Polarization-dependent ultrafast optical nonlinearities of *N*,*N*-dimethylformamide at 400 nm^{*}

ZHAO Xin¹**, XUE Zhiyong¹, LIU Qingyang¹, and YAN Xiaoqing²

1. School of Physical Science and Technology, Tiangong University, Tianjin 300387, China

2. Key Laboratory of Weak-Light Nonlinear Photonics, Ministry of Education, School of Physics, Nankai University, Tianjin 300071, China

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Ultrafast optical nonlinearities of *N*,*N*-dimethylformamide (DMF) are studied by using polarized light at 400 nm. Both nonlinear refraction (NLR) and stimulated Rayleigh-wing scattering (SRWS) depend on the polarization state of incident beam, while two-photon absorption (TPA) changes negligibly with polarization state. The polarization dependence of SRWS originates from that of NLR via self-focusing effect. Third-order susceptibility elements of DMF were determined, and a method to distinguish the multi-photon absorption signal from SRWS in Z-scan is provided. These results are helpful for the nonlinear optical research of the novel materials dissolved in DMF.

Document code: A **Article ID:** 1673-1905(2023)09-0541-7

DOI https://doi.org/10.1007/s11801-023-3081-2

Novel nonlinear optical (NLO) materials have attracted intense research due to both fundamental interest in the structure-properties relationship and their potential application in photonic devices^[1-6]. During optical measurements, generally, some novel materials (e.g., carbon nanotube, graphene oxide and perovskite) are needed to be dispersed/dissolved in solvents^[1,3-5,7,8]. Owing to the excellent solubility, N,N-dimethylformamide (DMF) has been widely used for novel materials fabrication and their optical measurements^[1,3-5,9]. To explore the broadband ultrafast optical nonlinearities of these novel materials or comprehensively understand their optical response process, short-wavelength laser pulses are used for optical excitation^[4,5,10-12]. And, short-wavelength pulse could realize the study of optical properties in large-bandgap materials and of the relaxation of carriers at high-energy state. Since most commercial femtosecond (fs) pulse lasers are at 800 nm, a simple and economical way to obtain short-wavelength fs pulses for ultrafast optical measurements is by converting the 800 nm pulses to 400 nm pulses via second-harmonic generation^[5]. So, the ultrafast optical response of novel materials in short-wavelength region is usually studied by using 400 nm pulses excitation^[4,5]. To avoid the influence of solvent in the measured optical signal and obtain the intrinsic optical nonlinearity of novel materials, the knowledge of NLO response in the solvents (especially DMF) at short wavelength region (including 400 nm) will be very helpful. However, such knowledge

on the optical nonlinearity of DMF at 400 nm is absent, as a result, some novel materials has to be prepared in films (It is hard to avoid the scattering induced by film heterogeneity in measurements) for optical measurements, such as reduced graphene oxide and black phosphorous quantum dots^[2,3,13].

Here, we study the polarization dependence of ultrafast nonlinear refraction (NLR), two-photon absorption (TPA) and stimulated Rayleigh-wing scattering (SRWS) in DMF at 400 nm by using polarized light Z-scan and time-resolved pump-probe measurements. The NLO response is analyzed in detailed and the physical mechanisms of polarization dependence are well explained. And the third-order susceptibility elements and TPA coefficient are determined.

The measured DMF was of analytical grade provided by Sigma-Aldrich, and the DMF was held in quartz cells during measurements. In both Z-scan and pump-probe measurements, the laser source was a Ti: sapphire regenerative amplifier (Spitfire Pro, Spectra Physics), which was operated at a pulse duration of $\tau_{FWHM} \approx 120$ fs with a repetition rate of 1 kHz, centered at the wavelength of 800 nm. The 800 nm pulse was converted to 400 nm pulse via a BBO crystal and a BG39 filter. After passing through a " $\lambda/2$ plate-Glan Taylor prism- $\lambda/4$ plate" combination, the temporal duration of 400 nm pulse was (230±30) fs (full width at half maxima (*FWHM*)) at the sample position determined from the instantaneous response of TPA in CS₂^[14]. The energy and polarization of

^{*} This work has been supported by the National Natural Science Foundation of China (No.12074202), and the Natural Science Foundation of Tianjin City (Nos.22JCYBJC00390 and 20JCQNJC00020).

^{**} E-mail: zx2013@tiangong.edu.cn

incident pulse in both Z-scan and pump-probe measurements were altered by rotating the corresponding wave plate in the combination.

Linear absorption spectrum of DMF is shown in Fig.1. Clearly, no absorption at 400 nm, but an absorption peak locates below 240 nm. Consequently, it is inferred TPA for DMF at 400 nm from the energy conservation requirement of TPA.

The Z-scan technique is applied to measure the NLR and TPA. The experimental arrangement used here is shown in Fig.2. The measurement system was calibrated by the open-aperture (OA) Z-scan measurement of $CS_2^{[14]}$. The laser beam was focused onto samples by using a 300 mm and a 200 mm focal-length lens with beam waist radius w_0 of (19±2) µm and (12±1) µm for OA and close-aperture (CA) Z-scan measurements, respectively. Neither laser-induced damage nor scattering

from quartz cells was observed in the experiment, and the ellipticity of the polarization ellipse was set to $e=\tan(5\pi/36)$ for elliptically polarized light without special physical purpose.



Fig.1 Linear absorption spectrum of DMF



BG39: filter; L1, L2, L3 and L4: lenses; BS: beam splitter; GT: Glan-Taylor prism; D1, D2: photodetectors; CA: closed-aperture Z-scan; OA: open-aperture Z-scan

Fig.2 Experimental setup for Z-scan measurements

First, the nonlinear refractive index is studied by CA Z-scan, and the sample length L is 1 mm. To eliminate nonlinear absorption (NLA) influence and get the pure NLR signal of DMF, an OA Z-Scan measurement at different pulse energy was also carried out. In addition, to exclude the NLR of the cell in the "DMF and cell" measurements, the CA Z-scan measurement of the empty quartz cell was also conducted for each polarization state. Fig.3 shows the linearly polarized light Z-scan traces for pulse energy of 64 nJ (i.e., $I_0=121 \text{ GW/cm}^2$). Clearly, considerable NLA of DMF and slight NLR of quartz cell contribute to the CA Z-scan trace. To determine the contribution of the pure NLR signal of "DMF and cell", the CA Z-scan trace was divided by the OA Z-scan trace (i.e., CA_{DMF and cell}/OA_{DMF and cell}). Then, we can get the approximate pure NLR signal of 1-mm-thick DMF liquid by subtracting the NLR signal of empty cell from that of "DMF and cell" (i.e., CA_{DMF and cell}/OA_{DMF and cell} - CA_{cell}) and show it in Fig.3(b). The approximate NLR index n_2 of DMF was obtained by least-square fitting between the CA Z-scan theory and the NLR trace of DMF^[15], the obtained n_2 value is listed in Fig.3(b). The experimental

data of differently polarized light was analyzed in the same way. These fitting curves are in good agreement with experimental data (Fig.3(b)). Clearly, the NLR depends on the polarization state of incident beam. Combining the n_2 values of linearly and circularly polarized light, the third-order susceptibility independent elements are determined and listed in Fig.3(b).

To further exploit the NLR of DMF, measurements were conducted at other pulse energies for each polarized light, and the dependence of n_2 on the intensity and polarization of incident pulse is shown in Fig.3(c). The n_2 decreases with ellipticity *e* and keeps nearly constant for each polarization in the measured intensity range, implying no higher-order NLR in our measurements. By constant fits of these n_2 values, the nonlinear refractive indexes could be determined for each polarized light (Tab.1). Furthermore, the real part of the third-order susceptibility elements can be calculated (Tab.1). These NLO parameters are in the same order of magnitude with those at 800 nm^[16], indicating the negligible dispersion in these parameters in the range of 400—800 nm due to no absorption for DMF in this range^[17].



Fig.3 (a) Linearly polarized light CA Z-scan traces of "DMF and cell", quartz cell, and DMF and OA Z-scan trace of DMF with pulse energy of 64 nJ and L=1 mm; (b) Pure NLR signal of DMF (the solid lines are the fitting curves); (c) Intensity dependence of n_2 (the solid lines are constant fits)

The ratio of $\operatorname{Re}(\chi_{xyyx}^{(3)})/\operatorname{Re}(\chi_{xyyy}^{(3)})$ is a little larger than 1 (Tab.1). It is known that the value of $\operatorname{Re}(\chi_{xyyx}^{(3)})/\operatorname{Re}(\chi_{xyxy}^{(3)})$ is 1 for electronic nonlinearity and 6 for nuclear nonlinearity (i.e., the nonlinearity induced by molecular orientation)^[17]. So, both electronic and non-instantaneous nuclear nonlinearity contribute to the NLR at the pulse width, and the electronic nonlinearity is dominant. The polarization dependence of NLR arises from the nonlinear polarization component related to $\operatorname{Re}\left(\chi_{xyyx}^{(3)}\right)^{[17]}$, leading to the variation of n_2 value with polarization state of incident beam.

Now, we turn to the NLA and nonlinear scattering (NLS) by performing OA Z-scan measurements with different levels of pulse energy and sample length. Using two sample lengths was aiming to reveal the influence of self-focusing effect on the measurements. The polarized light OA Z-scan traces at pulse energies of 11 nJ, 83 nJ and 168 nJ are shown in Fig.4. There were obvious signals from NLA or NLS in these traces. For both 1-mm-and 2-mm-thick DMF, the Z-scan signals change slightly with polarization state at low pulse energy, while changes obviously with polarization state at high pulse energy. And, the polarization dependence of Z-scan traces relies on sample length. The thicker the sample is, the stronger the polarization dependence is.

To explore the OA Z-scan signal source and analyze the physical mechanisms of polarization dependence, we first fit these traces with TPA model to extract the effective TPA coefficient β_{eff} . Since the self-focusing effect could affect the NLA of sample^[17], we need to consider the self-focusing effect in the data fitting. So, we turn to the nonlinear Schrödinger partial differential equation describing the propagation of the electric field envelope *E* in a nonlinear medium^[18]. In the case of Kerr nonlinearity and TPA, the equation is

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial E}{\partial r}\right) - 2ik\frac{\partial E}{\partial z} - ik\beta_{\text{eff}}\left|E\right|^{2}E + \frac{2k^{2}}{n_{0}}n_{2}\left|E\right|^{2} \cdot E = 0,$$
(1)

where $k=n_0\omega/c$ is the wave vector and the NLA $\Delta \alpha = \beta_{eff} I$. For each Z-scan trace, the normalized transmittance at position Z was calculated after the fs pulse passing through the sample by using Crank-Nicholson finite difference method for Eq.(1). In these fits, we try to make the calculated valleys of Z-scan traces agree with the measured traces, and then obtain the β_{eff} values.

The best Z-scan trace fits are shown as lines in Fig.4, and the extracted β_{eff} are listed in the corresponding figures. Among these fits, the fitting quality at low pulse energy is good (Fig.4(a) and (d)), while the TPA could not fit these Z-scan traces at high pulse energy well no matter what the polarization state is (Fig.4(c), (e) and (f)). At the same input energy and sample length, circularly polarized light Z-scan trace could be well fit with TPA model but linearly polarized light Z-scan trace could not be (Fig.4(c) and (e)). Or, for identical input energy and polarization state, Z-scan trace of 1-mm-thick sample could be well fit by the TPA model, but the 2-mm-thick case could not (e.g., elliptically polarized case in Fig.4(b) and (e)). Clearly, there is extra signal source besides TPA in these traces at high incident energy.

The dependences of β_{eff} on pulse energy, polarization state and sample length are given in Fig.5(a). However, the dependences of β_{eff} on polarization state and sample length are complicate. At low energy, the β_{eff} value is

Polarization	$n_2 (\times 10^{-16} \text{ cm}^2/\text{W})$	$\chi^{(3)}_{xyxy}$ (×10 ⁻¹⁵ esu)	$\chi^{(3)}_{xyyx}$ (×10 ⁻¹⁵ esu)	$\chi^{(3)}_{xxxx}$ (×10 ⁻¹⁵ esu)	$\frac{\operatorname{Re}(\chi^{(3)}_{xyyx})}{\operatorname{Re}(\chi^{(3)}_{xyxy})}$
Linearly	9.2±0.8	$(6.7 \pm 0.6) + (0.3 \pm 0.03)i$	10.3±2.5	$(23.7\pm2.2)+(0.3\pm0.03)i$	1.5±0.4
Circularly	5.2 ± 0.5				
Elliptically	7.2±0.8				

Tab.1 NLO parameters of DMF at 400 nm



Fig.4 OA Z-scan traces of DMF against polarization state, sample length and pulse energy (The solid lines are the fits with TPA model; These figures share the same *y*-axis label and legend)

independent on pulse energy and sample length, implying the presence of mere TPA at low energy. In addition, $\beta_{\rm eff}$ changes slightly with polarization state, thus the negligible dependence of the TPA coefficient on the polarization state could be concluded and the TPA coefficient could be obtained by constant fit at low pulse energy (Fig.5(a)). At high energy, the β_{eff} value increases with pulse energy for each polarization state, but less increase is found for circularly polarized light and thinner sample. In addition, the pulse energy threshold for extra signal decreases with sample length and increase with ellipticity. At the same time, the fitting quality become worse with sample length increasing (Fig.4(c) and (f)) and become better with ellipticity increasing. These results indicate that higher-order NLA or NLS would be the extra signal source^[16,17].

To verify the influence of NLS on these Z-scan traces (Fig.4), the transmitted light spectra were measured at different sample positions. The normalized light spectra for incident energy of 168 nJ are shown in Fig.6. From the comparison of spectra at different sample positions, we find that there is a forward Stokes-shifted super-broadening SRWS when the sample is placed near focus. And, the SRWS intensity changes with the polarization state of incident beam, i.e., largest (smallest) for linearly (circularly) polarized light. SRWS is the light

scattering process resulting from the tendency of anisotropic molecules to become aligned along the electric field vector of an optical wave^[17]. As discussed above, there was contribution from molecular orientation to the NLR of DMF, leading to SRWS signal in the Z-scan traces of high incident energy. Further, the SRWS results in the increase of β_{eff} with pulse energy.

It is known there is an intensity threshold for SRWS^[17]. To explain the polarization dependence of SRWS, we calculated the maximum light intensity at the exit face against position Z with accounting self-focusing effect, using the NLR parameters of Tab.1 in the simulation based on Eq.(1). In the simulation, the TPA had also been considered.

As shown in Fig.5(b), the maximum light intensity at the exit face increases with sample length and decreases with ellipticity at identical pulse energy. In the Z-scan measurements, NLS takes place once the light intensity exceeds the intensity threshold of SRWS. Combining the results in Fig.4 and Fig.5(b), the intensity threshold of SRWS is determined to be ~116 GW/cm², and the energy and polarization dependence of Z-scan results could be understood as follows. At the same pulse energy, the intensity increases with sample length and decreases with ellipticity. As a result, for the same polarized light, the SRWS signal is more obvious for 2-mm- than 1-mm-thick

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sample. And, for the same sample length, the SRWS signal intensity is stronger for linearly than circularly polarized light. The critical pulse energy for observing SRWS decreases with sample length and increases with ellipticity. Furthermore, SRWS results in that the β_{eff} at high energy increases with sample length and decreases with ellipticity (Fig.5(a)). For the same light polarization, to get the same maximum intensity the pulse energy for 2-mm-thick sample should be set smaller than that for 1-mm-thick sample, leading to that the energy threshold of SRWS is larger for the 1-mm- than 2-mm-thick sample. As pulse energy increase, the SRWS signal intensity increases more obvious for 2-mm- than 1-mm-thick sample, and the energy threshold of SRWS is lower for 2-mm- than 1-mm-thick sample. Furthermore, the $\beta_{\rm eff}$ increases faster with pulse energy for 2-mm- than 1-mm-thick sample (Fig.5(a)).



Fig.5 (a) Dependence of β_{eff} on pulse energy and sample length, and constant fit of TPA coefficient (thick cyan line); (b) The maximum intensities at the exit face of sample from simulation against position *Z* under incident energy of 168 nJ

So, the polarization and sample length dependences of both SRWS and $\beta_{\rm eff}$ have been well interpreted by the self-focusing effect. The polarization characteristic of self-focusing effect originates from the variation of n_2 value with polarization state (Tab.1)^[17].

To confirm NLA process of DMF, the time-resolved differential transmission (ΔT) measurements were carried out in DMF as in Ref.[14]. As shown in Fig.7(a), the ΔT

signal around zero delay time could be well fit by the cross-correlation function of pump and probe pulses, indicating instantaneous response of TPA^[19]. When the pump energy increases, the peak signal is linearly dependent on the pump energy (Fig.7(b)) while the normalized time-resolved curve does not change, confirming no higher-order NLA in DMF^[17].



Fig.6 Comparison of transmitted light spectra at different Z positions

Since the response time of nuclear nonlinearity is comparable with the pulse duration of most commercial fs laser, solvents are prone to generating SRWS signal during optical measurements at high energy. Therefore, when we use Z-scan to measure the NLA of novel materials dissolved in solvents with high pulse energy, it is necessary to avoid regarding the SRWS signal of solvents as NLA of novel materials. One simple way to avoid SRWS is by limiting the measurements to using very low pulse energy. If the extracted NLA coefficient increases with pulse energy, one way to judge whether it is caused by higher-order NLA or other nonlinear process is by studying the variation of NLA coefficient with sample length. If the increase of NLA coefficient is caused by higher-order NLA, the NLA coefficient should be independent on sample length. However, if the increase of NLA coefficient is caused by NLS, the NLA coefficient should increase significantly with sample length.



Fig.7 (a) Time-resolved ΔT curve of DMF at pump fluence of 0.097 mJ/cm²; (b) Linear dependence of the maximum ΔT on pump fluence

In summary, ultrafast optical nonlinearity of DMF has been systematically studied at 400 nm. In DMF, there is TPA at low intensity, and SRWS besides TPA at high intensity. The TPA is independent on the polarization state of incident beam, while the SRWS intensity varies with both polarization state and sample length. In addition, the nonlinear refractive indexes and susceptibility elements have been determined. When measuring the nonlinear optical properties of novel materials dissolved in DMF at short wavelengths, we should pay attention to not regarding the SRWS signal of DMF as NLA of novel materials, by measuring the NLA coefficient against sample length.

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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