

# First hyperpolarizabilities of several azobenzene derivatives studied by hyper-Rayleigh scattering (HRS)

Jing Zhu (朱菁)<sup>1</sup>, Xin Wang (汪昕)<sup>1</sup>, Changgui Lü (吕昌贵)<sup>1</sup>,  
Yiping Cui (崔一平)<sup>1</sup>, Chaozhi Zhang (张超智)<sup>2</sup>, and Guoyuan Lu (陆国元)<sup>2</sup>

<sup>1</sup>Advanced Photonics Center, Southeast University, Nanjing 210096

<sup>2</sup>Department of Chemistry, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210096

The first hyperpolarizabilities ( $\beta$ ) of four azobenzene derivatives are measured via hyper-Rayleigh scattering (HRS) technique at 1064 nm. These compounds show weak absorbance at 532 nm and neglectable two-photon fluorescence (TPF). Their static first hyperpolarizabilities ( $\beta_0$ ) are estimated by the classical two-level model. The effects of varying the variety and number of the acceptors from chloro to nitro substituents are studied. It is concluded that the first hyperpolarizabilities will be enhanced with increasing polarity or number of the acceptors, attributed to improved transferability of their  $\pi$ -conjugated electron clouds.

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Nonlinear optical (NLO) materials and techniques have received increasing attention for their applications involving optoelectronic devices, optical signal processing and telecommunications. Recently, organic NLO materials have been investigated quite intensively because of their advantages of synthetic flexibility and the fast purely electronic response<sup>[1]</sup>. Among these materials, azobenzene species with the donor-conjugated system-acceptor (D- $\pi$ -A) structures exhibit large second-order polarizabilities as well as photo-switching properties, which show good potential in applications in optical networks, storage and processing<sup>[2]</sup>. In general,  $\beta$  will increase with increasing donor (and/or acceptor) strength and with increasing separation as long as there is strong electronic coupling through the conjugated bridge<sup>[3]</sup>. Hyper-Rayleigh scattering (HRS) technique, a newly developed incoherent methodology, can be utilized to measure the  $\beta$  values of molecules in solution<sup>[4]</sup>. In comparison with the classical EFISHG technique, HRS is not only simple in apparatus and data processing, but also stronger with abilities to measure non-polar and ionic species<sup>[5]</sup>.

In this work, four azobenzene derivatives (denoted by Dye1, Dye2, Dye3, and Dye4) synthesized by us are studied by HRS technique. All the samples have been carefully characterized by <sup>1</sup>H nuclear magnetic resonance (NMR), <sup>13</sup>C NMR, ultraviolet (UV) visible absorption spectroscopy, element analysis, mass spectroscopy, and infrared (IR) spectroscopy. Details of the synthesis processes and characterization data will be published elsewhere. Samples' chemical structures are shown in Fig. 1. They are carefully designed D- $\pi$ -A conjugated organic molecules. The acceptor part of Dye1 or Dye3 consists of just one substituent of nitro or chloro, while two corresponding substituents construct the acceptor part of Dye2 or Dye4. The donor parts of the compounds are all with hydroxyl substituent, which is designed for further modifications and incorporation into other structures, for example, polymers.

UV-visible absorption spectra of the samples in tetrahydrofuran (THF) are shown in Fig. 2. The absorption peak of Dye3 (356 nm) is red shifted about 32 nm relative to that of Dye1 (388 nm) and about 42 nm from Dye4 (358 nm) to Dye2 (400 nm), which indicates the stronger electron-withdrawing ability of nitro termi-

nal than that of chloro. The addition of methyl to donor part of Dye1 might also increase the molecular polarity. The increase of number of substituent terminal will increase molecular polarity further, but the peak shifts in absorption spectra are quite small for above samples, especially for Dye3 and Dye4.

The HRS experimental setup we used is similar to that in the literature<sup>[4]</sup>. The Q-switched Nd:YAG laser pulse

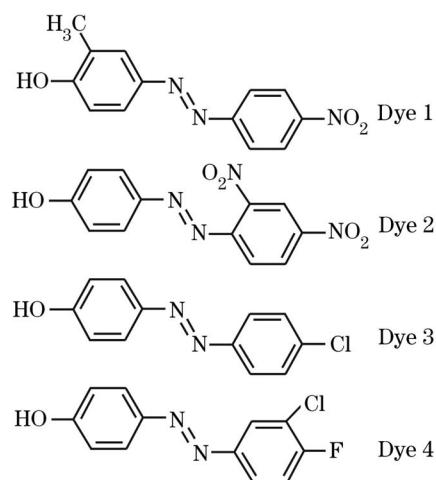


Fig. 1. Chemical structures of azobenzene derivatives studied in this work.

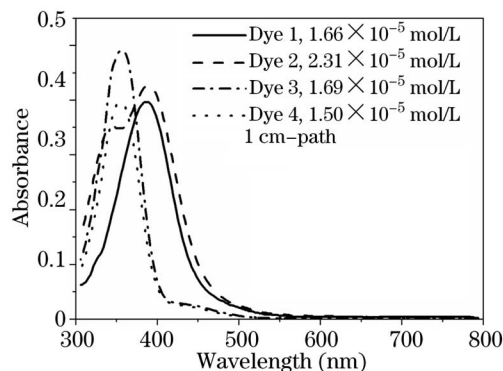


Fig. 2. UV-visible absorption spectra of the four azobenzene derivatives dissolved in THF.

(Continuum Precision II, 10 Hz, 8–10 ns pulse width) at 1064 nm was focused by a lens (focal length of 50 cm) into a cylinder cell (K9 glass, 50 mm in length, 3 mm in radius). The intensity of the fundamental beam could be adjusted by rotating a half-wave plate and was controlled under 0.1 mJ which was monitored by an energy meter. An interference filter at 532 nm (3-nm bandwidth) was mounted at the entrance of the photomultiplier tube (PMT, GDB159) to prevent luminescence at other wavelengths. The HRS signals were detected and averaged by a high frequency digital oscilloscope (Tektronix TDS 3052, 500 MHz). The two-photon fluorescence (TPF) around 532 nm were also checked and it was found that TPF contributions could be neglected in these HRS experiments, which is consistent with the fact that their absorption peaks are far away from 532 nm and their absorptions at 532 nm are rather weak.

An external reference method (EFM) is utilized in these HRS experiments by choosing *para*-nitroaniline (*p*NA) as standard. All the samples and *p*NA were dissolved in THF, and concentration gradients of the samples were prepared by successive dilution. The first hyperpolarizability of *p*NA in THF is known to be  $21.4 \times 10^{-30}$  esu<sup>[6]</sup>. For a two-component solution, the HRS intensity  $I_{2\omega}$  is given by<sup>[4]</sup>

$$I_{2\omega} = G(N_1 \langle \beta_1^2 \rangle + N_2 \langle \beta_2^2 \rangle) \cdot (I_\omega)^2 \cdot e^{-N_2 \alpha_2 l}, \quad (1)$$

where  $I_\omega$  is the incident intensity;  $G$  is a parameter reflecting experimental conditions such as instrumental factor, collection efficiency, and local field corrections;  $N$  is the number density and subscripts 1 and 2 refer to solvent and solute respectively. The brackets indicate the spatial orientational average of the chromophore molecules within the focus area with orientational fluctuations and density fluctuations. The factor  $e^{-N_2 \alpha_2 l}$  accounts for the losses of HRS signal due to the linear absorption and scattering of the solution at 532 nm, i.e. the Beer's law. For Dye3 and Dye4 the losses are negligible but for Dye1 and Dye2 the loss corrections are needed especially for higher concentrations in the concentration gradients. If we incorporate the  $e^{-N_2 \alpha_2 l}$  factor into  $G$ , then the HRS signal will scale linearly with the concentration, as shown in Fig. 3. The ratio of two slopes is directly proportional to the ratio of the averaged first hyperpolarizabilities. HRS experimental data for other samples are all similar to Fig. 3, and the experimental  $\beta(\omega)$  values are listed in Table 1.

All the azobenzene samples with D- $\pi$ -A structures studied in this work can be considered as line-type molecules, so the popular two-level model can be used to estimate their static first hyperpolarizabilities ( $\beta_0$ ) which reflect intrinsic polarizations of the molecules at zero frequency. The two-level model can be expressed as<sup>[7]</sup>

$$\beta(\omega) = \frac{\lambda^4}{[(\lambda^2 - \lambda_{gn}^2)(\lambda^2 - 4\lambda_{gn}^2)]} \beta_0, \quad (2)$$

where  $\lambda_{gn}$  is wavelength corresponding to the transition between the ground and the first excited state, which

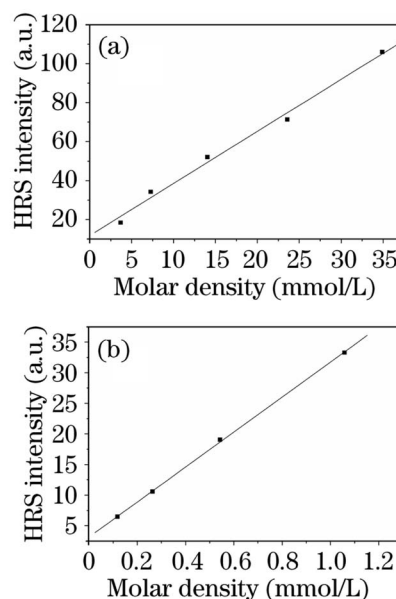


Fig. 3. HRS intensities versus molar densities. (a) For *p*NA; (b) for Dye1 after absorption corrections. Solid lines are linear fitting of the experimental data.

**Table 1. Samples' Absorption Peak Wavelength ( $\lambda_{\max}$ ), First Hyperpolarizabilities in HRS Experiments  $\beta(\omega)$ , and Intrinsic  $\beta_0$  Based on the Classical Two-Level Model**

Sample	$\lambda_{\max}$ (nm)	$\beta(\omega)$ ( $\times 10^{-30}$ esu)	$\beta_0$ ( $\times 10^{-30}$ esu)
Dye1	388	70.1	28.5
Dye2	400	125	46.5
Dye3	356	49.6	24.2
Dye4	358	72.0	35.2

can be estimate as the peak wavelength  $\lambda_{\max}$  in the UV-visible absorption spectra;  $\lambda$  is the wavelength of incident light.  $\beta_0$  is related to oscillator strength, transition energy and difference of the transition dipole moments between the ground and the first excited state.  $\beta_0$  values of the samples are also shown in Table 1.

The  $\beta(\omega)$  values of Dye1 and Dye2 show stronger enhancements due to (near) resonance effects because their absorption peaks are closer to 532 nm than Dye3 or Dye4. But the sequence of magnitude of  $\beta_0$  is still the same to  $\beta(\omega)$  as listed in Table 1. The  $\beta_0$  of *p*NA can be estimated to be  $10 \times 10^{-30}$  esu by the two-level model, so these azobenzene derivatives show large first hyperpolarizabilities several times of *p*NA. Results of Dye1 and Dye3 (or Dye2 and Dye4) show the enhancement of  $\beta_0$  for samples with nitro terminals, i.e., the stronger electron-withdrawing ability of nitro than that of chloro, which is in agreement with the quantum chemical mechanisms. By comparing the  $\beta_0$  values of Dye3 and Dye4 (or Dye1 and Dye2), it reveals that  $\beta_0$  will be enhanced with the increase of number of substituent terminals, which can also be understood by the increasing polarizable ability of the chromophore. So the second-order NLO experimental results can reflect some delicate structure-property relationships of the molecules, which might not be shown in the linear absorption spectra clearly.

In summary, the second-order NLO properties of four synthesized azobenzene derivatives have been studied by HRS technique. Molecular first hyperpolarizabilities will be enhanced with increasing polarity or number of the acceptors, attributed to improved transferability of their  $\pi$ -conjugated electron clouds. These azobenzene derivatives show good potential in applications for non-linear optical (NLO) materials and devices with not only large first hyperpolarizabilities but also excellent chemical properties for further modifications and synthesize.

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