

Photopyroelectric technique for the measurement of optical properties of pure liquids

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Photopyroelectric technique, in the transmission configuration, was shown adequate for the measurement of the optical properties of pure liquids. The analytical scheme involves the scanning of the photopyroelectric signal as a function of the sample thickness. Optical absorption coefficients, at four wavelengths in the near infrared region (904 nm, 980 nm, 1310 nm, and 1550 nm), were measured for eight pure substances, distilled water and glycerol, among them. Strong optical absorption was obtained, particularly for pure liquids with a hydroxyl group in their molecular structure. In order to figure out about the influence of this chemical group on optical properties as function of the size of the molecule, optical absorption coefficient for a series of linear alcohols at 1550 nm was also measured.

Introduction

Optical properties are widely used in analytical chemistry for quantification of substances in mixtures, the optical absorption coefficient β (also named as optical extinction coefficient), plays a fundamental role for this purpose [1]. This optical parameter characterizes at what extend monochromatic light is absorbed when it travels through a substance. When Beer-Lambert's model for light absorption is assumed for mixtures, optical absorption coefficient becomes $\beta = c\varepsilon$, where c and ε are the concentration and molar extinction coefficient (or absorptivity) of the absorbing substance, respectively. Only under this condition optical absorption coefficient is proportional to the absorbance, A . A calibration curve, showing linear relation between absorbance and sample's concentration is in practice required, moreover, a reference substance needs to be used (usually the solvent) as to compensate light reflections at the sample's container walls.

When dealing with pure liquids, an estimate of the optical absorption coefficient is usually done by measuring absorbance for a single sample thickness [2-4], other usual way is by a linear fitting on a number of absorbances obtained at different sample thicknesses [5,6]. In both cases; however, there is not an easy manner of compensate light reflections and more yet, compliance of the Beer-Lambert model cannot be ensured in advance.

Some photothermal techniques have been introduced for the optical absorption coefficient measurements of pure liquids: thermal lens spectroscopy [7-10], photothermal deflection spectroscopy [11] and the optothermal window [12], among them.

Thermal lens and photothermal deflection spectroscopies; however, share some experimental inconveniences: they are adequate only for low absorbing substances, aside of the requirement of special light sources for probe and excitation [9-11]. Optothermal window, on the other hand, has the problem of been adequate only for high absorbing fluids and, in addition, the requirement of knowing the sample's thermal diffusivity [12].

In this paper a photopyroelectric (PPE) technique in the transmission configuration, previously reported for optical properties measurements of liquid mixtures [13,14], is also shown very useful for the direct measurement of optical absorption coefficients for pure liquids. Neither reference sample nor calibration curve is required in this methodology

since it is introduced a mathematical model which provides of experimental criteria for validation purposes.

To show the convenience of using this photothermal methodology for optical characterization of pure liquids, optical absorption coefficients for a series of pure substances were measured at four wavelengths in the near infrared region (904 nm, 980 nm, 1310 nm and 1550 nm), good agreement with optical properties reported in literature was obtained.

the amplitude (in a semi-logarithmic scale) to a linear model. The slope of the linear adjustment corresponds to the optical absorption coefficient.

Basic theoretical aspects

Mathematical description of the PPE experimental setup for optical absorption measurements, shown in cross section in Figure 1, has been reported elsewhere [13,14], for which just the fundamental ideas behind the methodology are summarized here.

In the corresponding theoretical scheme, it has been shown that, under the adequate experimental conditions (thermally thick regime for the absorbing liquid), the PPE signal decrease exponentially as [13,14]

$$V(l) = C \exp(-\beta l) \quad (1)$$

while the corresponding PPE phase remains constant. In this equation β is the sample's optical absorption coefficient (at the wavelength used for the analysis), l its thickness and C is a complex expression, independent of the sample's thickness.

The experimental procedure consists of taking the PPE signal for a set of sample thicknesses, plotting the amplitudes (in a semi-logarithmic scale) and phases as function of this variable and, within the thickness' range where the phase remains constant (which is experimentally defined), adjusts the amplitude (in a semi-logarithmic scale) to a linear model.

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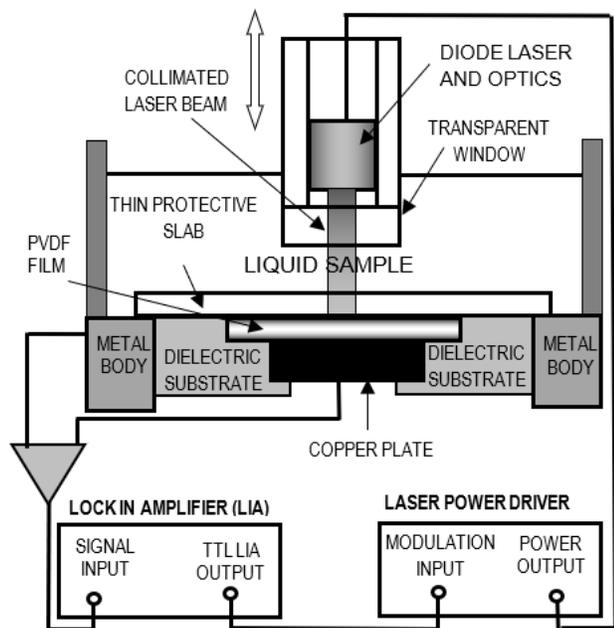


Figure 1. Cross section of the experimental photopyroelectric set up for optical absorption coefficient measurements for liquids.

The slope of the linear adjustment corresponds to the optical absorption coefficient.

Esperimental setup

The experimental setup consisted of a metalized thin foil of PVDF pyroelectric sensor (56 μm thickness) protected from the environmental liquids by means of a cover glass (160 μm thickness). Four different monochromatic light sources, from diode lasers, were used (Table 1). All measurements were made at fixed modulation frequency of 1 Hz, setting the Lock-In’s time constant at three seconds, and at room temperature of 20 °C. Thirty photopyroelectric signals were recorded for each liquid sample, starting from

Table 1. Monochromatic light sources, from diode lasers, used in this work for optical absorption coefficient measurements for pure liquids.

Thorlabs Model	Wavelength (nm)	CW Power (mW)
L904P010	904	10
L980P030	980	30
ML725B8F	1310	5
ML925B45F	1550	5

an unknown liquid’s thickness l_0 (absolute values of this length is not required for the analysis), increasing the thickness in steps of 50 microns.

Results and discussion

Figure 2 shows PPE signals at 980 nm, 1310 nm and 1550 nm (Figures 2a, 2c, and 2e for PPE phase, and Figures 2b, 2d, and 2f for PPE amplitude), as a function of the sample thickness, for some of the pure substances studied in this work. Figures 2a and 2b stand for distilled water, glycerol and linalool, at 980 nm (empty circles (o), squares (□) and triangles (Δ), respectively), figs. 2c and 2d stand for water, glycerol and ethanol, at 1310 nm (empty circles (o), squares (□) and triangles (Δ), respectively), finally figs. 2e and 2f stand for distilled water, methanol and ethanol, at 1550 nm (empty circles (o), squares (□) and triangles (Δ), respectively). It is evident in these plots a sample thickness range where the PPE phase remains approximately constant (Figures 2a, 2c, and 2e), and where Equation (1) applies, according with the theoretical scheme. The corresponding linear fittings to obtain the liquids’ optical absorption coefficients are shown as continuous lines in Figures 2b, 2d, and 2f.

Table 2 summarizes the set of optical absorption coefficients measured for all the liquid substances in this work (columns 2, 3, and 4, for 904 nm, 980 nm, and

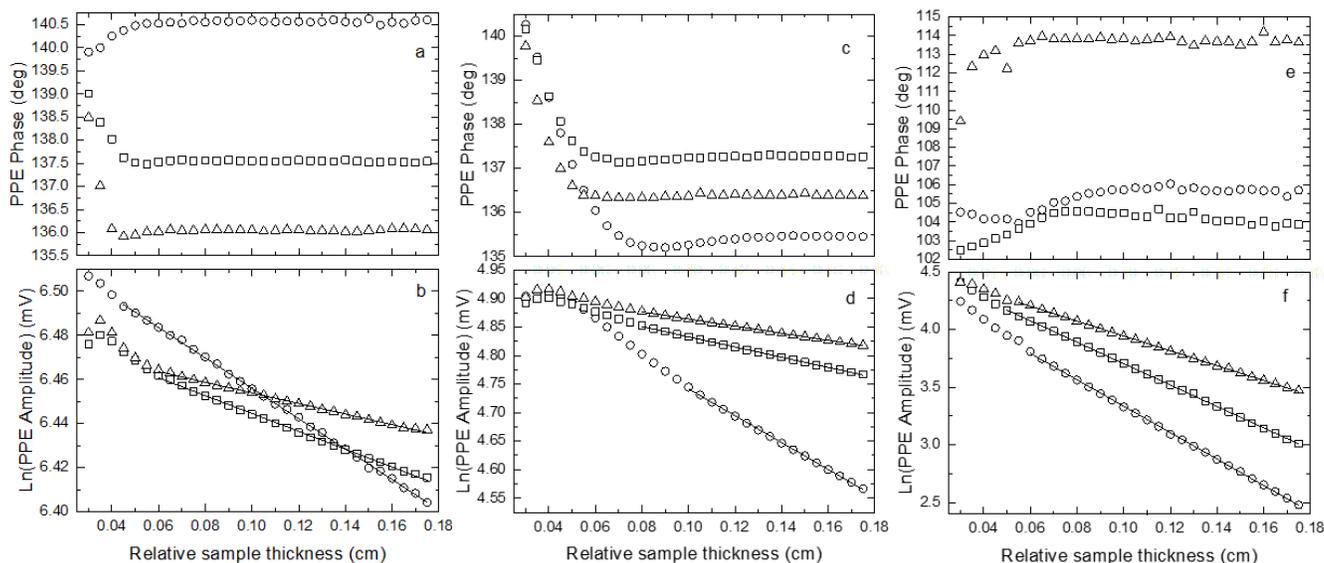


Figure 2. Photopyroelectric (PPE) signal at 980 nm (a,b), 1310 nm (c,d) and 1550 nm (e,f), as function of the relative sample thickness, for some of the liquid samples studied in this work. Continuous lines are best linear fits for optical absorption coefficient determination.

Table 2. Optical absorption coefficients, β , for the pure liquids studied in this work, measured by means of the presented photopyroelectric technique.

Pure Substance	β (cm ⁻¹)			
	904 nm	980 nm	1310 nm	1550 nm
Glycerol	0.163 ± 0.001	0.405 ± 0.004	0.893 ± 0.005	11.51 ± 0.03
Distilled water	0.134 ± 0.003	0.690 ± 0.004	2.36 ± 0.010	11.46 ± 0.04
Methanol	0.125 ± 0.005	0.317 ± 0.015	0.686 ± 0.005	9.28 ± 0.03
Ethanol	0.186 ± 0.002	0.298 ± 0.011	0.622 ± 0.003	6.44 ± 0.02
Linalool	0.133 ± 0.001	0.241 ± 0.003	0.547 ± 0.005	1.89 ± 0.01
Vitamin E (α -tocopherol)	0.153 ± 0.002	0.216 ± 0.004	0.426 ± 0.003	1.07 ± 0.01
Eucalyptol	0.199 ± 0.003	0.111 ± 0.003	0.386 ± 0.003	0.466 ± 0.006
Hexanes (mixture of isomers)	0.128 ± 0.004	0.104 ± 0.005	0.217 ± 0.006	0.404 ± 0.020

1310 nm, respectively). Each value in this table corresponds to the optical absorption coefficient obtained from the analysis on one typical sample for each liquid, the reported uncertainty is the error obtained from the fitting procedure.

The optical absorption coefficients obtained in this work resulted in good agreement with those reported in literature, for water, for instance, reported values are of 0.067 cm⁻¹, 0.46 cm⁻¹, 1.08 cm⁻¹, and 9.6 cm⁻¹, for wavelengths of 900 nm, 970 nm, 1300 nm, and 1550 nm, respectively [15]; these values compare well with the ones in Table 2 (which were obtained at the closest wavelengths). Optical absorption coefficients for methanol and ethanol at 1550 nm, on the other hand, are in good agreement with the ones estimated from reported absorption spectra for linear alcohols ($\beta=A/(l\log(e))$) [16].

It is interesting to note the relatively large absorption coefficients at 1550 nm for the first six substances. For alcohols, it is well known the existence of an absorption band, around 1460-1600 nm, corresponding to the first overtone of the hydroxyl group [17]. The existence of an absorption band for these first six substances in the neighborhood of 1550 nm (the maximum of this band depends on the molecule’s structure), attributed to this functional group, can then be inferred.

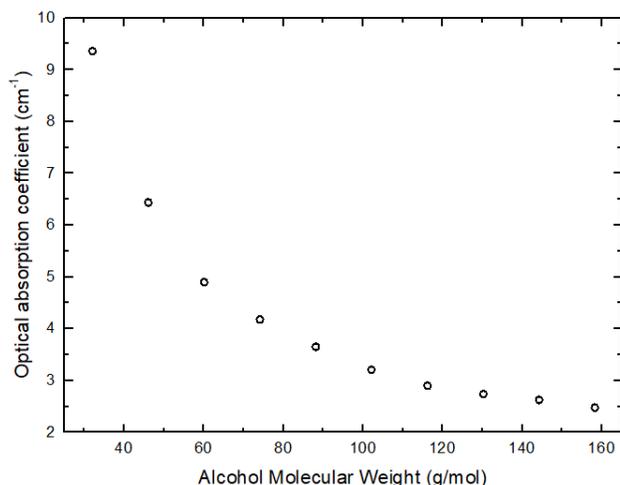


Figure 3. Optical absorption coefficient behavior, at 1550 nm, as a function of the molecular weight, for the ten linear alcohols studied in this work.

It seems also evident a “dilution” effect on the optical influence of this functional group as the molecule increase its size; this effect is evident for the two linear alcohols studied in this work, methanol and ethanol. In this case, the optical absorption coefficient decreases from 9.28 cm⁻¹ to 6.44 cm⁻¹ when the molecule’s size increase (32.04 g/mol for methanol to 46.07 g/mol). This effect is more evident for linalool and α -tocopherol, which have only one hydroxyl group and have a relative large molecular weight (154.25 g/mol and 430.71 g/mol, respectively). To figure out on the hydroxyl group effect on the optical absorption coefficient, this optical property was measured at 1550 nm for a complete series of linear alcohols from methanol to 1-undecanol. The results are summarized in Table 3 and the optical absorption coefficient behavior, as function of the alcohol molecular weight is shown in Figure 5.

Concluding remarks

A photopyroelectric (PPE) technique, in the transmission configuration, for the direct measurement of optical absorption coefficient for pure liquids has been presented. Since involves the scanning of the PPE signal as a function of sample’s thickness, is similar to other old techniques for measuring this optical property [4,5] but, on a difference to them, the signal in this case is generated directly from the

Table 3. Optical absorption coefficients, β , for the linear alcohols studied in this work, measured by means of the presented photopyroelectric technique.

Linear alcohol	β (cm ⁻¹) at 1550 nm
Methanol	9.28 ± 0.03
Ethanol	6.44 ± 0.02
1-Propanol	4.9 ± 0.02
1-Butanol	4.18 ± 0.02
1-Pentanol	3.65 ± 0.01
1-Hexanol	3.21 ± 0.01
1-Heptanol	2.9 ± 0.01
1-Octanol	2.74 ± 0.01
1-Nonanol	2.63 ± 0.01
1-Decanol	2.48 ± 0.01



absorbed radiation. At this way, light's reflections at the sample's container does not have significant contribution to the PPE signal for which reference sample is not required. Light sources for the implementation of this technique do not need to fulfill special requirements (aside of being monochromatic). Optical absorption coefficients, at any wavelength, can be obtained by just attaching to the system a monochromator and the appropriate continuous light source (with good emission inside the wavelengths' range of interest).

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