Thermal lens spectroscopy

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Abstract

This paper describes the basic principles behind the thermal lens technique. Although this photothermal spectroscopic method offers several advantages respecting conventional optical spectroscopy its very existence is practically unknown to most people, and references to it in textbooks are scarce, if not absolute. Due to its importance and widespread use during the last years, we believe it is a subject that should be included in the study curricula of optical spectroscopy topics at the university level.

Keywords: Thermal lens, photothermal, light thermal diffusivity.

Resumen

En este artículo, describimos los principios básicos detrás de la técnica de lente térmica. Aunque este método espectroscópico fototérmico ofrece algunas ventajas con respecto a la espectroscopia óptica convencional, es casi desconocido para muchas personas, y las referencias a él en los libros de texto son escasas, si no absolutas. Debido a su importancia y uso generalizado durante los últimos años creemos que es un tema que debe incluirse en los planes de estudio a nivel universitario cuando se tratan temas de espectroscopia óptica.

Palabras Claves: Lente térmica, fototérmica, luz, difusividad térmica.

I. INTRODUCTION

Optical spectroscopy is based on studying absorption and emission of light by matter [1]. In brief, this technique compares the intensity of light transmitted by a sample with the intensity of the incident light. Then, a spectrum is realized by plotting the quotient of these parameters, or any magnitude related to it (e.g., the optical absorbance, as shown in the next section), as a function of a light's characteristic such as its wavelength, or the energy, or the frequency, etc. [2]. In the last years, many methods have been developed that enlarged the scope of optical spectroscopy [3]. This paper aims to give an overview of the basics of Thermal Lens (TL) Spectroscopy (TLS) [4], a photothermal method almost unknown to many people despite its growing importance in many applications that include traces determination in environmental systems, chemical reactions studies, calorimetry, microfluidics, quantum yields measurement, among others. We believe it is a method that merits being included in the curricula of science and engineering careers when treating themes of optics and spectroscopy. Although we assume that the readers are quite familiar with the subject of optical absorption, in the first part of this paper we do a short reminder of this topic, which is intended to be useful for a better understanding of the thermal lens technique. The central part of the manuscript will be then focused to describe the experimental and theoretical fundamentals of TLS, making emphasis on its main advantage when comparing with the conventional optical spectroscopic method.

II. SOME BASIC CONCEPTS OF OPTICAL SPECTROSCOPY

Optical absorption processes by matter are often based on the Lambert-Beer law, which describes the linear relationship between optical absorbance (A) and the molar concentration (C_m) of an absorbing specie at a specific light wavelength. It is usually written as [1]

$$A = \chi \, L \, C_m, \tag{1}$$

where L is the optical path length (defined by the sample´s thickness), and χ is the molar extinction coefficient, with units of $cm^2 mol^{-1}$, which depends on the light wavelength [1]. The molar concentration is given as the quotient between the number of absorbing centers (e.g., molecules) per unit volume (n) and Avogadro's number, $N_A = 6,02 \times 10^{23} \, mol^{-1}$, so that

$$A = \chi L \, n/N_A \,. \tag{2}$$

Note that it is a unitless parameter defined for the optical path length used in its measurement.

Consider a homogeneous sample shown schematically in Fig.1. If light of intensity I_0 impinges on one face of the sample, the light intensity at a given distance (x) from the surface is given by

$$I = I_0 \exp(-\beta x) = I_0 \exp\left(-\frac{x}{\mu_\beta}\right), \tag{3}$$

where β is the optical absorption coefficient and $\mu_\beta = \beta^{-1}$ is the optical penetration depth, being the distance at which the intensity value at the illuminated sample's surface is reduced e times, i.e., the distance at which the light intensity is attenuated about 60%.
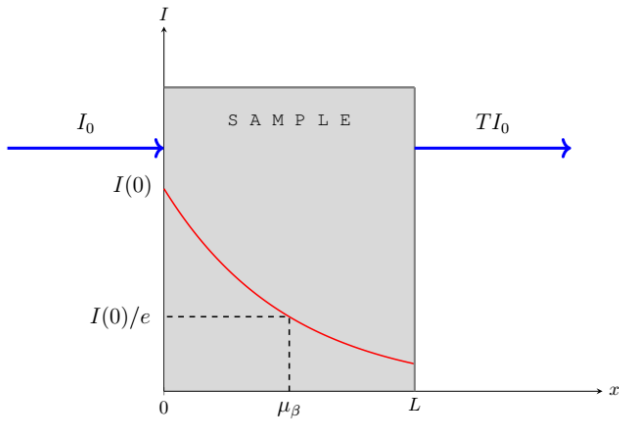

FIGURE 1. Illustration of optical transmission

At $x = L$ the sample's transmittance is defined by

$$T = I/I_0 = \exp(-\beta L) \,, \tag{4}$$

being

$$a = 1 - T = (I_0 - I)/I_0 = 1 - \exp(-\beta L) \,, \tag{5}$$

the fractional absorbance or absorptance.
The sample´s absorbance is defined as

$$A = -\log_{10}(T) = \log_{10}(I_o/I) = \beta L \log_{10}(e) = 0.43\beta L \tag{6}$$

Note from Eqs. (1) and (6) that

$$\beta = \chi \, C_m \, 2.30. \tag{7}$$

It is also a light wave-length dependent parameter.
The absorbance as a function of wavelength defines the optical absorption spectrum, a "fingerprint" for each substance, usually measured directly by commercial optical spectrometers. But the sensitivity of these instruments becomes compromised in the case of very weak optical absorption, as occurs for trace amounts of the optical

absorbing specie. In such a case we can say that we are in presence of the low optical absorption limit for which $\beta L << 1$. Then, Eq. (5) can be rewritten as

$$a = 1 - T = 1 - (1 - \beta L) = \beta L = ln(I_o/I) = \frac{log_{10}(I_o/I)}{log_{10}(e)} = \frac{A}{log_{10}(e)} \approx 2.30A. \tag{8}$$

Often people confound A with a. They are closely related parameters, but they are not the same thing.

III. THERMAL LENS SPECTROSCOPY

A.The experimental set-up

Thermal lens spectroscopy is a technique that allows the measurement of the optical absorbance in an indirect way, namely by measuring the amount of heat generated in the sample due to the optical absorption, instead of the light energy transmitted by the sample. The most widely used configuration of a thermal lens experiment is shown schematically in Fig. 2a.
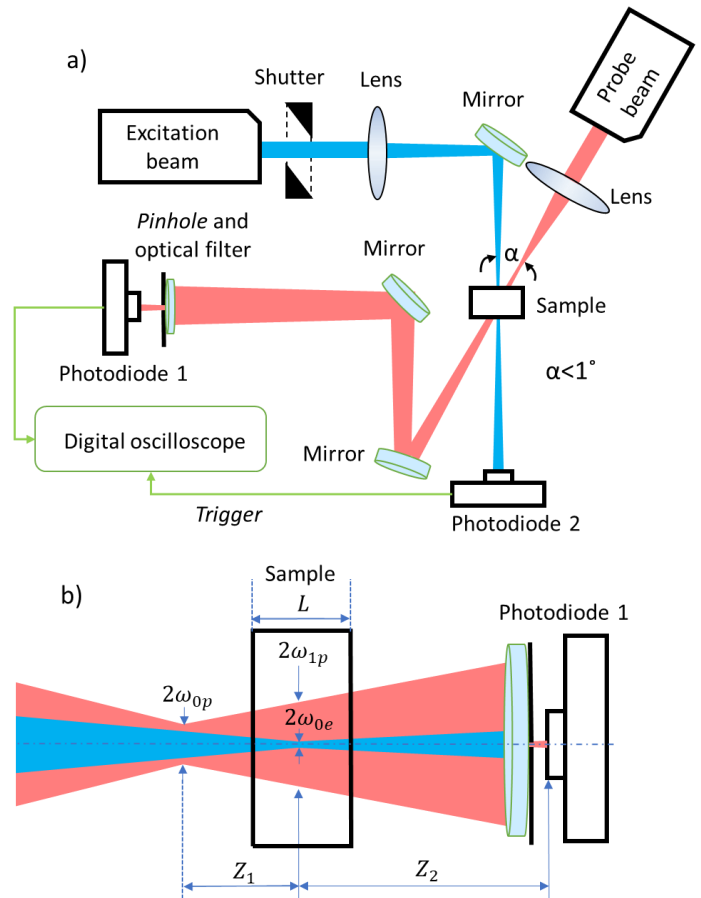

FIGURE 2. a) Schema of the dual beam transient mode-mismatched thermal lens spectroscopy set-up. b) definition of the optical geometrical parameters.

It is named the dual beam, mode-mismatched transient TLS configuration. Mode mismatched means that the waists of the pump and probe beams are different at the sample's position

(see schema at part b of the figure). In TLS, a light beam, often called the excitation or pump beam, is focused on the sample and its energy is partially absorbed and transformed into heat that diffuses through the sample. Consequently, the refractive index (n) is locally altered, causing a change in the phase of another light beam that pass through the same region of excitation. For this light beam, which is named the probe beam, a low intensity gaussian laser is chosen with a wavelength for which the optical absorption of the sample is minimal. The probe laser intensity is recorded at the far field with a photodiode as a function of the time elapsed since the beginning of pumping. The total fractional intensity change is often called the TL signal, which is proportional not only to the optical absorbance, but also to the amount of the light energy absorbed by the sample that is transformed into heat, i.e., the non-radiative photothermal conversion efficiency or photothermal quantum yield (φ). With this method, very weakly absorbing samples can be characterized, and lower limits of detection of the absorbing species can be achieved than with the conventional optical spectroscopy. However, despite this advantage and its easy instrumentation and description, TLS is an almost unknown method for many people and references to it in textbooks of optics and spectroscopy are very scarce.

Usually, the pump laser is highly focused on the sample while the probe beam with a greater diameter is defocused or collimated and passes through the same heated region of the sample. The probe beam's intensity is detected in the far-field by a photodetector and recorded by a digital oscilloscope. A pinhole in front of the detector makes it possible to detect only the central part of the probe laser beam, which contains useful information. A bandpass filter is used to ensure that only the probe laser beam was detected. A mechanical shutter is used to excite the sample during the measurement time. Usually, a second photodetector is used for triggering the oscilloscope reading from the beginning of the excitation.

B. Theory of thermal lens spectroscopy

The most accepted model for the calculation of the TL signal in this configuration was proposed by Shen *et al.* [5]. This model, which involves concepts of thermodynamics and electromagnetic theory, including optics, considers the aberrant nature of the TL to calculate the intensity evolution with time of the probe beam assuming optical absorption and heat diffusion as the unique factors influencing the generation of the TL signal (the model neglects effects such as convection, mass diffusion, etc.). The methodology involves the calculation of the temperature field induced in the sample by heating, for the calculation of the phase shift produced in the probe beam. From this phase shift, the Fresnel diffraction theory allows the calculation of the intensity as a function of time ($I(t)$) at the center of the probe beam in the detector plane. The result is a numerical expression, whose use requires large computing times when applied to fit huge experimental data. However, for a small phase shift and very weak optical absorption, the following analytical expression is proposed [6]:

$$I(t) = I(0)\left[1 - \theta\, arctan\left(\frac{\gamma}{\delta/t+\varepsilon}\right)\right]. \quad (9)$$

Here, $\gamma = mV$, $\delta = [(1+2m)^2 + V^2](t_c/2)$ and $\varepsilon = (1 + 2m + V^2)$ depend on the following optical geometrical parameters (see Fig. 1 b): $m = (\omega_{1p}/\omega_{0e})^2$, $V = Z_1/Z_{cp} + (Z_{cp}/Z_2)[1 + (Z_1/Z_{cp})^2]$, where ω_{1p} (ω_{0e}) is the probe (pump) radius at the sample position, Z_1 is the distance from the waist of the probe beam to the sample, Z_{cp} is the confocal distance of the probe beam, and Z_2 is the distance between sample and photodetector. These parameters can be measured using several methods, being the most accurate of them the use of an optical profilometer (ej, Coherent, LaserCam-HR II - 1/2"). The term $I(0)$ represents the probe beam intensity just before the pump beam is onset. From here on, without loss of the generality we will consider the sample as an absorbing dye dissolved in a solvent. The characteristic time t_c is related to the thermal diffusivity of the solvent, D, by $t_c = \omega_{0e}^2/4D$. Lastly, the thermal-lens parameter is defined as

$$\theta = -\frac{P_H\left(\frac{dn}{dT}\right)}{\lambda_p k}, \quad (10)$$

where P_H is the fraction of the incident light power (P_o) degraded to heat (energy per unit time), dn/dT is the temperature coefficient of the refractive index or optothermal parameter of the solvent (it has a negative value for most liquids at room temperature), λ_p is the probe beam wavelength and k is the thermal conductivity of the solvent [7].
Considering that

$$\varphi(\lambda) = P_H(\lambda)/P_{abs}(\lambda), \quad (11)$$

where P_{abs} is the pump light power absorbed by the sample, then the Eq. (10) can be rewritten as:

$$\theta = -\frac{\varphi P_{abs}\left(\frac{dn}{dT}\right)}{\lambda_p k}. \quad (12)$$

Neglecting light reflection and elastic scattering, the energy conservation law reads

$$P_o(\lambda) = P_T(\lambda) + P_H(\lambda) + P_L(\lambda_L), \quad (13)$$

where $P_T(\lambda)$ is the power of the light transmitted through the sample and $P_L(\lambda_L)$ is the total power of the photons that can be re-emitted by fluorescence with wavelengths $\lambda_L > \lambda$ (i.e., with lower energy than that of the incident light). Therefore,

$$P_{abs}(\lambda) = P_o(\lambda) - P_T(\lambda) = P_H(\lambda) + P_L(\lambda_L). \quad (14)$$

Then, substituting Eqs. (5) and (14) into Eq. (12) leads to

$$\theta = -\frac{\varphi P_o\left(\frac{dn}{dT}\right)}{\lambda_p k}\left(1 - e^{-\beta L}\right) = -\frac{\varphi P_o\left(\frac{dn}{dT}\right)}{\lambda_p k}\beta L_{eff}. \quad (15)$$

where

$$L_{eff} = \frac{(1 - e^{-\beta L})}{\beta}. \qquad (16)$$

Note that for a non-fluorescent sample one can consider that all absorbed energy is transformed into heat, so that $\varphi = 1$. Then, we have

$$\theta = -\frac{P_o \left(\frac{dn}{dT}\right)}{\lambda_p k} \beta L_{eff}. \qquad (17)$$

Assuming also very weak optical absorption, such that $\beta L \ll 1$, then $L_{eff} = L$ and Eq. (17) takes the form usually appearing in the specialized Literature [8]:

$$\theta = -\frac{P_o \left(\frac{dn}{dT}\right)}{\lambda_p k} \beta L = -\frac{2.30 P_o \left(\frac{dn}{dT}\right) A}{\lambda_p k} = -\frac{P_o \left(\frac{dn}{dT}\right) a}{\lambda_p k} = -EA. \qquad (18)$$

If the above-considered assumptions are not well met, care must be taken in applying this equation.
In Eq. (18) we defined the enhancement factor

$$E = \frac{2.30 P_o \left(\frac{dn}{dT}\right)}{\lambda_p \quad k} = \frac{2.30 P_o}{\lambda_p} F, \qquad (19)$$

and the figure of merit

$$F = \frac{\left(\frac{dn}{dT}\right)}{k}, \qquad (20)$$

because the reasons that we will see in the following section. The TLS signal is often defined as the total fractional change of the probe beam intensity, namely

$$S = \left| \frac{I_o - I(t \gg t_c)}{I_o} \right| = \theta G = GEA, \qquad (21)$$

where G is the value of the arctangent term in Eq. (9) for times much greater than the characteristic time (t_c is typically of the order of a few milliseconds while a typical $I(t)$ curve is recorded during several seconds as shown in the next section). As an example, for a highly focused pump beam and a perfect collimated probe beam, Marcano *et al* [6] demonstrated that $G = \pi/2$, while a value close to that was experimentally obtained by Marin and Isidro-Ojeda [7] using a non-collimated beam.

C. A typical experiment

Fig. 3a. shows a typical intensity evolution with time for a sample of 12.5 ppm of the Deyman's organic dye "Strawberry 2143 v.7" dissolved in distilled water. Part b of the figure shows the optical absorption spectrum of the same sample. This spectrum was recorded using an Ocean Optics spectrometer (Flame-T-UV-VIS-ES), and a 1 cm thick quartz cuvette, the same used in the TLS arrangement. For the pump laser wavelength, the 514 nm line of an Ar-ion laser (Edmund Optics Multi-Line, 4 Lines Selectable, Argon-Ion Laser) was chosen, which is near the absorption maximum of the solution.

The pump laser power was $P_o = (21.85 \pm 0.02)$ mW. A HeNe laser (Newport, Model R-30995) emitting at 632.8 nm

was used for the probe beam (~1mW power). At this wavelength, the optical absorption of the sample is negligible. The values of the optical geometrical parameters used in the described experiment are the same given in a recent paper [8]. The other components used in the experiments were a Tektronix, TBS 2000 Series model oscilloscope, THORLABS-DET36A/M and Newport 818-BB-21 photodetectors, a Thorlabs SHB1T mechanical shutter, and a Thorlabs, P200s pinhole, in addition to optical components such as mirrors, optical attenuators, lenses and filters. A classroom experiment can also be easily implemented using similar equipment available in the market at very accessible prices today. The solid line in Fig. 3a shows the result of the best least squares fit using Eq. (9), leaving t_c and θ as adjustable parameters, for which the values (3.62 ± 0.01) ms and (0.1027 ± 0.0002) were obtained, respectively. Using the t_c-value and $\omega_{0e} = (45 \pm 1)$ μm, the thermal diffusivity of the solvent was obtained as $D = (1.40 \pm 0.01) \times 10^{-7}$ cm^2/s, in good agreement with the literature reported value for water [9]. Using Eq. (1) and the values $k = 0.595$ Wm^{-1}K^{-1} [6] and $dn/dT = -0.8 \times 10^{-4}$ K^{-1} [10] reported for water, we obtained a sample´s absorbance of 0.087, in agreement with the value of Fig. 3b at the pump laser wavelength.
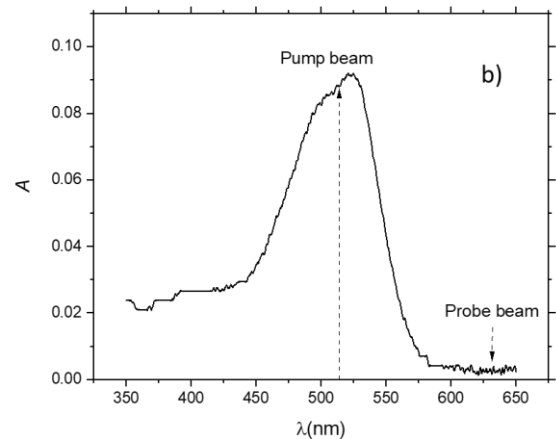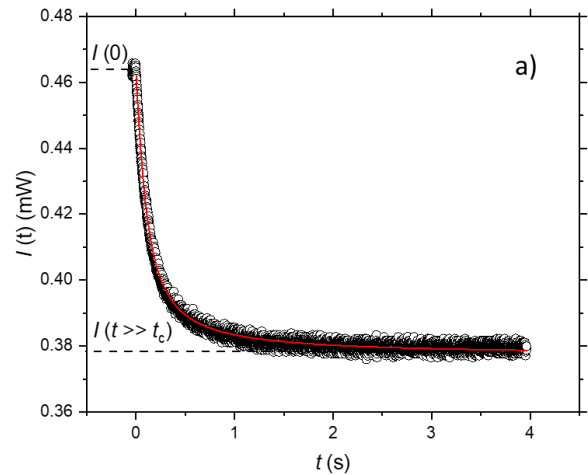

FIGURE 3. a) A typical probe beam intensity as a function of time obtained for 12.5 PPM Deyman/water sample. b) The optical absorbance spectrum of the same sample.

IV. THE ADVANTAGE OF THERMAL LENS OVER OPTICAL SPECTROSCOPY

Each method has its pros and cons. Conventional optical spectroscopy is easy to implement, and the interpretation of its results is relatively simple. It is a commercially available technique accessible to many scientific and teaching laboratories. But its application is limited in the case of very opaque samples that don't transmit light, for highly transparent samples where transmitted light intensity is comparable with that of the impinging light, and for samples exhibiting the light scattering phenomenon, for which must be aided by complicated sophisticated and expensive equipment such as integrator spheres. In these cases, techniques that measure the amount of absorbed energy by the sample, being less affected by scattering are the options of choice. Thermal lens spectroscopy is one of these methods.

Eq. (21) describes the main advantage of TLS over conventional optical spectroscopy in a simple way. Optical spectroscopy directly measures the sample's absorbance, while the TLS signal measures the same magnitude multiplied by the product of the parameters G and E. The first of them depends on geometrical optical parameters that are fixed and well-known in each experiment. The second one, the enhancement factor, depends on the probe laser wavelength and the pump laser power, which are also fixed parameters of the experiment, and on the enhancement factor, a solvent property. Because of the constancy of G, the larger be the enhancement factor, the greater be the parameter that multiplies the absorbance in Eq. (21) and, consequently, the thermal lens signal.

Because the thermal lens method is based on measuring with a probe laser the changes in the sample's refractive index induced by light absorption, several people choose a sample with a high photothermal parameter to increase the enhancement factor but forgot to consider the effects of the thermal conductivity value.

Fig. 4 shows the figure of merit as a function of thermal conductivity (a) and as a function of the photothermal parameter (b) for some solvents of interest (values were taken from [11]). The figure of merit has the largest value for a solvent with a lowest thermal conductivity (Carbon Tetrachloride). However, the solvent with the highest photothermal parameter (Benzene) is not that with the highest figure of merit. Therefore, Eq. (4) doesn't imply that the highest figure of merit can be achieved for a sample with the highest photothermal parameter and the lowest thermal conductivity, but for a solvent with a highest F.

On the other hand, note that the figure of merit for water is at least 20 times lower than that of the other solvents analyzed here. But water is the universal solvent in nature, so there are experiments in which it is not possible to substitute it with another solvent with a higher F, for example, in applications related to the determination of traces of contaminants in water.

Therefore, it is important to find variants to increase the enhancement factor. One obvious way to do that is by increasing the power of the excitation beam. But this variant has some disadvantages, for example, convective and non-linear effects can be produced at high laser energies, and the

boundary conditions imposed by the theoretical models used for data analysis cannot be well fulfilled. Changing the water temperature is another possibility to increase the figure of merit [12], but this is a complicated way from the experimental point of view and can alter other sample's properties, as can happens with the addition of some amounts of a solvent with a higher figure of merit to the sample.

A very simple way to increase the enhancement factor was discovered in a serendipitous way. As part of an international work team, some authors of the present work were making measurements using homemade thermal lens spectrometer when they noticed a very intense signal in one reflection of the probe laser beam coming from the sample. The signal was being amplified between two reflective surfaces, namely the exit mirror of the HeNe laser used to generate the probe beam and the sample itself. Then, the team understood that if they placed the sample between two properly arranged mirrors, this process could be reproduced because the multiple passes of the probe beam forth and back through the sample. In this way, the optical path length in Eq. (18) increases in a factor (p) proportional to the number of passes and the enhancement factor (Eq. (19)) becomes multiplied by p.
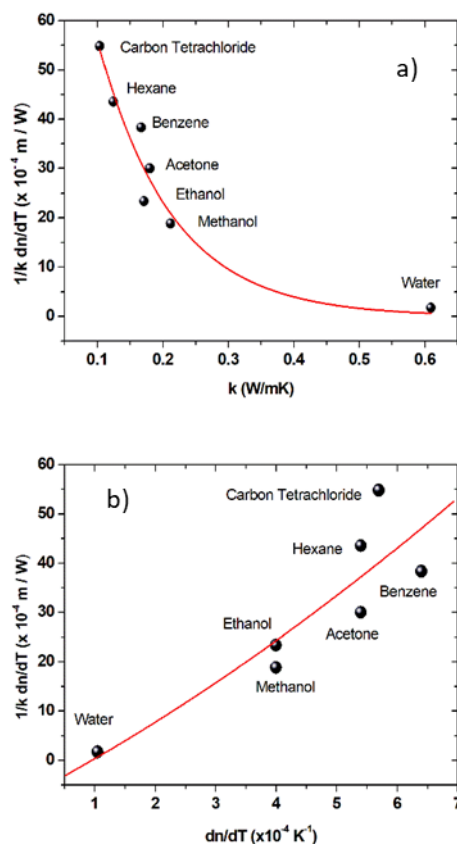

FIGURE 4. Thermal lens figure of merit $F = \frac{1}{k}\frac{\partial n}{\partial T}$ as a function of (a) the thermal conductivity and (b) the optothermal parameter for some solvents of interest at $300 K$ and $1\ atm$. Solid curves are shown only for visualization purposes.

An increase of ten in the factor p allowed to obtain limits of detection of three valent iron [13] and hexavalent chromium

[14] in water of the order of magnitude of parts per trillion, values well-below the limits established by international regulations for this pollutant in drink water [15]. In addition to trace measurements, recent applications of the improved method were the measurement of optical absorption spectra in very weak optical absorbers such as ethanol and water in the visible part of the electromagnetic spectrum [16], the monitoring of photocatalytic reactions in situ at low concentrations of the degraded specie [17], characterization of the thermo-diffusion of nanoparticles due to heating in photothermal therapy-oriented processes [18], among others.

In addition to those mentioned above, there are several applications of TLS that have been reviewed by several authors [19, 20, 21, 22] to which the interested people can be referred. Today it is very important to develop experimental methods with high sensitivity capable of measuring samples at very low concentrations and in very small sample volumes, that are based on compact and portable equipment, and be as non-invasive as possible. One of the most promising techniques for this is thermal lens spectroscopy. A modern area in analytical chemistry is the miniaturization of instruments and the integration of as many analysis steps as possible into a compact device, such as a microchip, in which both the sample quantity and the analysis time can be reduced without compromising the sensitivity of the technique. These systems known as lab–on–a–chip technologies, typically accommodate the detection zone and an interface with an external detector. The selection of the detection technique is one of the most important aspects that are being addressed worldwide due to the small sample volumes and the low concentrations to be measured, which require methods capable of detecting only a few molecules. Optical methods are very advantageous, but conventional optical spectroscopy is not useful due to the reduced optical paths imposed by miniaturization and some reasons addressed in this paper. One of the most widely used techniques is laser-induced fluorescence, but its application is limited to fluorescent samples. Because of this, and the advantages mentioned here, thermal lens spectroscopy results in an ideal variant that many research groups worldwide are addressing. Therefore, we believe that introducing this subject in modern courses of applied optics and related disciplines becomes necessary.

V. CONCLUSIONS

We reviewed, in a way that we hope can be accessible to teachers and students of science and engineering at university level, the experimental basis and equations describing thermal lens spectroscopy, a technique of growing interest due to its several applications in physics and analytical chemistry. We believe that this theme can be of interest for people dealing with spectroscopy and related items.

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