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# Theoretical study of the second-order nonlinear optical properties of oxazine derivatives

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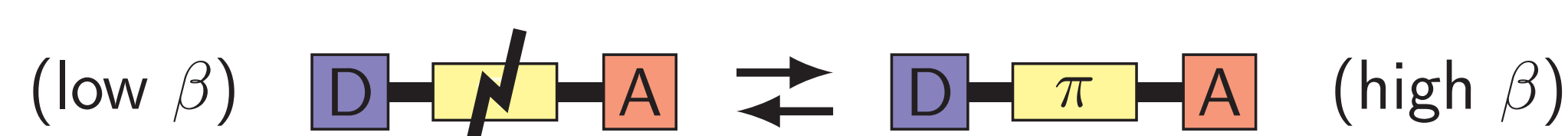
## Introduction

- **Molecular switches:** molecules showing large property variations in response to an external stimulus.<sup>1</sup>
- Triggering via irradiation of the molecule with a laser at given frequencies.
- The interaction between the dipole moment,  $\vec{\mu}$ , and the electric field,  $\vec{E}$ , is the dominant term in the interaction between matter and electromagnetic field. It can be described using a Taylor series, as

$$\vec{\mu}(\vec{E}) = \vec{\mu}_0 + \vec{\alpha}\vec{E} + \frac{1}{2}\vec{\beta}\vec{E}^2 + \dots$$

where  $\vec{\alpha}$  and  $\vec{\beta}$  are the polarizability and the first hyperpolarizability<sup>2</sup>

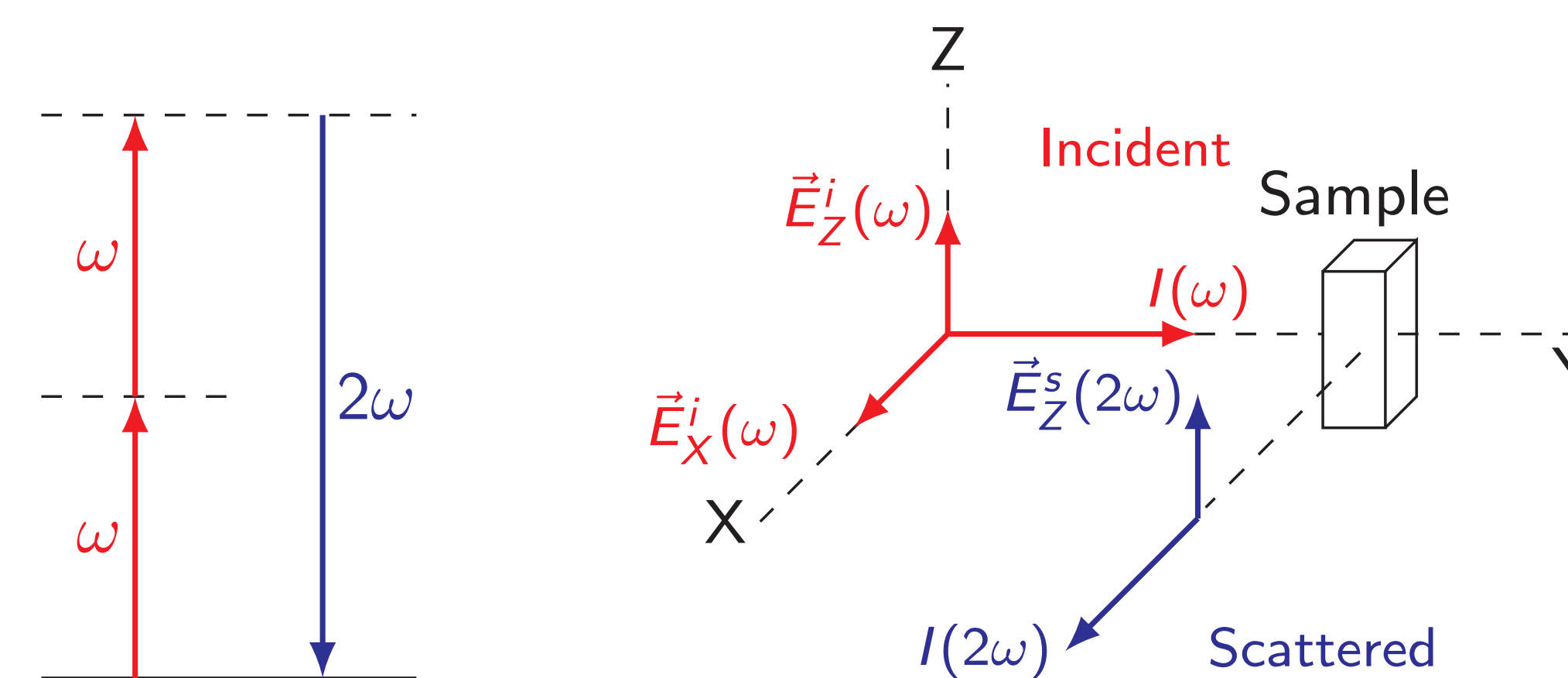
- $\pi$ -conjugated compounds (terminated by a donor and an acceptor): trigger can modify or even break the conjugation path, resulting in a large change of  $\vec{\beta}$ .



Those are called *second-order NLO switches*<sup>3</sup>

- Usage in data storage, imaging microscopy and optical communication

## Hyper Rayleigh Scattering (HRS)



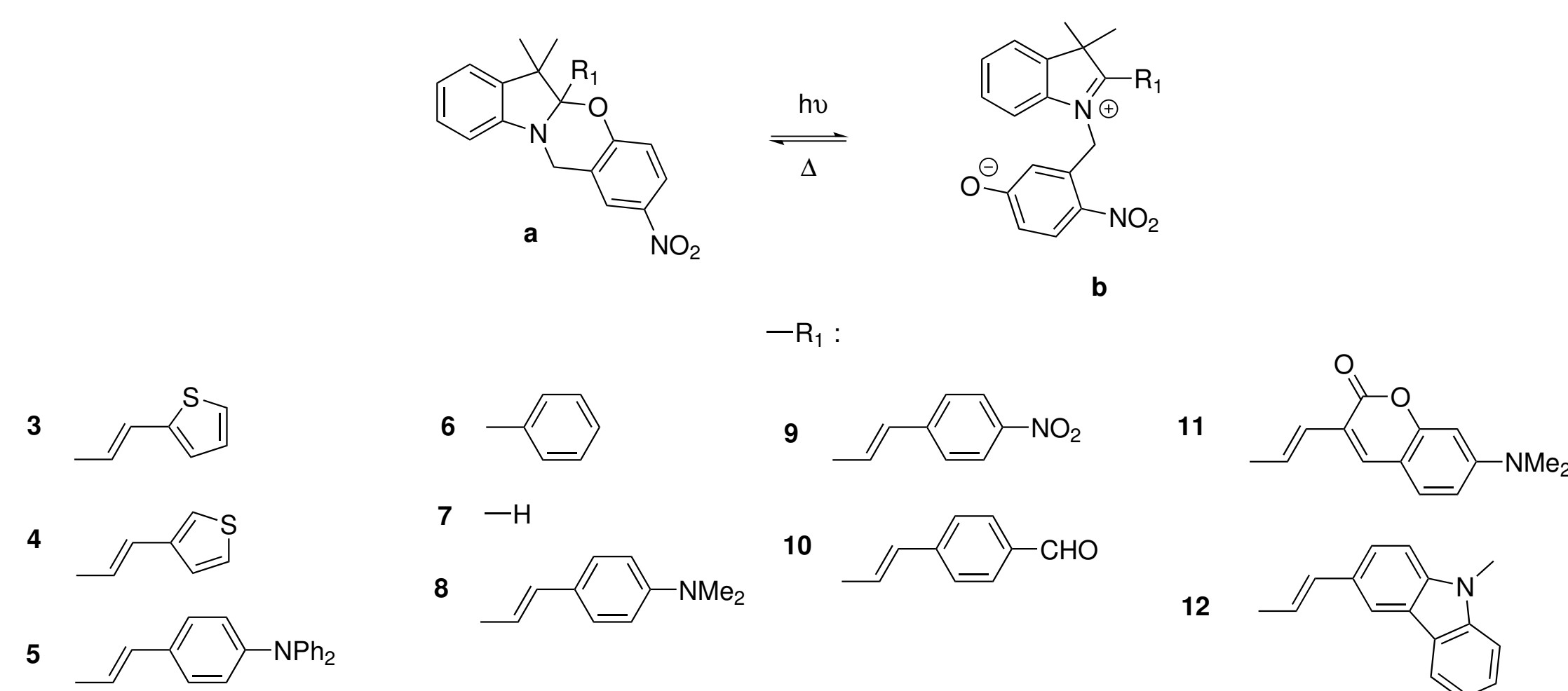
- HRS: nonlinear elastic scattering phenomenon where a molecule illuminated with photons of frequency  $\omega$  scatters photons of frequency  $2\omega$ .
- Measurement at  $90^\circ$  and scattered beam vertically polarized.  $I(2\omega) \propto \langle \beta_{ZZX}^2 \rangle$  (if incident beam polarized horizontally) or  $\propto \langle \beta_{ZZZ}^2 \rangle$  (if polarized vertically).
- Determination of the full HRS response ( $\beta_{HRS}$ ) and depolarization ratio (DR):

$$\beta_{HRS} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZZX}^2 \rangle} \quad DR = \frac{\langle \beta_{ZZZ}^2 \rangle}{\langle \beta_{ZZX}^2 \rangle}$$

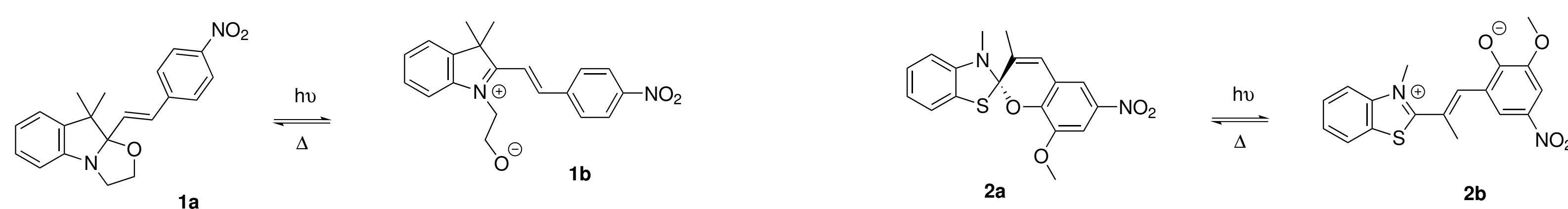
DR gives information on the geometry of the chromophore

## Goals and results

**Objective:** study a new family of NLO switches, the benzo[1,3]oxazines with donor and attractor substituents.

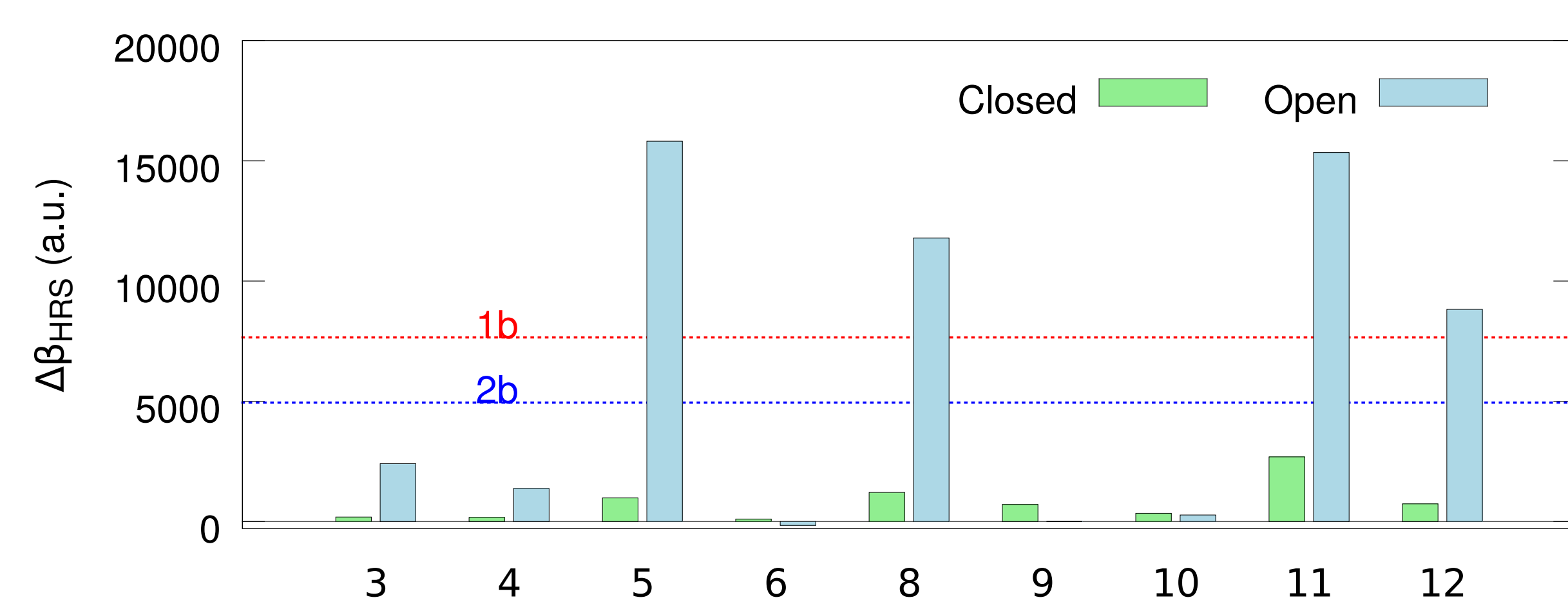


**3-6, 8 and 11-12** have recently been synthesized by Raymo and co-workers.<sup>4</sup> Comparison with value of reference compounds:<sup>5</sup>

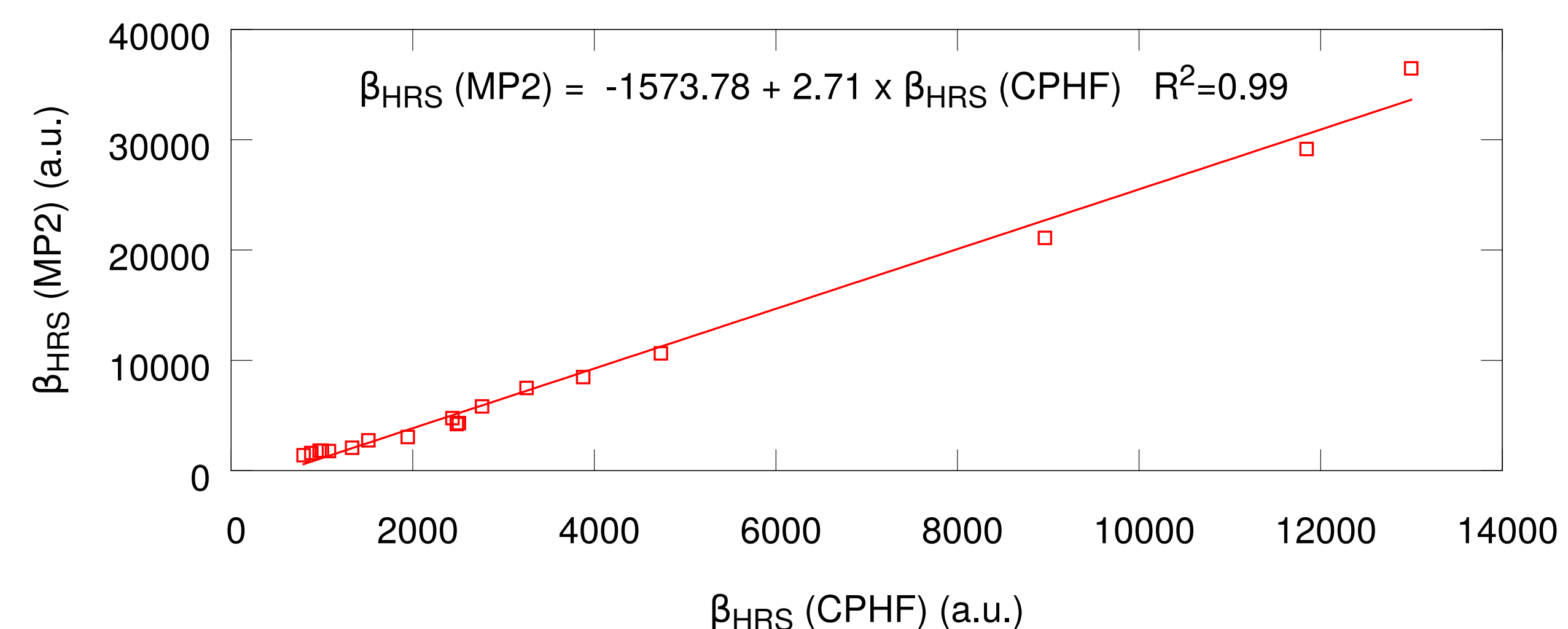


	Closed (a)		Open (b)		Contrast ratio		Closed (a)		Open (b)		Contrast ratio
	$\beta_{HRS}$	DR	$\beta_{HRS}$	DR			$\beta_{HRS}$	DR	$\beta_{HRS}$	DR	
<b>1</b>	1427	4.82	12637	4.64	<b>8.86</b>	<b>7</b>	725	3.12	1888	3.73	2.60
<b>2</b>	697	3.31	6833	3.17	<b>9.80</b>	<b>8</b>	1934	5.12	13682	5.31	<b>7.07</b>
<b>3</b>	914	3.94	4292	5.95	4.70	<b>9</b>	1432	3.05	1888	2.49	1.32
<b>4</b>	895	3.91	3261	5.96	3.64	<b>10</b>	1066	2.88	2161	4.20	2.03
<b>5</b>	1704	3.82	17705	5.21	<b>10.39</b>	<b>11</b>	3415	4.64	17236	4.63	5.05
<b>6</b>	828	3.40	1726	3.64	2.09	<b>12</b>	1462	4.52	10708	4.82	<b>7.33</b>

**Table:** IEF-PCM/TDHF dynamic first hyperpolarizabilities ( $\beta_{HRS}$ , a.u.) as well as the  $\beta_{HRS}$  (open) /  $\beta_{HRS}$  (closed) contrast ratios.



**Figure:** Substituent effect on the dynamic  $\beta_{HRS}$  estimated by the difference between the dynamic  $\beta_{HRS}$  response of the different compounds and that of **7** ( $R_1=H$ ), taken as reference ( $\Delta\beta_{HRS} = \beta_{HRS} - \beta_{HRS}^7$ )



**Figure:** Effect of the inclusion of electron correlation on the static  $\beta_{HRS}$  of some oxazines (**3-4** and **6-12**), as estimated at the IEF-PCM/MP2 level of calculation

- Attractor substituents on the oxazines lead to smaller  $\beta_{HRS}$  contrast ratios.
- Donor substituents show larger contrast ratios.
- Compounds **5, 8, and 12** demonstrate appreciable contrasts in comparison to references NLO switches (**1** and **2**)
- **11** has a large NLO response for both forms.
- Inclusion of electron correlation increases  $\beta_{HRS}$  of 170%

## Computational details

- Optimization: M06/6-311G(d)
- First hyperpolarizabilities: Static (CPHF and MP2 with a finite field, FF, approach) and dynamic ( $\lambda=1064$  nm, TDHF) with the 6-311+G(d) basis set
- Solvent effects on all calculations: IEF-PCM, in acetonitrile

## Acknowledgements

All calculations were performed using the Gaussian 09 package<sup>6</sup> as well as homemade code to carry out the FF (Romberg) scheme. Computational resources have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifique (F.R.S.-FNRS) under the Grant No. 2.5020.11.

## References

- [1] Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639–665.
- [2] Karna, S. P.; Yeates, A. T. *Nonlinear optical materials — Theory and modeling*; American chemical society: Washington, DC, 1996.
- [3] Castet, F.; Rodriguez, V.; Pozzo, J.-L.; Ducasse, L.; Plaquet, A.; Champagne, B. *Acc. Chem. Res.* **2013**, *46*, 2656–2665.
- [4] (a) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2005**, *70*, 8180–8189; (b) Deniz, E.; Tomasulo, M.; Cusido, J.; Sortino, S.; Raymo, F. M. *Langmuir* **2011**, *27*, 11773–11783; (c) Deniz, E.; Cusido, J.; Swaminathan, S.; Battal, M.; Impellizzeri, S.; Sortino, S.; Raymo, F. M. *J. Photochem. Photobiol., A* **2012**, *229*, 20–28; (d) Garcia-Amorós, J.; Swaminathan, S.; Raymo, F. M. *Dyes and Pigments* **2014**, *106*, 71–73.
- [5] (a) Plaquet, A.; Guillaume, M.; Champagne, B.; Castet, F.; Ducasse, L.; Pozzo, J.-L.; Rodriguez, V. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6223–6232; (b) Mançois, F.; Pozzo, J.-L.; Pan, J.; Adami-etz, F.; Rodriguez, V.; Ducasse, L.; Castet, F.; Plaquet, A.; Champagne, B. *J. Chem. Eur.* **2009**, *15*, 2560–2571.
- [6] Frisch, M. J. et al. Gaussian 09 Revision D.01. Gaussian Inc. Wallingford CT 2009.