

## Spectral dispersion of ultrafast optical limiting in Coumarin-120 by white-light continuum Z-scan

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Measurement of the wavelength dispersion of optical limiting in materials can provide invaluable information useful for laser safety device applications. However, it can be a tedious task when conventional tunable laser sources like the optical parametric amplifier are employed for excitation. Here we report the spectral dispersion of ultrafast optical limiting in the laser dye Coumarin-120 in the wavelength region 630 to 900 nm, measured in a single Z-scan, using the white-light continuum as the excitation source. Optical limiting is found to arise from two-photon absorption, and its spectrum agrees very well in shape with the linear absorption spectrum. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4807151>]

Among the various classes of materials studied for non-linear optical (NLO) applications, organic dyes are of special interest due to the presence of extended  $\pi$  electron conjugation in their molecules, which makes them highly polarizable. Depending on the excitation wavelength they may also have high optical damage thresholds and ultrafast optical responses.<sup>1</sup> The electronic structure of these materials usually support strong nonlinear absorption (NLA) in the visible as well as IR regions, which can be utilized in applications such as optical power limiting, multi-photon excited fluorescence imaging, and multi-photon photodynamic therapy.<sup>2,3</sup> Due to simplicity and high sensitivity, the Z-scan method is often used for the measurement of nonlinear absorption and nonlinear refraction in these materials.<sup>4,5</sup> But, conventional Z-scan method uses a monochromatic excitation source, which allows the measurement of nonlinearity only for a single wavelength at a given time. Since NLO properties of a material are wavelength dependent, optimization of the device performance often requires that the nonlinearity is measured over a wide spectral range. Determination of nonlinear spectra using conventional tunable light sources like the optical parametric amplifier (OPA) is tedious and time consuming. Moreover, exposure to laser radiation for prolonged time periods may affect the sample stability and result in faulty results.

In view of the above, an alternative technique which uses a white-light continuum (WLC) as the excitation source was developed by a few research groups in the past.<sup>6-9</sup> Here, the monochromatic excitation source used in the conventional Z-scan is replaced by a broadband WLC source. White-light continuum is generated by passing intense ultrafast laser pulses through a suitable transparent medium like water or quartz. Though the temporal coherence of such a broadened pulse is low, the spatial coherence remains high.<sup>10</sup> In the implementation by He *et al.*<sup>6</sup> the WLC is spatially dispersed by means of a prism before reaching the

sample. Since different colors are incident on the sample at different positions, a degenerate measurement of the nonlinearity can be made. Instead of spatially dispersing the WLC, Boni *et al.*<sup>9</sup> suggested that the inherent chirp of the WLC (which was measured to be 18 fs/nm in their case) is sufficient to measure a degenerate two-photon absorption (2PA) spectrum. However, from detailed studies Van Stryland and colleagues<sup>7,8</sup> concluded that both temporal and spatial dispersion of the WLC is desirable to measure the degenerate 2PA coefficients accurately. The major advantage of the WLC Z-scan is the large spectral bandwidth of the WLC, which allows the fast and simultaneous measurement of the NLA spectrum of a given material. Moreover, the good spectral resolution possessed by WLC makes it possible to observe subtle features in the NLA spectra, which otherwise cannot be detected by discrete sources.<sup>11</sup>

For the present investigations, we have chosen a commercially available laser dye, namely, Coumarin-120 (*4-methyl-7-aminocoumarin*). Coumarins are an important class of organic dyes which are well studied for applications such as fluorescence, pulse shortening, electrophotography, and electroluminescence.<sup>12,13</sup> Since their backbone is an asymmetric transmitter, the nonlinearity can be enhanced by electron donating and withdrawing group substitutions.<sup>14,15</sup> In the present study, we report measurements of the spectral dispersion of the nonlinear absorption coefficient in Coumarin-120, performed using the WLC Z-scan technique.

The linear absorption spectrum of Coumarin-120 (purchased from Sirah Lasertechnik GmbH) was recorded using a UV-Vis spectrometer (PerkinElmer, Lambda 35). Intense laser pulses required for WLC generation were derived from a regeneratively amplified Ti:Sapphire laser (TSA-10, Spectra Physics), which produces  $\sim 8$  mJ, 100 fs pulses at 780 nm (1.59 eV), at a 10 Hz repetition rate. The continuum is generated by focusing the laser pulses into a 5 cm long water cell, using a 10 cm focal length lens. A schematic of the experimental setup is given in Fig. 1. The WLC generated in the water cell is initially collimated using a plano-

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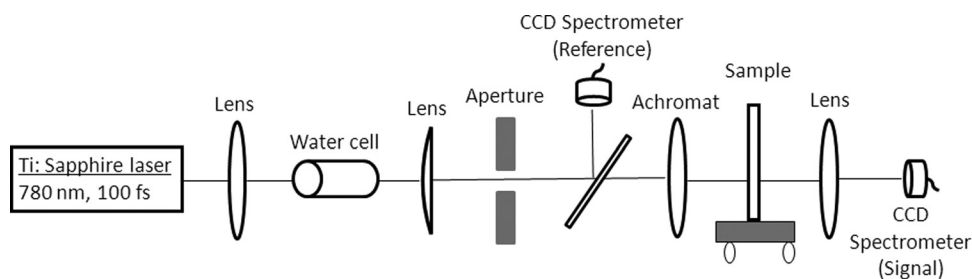


FIG. 1. The WLC Z-scan set up. White-light continuum generated in the water cell by 100 fs laser pulses is used as the excitation source for the Z-scan. Spectra of the generated white-light as well as transmitted white-light are measured on CCD spectrometers as shown.

convex lens of 10 cm focal length. After collimation, the conical emissions are removed by placing an iris aperture in the beam path, which restricts the output to the central WLC region. A small part of this continuum beam is directed to a CCD spectrometer using a beam splitter for reference. The main beam is focused onto the sample using an achromatic doublet, which converges all the wavelengths onto the same focal point in the sample. The sample taken in a 1 mm cuvette is mounted on a translation stage which can be moved along the beam propagation direction (taken as the z-axis). Light transmitted through the sample is fed into another CCD spectrometer using a converging lens. Both spectrometers are identical (AvaSpec 2048, Avantes BV), with a working wavelength range of 340-1100 nm and resolution of 0.8 nm. The spectrum of transmitted light is recorded at equal intervals while the sample is translated from  $z = -15$  mm to  $z = +15$  mm ( $z = 0$  is the focal point). The transmission spectrum recorded at each  $z$  position is normalized with the corresponding spectrum obtained by the reference spectrometer. This normalized spectrum, calculated for every  $z$  value, contains nonlinear transmission information over a wide wavelength range of approximately 630 nm to 900 nm, with a resolution of 0.8 nm. From this large dataset, by rearranging the data, it is possible to obtain the nonlinear transmission for any particular wavelength, for the full range of  $z$  values. This gives the Z-scan curve for that wavelength. For convenience, we calculated these Z-scan curves using a LabVIEW program. The Z-scan curves thus obtained are analyzed numerically to find the coefficient of nonlinear absorption at the corresponding wavelengths. The beam waist is taken to be approximately the same for all the wavelengths.<sup>9</sup>

The WLC spectrum obtained in water given in Fig. 2 extends approximately from 630 nm to 930 nm. The peak at 780 nm is due to the excitation pulse because we chose not to use any filters in order to get the complete spectrum including the near infrared (NIR) region. The mechanism of supercontinuum generation is generally considered to be related to self phase modulation and stimulated Raman scattering. When an intense laser pulse propagates through a medium, variations in the refractive index due to optical Kerr effect changes the instantaneous phase of the incident laser pulse, which results in the spectral broadening.<sup>16</sup> The intensity dependent refractive index is given by  $n(I) = n_o + n_2 I(t)$ , where  $I(t)$  is the intensity of the incident laser pulse,  $n_o$  is the linear refractive index, and  $n_2$  is the nonlinear refractive index coefficient. The instantaneous phase of the pulse can be written as,  $\phi(t) = \omega_o t - \frac{2\pi}{\lambda_o} n_o L - \frac{2\pi}{\lambda_o} n_2 I(t) L$ , where  $\omega_o$  is the frequency of the incident pulse,  $\lambda_o$  is the pulse wavelength, and  $L$  is the length of the medium. The instantaneous

frequency can be obtained from the time derivative of the instantaneous phase as  $\omega(t) = \frac{d\phi(t)}{dt} = \omega_o - \frac{2\pi}{\lambda_o} n_2 L \frac{dI(t)}{dt}$ , so that  $\omega(t) = \omega_o - \Delta\omega(t)$ , where  $\Delta\omega(t) = \frac{2\pi}{\lambda_o} n_2 L \frac{dI(t)}{dt}$ . Thus, the intensity dependent refractive index results in a frequency sweep of the pulse in time. For a material with positive  $n_2$ , the leading edge of a Gaussian pulse shifts to higher frequencies and the trailing edge to lower frequencies. Moreover, if the material is vibrationally active then laser pulses can excite coherent vibrational modes resulting in stimulated Raman scattering (SRS). The intense primary SRS lines act as excitation sources to generate their own Raman lines, thereby introducing new spectral components.<sup>17</sup>

The nonlinear transmission curves of Coumarin-120 obtained for different excitation wavelengths using the WLC Z-scan measurement are shown in Fig. 3. The transmittance is found to decrease with input intensity resulting in an optical limiting (OL) behavior. In general, NLA may occur from multiphoton and excited state absorption processes (MPA and ESA, respectively). ESA is a sequential process that requires the presence of *real* intermediate states. The UV-Vis absorption spectrum of Coumarin-120 given in Fig. 4(a) shows electronic absorption bands in the UV region, so that the material is transparent in the WLC spectral range (630 to 930 nm). Therefore, the most likely mechanism of NLA in this transparency region is MPA involving *virtual* intermediate states. It is important to note that the WLC in our case is not spectrally or temporally dispersed, and the beam is focused onto the sample using an achromatic doublet so that the optical limiting we observe is of a nondegenerate nature.

To confirm the mechanism of NLA, we numerically fitted the Z-scan curves with different nonlinear transmittance

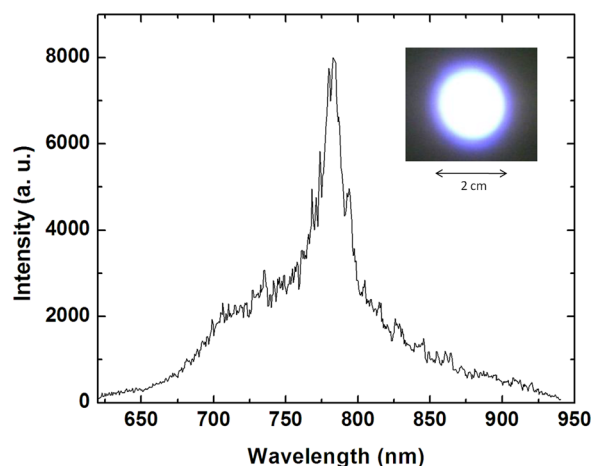


FIG. 2. Emission spectrum of white-light continuum generated in water upon irradiation by focused 100 fs laser pulses. Peak at 780 nm is due to the input laser radiation. Inset shows a photographic image of the WLC.

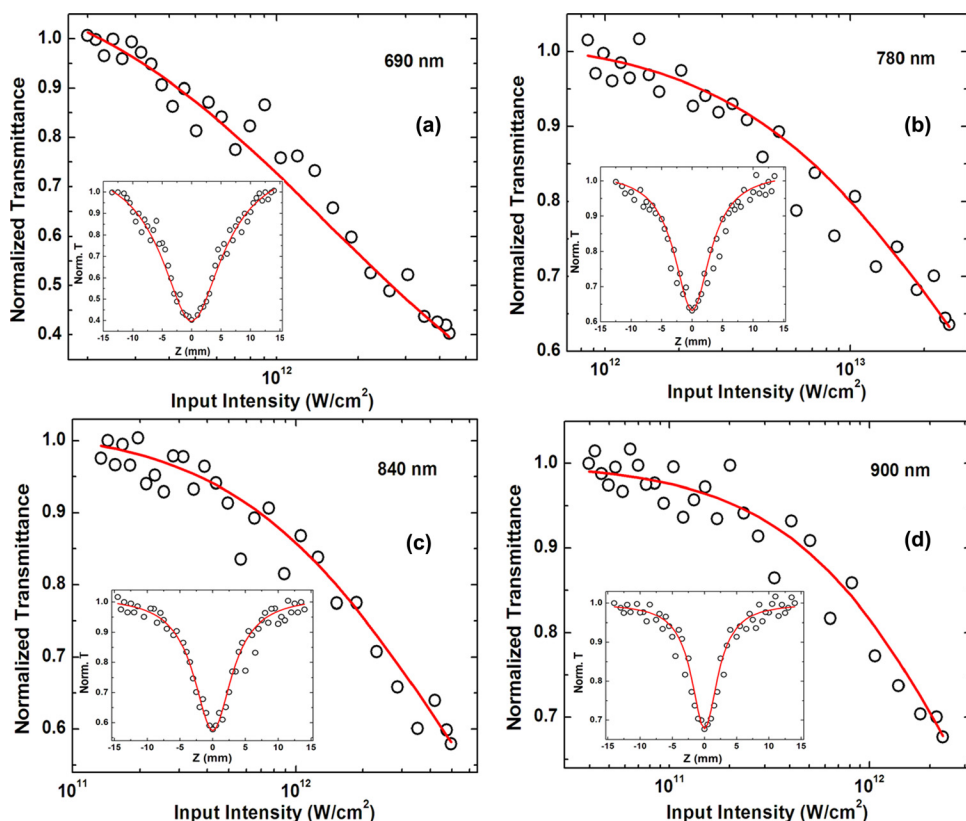


FIG. 3. Optical limiting curves of Coumarin-120 calculated for the wavelengths (a) 690 nm, (b) 780 nm, (c) 840 nm, and (d) 900 nm. These are obtained from the corresponding Z-scan curves given in the insets, which are in turn calculated from a single WLC Z-scan measurement. Open circles are experimental data and solid curves are numerical fits for two-photon absorption (Eq. (1)).

equations and found that the best fit is to a two-photon absorption (2PA) process. The sample transmittance in the case of 2PA is given by<sup>18</sup>

$$T = ((1 - R)^2 \exp(-\alpha_o L) / \sqrt{\pi q_o}) \int_{-\infty}^{+\infty} \ln[1 + q_o^2 \exp(-t^2)] dt, \quad (1)$$

which is obtained by solving the pulse propagation equation  $dI/dz' = -\alpha_o I - \beta I^2$ . Here,  $L$  and  $R$  are the sample length and surface reflectivity, respectively.  $I$  is the incident laser intensity,  $\alpha_o$  is the linear absorption coefficient, and  $z'$  is propagation distance within the sample.  $q_o$  is given by  $\beta(1 - R)I_o L_{eff}$ , where  $\beta$  is the 2PA coefficient, which characterizes the strength of nonlinear absorption, and  $I_o$  is the on-axis peak intensity. The effective length  $L_{eff}$  is given by  $(1 - \exp(-\alpha_o L)) / \alpha_o$ . The  $\beta$  values calculated from the best fits to the Z-scan curves corresponding to different wavelengths are plotted in Fig. 4(b).

In general, the selection rules applicable for one- and two-photon transitions are different due to the restrictions posed by the conservation of angular momentum. But for asymmetric molecules like Coumarin-120, the selection rules are relaxed so that both one-photon absorption (1PA) and 2PA result in same final state.<sup>19,20</sup> In conformity to this observation, we can see that the 2PA spectrum shown in Fig. 4(b) is almost a replica of the 1PA spectrum, except for the appropriate shift in the wavelength scale. The spectral dispersion of 2PA coefficient in the 630 to 900 nm range closely follows the strength of corresponding 1PA in the wavelength region of 315 to 450 nm. It may be noted that unlike ESA the 2PA process is a weak phenomenon, which does not result in substantial population redistribution within an absorbing system. The  $\beta$  values are hence mostly independent of the on-axis peak intensity seen by the sample.<sup>21,22</sup> Therefore, it can be ensured that the measured dispersion of nonlinearity is not an artifact due to intensity variations between the wavelengths (each wavelength in the WLC has a different intensity), but arises truly from the wavelength dispersion of the 2PA cross-section of the sample.<sup>21,23</sup>

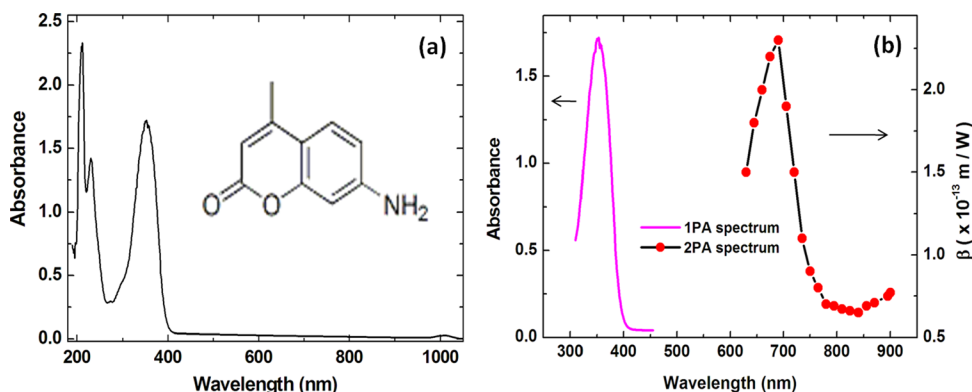


FIG. 4. (a) Linear absorption spectrum of Coumarin-120 (peak at 352 nm) showing negligible absorption in the WLC spectral range. Inset shows the structure of the asymmetric molecule. (b) Dispersion of the 2PA coefficient ( $\beta$ ) obtained from the best fit curves to the WLC Z-scan data given in Fig. 3. The 2PA spectrum peaks at 690 nm and is similar in shape to the corresponding 1PA spectrum.

It may be noted that the fluorescence emission of Coumarin-120, which is in the range of 400 nm to 490 nm,<sup>24,25</sup> will not be directly excited by the present WLC. Nevertheless, in general, some samples may be excited by a certain wavelength region of the WLC to emit Stokes-shifted photoluminescence (PL) in a longer wavelength region of the WLC. In such cases, it will be impossible for the CCD spectrometer to distinguish between WLC photons and PL photons of similar wavelengths. However, since PL emission is usually isotropic, its fraction reaching the detector placed in the far field on the z axis will be relatively small, and can be ignored. Moreover, the detector may be kept in the far field as far away from the sample as possible, and the WLC Z-scan may be limited to the shortest range possible near the lens focal region so that the magnitude and variation of PL photons reaching the detector can be minimized.

The strong nonlinearity observed in Coumarin-120 originates primarily from the peculiar structure of the molecule. As seen in the inset of Fig. 4(a), the amino (-NH<sub>2</sub>) group of the molecule acts as an electron donor and the benzopyrone moiety acts as electron acceptor. The existence of such a donor-acceptor (D-A) motif in the structure leads to strong delocalization of the  $\pi$  electron cloud through intramolecular charge transfer, resulting in large nonlinear polarization.<sup>26</sup> Previous studies done on Coumarin derivatives have revealed the polar nature of the first excited state arising from intramolecular charge-transfer resulting in a larger dipole moment compared to the ground state.<sup>27,28</sup> The large difference in dipole moments between the ground and excited states favors strong 2PA in these materials. In general, NLA in molecular materials can be explained using a five level energy diagram consisting of singlet and triplet state manifolds ( $S_0$ ,  $S_1$ ,  $S_2$ ,  $T_1$ , and  $T_2$ ).<sup>18</sup> Under strong laser excitation, molecules from the ground state  $S_0$  are excited to higher lying vibronic levels of  $S_1$  from where non-radiative scattering thermalizes them to the lowest vibronic level of  $S_1$ . Molecules undergoing ESA get excited to  $S_2$  instantaneously and decay back to  $S_1$  within a few picoseconds. In the nanosecond excitation regime, strong NLA happens *via* intersystem crossing as well, where molecules from  $S_1$  make a spin-flip transition to  $T_1$  followed by ESA to  $T_2$ . Since intersystem crossing takes several picoseconds to happen, the effect of triplet state ESA is negligible in the ultrafast excitation regime.

In the present case, 2PA in Coumarin-120 occurs due to transitions from  $S_0 \rightarrow S_1$  where the simultaneous absorption of two photons excites molecules to different vibronic levels of  $S_1$ . The strength of absorption at each wavelength is governed by the corresponding 2PA cross-section. The 2PA coefficient  $\beta$  is obtained by multiplying the 2PA cross-section with the ground state population density. It follows from perturbation theory that the 2PA cross-section ( $\sigma^{(2)}$ ) for a given excitation frequency  $\nu$  is given by

$$\sigma^{(2)}(\nu) = \frac{(2\pi)^4 \nu^2}{(ch)^2} g(2\nu) |S_{fg}|^2, \quad (2)$$

where  $c$  is the speed of light,  $h$  is the Planck's constant,  $g(2\nu)$  is the normalized 2PA line shape, which is usually Lorentzian, and  $|S_{fg}|^2$  is the 2PA tensor between the ground state  $|g\rangle$  and the final state  $|f\rangle$ .<sup>23</sup> Assuming a single virtual

intermediate state  $|i\rangle$ , the 2PA tensor can be obtained from sum-over-state calculations as

$$|S_{fg}|^2 = \frac{4}{5} \frac{|\mu_{ig}|^2 |\mu_{fi}|^2}{(\nu_{ig} - \nu)^2 + \Gamma_{ig}^2}, \quad (3)$$

where  $|\mu_{ig}|$  and  $|\mu_{fi}|$  are the transition moments,  $\nu_{ig}$  is the transition frequency, and  $\Gamma_{ig}$  is the damping constant for the  $g \rightarrow i$  and  $i \rightarrow f$  transitions, respectively. Therefore, for a given excitation, the 2PA cross-section of a molecule is determined by the line shape function, transition dipole moments, and transition frequencies. The frequency dependence determines the wavelength dispersion of  $\sigma^{(2)}$  (and thereby  $\beta$ ), and the dipole moments determine its overall magnitude.<sup>29</sup> It follows from Eq. (3) that resonance enhancement in the 2PA spectra of asymmetric molecules is a consequence of the increase in the 2PA tensor contribution, when the excitation frequency reaches the energy of the one photon transition (i.e.,  $\nu_{ig} - \nu = 0$ ).<sup>23</sup>

In summary, we have measured the spectral dispersion of ultrafast optical limiting in the laser dye Coumarin-120 in a single Z-scan measurement, using the nondegenerate WLC Z-scan method. The observed nonlinear absorption arises from two-photon absorption and its spectrum agrees very well in shape with the linear absorption spectrum due to the asymmetric nature of the molecule. The WLC Z-scan is extremely useful for the fast determination of nonlinear absorption spectra in materials, which is essential to optimize NLO materials for practical applications.

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