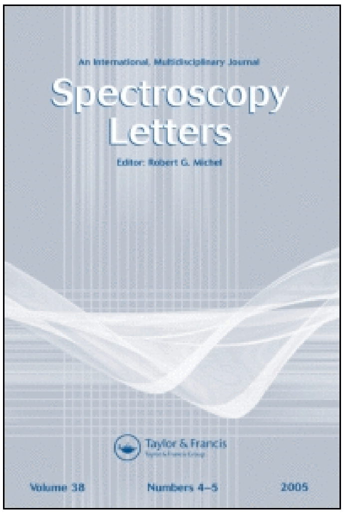

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Reflection Mode Photopyroelectric Spectfoscopy of Strongly Absorbing Liquids in the Near Infrared

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REFLECTION MODE PHOTOPYROELECTRIC SPECTROSCOPY OF STRONGLY ABSORBING LIQUIDS IN THE NEAR INFRARED

Key words: photopyroelectric spectroscopy, water, near infrared, photothermal spectroscopy

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ABSTRACT

Novel and simple technique suitable for spectroscopic studies of liquid samples is being described. Its validity has been experimentally verified using water as the specimen.

The sensitivity of the method allowed measurement of absorption coefficients (~ 200 cm^{-1}) in the near infrared with good signal to noise ratio values.

INTRODUCTION

To measure the absorption coefficient β of strongly absorbing liquids ($\beta > 10^3 cm^{-1}$) by means of conventional transmission spectroscopy presents a real problem since the signal, proportional to the transmitted radiation, becomes very small. Effective pathlengths as small as 0.5 μm have been achieved by a differential technique [1].

Alternatively, one can use the photo induced effect to generate a signal proportional to the absorbed, rather than to the transmitted radiation. An example is the nonradiative de-excitation in the absorbing medium, giving rise to photothermal phenomena. Reliable data for absorption coefficient β of organic liquids in the range $\beta \leq 300$ cm^{-1} using a CO_2 laser transverse mirage method have been reported [2].

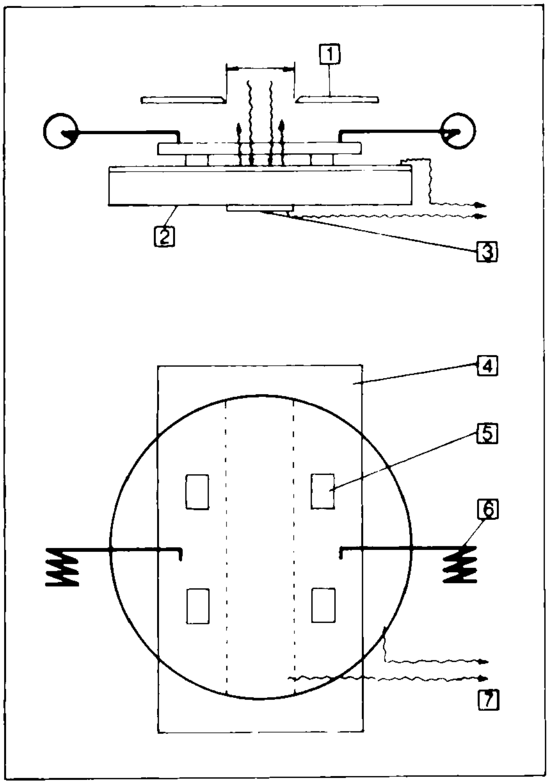
The use of an absorption cell in conjunction with a pyroelectric sensor to measure the heat developed upon absorption of radiation has led to the new experimental technique - the photopyroelectric spectroscopic method (PPE) that has been used to characterize solid samples [3,4]. The basic theory applicable to such a PPE cell operating in the transmission mode was described by Mandelis and Zver [5].

Similar cell arrangement intended for use with liquid specimens has been discussed [6]. The cell is essentially a pyroelectric detector provided with a reflecting electrode and the PPE signal is being generated solely due to the absorption within the sample studied without any interference resulting from the absorption process in the detector itself. This technique is termed as a reflection mode photopyroelectric PPE spectroscopy.

EXPERIMENTAL

The experimental cell shown in Fig. 1 consists of a lead zirconate titanate (PZT) ceramic pyroelectric disc (10 mm in diameter and 1 mm thick), provided with electrodes. Aluminium foil, 10 μm thick serving as the reflecting surface is glued to the front side of the PZT detector by means of a silicone grease.

Four mylar spacers of arbitrary thickness d (in this experiment $d = 60$ μm) define the volume that accomodates the injected liquid sample that is retained in the cell by the capillarity. A higly transparent glass (without hydroxyl radicals) window (150 μm thick) is placed atop the spacer to complete the cell. Two thin metal springs hold the assembled structure together. All of it is maintained in an enclosure provided with another transparent window in order to prevent the evapora-



1. exit slit of the monochromator
2. PZT material
3. rear electrode
4. glass window
5. thin spacer
6. joining spring
7. output signal to the lock-in amplifier

FIG. 1. Schematic view of the reflection mode photypyroelectric cell for liquids.

tion of the sample during the measurements and to reduce the effect of noise due to the air turbulence. The cell is placed closely to the exit slit of a Carl-Zeiss SPM-2 prism monochromator. The maximum equivalent slit width is 0.06 µm for the quartz prism used in the range 0.6 - 3.2 µm and 0.2 µm for the NaCl prism used in the range 3.2 - 4.2 µm. The radiation source is a quartz-tungsten lamp (supplied about half of the nominal voltage) chopped at 12 Hz and focussed with a NaCl lens onto the entrance slit of the monochromator. The preamplified pyroelectric signal is fed to a lock-in amplifier.

THEORY

As stated above, the reflection mode PPE spectroscopy method is based on detection of heat changes due to periodic absorption of radiation in a thin layer of liquid placed in thermal contact with a pyroelectric reflecting element (reflectance R). Since the radiation passes the liquid twice, the optical path length is numerically equal to a double of the spacer thickness (2d). The effect of higher order reflections and that of window transmittance do not have to be taken into consideration, as shown in the calibration procedure described below.

The heat quantities Q_i, developed successively are, (β is the absorption coefficient of liquid at a given wavelength):

$$\begin{array}{lll} Q_1 \propto 1 - e^{-\beta d} & \text{(liquid)} & \\ Q_2 \propto e^{-\beta d}(1 - R) & \text{(metal foil)} & (1) \\ Q_3 \propto Re^{-\beta d}(1 - e^{-\beta d}) & \text{(liquid)} & \end{array}$$

If the assembly is thermally thin, the temperature variation is homogeneous and the pyroelectric signal is proportional to the total heat

$$S(\lambda) \propto \sum Q_i = 1 - R\, e^{-2\beta d} \qquad (2)$$

and the absorption coefficient at given wavelength is

$$\beta(\lambda) = \frac{1}{2d} \ln \frac{1 - S_r(\lambda)}{1 - S(\lambda)} \qquad (3)$$

where $S(\lambda)$ and $S_r(\lambda)$ are the normalized signals for the cell obtained with and without the liquid, respectively.

If the sample is thermally thick, the PPE signal is given by the solutions of the appropriate heat diffusion equations for the system [5]. However, the correction factor $\eta(\beta,\omega)$ accounting for the efficiency of the transfer of the heat wave through the liquid towards the pyroelectric element can be introduced in eqn. (1) i.e. yielding a more general expression for the magnitude of PPE signal

$$S(\lambda) = (1 - R)\, e^{-\beta d} + \eta\, (1 - e^{-\beta d})\, (1 + Re^{-\beta d}) \qquad (2A)$$

Two extreme cases for β can be distinguished in equation (2A):

$$\beta \approx 0, \text{ hence } S(\lambda) = 1 - R = S_r \quad \text{and} \qquad (4)$$

$$\beta \to \infty, \text{ with } S(\lambda) = \eta = e^{-ad} \qquad (5)$$

where $a^{-1} = \sqrt{2\alpha/\omega}$ designates the thermal diffusion length while α and ω are the thermal diffusivity of the liquid and the modulation angular frequency. For large values of β ($\beta \to \infty$) the absorption is taking place at the front surface of the liquid and to assume that in such a case the coefficient η actually represents the attenuation e^{-ad} of the thermal wave in the liquid across the distance d is justified.

From these considerations it is clear that a spectroscopically useful condition is obtained when $ad \ll 1$, $\eta = 1$ and consequently eq. (3) for β is valid. The condition $ad \ll 1$ can be reached either by lowering the spacer thickness d or the modulation frequency ω.

The β dependent factor η in eq. (2A) can cause the appearance of the inverted peaks due to the competing absorption increase and a decreasing heat wave propagation efficiency, since the absorption takes place closer to the front liquid surface. The occurrence of inverted peaks in the PPE spectra was reported [4] and an adequate theory given [5].

RESULTS AND DISCUSSION

For quantitative determination of β, both $S(\lambda)$ and $S_r(\lambda)$ signals ought to be normalized. In doing so the pronounced, nonuniform spectra power density of the lamp and the monochromator has to be eliminated first. Consequently, measured $S(\lambda)$ and $S_r(\lambda)$ signals are ratioed to a signal $S_o(\lambda)$ obtained from a spectrally flat pyroelectric detector, as shown in Fig. 2. The shape of that curve resembles that of a black body radiator having a temperature of 2410 K, with superposed H_2O and CO_2 atmospheric absorption bands and an additional absorption (probably due to the monochromator) at 2.2 µm. The main problem is the availability of very low power levels between 2.7 - 2.8 µm thereby causing "noisy" measurements. The radiation power impinging on the detector ranges from 0.2 to 40 µW.

The magnitude of signal $S(\lambda)$ must be corrected by a constant factor due to the additional thermal capacity of the liquid and window when compared to the measurement performed with the empty cell. This factor is

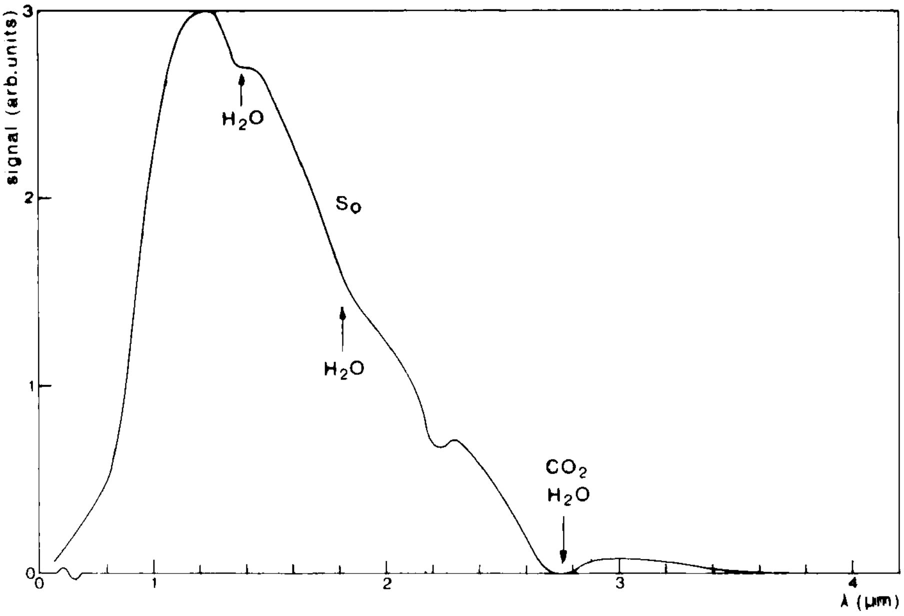


FIG. 2. The power spectrum $S_o(\lambda)$ of the source. Notice the atmospheric absorption bands. (See also the text).

obtained from the condition given by eq. (4) in the part of the spectrum characterized by $\beta \approx 0$.

Finally, both signals are normalized to the unity, this latter being based on the argument that $[1 - S_r(\lambda)]$ should represent the reflectance R of the Al foil, measured by other methods.

Signals $S_r(\lambda)$ and $S(\lambda)$ obtained with distilled water using two different spacer thicknesses (6 µm and 60 µm) are shown in Fig. 3. The absorption peaks of water at 1.43 µm, 1.92 µm and 3.0 µm are well observed. The peak at 0.8 µm is common to both curves and is characteristic for aluminium. The curve $S_r(\lambda)$ clearly shows that the PPE method enables the absorbance measurement of the non transparent materials as well [7].

The peak at 3 µm obtained with d = 60 µm is inverted as already discussed. The thermal diffusion length for water at 12 Hz is 62 µm and substitution of this value in eq. (5) yields $S(\lambda) = 0.36 \approx e^{-1}$. The

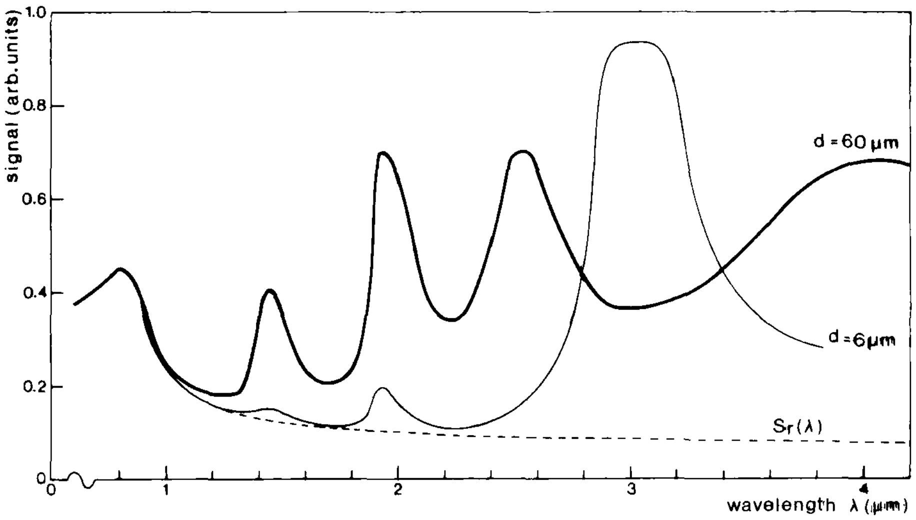


FIG. 3. The photopyroelectric signal of distilled water S(λ) and the residual cell absorption $S_r(\lambda)$ in the infrared region.

TABLE 1 Comparison of absorption coefficient β (computed via eq. (3)), and the experimental data from ref. 8 at different wavelengths. Phase lag φ is also presented.

d [μm]	λ[μm]	1.0	1.43	1.92	3.0
60	β [cm^{-1}] φ [°]	~ 0 0	32 -10	89 -15	– -80
6	β [cm^{-1}] φ [°]	~ 0 0	29 0	88 0	2030 0
Ref. [8]	β [cm^{-1}]	0.3	24	118	2860

explanation of the observed peak inversion as being due to the modification of the spatial absorption distribution of radiation in the liquid is consistent with the increasing phase lag of the PPE signal (see Table 1) as β increases in 1 μm to 3 μm wavelength range.

Values of coefficient β, computed via eq. (3) are also presented in Table 1. Good agreement with literature data is obained [8], even for the curve associated with d = 60 μm for which $\eta \neq 1$.

CONCLUSIONS

This communication presents a novel reflection mode PPE spectroscopic technique suitable for studies on heavily absorbing liquids. The method allows the quantitative β measurements provided the spectrum contains an optically thin region for calibration purposes. However, other calibration procedures (such as differential or substitution methods may be considered too). The range of measurable β values extends from optically thin to the optically thick 2d pathlengths.

In this work, water was chosen as the test liquid but with the appropriate cell modifications, a variety of liquids can be investigated. The wavelength range, the thickness of the liquid and the chopping frequency, may also be varied. By a suitable choice of these parameters one can perform the experiment in the desired optical and thermal modes, thereby simplifying the mathematical analysis and increasing the accuracy of the results.

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