



Thermal lensing and absorbance spectra of a fluorescent dye solution

J. Hung^a, A. Marcano O^{a,*}, J. Castillo^b, J. González^b, V. Piscitelli^b,
A. Reyes^b, A. Fernández^b

^a Centro de Física, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020 A, Venezuela

^b Escuela de Química, Universidad Central de Venezuela, Los Chaguaramos, Caracas 1020A, Venezuela

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Abstract

We compare thermal lensing and absorbance spectra of a fluorescent dye solution. When the dye solution shows a strong fluorescence, the thermal lensing spectrum is blue-shifted and broadened when comparing to the absorbance spectrum. No such differences between both types of spectra are reported when the fluorescence is quenched.

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1. Introduction

Light absorption spectroscopy is a powerful method for characterization and identification of materials. Absorption spectrum is usually determined by the measurement of the transmittance through the sample as a function of the wavelength of the incident light. Besides the transmittance method, a thermal lensing (TL) technique has been widely used for the characterization of absorption [1–3]. The TL is a photothermal technique that measures the distortion of the light wavefront induced by the heat deposited in the sample by the propagating beam. The light being absorbed generates in the sample a spatial distribution of temperatures. Since the refraction index depends on the temperature, a spatial distribution of the refraction index or thermal lens is generated. The generated thermal lens affects the beam propagation distorting its wave front. A magnitude of this distortion is determined by measuring the transmittance of a small aperture located at the far field. The relative transmittance of this aperture is a measurement of the absorption coefficient. The use of an excitation-probe variation of the TL technique allows for the implementation of TL spectroscopy studies [4–9]. The probe beam tests the thermal lens generated by a

excitation light beam. If the excitation source is tunable like a Dye laser, an F-center laser or an optical parametric oscillator (OPO), the TL signal is a function of the excitation wavelength (TL spectrum).

There is an important difference between the absorbance, measured through transmittance, and the TL spectra. The TL method measures the energy absorbed by the materials as heat. The absorbance method measures the total lost of energy of the electromagnetic wave when propagating through the medium. The absorbance spectrum and the TL spectrum are the same if there are not additional effects besides thermal heating in the medium. However, in a medium showing high fluorescence, Raman or other types of light scattering, the absorbance spectrum might not be same that the TL spectrum.

The purpose of this work is to compare the TL spectra and the absorbance spectra of a dye solution when a strong fluorescence is taking place. We compare also both types of spectra when the fluorescence process is depleted by addition of a quencher into the solution. We perform experiments on a low concentration ethanol solution of Rhodamine 6G. We show for the first time that in the presence of strong fluorescence, the TL spectrum is blue-shifted and broadened when comparing to the absorbance spectrum. The blue shift and the spectral broadening are not observed when adding a fluorescence depleting quencher into the dye solution.

* Corresponding author. Fax: +582125041148.

E-mail address: marcano@pion.ivic.ve (A. Marcano O).

2. Theoretical considerations

We consider that the absorption of excitation light generates in the dye solution only two types of effects: fluorescence and thermal heating. In this regard, we consider the losses on reflection, dispersion and possible photochemical reactions negligible. Using the conservation energy principle we can write

$$P_0(\lambda_e) = P_T(\lambda_e) + P_F(\lambda_e) + P_{Th}(\lambda_e), \quad (1)$$

where P_0 is the incident excitation power, P_T is the power transmitted through the sample and, P_F is the power of the fluorescence emission, P_{Th} is the power degraded to heat and λ_e is the wavelength of the excitation light. An ordinary transmission measurement determines the ratio

$$T(\lambda_e) = \frac{P_T(\lambda_e)}{P_0(\lambda_e)}. \quad (2)$$

The absorbance spectrum $A(\lambda_e)$ can be obtained by using the definition

$$A(\lambda_e) = -\log(T(\lambda_e)). \quad (3)$$

The fluorescence excitation spectra is defined as

$$F(\lambda_e) = \frac{P_F(\lambda_e)}{P_0(\lambda_e)}. \quad (4)$$

The fluorescence excitation spectrum is different from the fluorescence spectra usually measured, where the emission spectrum is obtained for a fixed value of the excited wavelength.

Finally, we define the thermal absorption coefficient as

$$A_{Th}(\lambda_e) = \frac{P_{Th}(\lambda_e)}{P_0(\lambda_e)}, \quad (5)$$

where $P_{Th}(\lambda_e)$ is the amount of absorbed light power degraded to heat. This coefficient measured as a function of the excitation wavelength λ_e gives the TL spectrum. The coefficient $A_{Th}(\lambda_e)$ can be obtained through the measurement of the TL signal. In the experiment described below, we use a excitation-probe method for the determination of the TL signal. The TL signal is usually defined as the relative change of the probe beam transmission of a small aperture located at the far field and at the axis of the probe beam. In this regard, the amplitude of the TL signal can be written as

$$S(\lambda_e) = \frac{T_a(\lambda_e) - T_{a0}}{T_{a0}}, \quad (6)$$

where $T_a(\lambda_e)$ is the probe light transmission of the aperture in the presence of the excitation beam and T_{a0} is the probe light transmission of the aperture in the absence of the excitation beam. Different authors have used a Fresnel diffraction approximation for the calculation of the TL signal given by Eq. (6) in the pulse regime [1,10,11]. These models show that for low absorption the TL signal is proportional to the thermal power. At the far field the TL signal amplitude is

$$S(\lambda_e) = GP_{Th}(\lambda_e), \quad (7)$$

where G is a proportionality parameter given by

$$G = \left(\frac{2\tau}{\pi\rho C_p} \frac{dn}{dT} \right) \frac{8k^2z}{k^2\omega_0^4 + 8k\omega_0^2z_c + 16(z_c^2 + z^2)}, \quad (8)$$

where τ is the excitation pulse width, ρ is the sample density, C_p is the sample heat capacity, dn/dT is the sample thermal gradient of the refraction index, $k = 2\pi/\lambda_p$, λ_p is the probe wavelength, ω_0 is the excitation beam radius, z is the sample position and z_c is the probe beam confocal parameter. By measuring the excitation wavelength dependence of the TL signal $S(\lambda_e)$ and by using Eqs. (5) and (6), we obtain the excitation wavelength dependence of the thermal coefficient $A_{Th}(\lambda_e)$ or TL spectrum. The proportionality coefficient G in Eq. (8) is usually determined after properly calibration of the TL experiment using a non-luminescence reference compound. This calibration can be performed also if the absolute value of the transmission spectrum $T(\lambda_e)$ and the relative values of the spectra $A_{Th}(\lambda_e)$ and $F(\lambda_e)$ are known.

Using Eqs. (2)–(5), the Eq. (1) can be transformed into

$$1 - T(\lambda_e) = 1 - 10^{-A(\lambda_e)} = F(\lambda_e) + A_{Th}(\lambda_e). \quad (9)$$

Eq. (9) states that absorbed light energy is redirected into fluorescence emission and thermal lens generation.

The thermal lens signal has been used in the past for the determination of the fluorescence quantum yield of dye solutions [12,13]. The quantum yield is [13]

$$\Phi_F(\lambda_e) = \frac{\lambda_F}{\lambda_e} \left(1 - \frac{A_{Th}(\lambda_e)}{1 - T(\lambda_e)} \right), \quad (10)$$

where λ_F is the averaged fluorescence wavelength.

3. Experimental method

In Fig. 1, we show the experimental set-up used for the measurements of absorbance, fluorescence excitation and TL spectra. The excitation field is derived from the output of an OPO laser (Continuum Surelite Optical Parametric Generator). This device is excited by the third harmonic from Nd:YAG laser, which generates 8 ns pulses at 10 Hz repetition rate (Continuum Surelite I, 355 nm emitting wavelength). For the purpose of the experiment, the light wavelength of the OPO laser is scanned between 450 and 560 nm. The maximal pulse energy is 0.1 mJ. A system of mirrors (M1 and M2) and a 20 cm focal length achromatic lens (L1) direct the excitation beam onto the sample cell. In front of the focusing lens we use the aperture P to limit the input excitation radius to 1 mm. To avoid bleaching of the absorption we locate the sample 20 cm away from the focal plane of the excitation beam. The beam spot radius

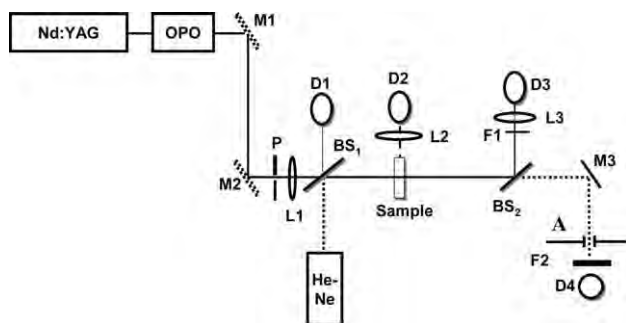


Fig. 1. Experimental set-up used for the measurement of the absorbance, fluorescence excitation and TL spectra consisting of: a Nd:YAG laser exciting an optical parametric oscillator OPO, mirrors M1 and M2, a 1 mm radius aperture P, a 20 cm focal length lens L1, a beam-splitter BS₁, a probe He–Ne laser. A solution sample contained in a 1 cm pathlength glass cell, lens L2 and detector D2 for collecting the fluorescence signal, detector D1 for registering the reference excitation beam, a lens L3 for collecting and a detector D3 for registering the transmitted excitation beam. A dichroic beam-splitter BS₂ for separation of the excitation and probe light, an optical neutral filter F1, a mirror M3, aperture A, an interference filter F2 for $\lambda = 632$ nm and a detector D4 for registering the TL signal.

at this position is estimated to be 1 mm. The maximal light irradiance in this condition is estimated to be 80 kW/cm^2 , which is much smaller than the saturation irradiance value. The beam-splitter BS₁ directs a small part of the beam into the detector D1, which monitors a signal proportional to the incident excitation power P_0 . After propagation through the sample, the transmitted light is directed onto the detector D3 by using the beam-splitter BS₂ and the lens L3. The filter F1 is used to reduce the power level of this light avoiding saturation of the detector. By using Eqs. (2) and (3) and the detected power values of the incident and transmitted signals, we determine the absorbance spectrum. Absolute values of the absorbance are determined by accurately recording the absolute values of P_0 and P_T . For calibration purposes, we also measured the absorbance spectrum of the sample using a commercial Spectrophotometer (Ocean Optics).

The fluorescence excitation signal is collected at 90° and focused by a 2 cm focal length lens L2 onto a silicon photodetector D2 (Thorlabs, Model DET210). By dividing the signal recorded by detector D2 over the signal recorder by detector D1 we determine the fluorescence excitation spectrum up to a constant factor, which is determined through calibration.

For measuring the TL signal we use a mode mismatched excitation-probe configuration. The excitation beam is the same excitation beam generated by the OPO laser. The beam from He–Ne laser (632 nm, 1 mW) is used as a probe. We use the beam-splitter BS₁ to direct the probe beam toward the sample collinearly with the excitation beam. Following the scheme of a mode-mismatched TL experiment recently proposed no focusing

optics is used in the path of the probe beam [14–16]. This configuration simplifies significantly the alignment of the excitation-probe TL experiment. Behind the sample, the probe beam passes through the beam splitter BS₂ toward the dichroic mirror M3, which reflects the light onto a 1 mm diameter aperture A. This dichroic mirror allows only the probe light to reach the detector. Behind the aperture, the interference filter F2 cancels the remaining excitation light letting through only the probe light toward the detector D4. This detector gives a direct measurement of the TL signal.

The achromatic character of the mode mismatched TL set-up needs a special discussion. Twarowski and Kligler [18] have reported that the spot radius of the excitation beam changes with the wavelength affecting the value of the TL spectrum. The geometrical factor G in Eq. (8) accounts for this dependence. However, this conclusion is only true if the sample is located at the beam excitation waist. We are performing the TL experiment 20 cm away from the excitation beam waist. In this situation, the dependence of the spot beam radius on the wavelength is significantly reduced. For the conditions of the experiment described below, we have estimated that the factor G decreases less than 2% when increasing the excitation field wavelength between 450 and 560 nm.

The TL and the fluorescence excitation signals are recorded using a digital averaging oscilloscope (100 MHz, Tektronix 3032), that provides a complete time domain representation of the signal. The transmission and reference is monitored using a digital oscilloscope (Hewlett–Packard 54610B).

The experiments are performed on Rhodamine 6G diluted in ethanol solution at room temperature and at different wavelength (450–560 nm) of the OPO laser. The ethanol solution concentration is 5×10^{-6} M. At this low concentration, no dimer formation is expected. The quenching experiments are performed with the same Rhodamine solution using potassium iodine as quencher, until reaching solution saturation. The solution samples cells are contained in a 1 cm path-length glass cell.

4. Results and discussion

Fig. 2 shows the absorbance (crossed circles), TL (solid triangles) and fluorescence excitation (crossed stars) spectra of the Rhodamine 6G–ethanol solution. The solid line is the absorbance of the same sample measured using the commercial spectrophotometer. The absorbance spectrum obtained using the pulse OPO laser reproduces the usual absorbance spectrum of Rhodamine 6G. Because of the high values of the fluorescence quantum yield of the Rhodamine 6G, the fluorescence dominates over the thermal absorption

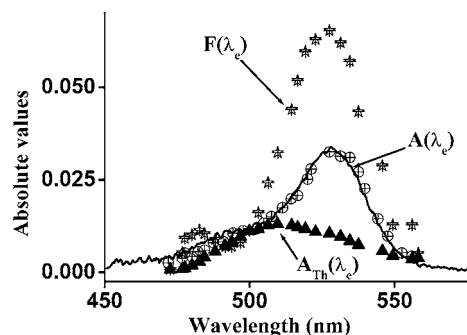


Fig. 2. Absorbance (crossed circles), fluorescence excitation (crossed stars) and TL spectra (solid triangles) of a 5×10^{-6} M ethanol solution of Rhodamine 6G. The solid line is the absorbance spectrum of the same sample obtained using a spectrophotometer.

process. The fluorescence excitation spectrum exhibits a peak at 527 nm coincident with the absorbance peak value. The thermal absorption is only a fraction of the absorbance. Besides this, the shape of the TL spectrum differs from the absorbance one: the TL spectrum is blue shifted by 22.3 nm and its spectral width (FWHM) is 42 nm, 30% wider than the FWHM of the absorbance spectrum (31.5 nm). The signal-to-noise ratio of the TL spectrum is estimated to be 30. For the results shown in Fig. 2, we estimate that Eq. (9) is observed within an experimental error of 7%.

The reason for the differences between the absorbance and the TL spectra can be understood as follows: the fluorescence excitation spectrum shows a minimum at 491 nm although the absorption remains relatively high for the same spectral region. The absorbed energy must be then redirected into heat through radiationless mechanisms. Different radiationless mechanisms can take place. The most important is the internal conversion or non-radiative decay of the lowest excited singlet state S_1 directly to the ground state S_0 . Intersystem crossing or non-radiative decay of the S_1 to the lowest triplet level T_1 can also deplete the fluorescence and increase the thermal output. Secondary absorption from excited states S_1 and T_1 are an additional fact to take into account in the fluorescence depletion. Finally, an important amount of non-radiative decay or cross-relaxation occurs within the spectral bands of the dye molecule. When changing the excitation field wavelength, different population distributions take place within the first excited band S_1 . After excitation, the radiation and radiationless channels of relaxation compete for the energy in different ways leading to different outputs in the fluorescence and thermal energy. In this regard, the maximal values for the thermal and fluorescence emission may not be coincident with the maximal value of the absorbance spectrum. For example, for large excitation wavelength, but still within the absorption band, the lower region of the excitation band S_1 is relatively more populated than the rest of the band. This

region contributes the most to the fluorescence emission. At shorter excitation wavelength, the upper region of the S_1 band is relatively more populated. From this region, the system must first decay without emitting light toward the lowest region of S_1 , where the fluorescence can take place. In other words, short excitation wavelength must favor the thermal conversion of the absorbed energy comparing with an excitation at large wavelength. In this regard, one can expect a blue shift for the thermal spectral response when comparing with the absorbance maximum position.

Despite all the complexity of the mechanisms involved in the dye molecule excitation and subsequent evolution, the results shown in Fig. 1 state that when a depletion of fluorescence is detected with not substantial change in the absorption, the absorbed energy is converted into heat through any of the radiationless decay mechanisms described.

The fluorescence quantum yields can be reduced considerably by adding a quencher into the solution. By adding amount of potassium iodine crystals (KI) into 1.5 ml of the sample, we reduce the fluorescence emission by a factor of 5. In this situation, the thermal absorption becomes dominant and the differences between the absorbance and the TL spectra are reduced. In Fig. 3, we show the absorbance (crossed circles), fluorescence excitation (crossed stars) and TL (solid triangles) spectra of the same sample after adding the quencher. The absolute value of the absorbance is decreased by a factor of 2. The absorbance and TL spectra show a similar peak position and a similar spectral width. We also determine that the absolute value of the thermal absorbance increases by a factor of 2 reaching approximately 80% of the total lost. We conclude that the fluorescence is being depleted and the absorbed energy is being redirected toward the thermal absorption process in accordance with Eq. (9). For the results shown in Fig. 3, we estimate that Eq. (9) is observed within an experimental error of 5%.

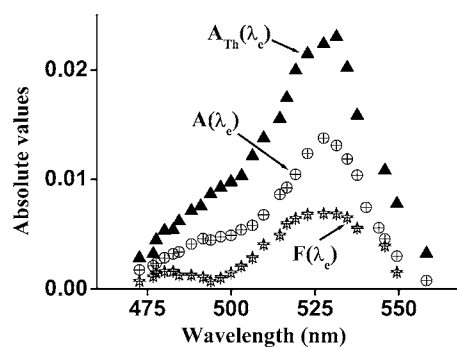


Fig. 3. Absorbance (crossed circles), fluorescence excitation (crossed stars) and TL spectra (solid triangles) of the same sample of Fig. 2 after adding of the quencher (KI). All the experimental conditions are as in Fig. 2.

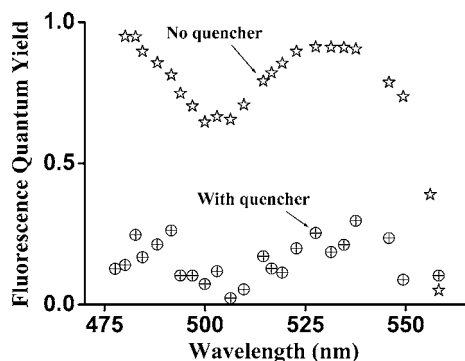


Fig. 4. Fluorescence quantum yield spectrum of the 5×10^{-6} M ethanol solution of Rhodamine 6G in presence of high fluorescence and in the presence of fluorescence quenching.

The obtained TL and absorbance spectra can be used for the estimation of the fluorescence quantum yield using Eq. (10). For this calculation, we use the averaged wavelength $\lambda_F = 562$ nm for all values of the excitation wavelength range. In Fig. 4 we show the fluorescence quantum yield dependence on the excitation wavelength for the data shown in Figs. 2 and 3. A maximal value of 0.92 ± 0.05 is obtained at 527 nm. This value is in good agreement with previous measurement of fluorescence quantum yield of Rhodamine 6G in the same spectral region [12,17,19]. After adding the quencher into the solution, the quantum yield decreases by a factor of 5 as corresponds to a depleted fluorescence situation.

The shape of the TL and fluorescence excitation spectra depends also on the solvent characteristics. Preliminary experiments performed on water and glycerol samples confirm this fact. As expected, the maximal values of the fluorescence excitation and TL spectra do not coincide with the maximum value of the absorbance spectrum. However, the sum of these spectra does reproduce the shape of the absorbance in accordance with Eq. (9). Experiments are under going in order to perform a more detailed study of the influence of the solvent properties on the shape of the TL and fluorescence excitation spectra.

5. Conclusions

We have performed a comparison between the TL and absorbance spectra of a fluorescent dye solution. We show, for the first time, that the TL spectra and the absorbance spectra differ substantially if the fluorescence is the dominant process. The TL spectrum is blue-

shifted and its spectral width is larger than the spectral width of the absorbance spectrum. These differences are the results of the competitive dynamics of the different radiation and radiationless decay mechanisms that act after the absorption has taken place. If the fluorescence is depleted by the use of a chemical quencher, the TL and the absorbance spectra are similar. In this situation, the thermal absorbance increases becoming the dominant process. We show that the TL experiment is a complementary spectroscopic method for the characterization of fluorescent materials. The TL spectrum can be used for the determination of the quantum yield spectrum of the fluorescent dye. In a similar way, the TL spectrum can be used for the complementary spectroscopic characterization of samples exhibiting high dispersion such as emulsions, Raman and other complex materials.

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