Volume 108, number 4 CHEMICAL PHYSICS LETTERS 13 July 1984

FREQUENCY-DOMAIN PHOTOPYROELECTRIC SPECTROSCOPY OF CONDENSED PHASES (PPES): A NEW, SIMPLE AND POWERFUL SPECTROSCOPIC TECHNIQUE

Andreas MANDELIS
Photoacoustics Laboratory, Department of Mechanical Engineering, University of Toronto, Toronto, Ontario, Canada M5S 1A4

Received 9 March 1984; in final form 17 April 1984

A new, powerful, and experimentally very convenient spectroscopic technique is described. The technique uses pyroelectric polyvinylidene difluoride (PVDF) thin film detectors in contact with solid or liquid samples. The instrumental and spectral characteristics of photopyroelectric spectroscopy (PPES) are presented, and its advantages over conventional photoacoustic spectroscopy (PAS) are discussed.

1. Introduction

Photoacoustic spectroscopy (PAS) has been used extensively in recent years with conventional microphones and piezoelectric detectors as signal transducers. The commonest piezoelectric transducers are usually made out of piezoelectric ceramic (e.g. lead zirconate titanate, PZT [1–3]). These ceramics exhibit a much higher frequency response than microphone transducers, and thus they became dominant in photoacoustic applications where fast transducer response is required, such as pulsed laser PAS [4]. Very recently Tam and Coufal [5] and Coufal [6] used polyvinylidene difluoride (PVDF) thin film piezoelectric transducers for pulsed and modulated photoacoustics. These films have distinct advantages over PZT transducers, the most important of which being their much higher, essentially flat frequency response between dc and tens of MHz [7]. In addition to piezoelectric behaviour, PVDF thin films (Pennwalt KYNAR™) exhibit strong pyroelectric properties [8] and, therefore, they can be used as detectors of thermal radiation. Coufal [6] utilized the pyroelectric character of 9 μm thin PVDF films to obtain pulsed and low modulation frequency spectra of Nd_2O_3 doped poly(methyl methacrylate) films. That application opened the way to the possibility of a new spectroscopic technique using pyroelectric films to detect optical absorption and non-radiative energy conversion processes in condensed phase matter. This paper is concerned with experimental studies aimed at demonstrating the potential of photopyroelectric spectroscopy (PPES) as a new, simple and sensitive spectroscopic method for the in situ study of physicochemical processes. Such processes may involve complex sample geometries which cannot be easily handled by conventional photoacoustic devices. Photopyroelectric data presented in this work suggest that PPES has distinct advantages over PAS.

2. Experimental

2.1. Photopyroelectric cell characterization

Fig. 1 shows the photopyroelectric sample cell design which was used for the present studies. The teflon cell was enclosed in aluminum foil to minimize ambient electromagnetic interference. The output of the cell was directly connected to the input of a variable gain ITHACO preamplifier (model 1201). The experimental assembly is shown in fig. 2. The photopyroelectric cell was first tested as an optical radiation detector. A thin layer of Xerox Toner black powder (≈1 μm) was spread on the 28 μm thick

0 009-2614/84/$ 03.00 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

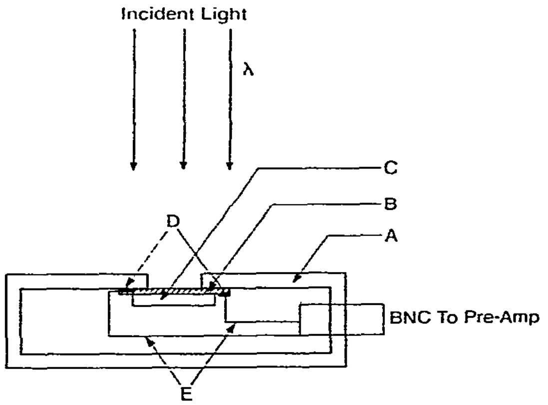

Fig. 1. Photopyroelectric cell with a 0.5" × 0.25" PVDF sample holder. (A) Teflon cell. (B) 25 μm thick PVDF film (Pennwalt KYNAR 5380-11-8 Piezo Film). (C) Teflon support. (D) Solderable copper foil electrodes with conductive adhesive. (E) Silver wires.

Pennwalt KYNAR PVDF film, which was located at the bottom of the cell as part of the sample chamber. Strong PPES signals were thus obtained throughout the whole UV–VIS spectral region (260–920 nm) of the xenon lamp.

The resulting spectrum (amplitude and phase) is similar to the one obtained photoacoustically using an EG&G PAS cell model 6003. The PPES phase, however, is essentially flat and constant throughout, whereas the PAS phase varies continuously by a few degrees from 250 to 900 nm due to phase shifts contributed by the complex microphone electronics. The frequency response of both cells is shown in fig. 3. The upper limit of the response is set by the mechanical chopper. The frequency response of the PPES cell, fig. 3a, exhibits essentially two linear regions, one below 50 Hz with a slope of −9.98 ± 0.03, and one above 50 Hz with a slope of −1.5 ± 0.1. This behavior is to be compared with the EG&G PAS cell frequency response curve fig. 3b. The photoacoustic cell exhibits non-linear Helmholtz-resonant behavior above 400 Hz. These resonances are difficult to eliminate from any microphone PAS chamber [9] and can seriously complicate frequency-domain studies of condensed matter specimens.

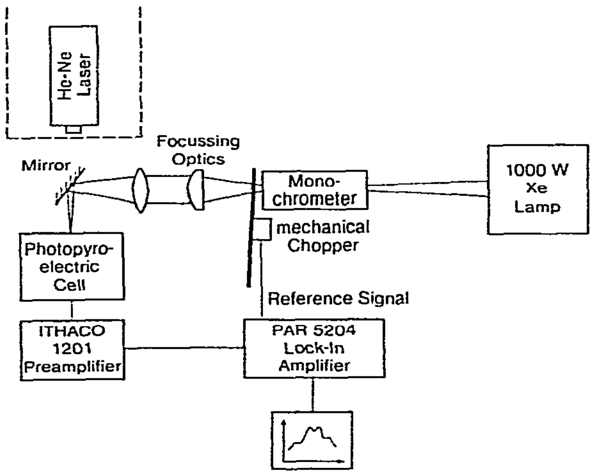

Fig. 2. Photopyroelectric experimental apparatus. Both broadband Xe lamp and He–Ne laser source are shown.

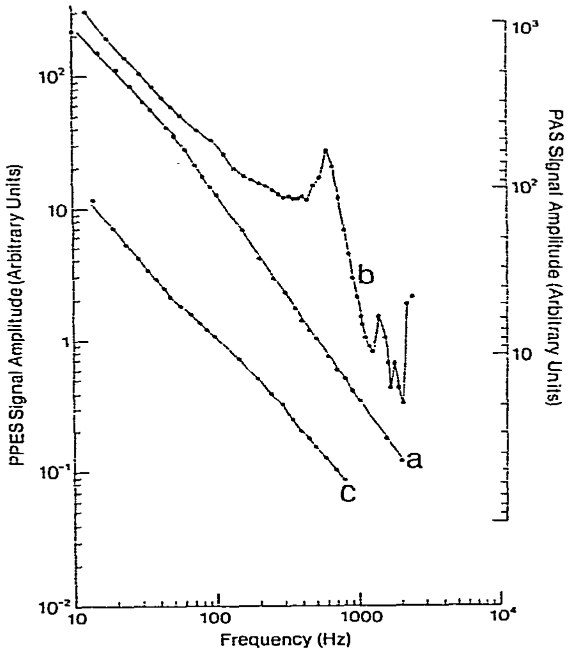

Fig. 3. (a) Frequency response of photopyroelectric cell using a 2 mW He–Ne laser flight source. Pre-amplifier gain: 10. Pre-amplifier high pass 3 Hz; low pass: 3 kHz. (b) Frequency response of EG&G PAS cell (model 6003) using a 2 mW He–Ne laser light source. (c) Frequency response of Cu plate after oxide removal. Light source: 2 mW He–Ne laser. Pre-amplifier gain: 5000.

2.2. Spectroscopic, chemical and materials PPES studies

Ho_2O_3 powder was used, mixed with tap water as a paste, so as to achieve a good thermal contact with the PVDF substrate film. Ho_2O_3 exhibits sharp absorption lines in the UV–VIS region and can be used to test and calibrate the photopyroelectric cell. The signal amplitude at 11 Hz, normalized by the Xe lamp spectrum, is shown in fig. 4a. The spectrum is identical to published PAS spectra of Ho_2O_3 powders [10] within the spectral resolution limitations of the slitwidth used for this experiment (2 mm slitwidth; 8 nm resolution). Fig. 4b is the normalized PPES signal of the Ho_2O_3 paste taken at 50 Hz. The amplitude and the phase correlate with each other and, upon comparison with fig. 4a, they are seen to anti-correlate with the features of the spectrum taken at 11 Hz.

The photopyroelectric probe was also used to monitor the kinetics of the chemical reaction:

$$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O. \qquad (1)$$

A 0.34 mm thick Cu plate was oxidized thermally, so as to form a dark, thin oxide film on the surface. The sample was then mounted between the holder opening and the PVDF film (i.e. between A and B in fig. 1). Physical contact of the pyroelectric with the back of the sample was achieved with the teflon backing plate C, fig. 1, and plastic screws. The oxidized copper specimen was further illuminated with a He–Ne laser at 632.8 nm and the lock-in output at 10 Hz was recorded. Reaction (1) was initiated upon introducing into the sample chamber a 0.1 M solution of HCl. Fig. 5 shows the time evolution of the PPES signal amplitude from the start of the reaction (t = 0) to its completion. Visual inspection showed metallic copper after ≈4 min. The lock-in output was essentially constant beyond this time. The discontinuity observed in fig. 5 at $t < 0$ is due to the sudden loss of the PPES signal immediately after the introduction of the dilute HCl in the chamber. After the recovery (≈30 s) the earliest recordable signal was already lower than the pre-mixing signal level by ≈10%.

Fig. 3c shows the frequency response of the metallic copper plate after the removal of the CuO. This curve exhibits a "knee" at ≈50 Hz, which was seen to be characteristic of the cell response. It also exhibits a clear break between 300 and 350 Hz with a subsequent change in the slope. By analogy to photo-

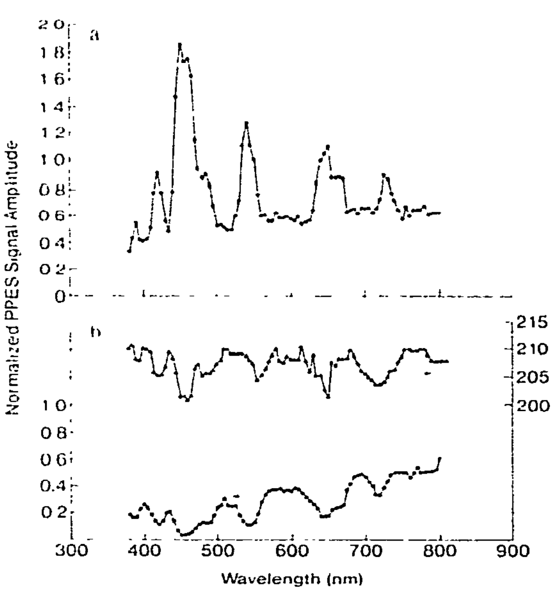

Fig. 4. (a) Photopyroelectric spectrum of Ho_2O_3 powder mixed with water. Chopping frequency: 11 Hz. Pre-amplifier gain: 500. Monochromator resolution: 8 nm. (b) Photopyroelectric spectrum (amplitude and phase) of Ho_2O_3 sample at 50 Hz. Pre-amplifier gain: 1000. Monochromator resolution: 8 nm.

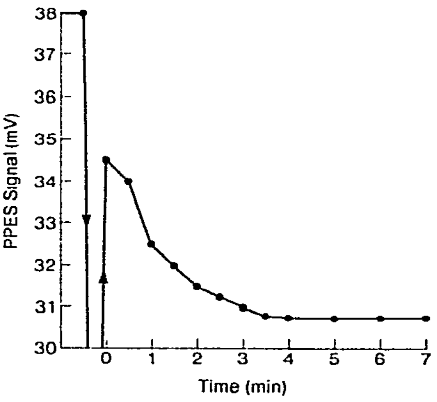

Fig. 5. Kinetics of eq. (1) monitored via photopyroelectric spectroscopy at 632.8 nm. Chopping frequency: 10 Hz. Pre-amplifier gain: 5000. Lock-in time constant: 1 s.

acoustic spectroscopy, the thermal diffusion length μ_{Cu} in the copper can be assumed equal to the plate thickness at the break frequencies, i.e. for $300 \leqslant f_b \leqslant 350$ Hz [11]:

$$\mu_{Cu}(f_b) = (\alpha_{Cu}/\pi f_b)^{1/2} \approx L_{Cu} . \qquad (2)$$

Eq. (2) gives the thermal diffusivity α_{Cu} of copper within the range

$$1.09 \leqslant \alpha_{Cu} \leqslant 1.27 \text{ cm}^2/\text{s}.$$

This value range is in agreement with published values of α_{Cu} using photoacoustic determination methods [11,12].

3. Discussion

The experimental results demonstrate the essentially thermal character of PPES. The PVDF Kynar films have been shown to be highly sensitive spectroscopic detectors in accordance with preliminary results by Coufal [6]. The basic mechanism of operation of this new spectroscopy is the pyroelectric effect: When the temperature of the sample–PVDF film interface increases by an amount ΔT due to nonradiative relaxation processes following optical absorption, the polarized film aligns its polar constituent crystallites along the temperature gradient field, thus producing a net dipole moment which results in a pyroelectric voltage given by [8]

$$\Delta V(\omega) = (pL/\epsilon)\Delta T(\omega), \qquad (3)$$

where p is the pyroelectric coefficient of the film, 3×10^{-9} coulomb/cm^2 K, L is the film thickness, ϵ is the film dielectric constant, $(1.06-1.13) \times 10^{-10}$ F/m, and ω is the angular frequency of modulation of the incident radiation.

The spectra obtained using this technique are of a quality similar to that of PAS. In fact PPES is related to photoacoustic spectroscopy in the sense that for a given sample geometry, PPES monitors the thermal energy transmitted to the substrate and gives a signal output proportional to the temperature of the interface between the sample and its backing. On the other hand, PAS monitors the thermal energy diffused to the sample surface and gives a signal output proportional to the spatial integral of the surface temperature [13]. It is, therefore, expected that PPES should be capable of providing more direct information about the sample than PAS which is an integrated and, therefore, an indirect technique. The phase profile obtained using a thin layer of Xerox Toner black powder is subject to optical absorption coefficient saturation considerations which are similar to those of PAS. The spectral feature reversal of figs. 4a and 4b can be understood qualitatively in terms of the simple mechanism proposed above. At low chopping frequencies for which the sample is thermally thin ($\mu_s > L$), thermal energy diffuses into the backing PVDF film and gives rise to a pyroelectric signal. Opaque spectral regions, such as those between 435 and 500 nm of Ho_2O_3, produce large amounts of heat due to their high absorption coefficient values. Nonradiative de-excitation processes then generate a larger PPES signal than that obtained from optically transparent spectral regions. Upon a spectral scan this signal produces a replica of the absorption spectrum of the sample, such as the one shown in fig. 4a. When the chopping frequency increases to levels such that the sample is thermally thick ($\mu_s < L$), only transparent regions can produce a pyroelectric signal through light penetration across the sample thickness and direct absorption by the backing PVDF film. Such a transparent region is in Ho_2O_3 between ≈560 and 630 nm. Strongly absorbing spectral regions retain the thermally converted optical energy close to the sample surface, as the condition $\mu_s < L$ prevents thermal communication with the backing. Such regions do not contribute to the generation of pyroelectric signals. Therefore, upon a spectral scan the pyroelectric effect produces a counter-spectrum, similar to a transmission spectrum, with strong signals at transparent regions and weak signals at opaque regions, such as shown in fig. 4b. The exact peak-by-peak anti-correlation of the spectra in figs. 4a and 4b demonstrates that at 11 Hz the Ho_2O_3 paste is thermally thin, whereas at 50 Hz it is essentially thermally thick. It may be concluded that PPES can be used as a conventional spectroscopic technique *only* at low chopping frequencies, *or* with very thin samples, so that the condition $\mu_s > L$ is valid. This is a restriction absent from photoacoustic spectroscopy, however, it is expected that an important contribution of PPES will arise in the study of thin film processes, such as the anodic growth of films on electrodes at the electrode–electrolyte interface. Physico-chemical interface processes cannot be studied efficiently using conventional microphone photoacoustics due to the exponential damping of thermal waves within the bulk of the upper medium [13]. Piezoelectric PAS can monitor such processes as a second-order effect, because the generation and launching of acoustic waves originating from thermal waves is required. PPES is sensitive to the thermal waves within the lower medium, i.e. it has the advantage of a first-order effect. The CuO experiment, summarized in fig. 5, substantiates the sensitivity of PPES to interfacial chemical processes and its power as a tool for kinetic studies which are otherwise difficult to monitor due to the complex, in situ requirements of the experimental configurations involved. The reaction rate constant of eq. (1) can be calculated approximately from the kinetic information of fig. 5, assuming a simple, first-order kinetic behavior of the form

$$[\mathrm{CuO}]_t = [\mathrm{CuO}]_0 \exp(-kt). \qquad (4)$$

Eq. (4), when fitted to the data of fig. 5, yields the following average value for k:

$$k = (1.55 \pm 0.6) \times 10^{-3}\ \mathrm{s}^{-1}.$$

Photopyroelectric spectroscopy can also provide additional information concerning thermal parameters of materials, as shown in fig. 3c. This capability appears to be of a degree similar to that of conventional photoacoustic spectroscopy.

Perhaps the most important advantages of PPES over other photothermal spectroscopies are the almost trivial ease of its implementation and the large amount of freedom allowed the experimenter regarding sample preparation, size, chemical and physical condition and pre-treatment.

In conclusion, a new spectroscopic technique, photopyroelectric spectroscopy, has been tested and characterized with respect to its spectral, chemical, and materials research capabilities. It was shown to be potentially more valuable than PAS (microphone and piezoelectric) for condensed phase samples, especially those involving complicated geometries. The main advantages of PPES are its extreme simplicity, sensitivity, in situ non-destructive probing ability, direct (i.e. first-order) cause–effect signal interpretation, and adaptability to practical restrictions imposed by experimental system requirements.

Acknowledgement

The author wishes to thank Dr. Hans Coufal of IBM Laboratories for fruitful conversations and a preprint of his pioneering paper concerning a preliminary investigation on the photothermal properties of PVDF thin films. He also wishes to acknowledge the financial support of the National Science and Engineering Research Council of Canada (NSERC), which made this research possible.

References

[1] A. Rosencwaig and G. Busse, Appl. Phys. Letters 36 (1980) 725.
[2] T. Sawada, H. Shimizu and S. Oda, Japan. J. Appl. Phys. 20 (1981) L25.
[3] A.C. Tam and C.K.N. Patel, Appl. Opt. 18 (1979) 3348.
[4] C.E. Yeack, R.L. Melcher and H.E. Klauser, Appl. Phys. Letters 41 (1982) 1043.
[5] A.C. Tam and H. Coufal, Appl. Phys. Letters 42 (1983) 33.
[6] H. Coufal, IBM Research Report RJ 4023 (45181) (1983).
[7] L. Bui, H.J. Shaw and L.T. Zitelli, Electron. Letters 12 (1976) 393.
[8] KYNAR™ Piezo Film Technical Manual, Pennwalt Corp. (1983) p. 17.
[9] N.C. Fernelius, Appl. Opt. 18 (1979) 1784.
[10] M.J. Adams, B.C. Beadle and G.F. Kirkbright, Analyst 102 (1977) 569.
[11] S.I. Yun and H.J. Seo, Technical Digest, 3rd. International Meeting on Photoacoustic and Photothermal Spectroscopy, Paris, France (1983), Paper 6.2/2.
[12] P. Charpentier, F. Lepoutre and L. Betrand, J. Appl. Phys. 53 (1982) 608.
[13] A. Mandelis, Y.C. Teng and B.S.H. Royce, J. Appl. Phys. 50 (1979) 7158.