Development of photoacoustic spectroscopy with a piezofilm

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Received 16 January 2007; accepted 20 February 2007;
posted 12 March 2007 (Doc. ID 79014); published 20 June 2007

We have developed photoacoustic spectroscopy with a piezofilm. A piezofilm is a piezoelectric element made from plastic polyvinylidene fluoride having piezoelectrical effect. Photoacoustic spectra (375–675 nm) of water, dye aqueous solution, and benzene, are measured with a xenon lamp. The piezofilm is directly immersed in the liquid samples for sensitive detection of the signal. The sensitivity of the method is shown to be as high as for photothermal deflection spectroscopy. Compared with the conventional methods such as photoacoustic spectroscopy with a piezoceramic and photothermal spectroscopy with a double beam configuration, the present method is favorable from its handy and simpler experimental setup. © 2007 Optical Society of America

OCIS codes: 160.1890, 190.4870, 230.0040, 300.6430.

1. Introduction

Understanding of nonradiative decay process due to electron-lattice interaction is essential for designing a highly luminescent material. For experimental research of such a material, photothermal or photoacoustic spectroscopy [1,2] is often employed because it offers a direct means to trace a nonradiative decay path. Photoacoustic spectroscopy is effective for extracting optical absorption from any material, such as strongly scattering solids, gelsol samples, powder samples, biomaterials, and optically opaque, nonluminescent materials [3–5].

A piezofilm is a piezoelectric element made from polyvinylidene fluoride (PVDF) having piezoelectrical effect. Piezofilms are used as various measurement elements and devices today [6–9]. In comparison with the conventional piezoceramic, they possess good flexibility, crash worthiness, high-voltage resistance, water resistance, and chemical stability. When bonded to any vibrating surface, the bulk waves in the vibrating object are converted to an electrical signal by the sensor, which accurately characterizes both frequency and amplitude of vibration. In this paper, we have applied a piezofilm to photoacoustic spectroscopy for the first time to the best of our knowledge.

2. Experimental

A piezofilm (LDT0-028K) was purchased from Tokyo Sensor. For the piezofilm, a PVDF film is sandwiched between silver electrode films coated with a thin protective plastic, so that it is resistant to water but not to a strong organic solvent. The samples measured were distilled water, a 0.04 wt. % aqueous solution of sodium copper chlorophyllin (CuChl), and benzene. Sodium CuChl (Kanto Chemical, Tokyo, Japan) and benzene (Wako Pure Chemical, Osaka, Japan) were used without further purification. For the measurement of liquid by conventional photoacoustic spectroscopy, a sensor is installed outside a liquid cell [10], and a light source is a tunable laser. In the present study, we used a 150 W xenon (Xe) lamp (Hamamatsu L2274) for the light source because we need the spectra in the whole visible region (375–675 nm). The average power of the excitation light after wavelength selection is much lower (by 2–3 orders of magnitude) than that of a laser. Therefore it is important to detect a photoacoustic wave with no intervention between a liquid sample and a piezoelement, so that the piezofilm is directly immersed in the liquid.

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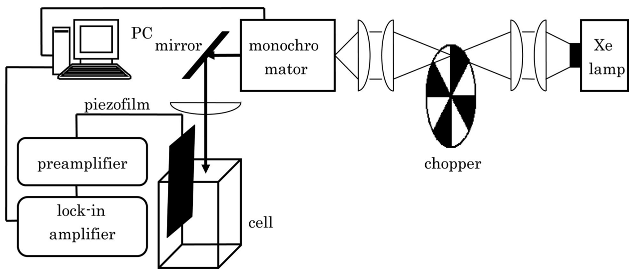

Fig. 1. Experimental arrangement in PFPAS. The intensity of the irradiation light is 0.2–0.65 mW/cm^2. The piezofilm is immersed in the liquid directly in the open glass cell of 20 mm × 10 mm × 38 mm in capacity. All the measurements are performed in a darkroom at room temperature.

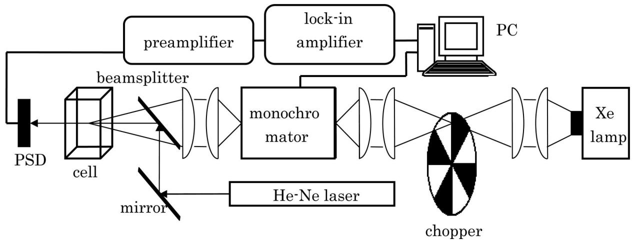

Fig. 2. Experimental arrangement in PBD spectroscopy. The intensity of the pump light is 0.4–0.9 mW/cm^2. The average power of the probe light is 146.3 mW, and it is 5.6 mW at the PSD. PSD is a position sensitive detector. The cell is an open quartz cell of 20 mm × 20 mm × 38 mm capacity. All the measurements are performed in a darkroom at room temperature.

Figure 1 shows the experimental arrangement. Since the optical system is simple, we can set it up easily. The cell, into which a sample was put, was an open glass cell of 20 mm × 10 mm × 38 mm in capacity. The thickness of the glass was 2.0 mm. To minimize the signal from the glass, the excitation light was irradiated from above (open side of the cell) to the sample. The piezofilm was wrapped in a protective film (semitransparent Parafilm) painted black. This film prevents scattered excitation light from hitting the piezofilm directly. The film may dampen a photoacoustic wave as well, but without the film, the contribution of the scattered light dominates the signal over that of the photoacoustic signal, resulting in the measurement of just the excitation light spectrum. To minimize visible-light absorption by the film, painting the protective film white would be better. The protective film also helps to reinforce the resistance of the piezofilm to an organic solvent. All lenses used were achromatic lenses. White light from the Xe lamp was chopped at 20 Hz and then monochromated through a 15 cm spectrometer (Acton SP-150) with wavelength resolution of 25 nm. The signal from the piezofilm was sent to a preamplifier and then to a lock-in amplifier (Signal Recovery 7265). The signal was recorded at every 2.5 nm with a time constant of 5 s.

For comparison, we applied photothermal beam-deflection spectroscopy (PBD) to the samples. PBD is one of the most effective photothermal spectroscopic methods, developed early in the 1980s to measure small absorption [2,11–13]. Because it is a noncontact method, it is best suited for the nondestructive measurement of absorption spectra of a sample, and it is useful for optical characterization of a semiconductor for which a dust and a flaw are harmful [14]. In addition, PBD is the most suitable for measuring optical absorption of polymers because it is insensitive to light scattering [15]. PBD now occupies the position of the standard method of photothermal spectroscopy, instead of photoacoustic spectroscopy using piezoelements.

Figure 2 shows the experimental arrangement for PBD. Surprisingly, there have been few reports on the absorption measurement of liquid itself by PBD [11], and the use of a broadband lamp source in PBD is exceptional as in Ref. 15, where a 1 kW Xe lamp is used. Here, the heating (pump) light source was a 150 W Xe lamp such that the measurement conditions were the same as in piezofilm photoacoustic spectroscopy (PFPAS), except for the chopping frequency, which was set at 120 Hz. The probe light source was a He–Ne laser (633 nm), and a position-sensitive detector [(PSD) Hamamatsu S5991-01] was used for detection. The pump and the probe beams were aligned almost collinearly with a beam splitter and were irradiated into a sample with a small angle. The pump light was focused through a lens into the sample, while the probe light was not, in order to get the maximum spatial overlap in the sample. The signal intensity of pump–probe-type measurements as in the case of PBD is inversely proportional to the focused area when both beams can be focused into the same spot size, but it is limited by the inverse of a larger spot size when the focusability is different between the two beams. Here, the signal intensity is limited by the focusability of the Xe lamp. The pump beam power is absorbed by the sample and is converted to heat. The temperature increase in the focused volume leads to the refractive index change, causing the probe beam deflection. The transmitted probe beam was detected on the PSD, which is placed 40 cm away from the cell in order to magnify the pump-induced deflection of the probe beam and to avoid the pump beam being incident on the PSD. The intensity change of the probe as a function of the pump wavelength is proportional to the absorption spectrum when it is normalized to the pump-light power spectrum. The pump-light intensity was almost the same as in PFPAS.

3. Results

Figure 3 shows the results of absorption measurement by PFPAS for distilled water, aqueous solution of sodium CuChl (0.04 wt. %), and benzene (100 wt. %). Since the intensity of irradiation light varies as a function of wavelength, the signal intensity was divided by the irradiation light intensity.

Water is a colorless transparent material, but it has weak absorption on the infrared side in the visible region due to overtones of OH stretching mode [16,17]. The measurement of light absorption of water is difficult by the conventional transmission spec-

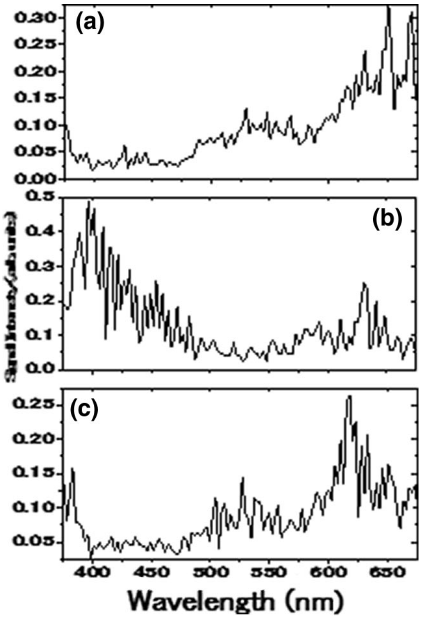

Fig. 3. Measurement results by PFPAS for (a) distilled water, (b) CuChl aqueous solution (0.04 wt. %), and (c) benzene (100 wt. %). The signal intensity was divided by the irradiation light intensity.

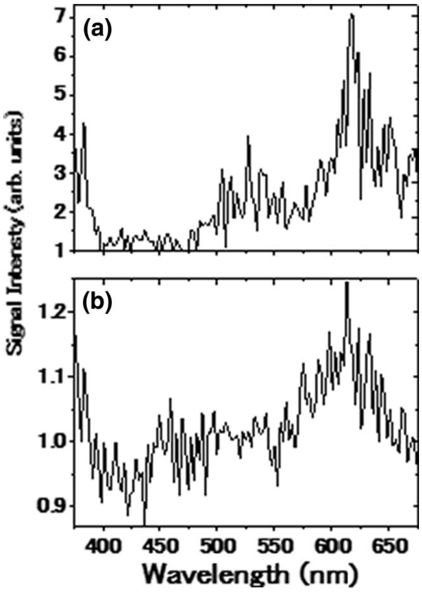

Fig. 4. Measurement results by (a) PFPAS and by (b) PBD for benzene (100 wt. %). The result is normalized so that signal intensity is 1 at 450 nm.

troscopy because reflection and scattering of light has much influence on the spectrum. The light absorption spectrum of water was measured previously by the photoacoustic spectroscopy with a pulsed dye laser and a specially designed cell in contact with a piezoelectric transducer [18]. We have obtained the similar absorption spectrum of water on the infrared side without using a laser or a complicated cell.

Sodium CuChl is a stable dye imitating chlorophyll and has two main absorption bands in the visible at ~400 and ~630 nm [19,20], known as B and Q bands. This dye has a very low luminescence quantum yield, so that it is suitable for confirming the validity of the present method. The photoacoustic spectrum shows the absorption peaks at the same wavelength region as the known dye absorption spectrum. In this way, it is demonstrated that the method is applicable to an aqueous dye solution. As it is not expected, however, despite its large absorbance, the signal quality is much lower than that measured with a spectral photometer, i.e., by the conventional transmission spectroscopy (not shown). The lower signal intensity for the dye solution suggests that the amplitude of photoacoustic wave decreases before it arrives at the piezofilm. The details of this mechanism are examined in Section 4.

The photoacoustic spectrum of benzene shows the peak in the vicinity of 615 nm. The signal originates from very feeble vibration of the sixth harmonic of C–H stretching mode [21]. This is an optically forbidden transition, so that the measurement of light absorption is difficult with the conventional transmission method. According to a former photoacoustic measurement, the peak arises at 607 nm [21], where a dye laser of 30 mW average power is used for excitation. By contrast, the Xe lamp is used in the present experiment, so that the intensity of the dispersed light after the spectrometer is very weak. It is typically 0.25 mW, by 2 orders of magnitude lower than in Ref. 21. The absorption peak position may depend on the intensity of excitation light, as supported by a report that the absorption peak of benzene measured with white light is located at ~610 nm [22]. The harmonic frequency may change if anharmonicity of the potential for the C–H stretching mode depends on the excitation light intensity. However, presently it is difficult to clarify the mechanism. In addition, the wavelength resolution must be further improved for confirming the result.

Figure 4 shows a comparison of the results for benzene between the two methods, PFPAS and PBD. The absorption peaks corresponding to the vibration of the sixth harmonic appear at the same position. The excitation light intensity and the wavelength resolution of the spectrometer are almost the same. Figure 4 shows that the signal-to-noise ratio (SNR) is similar for both the results in PFPAS and PBD. Therefore we can conclude that PFPAS is as effective as PBD. Considering the easier experimental setup with the single beam, the former has an advantage over the latter. Generally high SNR can be obtained in standard PBD, but it relies largely on the use of a laser light source, for which the excitation light can be tightly focused to enhance the refractive index change, which is proportional to the excitation intensity.

4. Discussion

For aqueous solution of CuChl, the signal intensity is low despite its large absorbance. As shown in Fig. 3, the ratio of signal intensity (measured in voltage by lock-in detection) of CuChl to water is ~10 at

~400 nm, which is much smaller than the absorbance ratio of them ~500.

To study the reason for the smaller signal for CuChl in piezofilm spectroscopy, we measured cobalt (II) chloride aqueous solution (0.1 M), where $[Co(H_2O)_6]^{2+}$ complexes are formed, by the same method in comparison. The result (not shown) shows that the signal intensity almost reflects the sample absorbance, which is ten times larger than for water. Therefore, it is suggested that CuChl solution is an exceptional case where the photoacoustic signal intensity is weakened for some reason. To study the reason further, we applied PBD to water, CuChl aqueous solution (0.04 wt. %), and cobalt (II) chloride aqueous solution (0.1 M). The results show that the signal intensity for each sample is almost proportional to its absorption strength. Since both PFPAS and PBD detect heat converted from the absorbed light in the samples, it is concluded that the generated heat quantity is proportional to the absorbed light intensity for all the samples.

The difference in the two methods resides in how to detect the heat. In PBD, the probe beam and the pump beam are focused in the same spot such that deflection of the probe is proportional to the heat generated in the spot, while in PFPAS, the heat is detected by the film distant from the spot where the acoustic wave is generated. It is therefore concluded that the photoacoustic signal decays during the propagation to the piezofilm for CuChl solution. We analyzed this phenomenon on the theory for the saturation effect of photoacoustic spectroscopy (PAS) [23,24] as follows.

The excitation light beam decays in intensity along the propagation distance and the absorbed light intensity is proportional to the light intensity at that position. For the absorption coefficient β, the generated heat distribution $F(x)$ is depicted by Fig. 5 as a function of x, distance from the solution surface ($x = 0$) toward the bottom ($x = d$) in the cell. Here, it is assumed that all the absorbed light is converted to heat. The piezofilm is positioned in parallel to the excitation beam and is immersed to the half ($x = d/2$) the cell depth. The beam cross section is ~10 mm × 5 mm, and the distance between the beam edge and the piezofilm is 3–5 mm. For simplicity, we neglected the cross section and the distance compared with $d = 38$ mm to reduce the problem to one dimension. Then, the heat detected at an arbitrary point $x = x'$ on the piezofilm is expressed by

$$F(x') = \int_0^{x'} \mathrm{d}x\, \beta \exp(-\beta x)\exp\left(-\frac{x'-x}{L}\right) + \int_{x'}^{d} \mathrm{d}x\, \beta \exp(-\beta x)\exp\left(-\frac{x-x'}{L}\right), \qquad (1)$$

where L is the thermal diffusion length of the solution given by [24]:

$$L = 2\pi\left(\frac{\alpha}{\pi f}\right)^{1/2}. \qquad (2)$$

Here, α is the thermal diffusion rate, and f is the modulation frequency of the excitation light. The total heat detected by the whole surface of the piezofilm is calculated by the integration:

$$Q(f) = \int_0^{d/2} \mathrm{d}x' F(x'). \qquad (3)$$

The results of calculation of Eq. (3) as a function of f are shown in Fig. 6, with substitution of the absorption coefficient of the three samples at 400 nm for β and the thermal diffusion length of water for L [24]. The ratio of Q/β for water and $[Co(H_2O)_6]^{2+}$ is almost the same, but that for CuChl is by 40 times smaller at $f = 20$ Hz. For a large absorption sample, therefore, the signal by PFPAS in the present experimental geometry is not proportional to the absorption coefficient due to the saturation effect. To verify the calculated results, we measured the frequency dependence of the signal for water and CuChl at 400 nm by PFPAS. The experimental results shown in Fig. 7 are

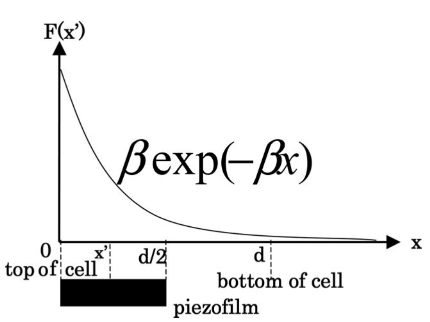

Fig. 5. Generated heat distribution and the position of the piezofilm in the cell. The liquid surface is at $x = 0$, the bottom of the cell is at $x = d$, and the end of the piezofilm is at $x = d/2$.

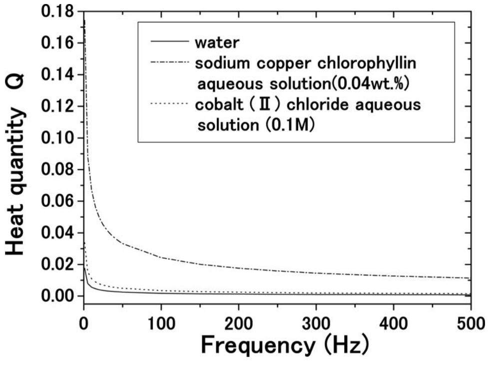

Fig. 6. Results of calculation of Eq. (3). Solid curve for water with $\beta = 0.035$ cm^{-1}, dashed–dotted line for aqueous solution of CuChl (0.04 wt. %) with $\beta = 17.3$ cm^{-1}, and dotted curve for cobalt (II) chloride aqueous solution (0.1 M) with $\beta = 0.07$ cm^{-1} at 400 nm.

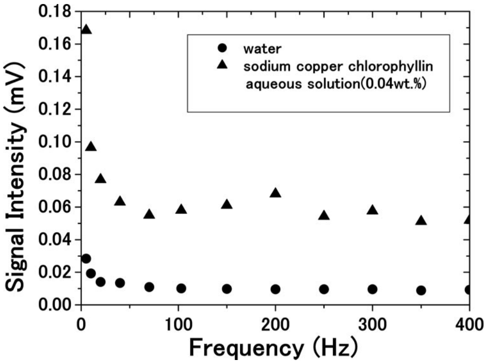

Fig. 7. Frequency dependence of the signal intensity by PFPAS for water and CuChl aqueous solution (0.04 wt. %). The signal is in the unit of voltage by lock-in detection.

semiquantitatively reproduced by the calculated results in Fig. 6, so that the proposed mechanism of the lower photoacoustic signal intensity for CuChl is verified.

5. Summary

We have introduced a piezofilm as a detecting element to photoacoustic spectroscopy and have measured liquid samples in a glass cell. For the experimental setup, it is enough to wrap the piezofilm in a protective film and immerse it in the liquid. The experimental setup is easier than the conventional method, such as photoacoustic spectroscopy with a photoacoustic cell of complicated structure and photothermal deflection spectroscopy with a double beam configuration. We showed that the sensitivity is comparable with that in photothermal deflection spectroscopy. For large absorption samples, the signal is not proportional to the absorption strength but saturates due to the geometrical reasons. The signal-to-noise ratio can be further improved by shielding the setup from external noise and by increasing the excitation light power through the use of a prism spectrometer, a higher power lamp with a retroreflector, and a larger light collection solid angle. In the present setup, there is much room for these improvements.

The authors thank Yoichi Ogo and Daisaku Ichitsubo for their help and advice on the experiment and Nobuhisa Ishii for the programming of the computer control software for the measurement.

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