研究速報

Photothermal Spectroscopy Using a Prism-Type Cell

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Photothermal deflection spectroscopy (PDS) which uses a prism-type cell is proposed and analyzed. This method consists of three conceptionally different schemes of deflection. The first one has a perfect collinear and on-axis arrangement, the principle of which involves bulk photothermal change in the refractive index. The second one is similar to a conventional longitudinal PDS scheme. The third one is a hybrid type. A simplified theory is presented and the characteristics of the first scheme are analyzed, the detectability of which is up to the same order of magnitude as that of conventional PDS schemes.

1. Introduction

The fundamental principle of photothermal deflection spectroscopy (PDS), originated by the group at Ecole Superieur de Physique et de Chemie Industriel (ESPCI) in Paris,$^{1-3)}$ involves the use of the spatial gradient of a refractive index caused by the absorption of an excitation beam by a sample and the successive change in the wave front of a probe beam. Two types of beam arrangement have been established to date, that is, longitudinal type and transverse type.$^{4)}$

This spectroscopic scheme achieved an extremely high level of sensitivity with many applications. However, not only is careful attention necessary in the alignment of two beams, but also the restriction of small beam overlap might be deleterious to some applications.

From the point of view described above, a PDS which uses a prism-type cell is proposed and analyzed in this paper.$^{5,6)}$ A simplified theory is presented, the characteristics of the PDS scheme using a prism-type cell are analyzed, and the detectability is estimated.

2. Basic Arrangement of the Photothermal Spectroscopy Using a Prism-Type Cell

In the conventional PDS scheme using a prism-type cell described in this article, there are three types of beam arrangements, two of which are shown in **Fig. 1** (a) and (b). The first one has a perfect collinear and on-axis arrangement, the principle of which involves bulk photothermal change in the refractive index. The second one is similar to a conventional longitudinal PDS scheme. In this type, the spatial gradient of a refractive index caused by the absorption of an excitation beam creates a probe beam which is deflected with inclined beam geometry, a prism working as the beam separator. The third arrangement is a hybrid type, which utilizes both the above-mentioned schemes. In this case, a parallel but partly overlapped beam arrangement and an inclined beam geometry are involved.

3. Signal Analysis

In this analysis, use of a right-angled trigonal prism and a perfect collinear and on-axis beam arrangement of excitation and probe beams is assumed for simplification (Fig. 1 a). The complete overlap of two laser beams makes the probe beam deflection possible due to the bulk effect alone. Signal amplitude in this scheme is derived and compared with the results of Jackson et al.$^{4)}$

Let us consider the situation shown in **Fig. 2.** Here, beam exit angles after refraction by a prism are r_0 and r, which correspond to those when the pump beam is OFF and ON, respectively. (Of course, sinusoidal modulation of the conventional PDS schemes will be available; however, to simplify the analysis we assume ON-OFF modulation here.) The deflection angle ϕ is equal to the difference of r_0 and r. After application of Snell's law, the signal amplitude is given by

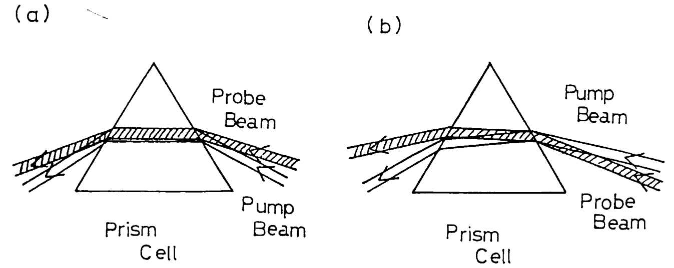

Fig. 1 Beam arrangement type. a) Perfect collinear and on-axis arrangement which utilizes bulk effect. b) Crossed-beam arrangement similar to the conventional PDS, which utilizes the spatial gradient of a refractive index caused by the absorption of an excitation beam. The third one, a hybrid type which utilizes both effects, is not shown here.

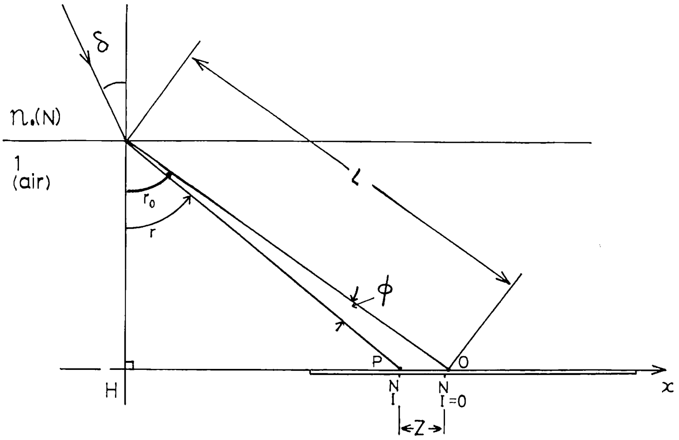

Fig. 2 Basic beam arrangement of the present analysis. δ is the angle of incidence of both the probe beam and excitation beam r and r_0 are angles of refraction of the probe beam when the excitation light is ON and OFF respectively, and ϕ is the angle of deflection. When the sample concentration is N, Z is the distance between positions of the probe beams P and 0, which are the detector positions when the excitation light is ON and OFF, respectively. Measurement is assumed to be performed on the x-axis, from the point H.

$$\begin{aligned}\phi &= r_0 - r\\ &= \sin^{-1}(n_0 \sin\delta) - \sin^{-1}(n \sin\delta) \qquad (1)\end{aligned}$$

where n_0 and n denote the refractive index of the bulk medium when excitation is absent and present, respectively, and δ means an angle of incidence into a prism cell.

If we expand arcsine with Taylor's formula, the signal amplitude is given by

$$\begin{aligned}\phi &= \frac{1}{\sqrt{1-n_0^2\sin^2\delta}}(\Delta n \sin\delta)\\ &\quad + \frac{1}{2}\frac{n_0 \sin\delta}{(1-n_0^2\sin^2\delta)^{3/2}}(\Delta n \sin\delta)^{3/2} + \cdots \qquad (2)\end{aligned}$$

where Δn $(=n_0 - n)$ represents the deviation of the refractive index from its equilibrium value.

The signal analysis in the case of a parallel but off-axis collinear arrangement using a nonfocused beam will be calculated in a similar way, if we can neglect the effect of heat diffusion across the inclined window at an interface between the absorbing medium and a cell window. In this case, the beam deflection formula of the theory of Jackson et al.[4] will be modified somewhat by refraction by a prism; however, no results significantly different from those of the conventional PDS will be obtained. Furthermore, the analysis for the hybrid type, in which all processes described above could possibly occur, will be more complicated and thus will be presented elsewhere.

In the analysis of collinear PDS,[4] a beam deflection angle for a Gaussian pump beam at low frequency, in which thermal diffusion length μ_s is much larger than the pump beam redius a, is given by

$$\phi=\frac{\mathrm{d}n}{\mathrm{d}T}\frac{P}{\kappa\pi^2 x_0}[1-\exp(-\alpha l)]\left[1-\exp\left(\frac{-x_0^2}{a^2}\right)\right] \tag{3}$$

where P is the power of an excitation laser beam, κ means the thermal conductivity of the medium, and x_0 denotes the distance between excitation and probe beams. The parameter α denotes the absorption coefficient of the medium under consideration.

In a high-frequency case, in which the thermal diffusion length is much smaller than radius ($\mu_s < a$), the results of a collinear PDS are rather modified as

$$\phi=\frac{\mathrm{d}n}{\mathrm{d}T}\frac{P}{\omega\rho c\pi^2 a}[1-\exp(-\alpha l)]\times\left[-\frac{2x_0}{a^2}\exp\left(-\frac{x_0^2}{a^2}\right)\right] \tag{4}$$

where ω and ρ denote the angular frequency of modulation and the density of the medium, respectively.

The formula of the deflection angle given by the theory of collinear PDS[4] is shown as

$$\phi=\frac{1}{n_0}\frac{\mathrm{d}n}{\mathrm{d}T}\int_0^l \nabla T(\bar{r})\mathrm{d}z=l\frac{\mathrm{d}n}{\mathrm{d}T}\frac{\mathrm{d}(\Delta T)}{dx_0} \tag{5}$$

where l denotes the optical path length of a probe beam within a cell. We regarded n_0 as unity for borderless media, and gradient of temperature T as equal to the gradient of temperature deviation ΔT.

In a high-frequency case, the simplified theory gives the temperature rise as

$$\Delta T=\frac{1}{\rho c}\int \alpha I_{\mathrm{p}}\mathrm{d}t=\frac{1}{i\omega\rho c}\frac{\alpha P}{\pi a^2} \tag{6}$$

where I_{p} represents the intensity of the pump beam.

We will derive a formula for the low-frequency case by the use of the relation

$$\frac{i\omega\rho c}{\kappa}=\frac{i\omega}{k}=K_1{}^2. \tag{7}$$

This is the ratio of Eqs. (3) and (4). Hence, the temperature rise is given by

$$\Delta T=\frac{1}{\rho c}\int \alpha I_{\mathrm{p}}\mathrm{d}t=\frac{1}{\kappa}\frac{\alpha P}{\pi a^2} \tag{8}$$

where the parameters used are the same as those used in Ref. 4.

The above relations will be compared with the results derived from Eq. (2). As a result, the formula for the deflection angle in linear theory in this configuration is given as

$$\phi=\frac{\sin\delta}{\sqrt{1-n_0^2\sin^2\delta}}\frac{\mathrm{d}n}{\mathrm{d}T}\frac{P}{\kappa\pi a^2}N\sigma(\lambda) \tag{9}$$

where the relation between absorption coefficient α and absorption cross section $\sigma(\lambda)$,

$$\alpha=N\sigma(\lambda), \tag{10}$$

is used, and N denotes the concentration of the sample. Equation (9) shows that the beam deflection angle ϕ is proportional to sample concentration N.

4. Estimation

In this section, the comparison between near collinear PDS, collinear prism-cell PDS and the experimental conditions for the latter case will be discussed and analyzed. The deflection angle for the near collinear PDS for Gaussian pump and probe beams in the low-frequency region is shown in Eq. (3); on the other hand, that of prism-cell PDS is shown in Eq. (9). The two equations are different by the factors

$$\frac{1}{x_0}\left[1-\exp\left(\frac{-x_0^2}{a^2}\right)\right] \tag{11}$$

and

$$\frac{1}{l}\frac{n_0^2\sin\delta}{\sqrt{1-n_0^2\sin^2\delta}}. \tag{12}$$

In the case of collinear PDS, in which maximum deflection will occur at $x_0=a$, Eq. (11) is equal to

$$\frac{0.864668}{a}$$

while, if we let $\delta=\pi/6$ (equilateral prism), $n_0=1.334$ (water), and $\sin\delta=1/2$, then Eq. (12) is equal to

$$\frac{0.3335}{l}.$$

If we assume the laser beam radius $a=40\,\mu$m and the length of the prism cell $l=20$ mm, then the ratio of the deflection angle of collinear PDS to that of PDS with a prism will be

$$\frac{\phi_{\text{prism}}}{\phi_{\text{collinear}}}=7.7\times10^{-4}. \tag{13}$$

The minimum detectable product of the absorption coefficient and sample length multiplied by laser power $(\alpha L)_{\min}\times P$ [W] for collinear PDS is estimated to be 10^{-7}-10^{-8} [W].[4] Thus, that of PDS with a prism cell will be on the order of 10^{-3}-10^{-4} [W], which is the same order of magnitude as that of transverse PDS.

5. Conclusions

In the present paper, a PDS scheme using a prism-type cell is proposed,[5,6] which liberates the restriction of rigorous beam alignment of the conventional PDS schemes because of its ease of optical alignment. This scheme consists of three types of beam arrangements and deflections. The first one has a perfect collinear and on-axis arrangement, the principle of which involves bulk photothermal change in the refractive index. The second one is similar to a conventional longitudinal PDS scheme. The third one is a hybrid type, which utilizes both the above-mentioned schemes. A simplified theory was presented for the first type and the characteristics were analyzed. The detectability on the same order of magnitude as that of a transverse arrangement is obtained.

The author suggests that this scheme is available not only for liquid phase trace chemical analysis but also for surface plasmon spectroscopy and solid state spectroscopy. Furthermore, even thermal lens measurement with a prism cell will be possible in which separation of the pump and probe beams plays a dominant role, where not only a conventional counter-beam arrangement but also a collinear beam arrangement will be feasible.

[Note] Very recently, the group at Okayama University presented calculations of PDS using a prism with excitation from the side of a prism cell⁷⁾. Their scheme is included in our general beam arrangements of three types, which can include excitation with an arbitrary angle between the probe light and excitation light. However, our pioneering work of the PDS with a prism cell (proposal, analysis and experiment)⁵,⁶⁾ was not mentioned in Ref. 7).

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