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Fluorescence quantum yield determination of molecules in liquids by thermally driven conical diffraction

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ABSTRACT

We report on a method to determine fluorescence quantum yield (η) of molecules in solution based on the observation of conical diffraction (CD) patterns induced by thermally driven self-phase modulation (SPM). In this approach, the central part of a laser beam is acquired as a function of its power after passing through the sample. If the thermal properties of the solvent are known, one can directly obtain η by measuring the sample optical absorption and the rings produced by CD. Otherwise, if the thermal properties of the sample are unknown, an additional measurement with the same solvent containing nonfluorescent molecules (blue-black ink, for instance) for thermal SPM generation is also needed. In this case, besides determination of η, one can also find the thermal conductivity (K) of the unknown solvent provided that the thermo-optic coefficient (dn/dT) is independently measured. K values obtained with this approach are in good agreement with the literature. CD technique was applied in rhodamine 6 G and a chromophore derivative of vitamin B6 in different solvents. Therefore, the present method may serve as a low-cost optical approach for η determination in liquid samples and for K measurements in unknown solutions.

1. Introduction

Fluorescence quantum yield (η) characterization is essential for the development of novel materials that can be used in light-emitting devices [1,2]. Several techniques based on emission spectra are used for the determination of η relative to a known reference chromophore [3]. Other optical techniques using an integrating sphere, photoacoustic spectroscopy and thermal lens (TL) are currently applied for η determination, but relatively sophisticated alignment or pump-probe configuration are needed [4,5]. Our group introduced the conical diffraction (CD) technique for nonradiative quantum efficiency (φ) determination in liquid samples [6,7]. Now, we present an improved CD procedure using a normalizing reference nonfluorescent sample for η determination. This low-cost technique is simple, and no additional information about thermal conductivity (K) and thermo-optic (dn/dT) coefficients of the samples are required.

In general, the propagation of the intense laser beam through a nonlinear medium leads to several transverse effects [6,8,9]. The spatial profile of the incident beam changes and ring patterns surrounding the central spot of the ray may be observed at the far-field region. The symmetry of the ring pattern is circular if distortion due to thermal convection is negligible [6,10]. Spatial self-phase modulation (SPM) can be mathematically modeled by using the Fresnel-Kirchhoff diffraction integral [6,11], and different studies of SPM effects are described in various materials [8–12].

The present work applies the normalized CD method for the determination of η in chromophores derivatives of vitamin B6 in different solvents (water, ethanol, chloroform, dimethyl sulfoxide (DMSO) or acetonitrile) and rhodamine 6 G. The vitamin B6 was characterized because their species as pyridoxal, pyridoxine, pyridoxamine and pyridoxal 5´-phosphate have been extensively researched due to their potential benefit to human health, as a key role in inflammatory diseases and antioxidant activity [13,14]. Derivatives of vitamin B6 materials are in continuous development, as they promise for a variety of novel applications as toxic metal ions sensing and pH sensor in aqueous media [15,16].

Also, the present automatized CD setup was used with the nonfluorescent ($\varphi \approx 1$) blue-black ink to determine the thermal

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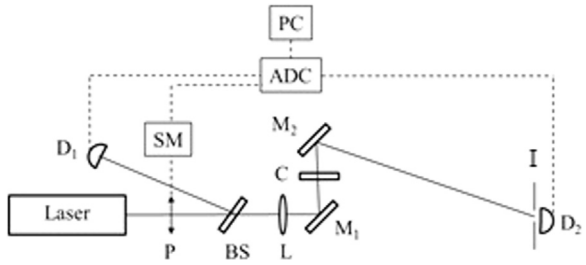

Fig. 1. Experimental setup used to measure CD. Here P is a polarizer, BS a beam splitter, L a lens, M_1, and M_2 are mirrors, C is the cuvette, D_1 and D_2 are detectors, I is an iris, SM is a stepping motor, ADC an analog to digital converter, and PC a personal computer.

conductivities of different solvents. Several techniques are used for thermal conductivity determination in liquids. They include the laser flash method, transient hot-wire method, methods of coaxial cylinders and parallel plates, with typical errors between 1% and 5% [17,18]. For the stationary hot-wire method, 10% errors for K are typical [18]. Since K values of liquid organic and inorganic compounds are sometimes unknown, not available at different temperatures, and the values obtained from the literature by various authors may differ [19,20], we think to be of interest to introduce a new simple technique to measure this parameter.

2. Material and methods

Fig. 1 shows the automatic setup used to measure CD in solutions. The light from a linearly polarized argon ion laser operating at 514.5 nm passes through a rotating linear polarizer that modulates the light intensity according to the Malus law. The polarizer rotation is controlled by a step motor driven by a personal computer interfaced to an analog to digital converter (ADC). In this way, the rotation speed can be chosen to be faster when the intensity varies slowly. A small fraction of the light (~10%) is picked up by a glass plate beam splitter (BS) and directed to a reference detector D_1 connected to the ADC. The incidence of the excitation beam in BS is close to normal (angle less than 10 degrees) and thus the s and p polarizations of reflected light contribute almost equally. This signal provides the input for the x-channel of intensity plots presented later. The voltage measured is converted to incident power by using a power meter just before the sample. After passing through a focusing lens (f = 20 cm) the beam is folded vertically by a dielectric mirror (100% reflectivity at the wavelength used, regardless of the polarization) and impinges on a 2-mm thick glass cuvette placed horizontally (to avoid convection effects). CD measurements were performed when the sample is positioned at the focus of the pump beam. CD signal was acquired only in the central part of the ring pattern, and to do so, an iris was placed before detector D_2 that receives light coming from mirror M_2.

For a given polarizer angle that defines the power incident on the sample, the PC reads and stores the values of the two detectors. Then, the step motor rotates to a new angle, and new values are measured. After acquiring some points enough to cover all power range available, we obtain a curve with several maxima, each one corresponding to a nonlinear phase shift of 2π. Finally, a peak detector routine was used to get the power corresponding to each of the maxima, which are used to yield the relevant thermal parameters.

As we mentioned previously, the thermal conductivity of solvents not yet characterized can be determined if the thermo-optic coefficient is also measured. K can be accomplished if a high accuracy refractometer is employed to measure the refractive index as a function of the temperature, and then taking the derivative. Instead, we chose to use a simpler and accurate technique based on a single arm double interferometer operating at wavelength value (λ) of the 532 nm, with the sample placed in a 2 mm-thick cuvette. This instrument allows the simultaneous measurement of interferences arising from a low-finesse

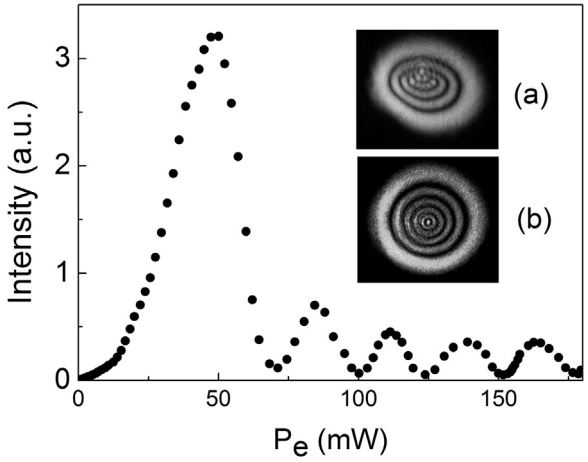

Fig. 2. The intensity of the CD obtained as a function of the incident laser power for blue-black ink diluted in aqueous solution (α = 4.6 cm^{-1}). The inset shows the ring pattern observed in the far field with sample cuvette at (a) vertical and (b) horizontal positions.

Fabry-Perot etalon and a Mach-Zehnder-type interferometer, in a common-path optical arrangement that makes the device compact and stable [21]. For the measurement of liquid samples, as is the case in the present work, it is necessary to use only the Mach-Zehnder part of the interferometer. In this case, the thermo-optic coefficient can be obtained using $dn/dT = \lambda/(2\,L\,\Delta T)$, where ΔT is the temperature spacing between two consecutive fringes and L is the cuvette thickness. Fluorescence spectra were obtained with a portable spectrometer (Ocean Optics USB2000+) by pumping the sample at 532 nm. The absorbance spectra were acquired by using a halogen lamp and the portable spectrometer.

Rhodamine 6 G and blue-black ink were purchased from Acros Organics and Sheaffer, respectively. Pyridoxal 5´-phosphate hydrate (vitamin B6) was obtained from Sigma Aldrich. The derivative of vitamin B6 was synthesized as described in reference [15].

3. Results and discussion

The intensity of the central part of the laser beam obtained with the CD setup as a function of the laser power (P_e) is shown in Fig. 2 for blue-black ink in aqueous solution. The insets in this figure show typical ring patterns obtained when the cuvette was placed horizontally and vertically. For a cuvette positioned vertically, the far field pattern observed consists of a set of distorted rings that are not concentric (Fig. 2a). This effect can be ascribed to the convection flow of the solution inside the cuvette, which may lead to distortions of the transmitted wavefront [10]. Otherwise, for a horizontal cuvette with a short path length, any convection can be neglected and the rings observed at the far field position are well concentric (Fig. 2b). Therefore, for the sake of automatizing the measurement, the CD setup used the horizontal configuration of the cuvette.

According to the general CD theory, the number of rings, N, is proportional to the nonlinear phase change, $\Delta\phi_{NL}$ [22,23], which in the case of thermal effects [24] is proportional to the power of the excitation laser beam, P_e. Therefore, $N = \beta P_e$ where [6,7,25]:

$$\beta = \frac{\alpha\varphi L_{eff}}{2\pi K\lambda}\left(\frac{dn}{dT}\right) \quad (1)$$

and α (cm^{-1}) is the optical absorption coefficient at the excitation wavelength (λ), L_{eff} = (1-exp(-αL))/α is the effective length, L (cm) is the sample thickness. φ called the absolute nonradiative quantum efficiency represents the fraction of the absorbed energy converted into heat and K is the thermal conductivity (W cm^{-1} K^{-1}). In this case, η can be determined according to the expression: