

# Frequency-resolved microscopic second-order hyperpolarizability of azochromophores: A study on nonlinear all-optical switches applications

Renato Mafra Moysés,<sup>†</sup> Emerson Cristiano Barbano,<sup>‡</sup> Daniel L. Silva,<sup>&</sup> Marcelo Gonçalves Vivas,<sup>\*</sup> and Lino Misoguti<sup>†</sup>

<sup>†</sup> Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

<sup>‡</sup> Departamento de Física, Universidade Federal do Paraná, CP 19044, 81531-980 Curitiba, PR, Brazil

<sup>&</sup> Departamento de Ciências da Natureza, Matemática e Educação, Universidade Federal de São Carlos, Rod. Anhanguera – Km 174, 13600-970 Araras, SP, Brazil

<sup>\*</sup> Laboratório de Espectroscopia Óptica e Fotônica, Universidade Federal de Alfenas, Poços de Caldas, MG, Brazil

Corresponding author: [misoguti@ifsc.usp.br](mailto:misoguti@ifsc.usp.br)

## 1 – Molecular Structure

Figure SI.1 shows the molecular structure of the azochromophores studied in this work: Disperse Red 1 (DR1), Disperse Red 13 (DR13), Disperse Red 19 (DR19) and Disperse Orange 3 (DO3).

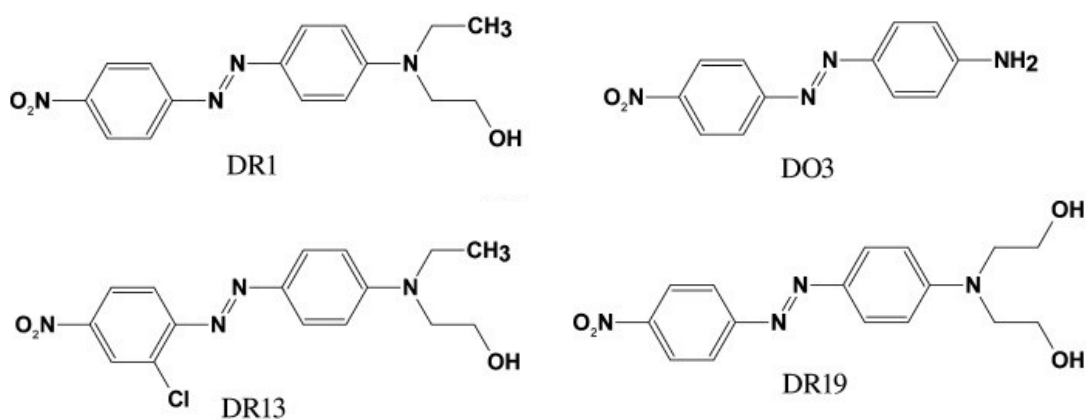


Figure SI.1 Molecular structure of azochromophores studied.

## 2 – Determination of dipole moments employed at the SOS model

According to  $n_2$ -SOS model reported in the Ref. <sup>1</sup>, the magnitude of the nonlinear refractive index ( $n_2$ ) for a noncentrosymmetric molecule is strongly dependent on the transition dipole moments ( $|\mu_{01}^r|$  and  $|\mu_{1n}^r|$ ) and the difference between permanent dipole moments ( $|\Delta\mu_{01}^r|$ ). In this context, the transition dipole moments from the ground state to the first excited state ( $|\mu_{01}^r|$ ) was obtained from the linear absorption spectrum by <sup>2</sup>

$$|\mu_{0n}|^2 = \frac{3 \times 10^3 \ln(10) hc}{(2\pi)^3 N_A} \frac{n}{L^2} \frac{1}{\omega_{0n}} \int \varepsilon(\omega) d\omega, \quad (1)$$

in which,  $\varepsilon(\omega)$  is the molar absorptivity and  $N_A$  is the Avogadro's number.  $\omega_{01} = (E_{11} - E_{00})/\hbar$  is the transition frequency,  $\omega$  is the excitation laser,  $\hbar$  is the Planck's constant divided by  $2\pi$ ,  $L$  is the local field factor ( $L = \frac{3n^2}{2n^2 + 1}$  is the Onsager local field factor), and  $n$  is the refractive index of the solution.

Figure SI.2 illustrates the ground-state absorption spectra (solid lines) for the azochromophores dissolved in chloroform and acetone. The dashed lines show the Gaussian decomposition method used to obtain the transition dipole moment.

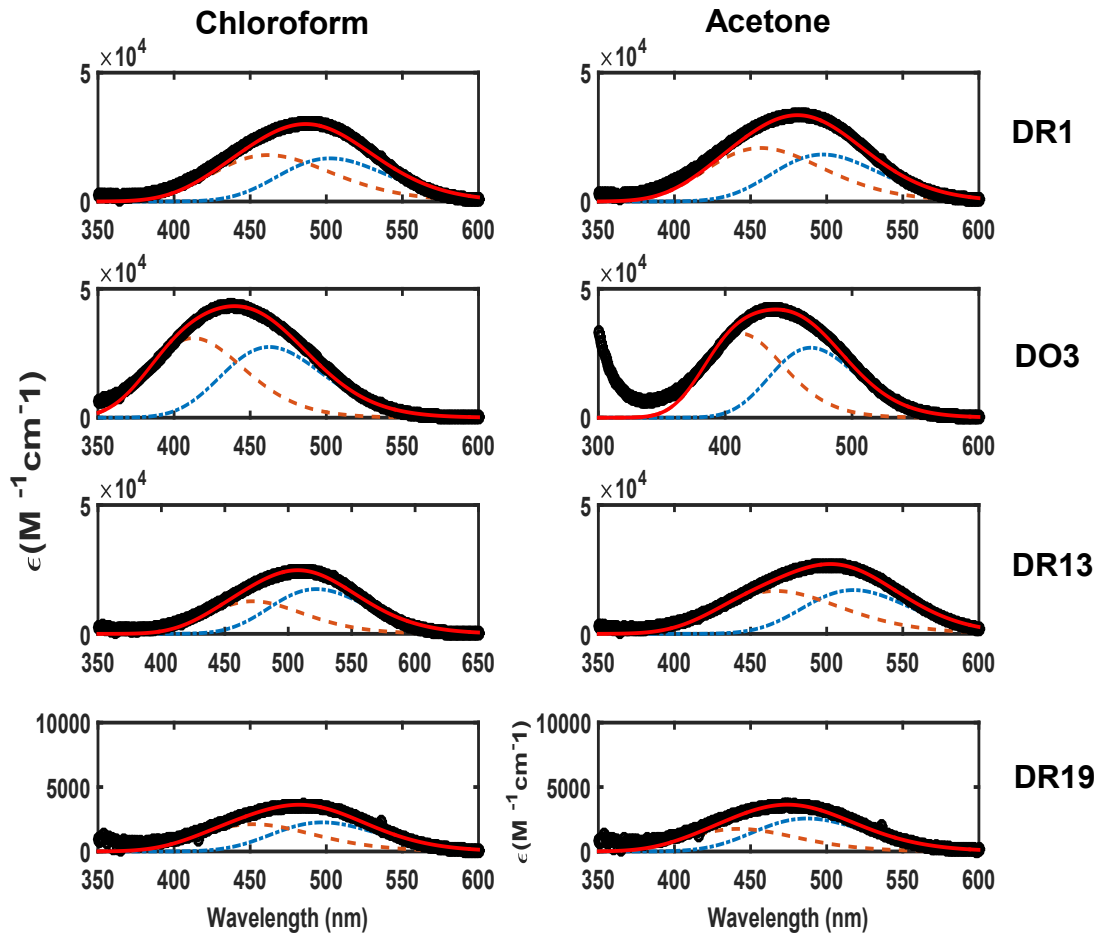


Figure SI.2: Gaussian decomposition used to obtain the dipole moments for the azo dyes. The other parameters were obtained from the 2PA cross section spectra from the rhodamine B and 6G dissolved in methanol reported in Ref. <sup>3</sup>. In the context of the SOS

approach, the value of the permanent dipole moment change is proportional to the 2PA cross section at the peak in the same transition and can be written as:

$$|\Delta\mu_{01}^r| = \left( \frac{5}{2} \frac{N_A hc}{(2\pi)^2 (3 \times 10^3) \ln(10)} \frac{n}{L^2} \frac{\omega_{01}}{\varepsilon_{\max}(\omega_{01})} \sigma_{01}^{(2PA-\max)}(\omega_{01}) \right)^{1/2} \quad (2)$$

To model the higher energy 2PA allowed band, attributed to transitions  $S_0 \rightarrow S_n$ , we considered a three-level energy system consisting of the ground-state ( $S_0$ ), one intermediate 1PA allowed excited state ( $S_1$ ) and the 2PA allowed final excited state ( $S_n$ ). For this system, the excited state dipole moment can be obtained from the 2PA cross-section can be written as (assuming linearly polarized light and that the dipole moments are parallel):

$$|\mu_{1n}^r| = \left[ \frac{5}{2} \frac{N_A hc}{(2\pi)^2 3 \times 10^3 \ln(10)} \frac{1}{R(\omega)} \frac{n}{L^2} \frac{\omega_{01}}{\varepsilon_{\max}(\omega_{01})} \sigma_{0n}^{(2PA)}(\omega_{0n}) \right]^{1/2} \quad (3)$$

in which,  $R(\omega) = \omega^2 / [(\omega_{01} - \omega)^2 + \Gamma_{01}^2(\omega)]$  is the resonance enhancement factor. For noncentrosymmetric molecules, Eq. (3) generally presents additional terms related to the permanent dipole moment change and the interference term between the two distinct excitation channels.<sup>4</sup> Table 1 illustrates the dipole moments value used to model the experimental results.

Table 1: Spectroscopy parameters obtained from the 1PA and 2PA spectra.

	$\mu_{01}$ (D)	$\mu_{02}$ (D)	$\mu_{1n}$ (D)	$\Delta\mu_{01}$ (D)	$\Delta\mu_{02}$ (D)	$\omega_{01}$ (nm)	$\omega_{02}$ (nm)	$\omega_{03}$ (nm)
DR1 (A)	5.2	5.9	8.3	12.0	12.0	505	465	330
DR1 (M)	5.4	6.3	8.3	10.0	10.0	500	460	325
DR13 (A)	5.4	4.8	7.8	13.0	13.0	525	475	335
DR13 (M)	5.1	5.7	7.0	9.0	9.0	520	470	330
DR19 (A)	1.9	2.0	10.8	20	20	500	455	330
DR19 (M)	2.1	1.9	10.3	16	16	490	445	330
DO3 (A)	6.7	7.3	7.0	9.0	9.0	470	415	320
DO3 (M)	6.7	7.5	7.0	9.0	8.0	465	415	315

As the permanent dipole moment obtained directly from the 2PA spectra is values high, we decide to estimate such values from the solvatochromic absorption measurements. In

this case, for higher energy transitions, one can use Eq. (4), which relates the shift of the maximum absorption ( $\nu_A$  ( $\text{cm}^{-1}$ )) with the solvent polarity ( $F(n, \xi)$ )<sup>5</sup>:

$$\Delta\mu_{fg}^r \cdot \mu_{gg}^r = -\frac{3}{4\pi} hc \frac{\partial \nu_A}{\partial F} \text{vol}, \quad (4)$$

in which vol is the volume occupied by the molecule surrounded by the solvent (estimated from the quantum chemical calculations), and  $\Delta F = 2\left(\frac{(\varepsilon - 1)}{2\varepsilon + 1} - \frac{(n - 1)}{2n^2 + 1}\right)$  is the Onsager polarity function. In this approach, it is convenient to use  $|\Delta\mu_{01}^r|$  from the Eq. (2) and  $\nu_A$  related with the first absorption band to found  $|\mu_{gg}^r|$ , assuming that the angle between the dipole moments is approximately zero for the dipolar molecule such as azochromophores studied here. Subsequently, we used this result and the absorption band shift data (to a higher energy band) to estimate  $|\Delta\mu_{fg}^r|$  the permanent dipole moment change related to the higher energy excited state. Figure SI.3 shows the solvatochromic measurements for the DR1 obtained from Ref. <sup>6</sup>.

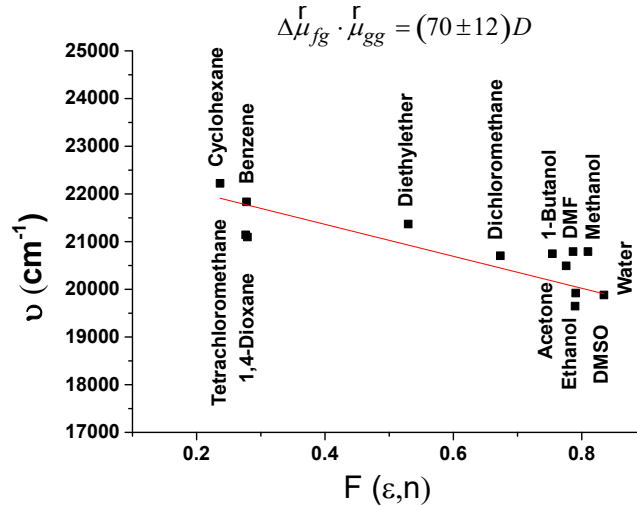


Figure S2 – Solvatochromic absorption measurements for DR1 in several solvents.

As can be noted, the scalar product between the permanent dipole moment change and the ground state dipole moment is approximately  $70 \pm 12$  D. In this case, we can substitute the  $\Delta\mu_{01}^r$  value obtained from the 2PA spectra in Eq. (4) to obtain  $\mu_{00}^r = (6.4 \pm 1.0)D$ . In

fact, as reported in the literature, linear azochromophores like DR1 have a large ground state dipole moment between 5-10 D depending on the trans or cis configuration<sup>7</sup>. Therefore, the values estimated from the 2PA spectra are in good agreement with the literature. As it can be seen up to now, several physical parameters that rule 2PA cross-section can be obtained from the linear optical properties. At the same time, the  $n_2$  dispersion relation can be obtained from the same data.

### 3 – 2PA-SOS results

Figure S3 illustrates the 2PA cross section spectra for all azochromophores given in GM units. The solid lines represent the SOS fitting using the parameters described in Table S1.

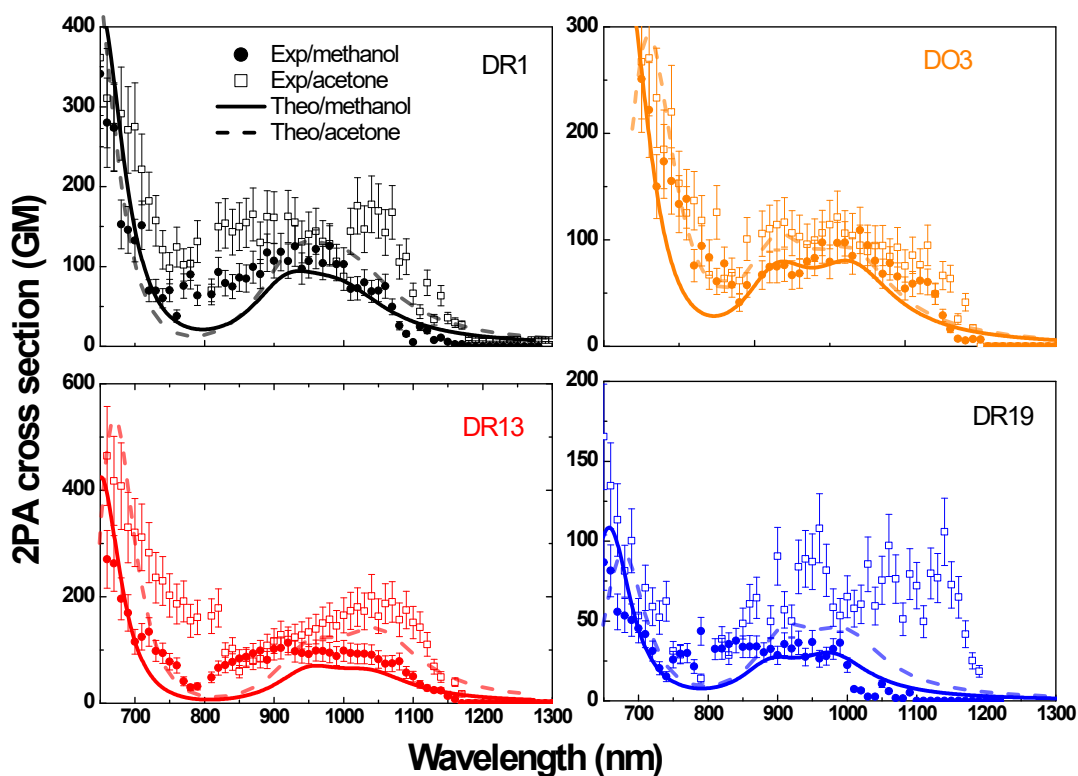


Figure S3 – The data correspond to the 2PA spectra in methanol (circles) and acetone (squares) solvent. The solid lines represent the SOS simulation.

### 4 – Computed second-order hyperpolarizability

Employing quantum-chemical calculations the averaged (isotropic) second-order hyperpolarizability ( $\langle \gamma(-3\omega; \omega, \omega, \omega) \rangle$ ) of the azoaromatic compounds was estimated for some excitation wavelengths. The  $\langle \gamma \rangle$  value can be written as a function of the molecular second-order hyperpolarizability tensor components ( $\gamma_{ijkl}$  – molecular coordinate framework). The essential formula to calculate  $\langle \gamma \rangle$  is

$$\langle \gamma \rangle = \frac{1}{5} [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \quad (5)$$

The value of the relevant tensor components from the Dalton program output are gathered in Table S2. The  $\langle \gamma \rangle$  values of the chromophores are also presented in Table S.1 (for second-order hyperpolarizability 1 a.u. =  $5.036238 \times 10^{-40}$  esu).

**Table S2.** The second-order hyperpolarizability tensor components ( $\gamma_{ijkl}$ ) computed using the B3LYP/6-311++G(d,p) approach in gas-phase.

Compound	Comp. ( a.u.)	$\omega = 0.0414$ a.u.	$\omega = 0.0456$ a.u.	$\omega = 0.0506$ a.u.	$\omega = 0.0570$ a.u.	$\omega = 0.0651$ a.u.
DO3	$\gamma_{xxxx}$	-200457	-780659	-217449	-8457820	-329169
	$\gamma_{yyyy}$	25271	20687	31810	5045	46338
	$\gamma_{zzzz}$	-46236151	-170762266	14246512	-60661083	6867460
	$\gamma_{xxyy}$	-6918	-61664	2455	-1540233	12707
	$\gamma_{xxzz}$	-3582643	-12506376	-2821733	-59372599	-1450702
	$\gamma_{yyzz}$	-299154	-1302877	81188	-1596896	-15968
	$\langle \gamma \rangle$	-10837753	-39852814	1716939	-38826663	735341
DR1	$\gamma_{xxxx}$	-168601	209755	2269835	469517	-634918
	$\gamma_{yyyy}$	-43542	158223	191864	171845	-236538
	$\gamma_{zzzz}$	-118537905	133424513	235448528	-1852524	18036986
	$\gamma_{xxyy}$	-153734	218563	811639	69267	316503
	$\gamma_{xxzz}$	-6249057	4884030	34856660	-22299	-10297954
	$\gamma_{yyzz}$	-3427490	3845592	6371210	504610	-2383337
	$\langle \gamma \rangle$	-27682122	30337772	64397849	-21602	-1512809

DR19	$\gamma_{xxxx}$	-80836330	134740652	309248604	-5070260	16406359
	$\gamma_{yyyy}$	43368	47774	59098	38783	165595
	$\gamma_{zzzz}$	-5314662	7439740	43615589	-1310636	-3818726
	$\gamma_{xxyy}$	-188061	407643	-353911	4302	-120821
	$\gamma_{xxzz}$	-20836106	33368564	100335230	-1521776	3393646
	$\gamma_{yyzz}$	-29803	96572	294901	3134	348611
	$\langle \gamma \rangle$	-25643113	41994744,6	110695146	-1874158	3999220
DR13	$\gamma_{xxxx}$	-170401	944729	1431308	153745	1083737
	$\gamma_{yyyy}$	-68406	-452156	134605	89888	-460247
	$\gamma_{zzzz}$	-175855703	467324702	-5484821	1687490	519151556
	$\gamma_{xxyy}$	-149487	2140780	405491	66802	519264
	$\gamma_{xxzz}$	-6902758	42978674	19587661	-503408	14720177
	$\gamma_{yyzz}$	-6618063	-25810092	-924167	-166475	-8667
	$\langle \gamma \rangle$	40514553	103514700	3181895	455496	114913862

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