

Origin of Kerr effect: investigation of solutions by polarization dependent Z-scan

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Abstract: The nonlinear refractive index dependence on the incident light polarization state have been studied for pure chloroform and chloroform solutions of aminobenziliden-1,3-indandione derivatives. Measurements were done with linearly, elliptically and circularly polarized light using an 8 ns and 30 ps pulse duration 1064 nm lasers. This allows us to separate electronic, molecular reorientation and thermo-optical components of the nonlinear refractive index. The refractive index variations with the change of laser pulse repetition rate were employed to identify the presence of the thermo-optical effect. Quantum chemical calculations of linear polarizability were used to estimate the magnitude of molecular reorientation induced refractive index changes for solvents and solutions. Overall, in this paper we have outlined various essential aspects that need to be taken into account to correctly interpret Z-scan measurement results for organic solvents and solutions.

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1. Introduction

In the last year's third-order nonlinear optical (NLO) research has increased as the demand for information transfer bandwidth and all-optical telecommunication systems has grown tremendously with the main focus on designing devices for optical data transfer, storage, and processing. While the former has already been implemented in everyday life, the latter two are still in the development phase. Although the experimental demonstration of all-optical switching [1] and data storage [2] has been presented, these devices are still not good enough to compete with the electro-optical (EO) systems. One of the main issues is a lack of highly efficient third-order NLO materials that can serve as media for light interaction, especially materials possessing Kerr and Two-photon absorption (2PA) effects [3]. Due to this studies of NLO materials are still very relevant these days as well as correct evaluation of NLO properties magnitude [4-8].

Through the years many different experimental methods have been implemented to study the NLO properties, such as degenerated four-wave mixing method [9], nonlinear ellipse rotation method [10], Mach-Zehnder interferometer [11], Beam-deflection method [12,13] and others. One of the most popular approaches to study organic materials for third-order NLO applications is by using the Z-scan method, firstly proposed by M. Sheik-Bahae group [14]. The main advantages of the Z-scan are the possibility to simultaneously study the Kerr effect and the 2PA, as well as simple experimental setup. While the Z-scan method is fairly simple to implement experimentally, ensuring correct experimental conditions for correct estimation of both effects is not that straightforward. As the Kerr effect is detected through refractive index changes due to laser irradiation, it is not the only NLO effect that can induce such changes. Free charge carriers, thermo-optical effects, and other aspects can lead to significantly larger refractive index changes compared to the Kerr effect, complicating the correct estimation of the Kerr effect amplitude [6,15,16]. A great focus has been given to studies on how to separate the thermo-optical effects from the Kerr effect. The simplest way to separate these effects is by using laser sources with different pulse lengths and repetition rates. The Kerr effect has a much faster response time (10^{-12} - 10^{-15} s) compared to the

thermo-optical effects (10^{-3} s) and by using lasers with pulse length with an order of few tens of picoseconds, the measured refractive index should only be due to the Kerr effect [17].

When studying organic compounds one of the most popular approaches is to dissolve the selected compound in a solvent and study the NLO properties of solution. The most popular choice for the solvent is chloroform as most organic dyes dissolve well in it. Studies of solutions also lead to a significant solvent contribution to the NLO response and need to be taken into account when evaluating the Kerr effect magnitude of organic dye. Usually, solutions are contained in optical cells with optical path shorter than the Rayleigh length of experimental setup. This allows to use a simple method for data approximation – the thin sample model [14]. It is important to emphasize that the Z-scan method is not limited to the thin sample approach and many different analytical models have been derived for other situations [18].

When discussing a more fundamental aspect of the Kerr effect origins, the NLO response of materials can be mainly separated into two parts – electronic response and nuclear effects. As the electronic contribution is instantaneous compared to the nuclear effects, by measuring the Kerr effect at different pulse widths, it is possible to separate these contributions. This has already been reported in the scientific literature by measuring the Kerr effect with pulse width from 100 fs to a few ps [19,20]. This allows for more in-depth studies of the NLO properties and for better understanding in which cases measured NLO properties resemble materials applicability in solid form as specific nuclear responses such as molecular reorientation will be much more limited. Another way to separate both types of responses is by measuring the Kerr effect at different light polarizations – linear, elliptic and circular. Recently scientific groups have started to study the NLO properties of materials depending on incident laser beam polarization, by introducing $\lambda/4$ plate into the Z-scan setup [21]. Many works of polarization studies for inert gases [22], CS_2 [23,24] and various solvents [19,23] have already been presented in the scientific literature, but similar in-depth studies of the NLO active organic dyes are insufficient, especially implementing the Z-scan method. Recently a paper was published regarding the separation of the thermal and the electronic contributions of Rhodamine B dissolved in methanol using polarization-resolved Z-scan measurements giving more insight for these effects in organic dyes [25]. Still, a similar study using chloroform as the solvent is lacking in the scientific literature. As chloroform is an anisotropic molecule, a specific nuclear effect – molecular reorientation - gives a significant contribution to the NLO response of the sample. Altogether, polarization-dependent measurements are a simple alternative to the pulse width measurements to separate the electronic and the nuclear parts of the Kerr effect.

In this work, we measured the 3rd order NLO efficiency dependence on light polarization for solutions of two organic compounds with picosecond and nanosecond lasers. This allows us to give a more in-depth explanation of processes influencing the nonlinear refractive index changes of the solution in each case – with the main focus being on electronic, molecular reorientation and thermo-optical effects. Measurements were carried out with mainly two goals. Firstly, to identify what processes induce the Kerr effect in organic solvents and dyes. This is essential not only for correct estimation of material applicability but also for structure-property studies and validation of quantum chemical calculation (QCC) results with obtained experimental results. Secondly, if one can do, to understand how the thermo-optical effects and the Kerr effect can be separated when using laser with ns pulse length. The experimental measurements were carried out using two 1064 nm Nd:YAG lasers, one with 30 ps pulses at 10 Hz repetition rate and second with 8 ns pulses at 200 – 40 000 Hz repetition rates. The QCC was used to calculate linear polarizability and the second-order hyperpolarizability of compounds. Values for the linear polarizability were used to evaluate the molecular reorientation contribution to the refractive index changes.

2. Experimental section

In this work, we have studied two aminobenziliden-1,3-indandione (ABI) derivatives – MeSBI and DMABI. Structures of the selected molecules are shown in Fig. 1. To study the NLO properties of selected molecules, they were dissolved in chloroform and contained in 2 mm thick photometric quartz cells. MeSBI and DMABI have insignificant linear absorption at 532 nm and 1064 nm and do not possess the 2PA effect at 1064 nm allowing to purely study the Kerr response at this wavelength [6,26]. Our previous [6,26] research has also shown that both molecules have a positive Kerr effect coefficient.

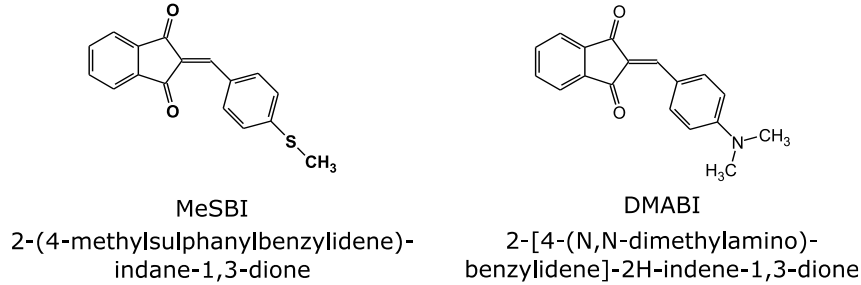


Fig. 1. Molecular structures and names of studied compounds.

To describe the refractive index dependence on the optical intensity, we used the following equation:

$$n = n_0 + n_2 \cdot I \quad (1)$$

where I is the optical intensity, n_2 is the Kerr coefficient and n_0 the linear refractive index. To simultaneously measure the 2PA and the Kerr effect, the Z-scan method employs two detection methods – open aperture and closed aperture. The open aperture detects just overall power deviations of the transmitted beam and represents the 2PA effect. The closed aperture senses two effects simultaneously - overall transmitted power changes and any variations in the laser beam size due to the refractive index changes. If the Kerr effect and the 2PA are present in media, closed aperture measurement will be influenced by both effects. To separate the Kerr effect and the 2PA we divide the closed aperture data with the open aperture data. The Kerr effect influence on the closed aperture measurement can be expressed as:

$$T(z) = 1 + \frac{4 \cdot \Delta\Phi \cdot \frac{z}{z_0}}{\left(1 + \frac{z^2}{z_0^2}\right) \cdot \left(1 + \frac{z^2}{z_0^2}\right)} \quad (2)$$

Where phase change $\Delta\Phi$ is defined as:

$$\Delta\Phi = k \cdot n_2 \cdot I \cdot L_{eff} \quad (3)$$

In the general case, the Kerr coefficient is linked to the third-order susceptibility that is expressed as a fourth-order tensor. In isotropic media, this tensor has only two independent components χ_{xyyx} and χ_{yyxx} . The contribution of the both elements can be separated by measuring the refractive index changes at linear, elliptical and circular polarized light. In case

when linearly polarized light passes through $\lambda/4$ plate, the Kerr coefficient is expressed as [17]:

$$n_2 = \pi \cdot \left(12 \cdot \chi_{xxyy} + 6 \cdot \chi_{xyyx} \cdot (\sin 2\theta)^2 \right) \cdot \frac{|E|^2}{n_0} \quad (4)$$

where E is electrical field amplitude and θ is the angle between slow axis of $\lambda/4$ plate and linear polarization direction. By measuring the ratio of the Kerr coefficient at linear and circular polarized light we can determine what effects induce refractive index changes. According to literature [27] ratio χ_{xyyx} and χ_{xxyy} equal to 6 indicates that molecular reorientation causes refractive index variation, in the case of 1 – electronic response dominate and for 0 – thermo-optical or electrostriction.

To characterize the Kerr effect of a single molecule we used nonlinear refractive cross-section defined as [28]:

$$\delta_{NLR} = \frac{\hbar \cdot \omega \cdot k \cdot n_2}{N} \cdot 10^{58} \quad (5)$$

where $\hbar \cdot \omega$ is photon energy and N is number density of molecules per volume unit. The acquired values have refractive Göppert-Mayer (RGM) as units of measure.

In our Z-scan experimental setup, we used an 11 cm lens to focus the laser beam. Laser beam waist size at the focal point was $w_0=26 \mu\text{m}$. Aperture with 1 mm diameter was used for the closed aperture measurements. The used aperture isolated less than 1 % of the incident laser beam. A more detailed description of the experimental setup can be found in reference [6].

To verify that our experimental Z-scan setup can be used to correctly measure the magnitude of the Kerr effect, we firstly measured chloroform and CS_2 with a linearly polarized laser beam and compared acquired values with the scientific literature. An example of the experimental measurement of pure chloroform can be seen in Fig. 2. Measured values of the nonlinear refractive index were $n_2=1.9 \pm 0.1 \cdot 10^{-15} \text{ cm}^2/\text{W}$ for chloroform and $n_2=3.1 \pm 0.2 \cdot 10^{-14} \text{ cm}^2/\text{W}$ for CS_2 that agree with values in literature measured at the same pulse width – 30 ps [14,29]. Also, pulse width dependent measurements of both of these compounds has been presented in the literature [13,19] indicating the separation between the electronic and the molecular reorientation contributions.

To describe the NLO properties of solutions containing multiple materials, each individual compound contribution to overall the nonlinear refractive index is estimated to be proportional to its weight fraction in the sample [30]:

$$n_{2,Solution} = (1 - \rho) \cdot n_{2,Solvent} + \rho \cdot n_{2,Organic} \quad (6)$$

where ρ is mass ratio of an organic compounds in solution. Similar linear approximations can be used for the phase change $\Delta\Phi$ on the sample concentration.

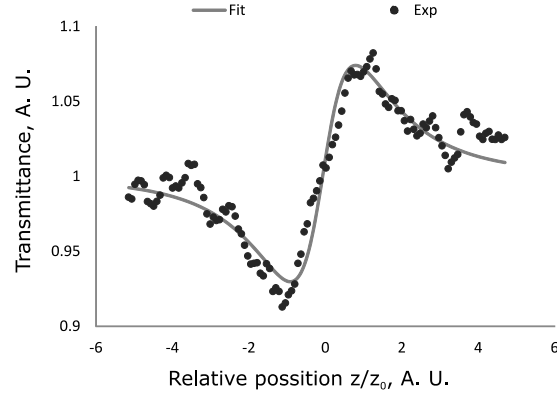


Fig. 2. Example of the closed aperture measurement of pure chloroform.

The molecular reorientation contribution to the refractive index changes is mainly present for materials that have anisotropic linear polarizabilities. Theoretically, this contribution can be described as [17]:

$$n_2 = \frac{4 \cdot \pi \cdot N}{45 \cdot n_0} \cdot \left(\frac{n_0^2 + 2}{3} \right)^4 \frac{(\alpha_2 - \alpha_1)^2}{k_B \cdot T} \quad (7)$$

where N is the number density of molecules per volume unit, T is temperature, k_B is Boltzmann constant and α_1 and α_2 are the linear polarizabilities in different directions. In the case of a molecule that has different polarizabilities in all three directions the general expression needs to be used of the form [31]:

$$n_2 = \frac{\pi \cdot N}{45 \cdot n_0} \cdot \left(\frac{n_0^2 + 2}{3} \right)^4 \frac{\left((\alpha_2 - \alpha_1)^2 + (\alpha_3 - \alpha_1)^2 + (\alpha_2 - \alpha_3)^2 \right)}{k_B \cdot T} \quad (8)$$

To test this model, we used the QCC to calculate values of the linear polarizabilities and the second-order hyperpolarizability of chloroform and organic dyes and compare them to the experimental results. The QCC were carried out using Gaussian 09 software package and more information about calculation details can be found in our previous work [6]. The second-order hyperpolarizability characterizes a single molecule's contribution to NLO properties and can easily be converted to the third-order susceptibility [32].

3. Results and Discussion

Firstly, we measured chloroform nonlinear refractive index dependence on polarization using the ps laser. Acquired results are shown in Fig. 3. Using the equation (4) we calculated the ratio between χ_{xyyx} and χ_{xxyy} to be 6.09. This indicates that the refractive index changes are mainly induced by the molecular reorientation for pure chloroform. To further investigate this, we used the linear polarizabilities calculated by the QCC ($\alpha_{xx}=\alpha_{yy}=56$, $\alpha_{zz}=29$) and used the equation (7) to calculate the nonlinear refractive index due to molecular reorientation. Calculated value $n_2=2.0 \cdot 10^{-15}$ cm²/W is close to experimentally measured value (see Table 1), indicating that employed QCC method can be used to predict the molecular reorientation contribution to refractive index changes. Next, we carried out similar measurements for DMABI and MeSBI. For DMABI solution in chloroform (0.54 wt%), the ratio between χ_{xyyx} and χ_{xxyy} was calculated to be 4.39. By assuming, that chloroform contributes with ratio 6, for

pure DMABI we acquired a ratio value of 2.85 that indicates that the measured Kerr value is due to both the electronic response and the molecular reorientation contribution. A similar value was acquired for MeSBI. Through these measurements, it is possible to separate the electronic and the molecular reorientation parts. This is important in cases when the comparison to third-order susceptibility acquired with the QCC is made as they provide value for the electronic contribution. By assuming that the electronic response is characterized by ratio 1 and molecular reorientation by ratio 6, we could estimate the magnitude of both effects. Such separation was done for DMABI as we have previously reported the QCC results of second-order hyperpolarizability for this molecule. The results are shown in Table 1. As DMABI has different linear polarizations at all three directions ($\alpha_{xx}=609$, $\alpha_{yy}=277$, $\alpha_{zz}=111$) we calculated the molecular reorientation using the equation (8) to estimate the theoretical value of the molecular reorientation. The experimental value is smaller than the theoretical but of a similar order. This could be due to DMABI having a larger time constant for the molecular reorientation compared to chloroform and 30 ps measurement cannot be used to determine the maximal value. Also, the separated electronic contribution is much closer to the QCC results, showing how essential is this separation.

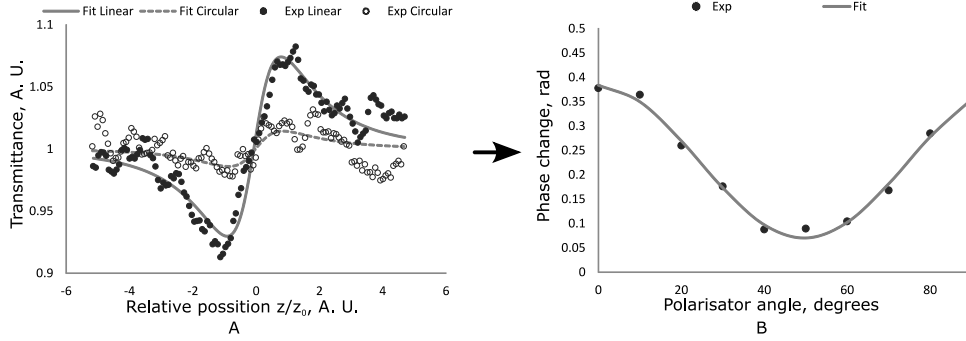


Fig. 3. Polarization measurements for chloroform. A – The closed aperture measurement at linear and circular polarizations, B – Induced phase change at different $\lambda/4$ plate angles. Data are fitted with the equation (4).

Table 1: Nonlinear refractive index values.**

	B/A	$n_{2:Exp}, cm^2/W$	$n_{2:Exp/MR}, cm^2/W$	$n_{2:Exp/E}, cm^2/W$	$n_{2:QCC/MR}, cm^2/W$	$n_{2:QCC/E}, cm^2/W$
Chloroform	6.09	$1.9 \pm 0.12 \cdot 10^{-15}$	$1.9 \pm 0.12 \cdot 10^{-15}$	-	$2.0 \cdot 10^{-15}$	$1.4 \cdot 10^{-15}$
DMABI	2.85	$2.5 \pm 0.1 \cdot 10^{-13}$	$1.5 \pm 0.1 \cdot 10^{-13}$	$9.7 \pm 0.5 \cdot 10^{-14}$	$2.0 \cdot 10^{-13}$	$9.4 \pm 0.4 \cdot 10^{-14}$

**QCC denotes quantum chemical calculation values and Exp denotes experimental values. E denotes electronic values of Kerr effect and MR denotes molecular reorientation values of Kerr effect. As for chloroform B/A ratio was close to 6, all of the experimental value was assumed to be only due to molecular reorientation and experimental electronic value was assumed to be insignificant.

Next, we carried out similar measurements using the ns laser. An example of chloroform measurements at different polarizations for 200 Hz pulse repetition rate is shown in Fig. 4. Compared to the ps measurements, it is evident that the induced phase change value increases by going from linear to circular polarization. In this case, the measured changes consist of the

thermo-optical contribution and the Kerr effect that have opposite signs. For circular polarization the Kerr effect contribution decreases while the thermo-optical does not change, leading to the overall increase. By assuming that the Kerr contribution still holds the same ratio for polarization measurements, we calculated the magnitudes of the Kerr and the thermo-optical coefficients and acquired values of $n_{2;\text{Kerr}}=1.8\pm 0.3\cdot 10^{-15}$ cm^2/W and $n_{2;\text{TO}}=-7.6\pm 0.6\cdot 10^{-15}$ cm^2/W . Acquired Kerr value is similar to one acquired with the ps laser proving that for chloroform the refractive index changes are due to the thermo-optical and the Kerr effects at the ns scale. By increasing the repetition rate, polarization influence decreased and it became more difficult to evaluate the Kerr contribution. Carrying out similar experiments at different repetition rates, we noticed that reaching about 1000 Hz, it becomes almost impossible to observe any systematic dependence on polarization within the margin of error. While at low pulse repetition rates by carrying out extra measurements at different incidence light polarization states it is possible to separate the Kerr effect and the thermo-optical effects.

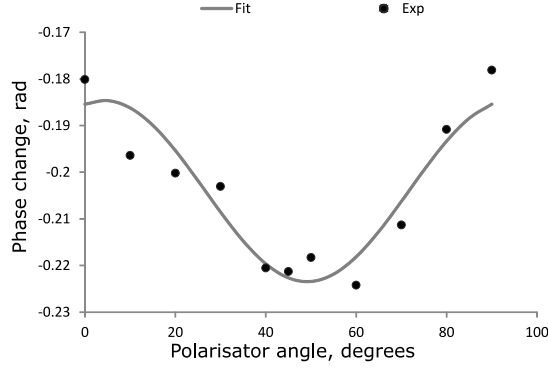


Fig. 4. Induced phase change for chloroform at different $\lambda/4$ plate angles. Data are fitted with the equation (4). Measurements were carried out with the ns laser at 200 Hz.

For the ns measurements we used both MeSBI and DMABI as they possess insignificant 2PA effect. We firstly measured MeSBI dissolved in chloroform with the ns laser at a 40 kHz repetition rate. An example of experimental measurements of pure chloroform and MeSBI sample can be seen in Fig. 5. From the experimental data, it is evident that MeSBI possesses a negative nonlinear refractive index that contradicts our previous results with the ps laser. By measuring polarization dependence, no variation in the nonlinear refractive index value was observed indicating that these changes are only due to the thermal effects. We calculated the thermal refractive index changes to be $n_{2;\text{TO}}=-2.8\pm 0.3\cdot 10^{-10}$ cm^2/W that is few orders higher than value measured with the ps laser $n_{2;\text{Kerr}}=2.5\pm 0.6\cdot 10^{-13}$ cm^2/W described in our previous work [26]. Corresponding nonlinear refractive cross-section values would be $\delta_{\text{NLR}}=1.1\pm 0.1\cdot 10^5$ RGM for the ns case and $\delta_{\text{NLR}}=9.5\pm 2.3\cdot 10^3$ RGM for the ps case. To test this we carried out experiments at different pulse repetition rates and observed that the magnitude of the nonlinear refractive index decreased with the repetition rate that coincides with previous observations of the thermal effect dependence on the pulse repetition rate [6]. While measuring the absorption spectrums of MeSBI, no significant absorption at 1064 nm was observed. Although a similar conclusion was made about chloroform, the refractive index changes were still mainly due to thermo-optical effect. This indicates that the overestimation of the Kerr effect magnitude for organic dyes can be easily made at the ns scale if not enough thorough study is made.

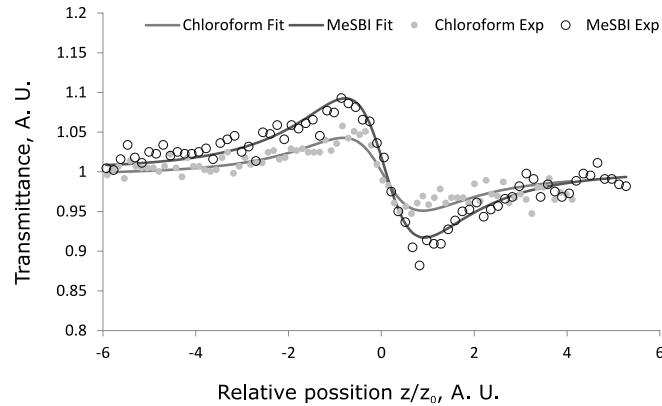


Fig. 5. Example of experimental measurement of MeSBI sample compared to pure chloroform.

For solutions containing DMABI, we started our measurements with the ns laser at 40 kHz repetition rate. An example of experimental data can be seen in Fig. 6. We acquired nonlinear refractive index value of $n_2=1.3\pm 0.2\cdot 10^{-10}$ cm²/W for DMABI corresponding to the nonlinear refractive cross-section of $\delta_{\text{NLR}}=4.4\pm 0.7\cdot 10^5$ RGM. Compared to value acquired with the ps laser [6] $n_{2;\text{Kerr}}=2.5\pm 0.2\cdot 10^{-13}$ cm²/W and $\delta_{\text{NLR}}=8.5\pm 0.7\cdot 10^3$ RGM, ns value is two orders larger. In our previous experiments, we have observed that the 2PA increases with pulse repetition rate for other ABI derivatives indicating that a real molecular level is involved in these processes [6]. The same processes could apply to the two-photon contribution to the Kerr effect leading to a similar increase. Polarization dependence measurements gave ratio 1.18 indicating mainly electrical contribution that fits the theory of two-photon contribution increase as it would increase electronic contribution to refractive index changes. By measuring dependency on the pulse repetition rate no significant changes were observed.

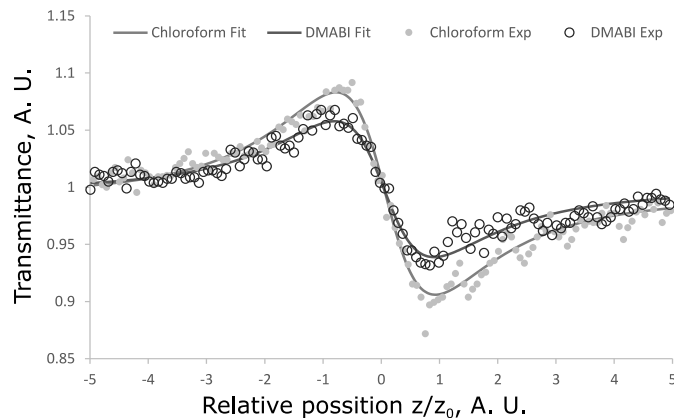


Fig. 6. Example of experimental measurement of DMABI solution in chloroform and pure chloroform. Samples concentration was 0.65 wt%.

4. Conclusions

In this work, we studied chloroform and solutions of organic dyes in chloroform with the Z-scan method using linear, elliptic and circularly polarized light. Through these experiments,

we have outlined various essential aspects that need to be taken into account to correctly interpret Z-scan measurement results. Overall the nonlinear refractive index dependence on the laser beam polarization as well as the pulse repetition rate can give more insight in origins of observed effects and separate the Kerr effect from the thermo-optical contribution as well as identify the physical processes inducing the Kerr effect. This is essential also for correct comparison between QCC and the experimental values. We showed that: i) when employing for Z-scan measurement laser with ps pulse length, the polarization dependence of refractive index changes can be used to identify what type of processes – electrical or molecular reorientation – gives rise to refractive index changes and we have demonstrated the possibility to separate them; ii) for DMABI after separation, the value of the electronic contribution of refractive index changes fits very well with QCC results; iii) molecular reorientation value can be calculated from linear polarizabilities calculated by QCC as presented in this work (for chloroform the QCC value fits very well with experimental results); iv) when using ns laser, thermal effects will strongly influence refractive index changes, but through polarization measurements, it is possible to separate Kerr and thermal effects; v) although no strong absorption at an incident wavelength for specific organic compound could be detected, thermo-optical effects can still strongly influence refractive index changes; vi) Kerr coefficient can change with pulse repetition rate due to two-photon contribution becoming stronger.

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Disclosures

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