samples, the optical absorption occurs through the sample from \( x = 0 \) to \( l_s \), and so does the temperature rise. The adiabatic approximation might be applied to both front and rear surfaces of the transparent sample if \( t \) were short. Air is the common deflecting medium in PD experiments. In this medium, one may expect that the adiabatic–isothermal (AI) approximation for opaque samples and the adiabatic–adiabatic (AA) approximation for transparent samples will be effective when \( t \) is short because of the lack of conductivity and consequent small value of the heat transfer coefficient \( h \) with air (Ref. 15, p. 20).

With the AI approximation, we can easily solve Eq. (11) without knowledge of sample properties:

\[
\delta_m = (2m - 1) \pi/2l_s, \quad m = 1, 2, 3, \ldots \tag{24}
\]

Similarly, we can determine the solution for Eq. (11) with the AA approximation:

\[
\delta_m = m \pi/l_s, \quad m = 1, 2, 3, \ldots \tag{25}
\]

The mathematical expressions of the temperature rise in the sample and the medium, as well as the PD signal with these two important approximations, are also simplified. The analytical expressions with the AA approximation can be found in Appendix A.

B. Simulations

In the following simulations, we will discuss the conditions and validity of the AI and AA approximations. Glassy carbon\(^{19}\) will be used as an opaque sample and lime glass (72% SiO₂, 18% Na₂O, and 10% CaO in weight)\(^{10}\) as a transparent sample in the simulations. The optical and thermal properties of these two samples can be found in Table 1. In the simulations, the total time, i.e., the sum of the active heating interval (\( t < \tau_0 \)) and the relaxation interval (\( t > \tau_p \)), does not exceed the characteristic diffusion time constant \( \tau_0 \) of the sample. The thickness \( l_g \) of the thin-skin layer in the deflecting medium is estimated by \( l_g \approx \sqrt{4\pi\alpha/\tau_0} \). The parameters we used in the simulations with air and water as the deflecting media are listed in Table 2. The thermal properties of the media can be found in Ref. 20. In our simulations, we will discuss three possible boundary condition cases: (1) the normal (real) boundary case (\( h_1 = h_2 = k_p/l_g \)), (2) the AA approximation (\( h_1 = h_2 \rightarrow 0 \)), and (3) the AI approximation (\( h_1 \rightarrow 0 \) and \( h_2 \rightarrow \infty \)). In the simulation, the criterion for ceasing the summation in

Table 2. Parameters Used in the Simulations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deflection Medium</th>
<th>( l_s ) (mm)</th>
<th>( h ) (W/m²K)</th>
<th>( \tau_0 ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy Carbon</td>
<td>Air</td>
<td>1.0</td>
<td>12.44</td>
<td>0.020</td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td>Water</td>
<td>1.0</td>
<td>3540</td>
<td>0.020</td>
</tr>
<tr>
<td>Lime Glass</td>
<td>Air</td>
<td>3.0</td>
<td>1.255</td>
<td>1.98</td>
</tr>
<tr>
<td>Lime Glass</td>
<td>Water</td>
<td>3.0</td>
<td>357.4</td>
<td>1.98</td>
</tr>
</tbody>
</table>

Eqs. (13), (14), (19), (20), (22), and (23) will be the ratio \( m \)th term: first term < 10⁻³.

1. Temperature Rise in the Samples

The temperature rise in the sample in the active heating interval (\( \tau_p = \tau_0 \)) for different times \( t \) is shown in Fig. 2. For glassy carbon in air, the temperature rises in the three cases at the front surface of the sample almost the same [see Fig. 2(a)]. The relative difference between case (1) and case (2) and between case (1) and case (3) is less than 0.5%. However, at the rear surface of the sample, the AI approximation keeps the temperature rise always at zero, accounting for the difference between case (1) and case (3) when \( t > 0.5\tau_0 \). For an opaque sample such as glassy carbon, the heat source produced after absorption of the heating beam energy is located very close to the front surface of the sample. When \( t \leq \tau_0 \), the heat flow does not reach the rear surface; as a result there is no temperature rise at the rear surface. Thus the AI approximation is valid only when \( t < \tau_0 \).

For the AA approximation, the temperature rise in the sample is almost the same as in case (1) with small relative difference < 1% because of the low value of the thermal conductivity \( k_p \) of air and consequent low heat flux from the sample to air, which is close to the adiabatic situation. Figure 2(b) shows the temperature rise in the glassy carbon sample in water. There is no big difference between case (2) and case (3) at the front surface of the sample. However, there are differences of 4%, 9%, and 13%, between case (1) and case (2) or case (3) when \( t = 0.1\tau_0, 0.5\tau_0, \) and 1.0\( \tau_0 \), respectively, because of the high value of the thermal conductivity of water. One may notice that at the rear surface the difference between case (1) and case (2) is not as great as the differences at the front surface. This smaller difference may be due to the temperature rise at the rear surface and the consequent heat flux from the sample to the medium, which are much lower than that at the front surface.
As opposed to the glassy carbon sample, lime glass is optically transparent, and the heat source is spread over the sample in the direction of its thickness. The low value of \( k_g \) and the small difference in the temperature rises at the front and rear surfaces are the reasons the temperature rises calculated in case (1) and in the AA approximation [case (2)] are almost the same (difference <0.5%) for lime glass in air, as shown in Fig. 2(c). There is a big difference at the rear surface between case (1) and case (3) because the AI approximation keeps the temperature rise at zero at the rear surface of the sample, which is unrealistic for the transparent sample, even with short \( t \). For lime glass in water, Fig. 2(d), the temperature rise at the middle of the sample along the thickness direction is higher than that at its surfaces, and all the approximations deviate from case (1) because of the high thermal conductivity of water and the consequent high heat flux from the glass to water. For \( t < 0.1 \tau_g \), the difference between case (1) and case (2) is smaller than 8%.

2. Temperature Rise and Photothermal-Deflection Angle in the Deflecting Media

The temperature rise in the deflecting medium is dependent on the temperature rise at the front surface of the sample, as predicted by Eq. (18). The photothermal-deflection signal is proportional to the derivative of the temperature rise in the medium, as predicted by Eq. (21). One may expect that if there is good agreement between case (1) and an approximation [case (2) or case (3)] in the temperature rise at the front surface, there will be good agreement in the prediction of the temperature rise in the medium and the PD signal. Figures 3 and 4, in general, meet this expectation. Figure 3 shows the temperature rise in the deflecting media with \( \tau_p = 0.5 \tau_g \) for the active and relaxation intervals. The temperature rises at the front surfaces of the samples in Figs. 3(a) and 3(c) reach a maximum when \( t = 0.5 \tau_g \) and start to fall thereafter. The temperature rise in air falls faster with glassy carbon than it does with lime glass because of the different heat source distributions. It is worth noting that for both samples, the temperature rises at \( x = \sqrt[4]{4 \alpha_g \tau_g} \) in the deflecting medium (air) deviate more from zero with increase of time \( t \), which means that Eqs. (7), (6c'), and (6d') are not applicable when \( t \geq \tau_g \).

Figure 4 shows the time-resolved PD signals with \( \tau_p = 0.5 \tau_g \), at the different positions in the deflecting media. The prediction by AA approximation [case (2)] is in good agreement with that by AI for both samples in air, as shown in Figs. 4(a) and 4(c). It is interesting to note that when the heating beam shuts off, the PD signal does not decrease instantaneously, and the maxima of the signals with different positions in the deflecting media take place at different times. This phenomenon is probably due to

![Fig. 2](image-url)  
![Fig. 3](image-url)  
![Fig. 4](image-url)
the time delay for the probe beam to sense the effect of the termination of the heating beam, depending on the distance \(a\) between the probe beam and the sample front surface in Fig. 1. When the distance \(a\) is small, e.g., \(x = 0.1\sqrt{4\alpha_0 \tau_s}\), the PD signal starts to fall almost immediately. For a larger distance \(a\), the time delay is longer because it takes more time for the heat to diffuse through a longer distance. For the lime glass sample, the time-resolved PD signal decays slower after the termination of the heating beam than the PD signal does with the glassy carbon sample. For the transparent lime glass, the heat source is distributed throughout the sample, while for the opaque glassy carbon it is only within a thin layer close to the front surface. Heat conduction from the inside of the lime glass sample to the deflecting media after termination of the heating beam slows down the PD signal decay. Figure 4(c) shows that the prediction by the AI approximation is not as good as that by the AA approximation for the lime glass sample; this is because of the unrealistic isothermal approximation for the transparent sample.

Concerning the temperature rise in water, Figs. 3(b) and 3(d), neither approximation is very close to case (1). The difference increases with distance \(x\) from the samples to water, especially when \(t > 0.1\tau_s\). Correspondingly, for the PD signals in Figs. 4(b) and 4(d), relative differences of more than 8% can be found at \(x = 0.5\sqrt{4\alpha_0 \tau_s}\) and \(t = 0.5\tau_s\) for both approximations compared with case (1). The difference increases with the decrease of \(|x|\) in the medium.

4. CONCLUSIONS
A novel time-resolved, photothermal-deflection spectrometry with step optical excitation has been proposed with a set of closed-form analytical solutions. For the purpose of the practical application and the simplification of the theory, the adiabatic–adiabatic (AA) and adiabatic–isothermal (AI) approximations have been fully explored to determine their validity. The numerical simulations reveal that for deflecting media with low values of thermal conductivity, such as air, the AA approximation is well suited for both opaque and transparent samples used in the simulations if \(t\) is short, while the AI approximation is applicable only to the opaque sample. For media with high thermal conductivity, e.g., water, neither approximation is very effective. We conclude that these approximations can be effectively used for characterizing solid materials, such as measuring their optical and thermal properties, with this novel spectrometry.

APPENDIX A
With the AA approximation \(h_1 \to 0\) and \(h_2 \to 0\)

\[
\delta_m = m\pi l_s, \quad m = 1, 2, 3, \ldots \quad (A1)
\]

With these boundary conditions, the Green’s function is (Ref. 15, p. 361)

\[
G(x, x', t, \tau) = \frac{1}{l_s \tau_0} \sum_{m=1}^{\infty} \exp\left(-m^2 \frac{t}{\tau_0}\right) \cos \left(\frac{m\pi x}{l_s}\right) \cos \left(\frac{m\pi x'}{l_s}\right).
\]

\[ (A2) \]

By using Eq. (12), the temperature rise in the sample is found to be

\[
T_s(x,t) = q t + \sum_{m=1}^{\infty} E_m[1 - \exp(-m^2 t/\tau_0)] \cos \left(\frac{m\pi x}{l_s}\right),
\]

\[ (A3) \]

\[
T_r(x, t) = q \tau_p + \sum_{m=1}^{\infty} E_m[\exp(m^2 \tau_p/\tau_0) - 1] \times \exp(-m^2 t/\tau_0) \cos \left(\frac{m\pi x}{l_s}\right).
\]

\[ (A4) \]

Here

\[
E_m = \frac{2\beta^2 l_0}{k_s l_s (m\pi l_s)^2[(m\pi l_s)^2 + \beta^2]},
\]

\[ (A5) \]

\[
q = \frac{I_0}{\rho c v^0_s} [1 - \exp(-\beta l_s)].
\]

\[ (A6) \]

The temperature rise in the deflection medium is

\[
T_{g,a}(x, t) = q t \left[1 + \frac{x^2}{2\alpha_g t} \text{erfc}\left(-\frac{x}{2\sqrt{\alpha_g t}}\right)\right.
\]

\[
\left. + \frac{x}{\sqrt{\pi\alpha_g t}} \text{exp}\left(-\frac{x^2}{4\alpha_g t}\right)\right]
\]

\[
+ \frac{E_m}{2} \left[2 \text{erfc}\left(-\frac{x}{2\sqrt{\alpha_g t}}\right)
\right.
\]

\[
\left. - \exp\left(-m^2 t/\tau_0\right)\right]
\]

\[
\times \left[\exp\left(jm \pi \alpha_g x \alpha_g l_s\right) \text{erfc}\left(-\frac{x}{2\sqrt{\alpha_g t}}\right)
\right.
\]

\[
\left. - j m \sqrt{\frac{t}{\tau_0}}\right]
\]

\[
+ \exp\left(-j m \pi \sqrt{\alpha_g x / \alpha_g l_s}\right) \text{erfc}\left(-\frac{x}{2\sqrt{\alpha_g t}}\right)
\]

\[
\left. + j m \sqrt{\frac{t}{\tau_0}}\right]\right], \quad t \leq \tau_p \quad (A7)
\]

\[ T_{g,a}(x, t) = T_{g,a}(x, t) - T_{g,a}(x, t - \tau_p), \quad t > \tau_p \quad (A8) \]

The deflection angles in the active and relaxation intervals are, respectively,
\[ \varphi_a(x, t) = \frac{1}{n} \frac{\partial n}{\partial T} \int \frac{x}{\alpha_s t} \text{erfc} \left( \frac{x}{2 \sqrt{\alpha_s t}} \right) \]
\[ - \frac{2}{\sqrt{\pi \alpha_s t}} \exp \left( -\frac{x^2}{4 \alpha_s t} \right) \]
\[ + \sum_{m=1}^{\infty} D_m \exp \left( -\frac{m^2 t}{\tau_s} \right) \]
\[ \times \left[ \exp \left( jm \pi \sqrt{\frac{\alpha_s x}{\alpha_g l_s}} \right) \text{erfc} \left( \frac{x}{2 \sqrt{\alpha_s t}} \right) \right. \]
\[ - jm \sqrt{\frac{t}{\tau_s}} \]
\[ \left. \exp \left( -jm \pi \sqrt{\frac{\alpha_s x}{\alpha_g l_s}} \right) \text{erfc} \left( \frac{x}{2 \sqrt{\alpha_s t}} \right) \right] \]
\[ + jm \sqrt{\frac{t}{\tau_s}} \right), \quad t \leq \tau_p, \quad (A9) \]
\[ \varphi_r(x, t) = \varphi_a(x, t) - \varphi_a(x, t - \tau_p), \quad t > \tau_p. \quad (A10) \]

Here
\[ D_m = \frac{j}{n} \frac{\partial n}{\partial T} \frac{m \pi}{l_s} E_m, \quad (A11) \]

and \( n \) is the optical refractive index of the deflecting medium.

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