Photoacoustic Spectrometry Coupled with Total Internal Reflection Technique: Theory and Experiment

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Theoretical expressions of photoacoustic signals generated in liquid in normal and oblique incidences of a laser beam are derived by modifying the Rosencwaig and Gersho theory for the investigation of distribution profiles of light absorbing species at solid-liquid interfaces. Expressions for both incidences show that the photoacoustic signal magnitudes are dependent on instrumental, solvent and thermal diffusion factors. The results expected from the expressions are in agreement with experimental results. This modified theory is expected to be applicable to liquid samples with any transparency.

Keywords Photoacoustic spectroscopy, total internal reflection, modulated laser excitation, solid-liquid interface

In previous studies^{1,2}, we developed photoacoustic spectrometry coupled with a total internal reflection technique (TIR-PAS) with the aid of a direct coupling method in which a piezoelectric transducer is in contact with a sample liquid, applied it to the measurement of a concentration distribution profile of light absorbing species at a glass-aqueous solution interface with a high spatial resolution of submicron, and showed experimentally that the photoacoustic (PA) signal magnitude was proportional to optical path length (effective thickness) and dye concentration. In addition, the PA signal is dependent on thermal and mechanical properties of a sample solution as well as on instrumental characteristics. Therefore, when TIR-PAS is applied to investigation of PA signal generation in different solvents, the PA signal magnitudes should be normalized for the different solvents. Many authors have treated PA signal generation in liquid by pulsed³⁻⁶ or modulated excitation^{3,7-10} theoretically, and have applied PA spectroscopy with the direct coupling method to trace analyses¹¹⁻¹³, measurements of weak absorptions^{4,14,15} and similar studies.^{3,6} However, there are no theories to be applied to TIR-PAS where the PA signal is induced by evanescent light emerging from the glass into an extremely thin region of the solution close to the interface. In order to obtain theoretical expressions of PA signal generation in TIR-PAS, a one-dimensional model where a sinusoidally modulated laser beam impinges on one side and a PA signal is detected on the other side has been adopted by modifying the Rosencwaig and Gersho theory (RG theory).^{16,17} The present paper reports theoretical expressions for normal and oblique incidences of a laser beam derived mathematically. Experimentally, the PA signal magnitude depends on an instrumental term

in the expressions, including light source power and modulation frequency.

Theoretical

Theoretical treatments of PA signal generation in liquids have been carried out for a transparent sample

Fig. 1 Schematic cross sectional view of PA cell. P, S and D mean a glass prism, a sample solution and a piezoelectric transducer, respectively. l , d , $\mu_\beta (=1/\beta)$ and $\mu_a (=1/a_s)$ denote thickness, penetration depth, optical penetrating length and thermal diffusion length, where β and a_s are optical absorption coefficient and thermal diffusion coefficient. The values of μ_β and μ_a are arbitrary.

occupying a cylindrical piezoelectric transducer.⁷⁻¹⁰ However, when the light beam travels in an opaque sample solution or when total internal reflection generates evanescent light in the sample solution, the light power may be attenuated remarkably at a distance as short as a thermal diffusion length of the sample. In such cases, it is useful to express the PA signal as a function of distance along the axis of the light beam and it is expected that the PA signal will depend on thermal diffusion. Figure 1 shows schematic cross sectional views of the PA cell for normal and oblique incidences. A hemicylindrical glass prism, P, serves as an optical window and an internal reflection element, D is a piezoelectric transducer for detecting pressure change and between them is a sample solution, S. The origin of the coordinate is located at the P-S boundary. According to expressions by Nowacki¹⁸, the temperature change caused by an acoustic wave being neglected^{7,8}, the temperature difference from surroundings in each matter, $T(x,t)$ [K], the scalar potential, $\Phi(x,t)$ [m²] and the heat produced by light absorption, $H(x,t)$ [W/m³], satisfy the following equations:

$$\partial T_p(x, t)/\partial t = \alpha_p[\partial^2 T_p(x, t)/\partial x^2] \quad (-l_p \leq x \leq 0) \quad (1a)$$

$$\partial T_s(x, t)/\partial t = \alpha_s[\partial^2 T_s(x, t)/\partial x^2] + H_s(x, t)/C_{ps}\rho_s \quad (0 \leq x \leq l_s) \quad (1b)$$

$$\partial T_d(x, t)/\partial t = \alpha_d[\partial^2 T_d(x, t)/\partial x^2] \quad (l_s \leq x \leq l_s + l_d) \quad (1c)$$

$$\partial^2 \Phi(x, t)/\partial x^2 - (1/v^2)[\partial^2 \Phi(x, t)/\partial t^2] = \alpha_T T_s(x, t) \quad (0 \leq x \leq l_s), \quad (2)$$

where x [m] denotes the coordinate, t [s] time, $\alpha = k/C_p\rho$ [m²/s] the thermal diffusivity, k [W/(m K)] the thermal conductivity, C_p [kJ/(kg K)] the specific heat, ρ [Mg/m³] the density and l [m] the thickness. The three subscripts, p, s and d, stand for the glass prism, the sample solution and the transducer. In addition v [m/s] and α_T [K⁻¹] denote the sound velocity in the sample solution and its isothermal expansion coefficient, respectively. In eqs. (1a) and (1c), $H_p(x,t)$ and $H_d(x,t)$ are equal to zero, because no heat generates due to the transparency of the glass prism and no light beam reaches the S-D boundary due to the opaqueness of the sample solution. However, when the sample solution is transparent, $H_d(x,t)$ is not equal to zero. This case will be treated only theoretically on the assumption that no heat generates in the transducer. Continuity of temperature and of heat flux are assumed as boundary conditions at both ends of the sample solution for the thermal diffusion equations (1), thus

$$T_s(0, t) = T_p(0, t) \quad (3a)$$

$$k_s \times \partial T_s(x, t)/\partial x|_{x=0} = k_p \times \partial T_p(x, t)/\partial x|_{x=0} \quad (3b)$$

$$T_s(l_s, t) = T_d(l_s, t) \quad (3c)$$

$$k_s \times \partial T_s(x, t)/\partial x|_{x=l_s} = k_d \times \partial T_d(x, t)/\partial x|_{x=l_s} \quad (3d)$$

And conditions of rigidity at both boundaries can be applied to the wave equation (2), because the acoustic impedance of the transducer is several dozen times higher than those of the sample solutions tested in this work. Thus the displacement $U(x,t)$ [m] is expressed as

$$U(0, t) = 0 \quad (4a)$$

$$U(l_s, t) = 0, \quad (4b)$$

where $U(x, t) = \partial \Phi(x, t)/\partial x$. The PA signal, $P(x, t)$ [N/m²] is expressed as $P(x, t) = \rho_s \times \partial^2 \Phi(x, t)/\partial t^2$ and the observed PA signal magnitude, P_{obs} [V], is given as follows:

$$P_{obs} = K \times |\rho_s \times \partial^2 \Phi(x, t)/\partial t^2|_{x=l_s} = K \times |P(l_s, t)|. \quad (5)$$

Here K [V m²/N] is the conversion coefficient which includes an output voltage coefficient of the piezoelectric transducer and circuit characteristics of the amplification instruments used.

In the case of normal incidence

The power of a sinusoidally modulated monochromatic light beam with an angular frequency of ω [rad/s] is expressed as follows:

$$I = (1/2)I_0[1 + \exp(i\omega t)]. \quad (6)$$

When the light beam falls normally upon the P-S interface and the light is absorbed by the sample solution, the heat generated at x is

$$(1/2)\beta I_0 \exp(-\beta x)[1 + \exp(i\omega t)]$$

where I_0 [W/m²] and β [m⁻¹] are the light source power and the optical absorption coefficient, respectively. When the above term is substituted for $H_s(x,t)$ in eq.(1b), the resulting thermal diffusion equation is quite similar to that in the RG theory. An alternating component of a solution of the equation is given for $0 \leq x \leq l_s$ by

$$T_s^{ac}(x, t) = B[D_1 \exp(\sigma_s x) + D_2 \exp(-\sigma_s x) - \exp(-\beta x)] \exp(i\omega t), \quad (7)$$

where $B = \beta I_0 / 2k_s(\beta^2 - \sigma_s^2)$ and D_1 and D_2 are coefficients determined by the boundary conditions of eqs. (3). The complex σ_s is $(1+i)a_s$, where $a_s = \sqrt{\omega/2\alpha_s}$ [m⁻¹] is the thermal diffusion coefficient. Substitution of eq. (7) into eq. (2) leads to a solution for the scalar potential,

$$\begin{aligned} \Phi^{ac}(x, t) = & \alpha_T B \{ E_1 \exp(ikx) + E_2 \exp(-ikx) \\ & + [D_1/(\sigma_s^2 + k^2)] \exp(\sigma_s x) \\ & + [D_2/(\sigma_s^2 + k^2)] \exp(-\sigma_s x) \\ & - [1/(\beta^2 + k^2)] \exp(-\beta x) \} \exp(i\omega t), \end{aligned} \quad (8)$$

where $k=\omega/\nu$ [rad/m] is the angular wave number and E_1 and E_2 are determined by the boundary conditions of eqs. (4). Consequently, the sinusoidal PA signal is derived from the expression $P(x, t)=\rho_s \times \partial^2 \Phi(x, t)/\partial t^2$, as follows:

$$P(l_s, t) = -\rho_s \omega^2 \Phi^{ac}(l_s, t). \quad (9)$$

The general equation (9) can be transformed into two typical forms according to relative magnitudes of the thermal diffusion coefficient, a_s , the optical absorption coefficient, β , and the angular wave number, k . Because a_s is several orders of magnitude larger than k at the angular frequencies from 10 Hz to 1 kHz, a_s can be made comparable with β . (Hereafter the ratio β/a_s will be represented by q .) In addition, because the product of kl_s is much smaller than unity for tested systems where $\nu=1.5 \times 10^3$ m/s, $\omega < 2\pi \times (1 \text{ kHz})$ and $l_s = 2 \times 10^{-3}$ m, and thus $kl_s < 8.4 \times 10^{-3}$, the approximation that $\sin(kl_s) \approx kl_s$ will be used.

Transparent sample solution ($q \approx 0, k \gg \beta$). When $q \approx 0$, the last term in the right hand side of eq. (8) contributes to $\Phi^{ac}(l_s, t)$ most significantly and thus

$$P(l_s, t) \approx (i/2)(I_0/\omega)(\alpha_{TV}^2/C_{ps})\beta \exp(i\omega t). \quad (10)$$

Equation (10) shows proportionality between the PA signal magnitude and the absorption coefficient and consequently suggests that our PA spectrometry can be applied to PA spectrometric determination. However, our PA cell can not be used for normal incidence owing to its configuration (Fig. 2).

Opaque sample solution ($q \geq 1$). When $q \geq 1$, the first two terms of the right hand side of eq. (8) contribute to $\Phi^{ac}(l_s, t)$ most significantly and thus

$$P(l_s, t) \approx -\rho_s \omega^2 \alpha_{TV} \beta I_0 / 2kk_s (\beta^2 - \sigma_s^2) \sin(kl_s) \times [(p+r)/\sigma_s(p+1) - (1/\beta)] \exp(i\omega t), \quad (11)$$

where $p=k_p\sigma_p/k_s\sigma_s$ and $r=(\beta/2a_s)(1-i)$. In the approximation that $\sin(kl_s) \approx kl_s$,

$$|P(l_s, t)| \approx (1/2)(I_0/l_s\omega)(\alpha_{TV}^2/C_{ps})N(p, q), \quad (12)$$

where

$$N(p, q) = [1/(p+1)] \times \sqrt{[q^4 + 2pq^3 + 2p^2q^2 - 4p(p+1)q + 4(p+1)^2]/(q^4 + 4)}.$$

It can be seen from eq. (12) that the PA signal magnitude has a tendency to saturate with increasing β , because $N(p, q)$ approaches $1/(p+1)$ with increasing q . This case has some significance as a reference to the case of oblique incidence, as described later, though it is not so useful for analytical applications due to the signal saturation.

In the case of oblique incidence (total internal reflection)

When a light beam impinges on the sample solution through the glass prism at any angles of incidence, it is partly reflected and partly transmitted. When the angle of incidence exceeds the critical angle, that is, in the case of total internal reflection, most of the light energy is reflected at the P-S boundary, with evanescent light being generated in the sample solution at the interface. The distribution of the evanescent light power, I_e [W/m²], which is localized in an extremely thin region on the solution side of the interface, is expressed as follows^{19,20}:

$$I_e = I(n_s \langle E_s^2 \rangle / n_p \cos \theta) \exp(-x/d). \quad (14)$$

Here n and θ [deg] denote the refractive index and the angle of incidence, respectively. The term $\langle E_s^2 \rangle$ shows the ratio of the light power in the solution at the interface to that in the glass prism and depends on the relative orientation of the plane of polarization to that of incidence. The quantity d is called the penetration depth, the distance at which the evanescent light power falls off to $1/e$ of that at the interface. In addition to eq. (14), the optical path length (effective thickness) is written as²⁰

$$b_e = n_s \langle E_s^2 \rangle d / n_p \cos \theta. \quad (15)$$

Here b_e depends on polarization through $\langle E_s^2 \rangle$ and was calculated in the same manner as in the Appendix of Ref. 2. The absorbed energy of the evanescent light is transformed into heat, its magnitude is

$$(1/2)\beta I_0 (n_s \langle E_s^2 \rangle / n_p \cos \theta) \exp(-\beta' x) [1 + \exp(i\omega t)]$$

where $\beta'=1/d$. When the above term is substituted for $H_s(x, t)$ in eq. (1b) and eqs. (1) and (2) are simultaneously solved in the same manner as those for normal incidence, the alternative component of a scalar potential is of the same form as eq. (8). Thus

$$P(l_s, t) \approx [-\rho_s \omega^2 \alpha_{TV} \beta I_0 / 2kk_s (\beta'^2 - \sigma_s^2) \sin(kl_s)] \times [(p+r')/\sigma_s(p+1)] (n_s \langle E_s^2 \rangle / n_p \cos \theta) \times \exp(i\omega t) \quad (16)$$

where $r'=(\beta'/2a_s)(1-i)$. In the approximation that $\sin(kl_s) \approx kl_s$,

$$|P(l_s, t)| \approx (1/2)(I_0/l_s\omega)(\alpha_{TV}^2/C_{ps})\beta b_e N(p, q') \quad (17)$$

where $q'=\beta'/a_s=1/da_s$. Equation (17) is fundamental in PAS-TIR. The proportionality of the PA signal magnitude to β and b_e suggests that PAS-TIR is applicable not only to investigations of concentration distribution profiles at the interface but also to the examinations of opaque sample solutions causing the signal saturation in normal incidence.

Now we have three expressions. Of these expressions of the PA signal magnitude, eq. (12), standing for the opaque sample solution in normal incidence, and eq. (17), standing for any sample solution in oblique incidence, are closely related to each other, because both of them arise from two terms of $\exp(ikx)$ and $\exp(-ikx)$ in the scalar potential. Division of both sides of eq. (17) by the corresponding sides of eq. (12) and substitution of the relationship, $-\ln(R) = \beta b_e^{20}$ give

$$-\ln(R) = [|P(l_s, t)|_{\text{obl.}} / |P(l_s, t)|_{\text{nor.}}] \times [N(p, q) / N(p, q')] \quad (18)$$

where R is the reflectivity. That is, if the PA signal magnitudes are measured for the same opaque sample solution in both incidences, their ratio will yield the reflectivity corrected by the term of $N(p, q) / N(p, q')$ at a particular angle of incidence. Furthermore, resonance conditions are derived from eqs. (11) and (16). Over a

wide range of the modulation frequency, the term $\sin(kl_s)$ in the denominators in eqs. (11) and (16) can not be assumed to be kl_s . Thus the signal magnitudes can increase infinitely under the resonance conditions given by

$$\omega = 2\pi f = (v/l_s)m\pi \quad (m=0, 1, 2, \dots), \quad (19)$$

where f [Hz] denotes the modulation frequency.

Experimental

Apparatus

The experimental arrangement for measuring PA signals was similar to that previously used², except for the use of a He-Ne laser (Spectra Physics Model 105-1). The beam with nominal power of 5 mW at 632.8 nm was usually modulated at 12.5 Hz by an optical chopper and was made to irradiate the sample solution so that the plane of polarization was perpendicular to that of incidence. The PA signal was detected with a discoid piezoelectric transducer, 10 mm in diameter and 1 mm thick, supplied by Murata Mfg. Co., Ltd. and measured with a preamplifier (NF Co., Ltd., Model LI75A) and a lock-in amplifier (NF Co., Ltd., Model LI574 and PAR Model 5101). The light power was attenuated by four neutral density filters (Nippon Shinku Co., Ltd.) with calibrated transmissivities of 21.8, 40.7, 60.7 and 82.3% at 632.8 nm. Figure 2 shows an exploded view and a cross sectional view of the PA cell. The sample solution was packed into a cylindrical space (1), approximately 2 mm thick, between a demountable hemicylindrical glass prism (2) and the transducer (3), which was attached to a stainless steel disc (4) with epoxy cement. The glass prism was attached to a holder (5) with a packing sheet (6) by two springs (7) and screws (8).

Fig. 2 Exploded view and cross sectional view of PA cell. 1, sample solution compartment; 2, glass prism; 3, piezoelectric transducer; 4, stainless steel disc; 5, holder; 6, packing sheet; 7, spring; 8, screw.

Table 1 Thermal, mechanical and optical constants of water^a and glass

	Water	Glass
α_t / K^{-1}	0.207×10^{-3}	
$\nu / m s^{-1}$	1.483×10^3	
$C_p / kJ kg^{-1} K^{-1}$	4.184	0.84 ^b
$\rho / Mg m^{-3}$	0.998	2.52 ^c
$k / W m^{-1} K^{-1}$	0.6121	0.711 ^d
n^e	1.333	1.525

a. "Kagaku Binran, Kisohe II", 2nd Ed., Maruzen, Tokyo (1975).

b. G. Sameshima, "Butsurikagaku Jikkenho", 5th Ed., Shokabo, Tokyo (1977).

c. Density calculated from volume and weight of prism.

d. "Jikken Kagaku Binran", 1st Ed., Kyoritsu Shuppan, Tokyo (1970).

e. Refractive index at 632.8 nm.

Reagents

Brilliant Blue FCF (BB) (Tokyo Kasei Kogyo Co., Ltd.) was used without further purification. Sample dye solutions were prepared by dilution of a 0.100 M ($M = \text{mol dm}^{-3}$) BB stock solution with distilled water. Table 1 lists thermal, mechanical and optical constants of water and the glass for the prism.

Results and Discussions

Equation (17) is the fundamental expression for TIR-PAS and eq. (12) has some significance as a reference to eq. (17). These equations consist of a number of parameters and seem to be complex. However, eq. (17) and eq. (12) can be divided into four and three simple terms. The first is an instrumental term, $I_0/l_s\omega$, which is determined only by the instruments used. The second is a solvent term,

$\alpha_T v^2 / C_{ps}$, depending on thermal and mechanical properties of the sample solution. The third is an optical absorption term, βb_e , appearing only in eq. (17); this term is concerned with optical properties of the sample solution. The last is a thermal diffusion term, $N(p, q)$ in eq. (12) and $N(p, q')$ in eq. (17). Here the term $N(p, q)$ depends only on the thermal diffusion coefficient and the optical absorption coefficient of the sample solution provided the same glass prism is used, and the term $N(p, q')$ is approximately equal to $1/(p+1)$, because $q' (=1/da_s)$ always has a large value, that is $q' \sim 1/(10^{-7} \text{ m} \times 10^5 \text{ m}^{-1}) = 10^2$ at 1 kHz, and $p (=k_p \sigma_p / k_s \alpha_s)$ is approximately in the order of 10^0 , for example, when $k_p = 0.711 \text{ W/(m K)}$, $C_{pp} = 0.837 \text{ kJ/(kg K)}$ and $\rho_p = 2.52 \text{ Mg/m}^3$, the parameter p is equal to 0.766 for water and 3.23 for carbon tetrachloride. The first three terms of eq. (17) are independent of one another; moreover, the term $N(p, q')$ can be approximated by a constant. Thus TIR-PAS can practically be used as a tool for measuring a surface concentration of a light absorbing species at a solid-liquid interface and for estimating thermal and mechanical properties of a sample solution with the aid of eq. (17). The dependence of the PA signal magnitude on the optical absorption term, βb_e , has been proved in the previous paper.² In the present paper, the instrumental terms will be experimentally examined. The experimental investigations of the others will be presented in later papers.

Light source power

Many authors have proved that the PA signal magnitude increases with the source power in a proportional manner.^{12,13,22,23} And eqs. (12) and (17) imply the existence of the proportionality. Figure 3 shows plots of the signal magnitude of a 5 mM BB solution vs. the source power. The plots are linear through the origin, regardless of the angle of incidence and the modulation frequency, as expected. Equation (17) shows not only that the signal magnitude is proportional to β and hence to the concentration of light absorbing species, but also that the proportionality exists in a sample solution with any transparency. Therefore, it is expected from the proportionality to the source power that the use of a high power source will allow the determination of the absorbing species from the very dilute solution to the concentrated solution without the PA signal saturation.

Besides the source power dependence, it is expected

in oblique incidence that the signal magnitude depends on a relative orientation of a plane of polarization to that of incidence through b_e containing the term $\langle E_e^2 \rangle$ depending on polarization, as can be seen in eq. (17) and eq. (15). Table 2 shows results of the signal magnitudes divided by b_e calculated for perpendicular and parallel polarizations at each angle of incidence. The results for both polarizations agree with each other at each angle. This agreement proves that the PA signal magnitude depends on the polarization in the same manner as the reflectivity in conventional internal reflection spectroscopy.^{19,20}

Modulation frequency

Kitamori *et al.*^{9,10} showed that the signal magnitude was inversely proportional to the modulation frequency for transparent liquid samples at frequencies below 1 kHz, because the photoenergy per light pulse was inversely proportional to the frequency. The inverse proportionality might also be expected from the present analysis, because $\sin(kl_e)$ in eqs. (11) and (16) can be approximated to kl_e . However, the existence of

Fig. 3 Plots of PA signal magnitude vs. source power. ○, normal incidence at 10 Hz; ●, normal incidence at 180 Hz; ○, oblique incidence (70°) at 10 Hz; ●, oblique incidence (63°) at 60 Hz. The sample was 5 mM BB aqueous solutions. The critical angle of the system was 60.9°.

Table 2 Polarization dependence of PA signal magnitude^a

θ /deg	63	64	65	67	70	73	77
$P_{\text{obs.}}/b_e(\perp) / 10^{-3} \text{ V m}^{-1}$	0.264	0.266	0.270	0.271	0.267	0.273	0.273
$P_{\text{obs.}}/b_e(\parallel) / 10^{-3} \text{ V m}^{-1}$	0.245	0.268	0.274	0.274	0.276	0.280	0.257

a. In perpendicular ($\perp$) and parallel ($\parallel$) polarizations, the planes of polarization are perpendicular and parallel to that of incidence, respectively.

either $N(p, q)$ or $N(p, q')$ causes modification of the frequency dependence, because the parameters q and q' include a thermal diffusion coefficient which is proportional to the square root of the modulation frequency. For each incidence, the plot of the signal magnitude vs. the reciprocal angular frequency multiplied by $N(p, q)$ or $N(p, q')$ in the frequency range below 500 Hz is shown in Fig. 4. Each plot shows a straight line at the higher frequencies and lowering tendency at the lower frequencies below several tens of Hz. Each straight line shows the inverse proportionality expected from eqs. (12) and (17). Oda *et al.*^{12,13} have also reported the observation of a similar lowering tendency. Although this lowering has not been clarified yet, it seems to be due to frequency characteristics of both the preamplifier and the piezoelectric transducer.

Sample thickness

As shown in eq. (19), the sample thickness is related to the resonance condition. However, at low frequencies below 1 kHz, inverse proportionality of the signal magnitude to the thickness is expected, as can be seen in eqs. (12) and (17). Qualitatively the signal magnitude was higher for the thinner sample thickness, although the sample thickness dependence was not examined in detail, because it was difficult to keep all conditions of the cells constant among the cells designed. Thinner sample thickness is recommended especially for TIR-PAS, because the evanescent light generated by the total internal reflection exists only at the glass-solution interface and therefore little light impinges on the transducer surface.

Fig. 4 Plots of PA signal magnitude vs. $N(p, q)/\omega$ or $N(p, q')/\omega$. O, normal incidence; ●, oblique incidence (63°). The sample was 5 mM BB aqueous solutions. The solid line shows the theoretical curve. The parameter p was 0.7661 for this calculation.

As mentioned above, the present theory can well explain the dependence of the PA signal magnitude on the instrumental factors. Dependences of the PA signal magnitude on the thermal diffusion and the solvent terms will be described in detail in the next papers.

We wish to thank Murata Mfg. Co., Ltd. for supplying the piezoelectric pieces.

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(Received April 8, 1986)

(Accepted June 30, 1986)