Measuring the Two-Photon Absorption Spectra of Organic Solutions Via Two-Photon Induced Fluorescence Spectroscopy

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This customer written application note describes how to measure the two-photon absorption spectra of fluorescent chromophores by using an external short-pulsed laser source in an Edinburgh Instruments FS5 Spectrofluorometer. A procedure on how to calculate the nonlinear refraction dispersion from the measured spectra is also given.

1. Introduction

Organic chromophores have long been sought out due to the ability to tailor not only their linear but nonlinear optical properties [1]. This is especially important in the case of third-order nonlinearities in which the response of the material is irradiance-dependent and, thus, effectively instantaneous. In terms of a material's absorption (α), the irradiance-dependent coefficient can be written as:

$$\alpha(I) = \alpha_0 + \alpha_2 I + \cdots \qquad (1)$$

where α_0 is the linear absorption coefficient in units of m^{-1}, I is the irradiance in units of W/m^2, and α_2 is the two-photon absorption (2PA) coefficient in units of m/W. This 2PA coefficient describes the simultaneous absorption of two photons from the ground state to a higher-lying excited state. There have been many efforts to identify structure-property relationships for the rational design of chromophores that exhibit large 2PA coefficients [2]. As such, a chromophore possessing large 2PA can have utility in a wide range of applications such as optical data storage [3] and microfabrication [4].

In this note, we will utilize a technique called two-photon induced fluorescence (2PF) spectroscopy to describe how to measure the 2PA spectrum of an organic molecule in solution. This method, first introduced by Xu and Webb [5], provides a rapid means of measuring a molecule's 2PA spectrum as opposed to other more conventional means such as the Z-scan technique [6].

2. Experimental setup

To perform 2PF measurements, a high-intensity pump beam excites a sample via 2PA and then the material radiatively relaxes back down to the ground state [5]. Thus, for 2PF to be an efficient means to extract the 2PA coefficient, the sample should be highly fluorescent. This means the fluorescence quantum yield (QY) should be ≫ 1%. The magnitude of the 2PF signal for each wavelength measured allows for the

construction of the 2PA spectrum of a given material. Both QY and 2PF measurements are performed in 1 cm path length matched quartz cuvettes.

For the 2PF measurements conducted in this note, the external laser pulses are derived from an amplified Ti:sapphire system (Spectra-Physics, Solstice) producing 3.5 mJ, 100 fs (full-width at half-maximum, FWHM) pulses at a 1 kHz repetition rate at a wavelength (λ) of 800 nm. The laser pulses are directed into the spectrofluorometer (Edinburgh Instruments, FS5) via a modified SC-05 cassette as shown in Fig. 1. The cassette has an opening drilled in the front to allow laser light entry as well as a custom fitted optical breadboard (1/4"-20 taps on 1" centers) in which mirrors direct the laser light into the sample cuvette. The last mirror (top right in Fig. 1) is an off-axis parabolic mirror to focus the laser light into the sample. The 2PF emission is collected in the same manner as with the standard steady-state acquisition excited with a Xenon lamp. To control the fluorescence intensity reaching the PMT, the emission bandwidth is adjusted and attenuation is placed in the laser light beam path prior to entering the SC-05. The attenuation consists of neutral density (ND) filters and/or a half-wave plate/polarizer combination. To generate other excitation wavelengths to complete the 2PA spectrum, approximately 1.8 mJ from the laser output is used to pump an optical parametric amplifier, OPA (Light Conversion, Ltd., TOPAS PRIME). The wavelengths of interest are generated via frequency mixing from the output of the OPA.
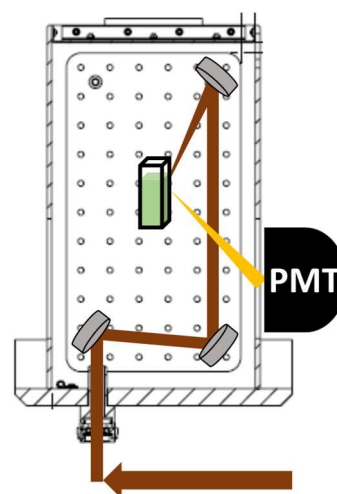

Figure 1. Modified SC-05 cassette allowing for an external laser source to excite a solution via two-photon absorption (2PA).

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3. Methodology

3.1 QY determination

In order to determine 2PA coefficients via 2PF measurements, first the QY of the chromophore via one-photon fluorescence (1PF) spectroscopy must be known with high accuracy. The FS5 allows determination of this value either via absolute QY measurements using the SC-30 Integrating Sphere or via comparative actinometry with the SC-05 Standard Cuvette Holder. For information on how to obtain absolute QY values, refer to the SC-30 Integrating Sphere Manual and Edinburgh Instruments Technical Note TN_P21 [7].

To measure QY via comparative actinometry, we use a reference standard with a known QY to determine the QY of the unknown. In order to do this, we use the following relation:

$$\phi = \phi_{ref} \frac{f_{ref}^{\lambda_{exc}}}{f^{\lambda_{exc}}} \frac{\left(n_0^{\lambda_{exc}}\right)^2}{\left(n_{0,ref}^{\lambda_{exc}}\right)^2} \frac{\langle F \rangle}{\langle F_{ref} \rangle} \frac{P_{ref}^{\lambda_{exc}}}{P^{\lambda_{exc}}} \qquad (2)$$

where ϕ is the QY of the unknown sample, $f = 1 - 10^{-OD}$ with OD being the optical density at the excitation wavelength (λ_{exc}), n_0 is the linear refractive index of the solvent, $\langle F \rangle$ is the integrated fluorescence intensity, and P is the lamp power. The subscript "ref" refers to the reference standard. The refractive index of many solvents can be readily found in references such as [8]. It's important to note that the ratio of the lamp power is a correction factor used when the reference and unknown sample cannot be excited at the same wavelength. The FS5 allows this ratio to be easily determined, if needed, by observing the excitation in the signal counts dialog window. As is the case for all QY measurements, the peak OD of both the reference solution and unknown solution should be kept below 0.1 to minimize re-absorption of the fluorescence signal. Ideally, the absorption spectrum of the chosen reference standard should have overlap with that of the unknown sample in order to excite at the same wavelength. But if not, as mentioned prior, a correction factor can account for this discrepancy. For a list of common reference standards and their QY values, see Ref. [9] and references therein.

3.2 2PF Measurements

Once the QY of the sample is measured, the 2PA can be determined. In order to do so, the 2PA spectrum of a well-studied molecule is used to determine the 2PA spectrum of the unknown by using the following relation:

$$\delta = \delta_{ref} \frac{n_0^2}{n_{0,ref}^2} \frac{\phi_{ref}}{\phi} \frac{\langle F_2 \rangle}{\langle F_{2,ref} \rangle} \frac{C_{ref}}{C} \frac{E_{n,ref}^2}{E_n^2} \qquad (3)$$

where δ is the 2PA cross section, $\langle F_2 \rangle$ is the integrated 2PF intensity, C is the concentration, and E_n is the energy of the laser pulses incident on the sample. The 2PA coefficient is related to the 2PA cross section by:

$$\delta = 10^{58} \frac{\hbar \omega \alpha_2}{N} \qquad (4)$$

where $\hbar$ is the reduced Planck's constant, ω is the optical frequency defined as $2\pi c / \lambda$ where c is the speed of light, and N is the number density of molecules. Note that all physical quantities in Eqn. (4) are in mks units. The multiplicative factor in Eqn. (4) expresses δ in units of Göppert-Mayer, GM $\left(= 10^{-50} \text{ cm}^4\text{s/photon}\right)$ [10]. Eqn. (3) is utilized at each of the measured wavelengths to construct the 2PA spectrum.

Rhodamine B (CAS: 81-88-9) dissolved in spectroscopic grade MeOH can be used as a standard for both QY [11] and 2PF measurements [12, 13]. Since the 2PF intensity is directly related to the incident irradiance and the concentration, it is imperative that the concentration used for 2PF measurements be much higher than that used for QY determination to maximize the generated signal. For instance, in this note, the concentration of Rhodamine B used for QY measurements is 0.79 μM whereas for 2PF measurements the concentration is 5.1 mM.

Thus, for 2PF measurements, the maximum soluble concentration achievable (without aggregation) should be used. As mentioned in Section 2, attenuation of the external laser source is also used to control the 2PF intensity. The dynamic range of the visible PMTs in the FS5 allows for adequate signal-to-noise ratios while maintaining the same excitation energy used for 2PF generation in both the reference and unknown sample, in most cases. If the attenuation needs to be adjusted for adequate 2PF generation, an energy sensor should be placed prior to the sample to record the energy ratio of the different excitation intensities.

Figure 2a shows the normalized absorption and fluorescence spectra of a dilute solution (0.79 μM) of Rhodamine B in MeOH. There is significant overlap between the absorption and fluorescence spectra demonstrating the need for dilute sample concentrations for QY determination as stated previously. Fig.2b shows the difference between the fluorescence

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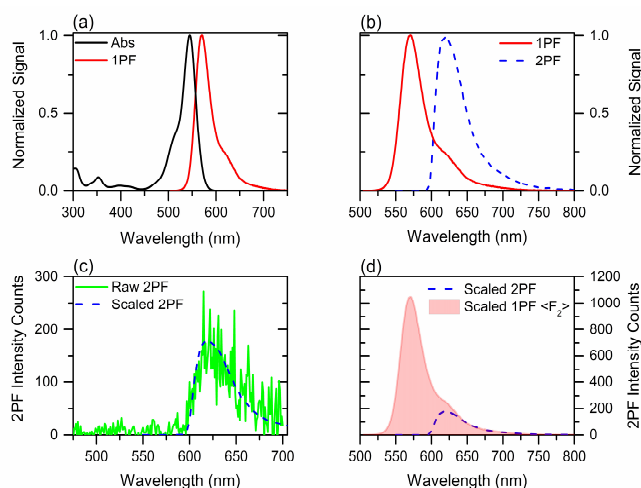CCDC – U.S. Army Research Laboratory, Sensors and Electron Devices Directorate, Adelphi, MD 20783, USA

Figure 2. (a) Normalized absorption (Abs) and 1PF spectra of a dilute concentration of Rhodamine B dissolved in MeOH. (b) Comparison of 1PF signal from dilute solution to 2PF signal of concentrated solution. (c) Raw 2PF signal of concentrated solution excited with 800 nm pulses with scaled 2PF signal matching the peak intensity counts of the raw 2PF signal. (d) Scaled 1PF signal to the tail of the scaled 2PF signal. The area under the curve of the scaled 1PF signal is $\langle F_{2,ref} \rangle$ in Eqn. (3).

spectra measured with the dilute concentration in Fig. 2a and the concentrated solution (5.1 mM) used for 2PF measurements. Note that the shape of the fluorescence is highly distorted compared to the 1PF spectrum as well as the dramatic Stokes shift of the peak. This is due to significant reabsorption of the fluorescence signal as a result of the high concentration. The fluorescence curves in Figs. 2a and 2b are obtained via emission scans using the standard FS5 Xe lamp as the excitation source.

Figure 2c shows the raw 2PF signal obtained using external laser pulses from the fs laser source. The 2PF signal is highly susceptible to intensity fluctuations of the external laser source and the instability results in the noise seen in Fig. 2c. Therefore, it's important to average multiple scans in order to reduce the noise. From Ref. [12], the 2PA cross-section of Rhodamine B at 800 nm is 120 GM. For the given concentration of 5.1 mM, this corresponds to $\alpha_2 = 1.5 \times 10^{-13}$ m/W. For the given experimental conditions, the peak irradiance, $I_0 (\approx En/(w_0^2 \tau)$ where w_0 is the minimum spot size at focus and τ is the pulse width of the laser source), required to observe an adequate 2PF signal (in Fig. 2c) is ~10 GW/cm². Note, however, that the irradiance needed to observe a 2PF signal will vary drastically depending on the concentration and 2PA characteristics of the molecule.
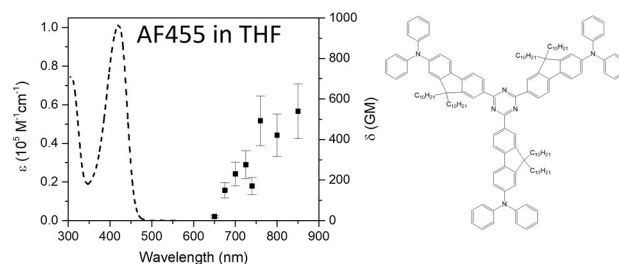

Figure 3. Molar absorbance, ε, spectrum (dashed black line) and 2PA cross sections (solid black squares) of an organic choromophore dissolved in tetrahydrofuran (THF).

Once an adequate 2PF signal is obtained, the distorted fluorescence spectrum of the concentrated solution (see Fig. 2b) is scaled to match the peak of the raw 2PF signal (see Fig. 2c). Note that the 2 curves are identical in shape and should match point-by-point within the noise of the signal. The normalized 1PF curve is then scaled to the tail of the scaled 2PF curve (Fig. 2d) which represents the "true" 2PF intensity due to 2PA. Integrating over this scaled 1PF curve yields $\langle F_{2,ref} \rangle$ in Eqn. (3).

The methodology presented in Fig. 2 and described in the text is the same for all wavelengths of measure for both the reference and unknown sample. Figure 3 shows an example of the molar absorbance spectrum and the 2PA spectrum of an organic chromophore obtained via 2PF measurements. This molecule has been the subject of previous studies [13-15]. As stated previously, the 2PF signal of both Rhodamine B in MeOH as the standard and AF455 in THF as the unknown were taken at all wavelengths of measure as shown in Fig. 3 to obtain the full 2PA spectrum using Eqn. (3).

4. Calculating the nonlinear refraction (NLR) dispersion from the measured 2PA spectrum

Another phenomenon arising from the third-order response of materials is the irradiance-dependent refractive index (n). To third-order, the refractive index is expressed as:

$$n(I) = n_0 + n_2 I \qquad (5)$$

where n_2 is the third-order nonlinear refraction (NLR) coefficient. The n_2 is a quantifiable parameter that determines the amount of phase change in materials in the presence of high-irradiance

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radiation. As is the case for materials with large 2PA, there have been many studies aimed at identifying materials systems with large n_2 values [16, 17] since they have utility in a variety of applications such as all-optical switching [18].

The standard method to describe the NLR dispersion of organic molecules is the sum-over-states (SOS) model. This model takes into account the ground state and all possible excited states and their corresponding transition dipole moments [19]. Since the inclusion of all states would be computationally difficult to handle, a simplification was introduced which only contains the 3 most important transitions for molecules that possess centrosymmetry [20]. These transitions include those from the ground state (g) to the first excited state (e, linear absorption) and those from the first excited state to a higher-lying excited state (e', 2PA). Parity rules dictate that direct transitions from the ground state to the 2PA state are forbidden. Thus, this is referred to as a 3-level SOS model. The inclusion of multiple 2PA states is referred to as the quasi 3-level model.

Following the procedure in Ref. [21], a simplified expression for the second hyperpolarizability, γ, deduced from the 3-level SOS model that includes only the dominant transitions can be written as:

$$\gamma(\omega) \cong$$

$$\frac{1}{3\hbar^3} \sum_{e'} \left(\frac{\mu_{ge}^2 \mu_{ee'}^2}{(\overline{\omega}_{eg} - \omega)^2 (\overline{\omega}_{e'g} - 2\omega)} \right.$$

$$+ \frac{\mu_{ge}^2 \mu_{ee'}^2}{(\overline{\omega}_{eg}^* - \omega)(\overline{\omega}_{e'g} - 2\omega)(\overline{\omega}_{e'g} - 2\omega)} \right) \quad (6)$$

$$- \left(\frac{\mu_{ge}^4}{(\overline{\omega}_{eg} - \omega)^2(\overline{\omega}_{eg}^* - \omega)} + \frac{\mu_{ge}^4}{(\overline{\omega}_{eg} - \omega)^3} \right)$$

where the transition dipole moments, μ_{ge} and $\mu_{ee'}$ are defined as $\langle g|\mu|e \rangle$ and $\langle e|\mu|e' \rangle$, respectively, and describe the transition between states g and e and e and possible multiple 2PA states e'. The complex frequency $\overline{\omega}_{nm} = \omega_{nm} - i\Gamma_{nm}$ defines the resonant transition frequency between states n and m (with n and m representing states g, e, or e'), Γ_{nm} is the damping factor related to the linewidth of the transition, and "*" is the complex conjugate. Note that this expression assumes polarizability along one molecular coordinate axis. The first 2 terms are called the "Two-photon terms" (T-terms), corresponding to the transition between the states g and e' with

the summation allowing for the inclusion of multiple 2PA states. The last 2 terms, which always show a negative contribution, are called the "Negative terms" (N-terms), corresponding to the transition between the states g and e. The overall nonlinearity is due to the interaction of these terms, and is determined by the magnitude of the transition dipole moments and the relative energies of the relevant states. In relating these terms to the measured third-order quantities, the $Re(\gamma) \propto n_2$ and $Im(\gamma) \propto \alpha_2$.

The molar absorbance spectrum allows for the determination of the ground state parameters: μ_{ge}, ω_{eg}, and Γ_{eg}. To calculate the ground state dipole moment, μ_{ge}, the following relation is utilized [22, 23]:

$$\mu_{ge} = 3.563 \cdot 10^{-33} \sqrt{\int \varepsilon(v)dv / E_{ge}} \left[f^{(1)} \right]^{-1/2} \quad (7)$$

where $\varepsilon(v)$ is the molar absorbance spectrum as a function of wavenumbers v (cm^{-1}), $E_{ge} = \hbar\omega_{eg}$ represents the energy of the peak absorption in eV, and $f^{(1)} = (n_0^2 + 2)/3$. The ground state linewidth, Γ_{eg}, is determined by fitting the main linear absorption peak with a single Lorentzian. The half-width at half-maximum of the fit is the linewidth used in Eqn. (6).

To obtain the excited state dipole moment(s) and associated parameters, $\mu_{ee'}$, $\omega_{e'g}$, and $\Gamma_{e'g}$, the 2PA spectrum (in GM) obtained from 2PF measurements is fit using Eqn. (6) by the following relation:

$$\delta(\omega) = \frac{3 \times 10^{58}}{10} \frac{\hbar\omega^2 f^{(3)}}{\varepsilon_0^2 c^2 n_0^2} Im(\gamma_T) \quad (8)$$

where $f^{(3)} = (n_0^2 + 2)^4/81$ and ε_0 is the vacuum permittivity.

Table 1. Fit parameters for the 2PA spectrum in Fig. 4a using Eqn. (8) where the transition dipole moments are given in Debye (D) (1 D $\cong$ 3.33 · 10^{-30} Coulomb·m).

μ_{ge}	$10.9\ D$
ω_{ge}	3.0 eV/$\hbar$
Γ_{ge}	0.26 eV/$\hbar$
$\mu_{ee'}^{(1)}$	$14\ D$
$\omega_{ge'}^{(1)}$	2.95 eV/$\hbar$
$\mu_{ee'}^{(2)}$	$11\ D$
$\omega_{ge'}^{(2)}$	3.33 eV/$\hbar$
$\Gamma_{ge'}^{(1)} = \Gamma_{ge'}^{(2)}$	0.13 eV/$\hbar$

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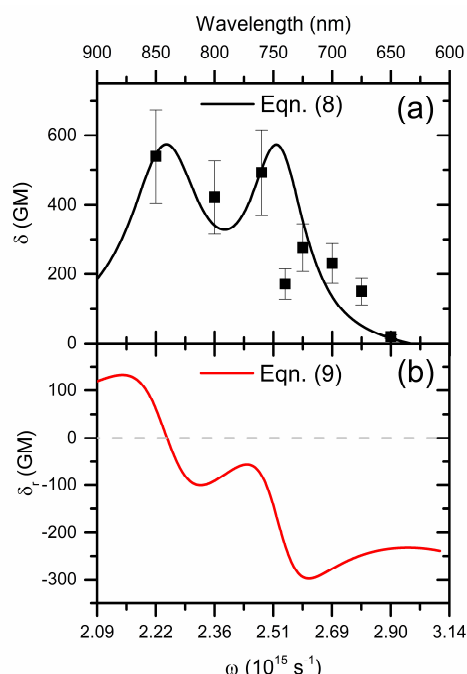

Figure 4. (a) 3-level SOS fit of the 2PA spectrum of AF455 by using Eqn. (8) and the parameters listed in Table 1. (b) Nonlinear refraction spectrum of AF455 calculated from Eqn. (9). The dashed gray line in (b) refers to $\delta_r = 0$.

The subscript "T" means that only the imaginary component of the T-terms, i.e. the first 2 terms in the summation, are included when fitting the 2PA spectrum and the imaginary component of the N-terms, i.e. the last 2 negative terms, are excluded. For a detailed explanation of why the N-terms are excluded when describing 2PA, see Section 4 and Appendix A in Ref. [21].

Figure 4a shows the fit of the 2PA spectrum measured via 2PF measurements using the fit parameters listed in Table 1. As stated previously, the ground state parameters (μ_{ge}, ω_{eg}, and Γ_{eg}) are determined from the molar absorbance spectrum while the excited state parameters ($\mu_{ee'}$, $\omega_{e'g}$, and $\Gamma_{e'g}$) are determined from the best fit of the 2PA spectrum. The superscripts (1) and (2) in Table 1 indicate that the spectrum was fit with multiple 2PA states via the summation in Eqn. (6).

The positions of the 2PA states are determined to be $\omega_{ge}^{(1)} = 2.95$ eV/$\hbar$ and $\omega_{ge'}^{(2)} = 3.33$ eV/$\hbar$ corresponding to ~840 nm and ~745 nm, respectively. The linewidths of the 2PA states are assumed to be the same, i.e. $\Gamma_{e'g}^{(1)} = \Gamma_{e'g}^{(2)}$.

After extracting all the parameters via fitting the 2PA spectrum, the following relation can be used to calculate the NLR dispersion:

$$\delta_r(\omega) = \frac{3 \times 10^{58}}{20} \frac{\hbar \omega^2 f^{(3)}}{\varepsilon_0^2 c^2 n_0^2} Re(\gamma) \qquad (9)$$

where we include all terms in Eqn. (6) and have introduced the NLR cross section $\delta_r (= 10^{58} \hbar \omega^2 n_2 / (cN))$ [24]. Fig. 4b shows the calculated NLR dispersion of AF455. For context, using the concentration for the 2PF measurements (1.4 mM), the max positive $\delta_r (\sim 125$ GM) at 875 nm corresponds to $n_2 \cong 0.65 \times 10^{-16}$ cm^2/W whereas the max negative $\delta_r (\sim -300$ GM) at 725 nm corresponds to $n_2 = -1.1 \times 10^{-16}$ cm^2/W. These values are more than a factor of 2 smaller than that of fused silica in this wavelength regime [25].

5. Final notes

The analysis presented in Section 4 was derived specifically for molecules that can be approximated as centrosymmetric in Ref. [21]. But this procedure has shown to be robust even for non-centrosymmetric molecules such as Rhodamine B and Rhodamine 6G by incorporating additional terms [26]. While the NLR can be calculated by the reduced form of the 3-level SOS model presented in Eqn. (6) with good accuracy from the 2PA spectrum, it is recommended to use the more complete form presented in Eqns. (13) and (14) in Ref. [21].

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