

## Measurement of group velocity dispersion of solvents using 2-cycle femtosecond pulses: Experiment and theory

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(Received 15 July 2011; accepted 7 September 2011; published online 22 September 2011)

Second and third-order dispersion for water, methanol, cyclohexane, carbon tetrachloride, dimethyl sulfoxide, toluene and carbon disulfide are measured with high accuracy and precision in the range of 700-900 nm using two-cycle long femtosecond laser pulses. The ratio between second and third-order dispersion, which is predicted to vary linearly, is experimentally confirmed and this observation is examined theoretically. A method to predict second and third-order dispersion of unknown transparent media with accuracy that is comparable to the best experimental methods is proposed and tested. The information provided is important for applications of ultrafast lasers in science, medicine and industry. *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:10.1063/1.3646462]

### I. INTRODUCTION

A number of applications such as nonlinear optical microscopy, nonlinear spectroscopy, femtosecond laser eye surgery and femtosecond micromachining, require the delivery of minimally dispersed pulses at the intended target. Unfortunately, short pulses undergo chromatic dispersion, which results in temporal broadening, as the pulses are transmitted through a medium. Applications as well as scientific experiments with femtosecond laser pulses require knowledge of the dispersive properties of gaseous, liquid and solid state media. This need was predicted 25 years ago, when a landmark theoretical study was published that compared the second, third and fourth derivative of refractive indices of the most common optical media.<sup>1</sup> Remarkably, at the time there appeared to be a linear relation between the different orders of derivatives of refractive indices. Moreover, this ratio between the different orders seemed independent of optical media. This supposed linear relationship has been used to estimate the extent of high order correction to the wavelength dependent refractive index when no dispersion measurements are available. Alternatively, index of refraction measurements numerically fitted by phenomenological (Sellmeier's) equation are also used to determine dispersion.<sup>1,2</sup> However, given that dispersion depends on high-order derivatives of the index of refraction, such estimates are not very accurate.

In this study, we revisit the relation between second and third order dispersion (SOD and TOD, respectively), and provide a new formulation that can be used to determine TOD for any medium (gas, liquid, or solid) provided the region of interest is far from optical resonances. The new formulation is tested for different media, including some of the most common optical media used for ultrafast laser studies.

Dispersion results when a pulse of light transmits through a medium with a frequency dependent refractive index, as illustrated in Fig. 1. Note that as the pulse propagates, the term  $k(\omega)$  is frequency

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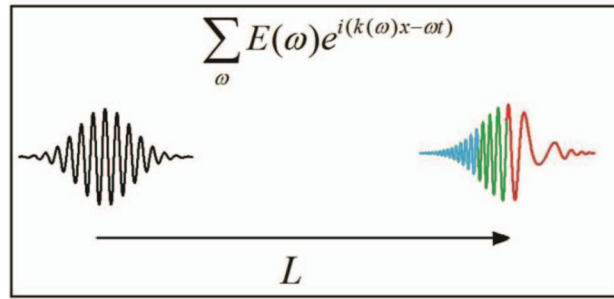


FIG. 1. Schematic diagram representing the phase distortions of a pulse as it propagates through a medium with a frequency-dependent wavenumber vector  $k(\omega)$ .

dependent. Therefore an ultrashort laser pulse, with a broad spectral bandwidth, experiences different  $k(\omega)$  values. The refractive index, which is proportional to  $k(\omega)$ , is affected by the oscillator strength and frequency of electronic and vibrational resonances of the medium. For transparent media, one may assume that there is a single resonance in the vacuum ultraviolet region and dispersion primarily depends on the oscillator strength of that resonance. Beyond this simple, single electronic resonance explanation, only accurate experimental methods are able to provide SOD and TOD values for media of interest. Here we present a series of such measurements and provide a method to predict the dispersion of other transparent media.

As the pulse duration of femtosecond lasers available commercially continues to get shorter, reaching the single cycle regime in some cases, higher order dispersion of optical media become important and can cause significant pulse broadening. In determining the need for considering third order dispersion correction, we find it useful to consider the ratio between the bandwidth  $\Delta\omega$  and the carrier frequency of the pulse  $\omega_0$ . For pulses with  $\Delta\omega/\omega_0 > 0.1$ , third order dispersion begins to play a role, and for octave spanning lasers  $\Delta\omega/\omega_0 < 0.25$  even higher order terms must be determined. White light interferometry has been the method of choice to measure dispersion with very good accuracy.<sup>3,4</sup> More recently method that measures directly higher order dispersion<sup>5</sup> based on multiphoton intrapulse interference phase scan (MIIPS) was introduced,<sup>6,7</sup> and here we use this method to measure the second and third order dispersion of common solvents used in femtosecond research.

## II. THEORY

We begin our discussion from fundamental definitions. The wave number is defined as  $k(\omega) = \omega n(\omega)/c$ , where  $\omega$  is the angular frequency of light,  $n(\omega)$  is the refractive index of the medium,  $c$  is the speed of light. As a pulse propagates through a medium it undergoes chromatic dispersion as illustrated in Fig. 1. The phase accumulated by a pulse as it propagates through a medium of length  $L$  can be expressed as the Taylor series expansion near the carrier frequency  $\omega_0$

$$\varphi(\omega) = \left[ k_0 + k'(\omega - \omega_0) + \frac{1}{2}k''(\omega - \omega_0)^2 + \frac{1}{6}k'''(\omega - \omega_0)^3 + \dots \right] L \quad (1)$$

In the expression above, the first two terms cause no dispersion. The first order term causes a time delay of magnitude  $k'(\omega) = dk(\omega)/d\omega = \varphi'(\omega)/L = d\varphi(\omega)/d\omega/L$ . The second and higher order terms cause dispersion. For a given unit length, the second order phase distortion ( $k''(\omega) = d^2k(\omega)/d\omega^2 = \varphi''(\omega)/L = d^2\varphi(\omega)/d\omega^2/L$ ) is defined as SOD, also known as group velocity dispersion (GVD). The third order term ( $k'''(\omega) = d^3k(\omega)/d\omega^3 = \varphi'''(\omega)/L = d^3\varphi(\omega)/d\omega^3/L$ ) is known as TOD. For carrier frequencies far from resonance and pulses longer than two optical cycles, GVD and TOD are sufficient to predict pulse broadening. In the presence of resonances or when a pulse is transmitted through or reflected from artificially constructed optics such as fibers or dielectric mirrors, higher order terms are required to account for abrupt changes in dispersion, within the bandwidth of the pulse regardless of pulse duration.

As mentioned earlier, a relation between different orders of dispersion has been explored in order to predict higher order terms, which until recently have been difficult to measure. This was illustrated theoretically in 1985 by Bor and Racz.<sup>1</sup> However deviations from that theoretical prediction have been noted when compared to values derived from the best available index of refraction data and its approximation by Sellmeier equations. Exploring dispersion in the frequency domain allows us to explain the parameters of the medium that affect the ratio between different orders of dispersion and gives us a general insight into dispersion.

For media with only one strong resonance with oscillator strength  $A$  and at frequency  $\omega_1$ , the refractive index may be expressed as

$$n(\omega) = \sqrt{1 + \frac{A}{1 - \omega^2/\omega_1^2}}, \quad (2)$$

this expression is similar to a single term Sellmeier equation. It is interesting to note that for frequencies far from optical absorption ( $\omega \ll \omega_1$ ),  $k''(\omega)$ , and  $k'''(\omega)$  obey the following relation<sup>8</sup> (see Supplementary Information Sec I for the derivation).

$$\omega \frac{k'''(\omega)}{k''(\omega)} = 1 + \frac{5\omega^2}{\omega_1^2} \left[ 1 + \frac{1}{3(1+A)} \right] \quad (3)$$

We see from equation (3) that  $\omega_1$ , plays an important role in determining the ratio between  $k''$  and  $k'''$ . For gases, with approximately three orders of magnitude lower density than liquids,  $A$  is negligible and can be ignored. Thus for gases:

$$\omega \frac{k'''(\omega)}{k''(\omega)} \approx 1 + \frac{20\omega^2}{3\omega_1^2}. \quad (4)$$

A gross approximation could be made by setting  $\omega_1 = \infty$ , based on the fact that typically  $\omega_1 \gg \omega$ . If one assumes the resonance frequency is much higher than the carrier frequency then one obtains the simplest expression given as Equation (5), however significant deviations occur even when Ti:Sapphire laser interacts with a transparent media with a resonance near 200 nm, as will be shown in the results section.

$$\omega \frac{k'''(\omega)}{k''(\omega)} = 1. \quad (5)$$

Here we explore the ratio between  $k''$  and  $k'''$  for various media commonly used in femtosecond time-resolved spectroscopy and relevant to the design of ultrafast laser applications. We evaluate the different approximations using experimentally determined values and provide a guideline to estimate GVD and TOD for all media studied here and even for media for which no dispersion information is available.

### III. EXPERIMENTAL

Measurements are performed using an ultrabroad bandwidth femtosecond Ti:Al<sub>2</sub>O<sub>3</sub> (Venteon) laser oscillator with specially designed chirped mirrors, having a spectrum spanning 630–1050 nm (see Fig. 2(a)), capable of producing sub-5 fs pulses.<sup>9</sup> For pulses centered at 800 nm, a two-cycle long pulse corresponds to a pulse duration of 5.3 fs Full Width at Half Maximum (FWHM). The pulse duration obtained with this laser oscillator was found to be as short as 4.3 fs FWHM, reported in our earlier publication.<sup>7</sup> The oscillator output is directed to a pulse shaper for phase measurement and elimination of high order dispersion using MIIPS.<sup>6,7</sup> The high resolution pulse shaper used for this work has all-reflective optics and a 640-pixel dual-mask spatial light modulator (640 DM SLM, CRi.). After the shaper, the pulses are focused onto a 20  $\mu$ m type-I KDP crystal, and the SHG signal is detected by a spectrometer (QE65000, Ocean Optics Incorporated). The resulting SHG spectrum after compensation for chromatic dispersion is shown in Fig. 2(b).

For the phase measurements, the medium is introduced between the pulse shaper and the SHG crystal (Fig. 2(c)). Note the beam was not focused on the sample; it had a diameter of 8mm and

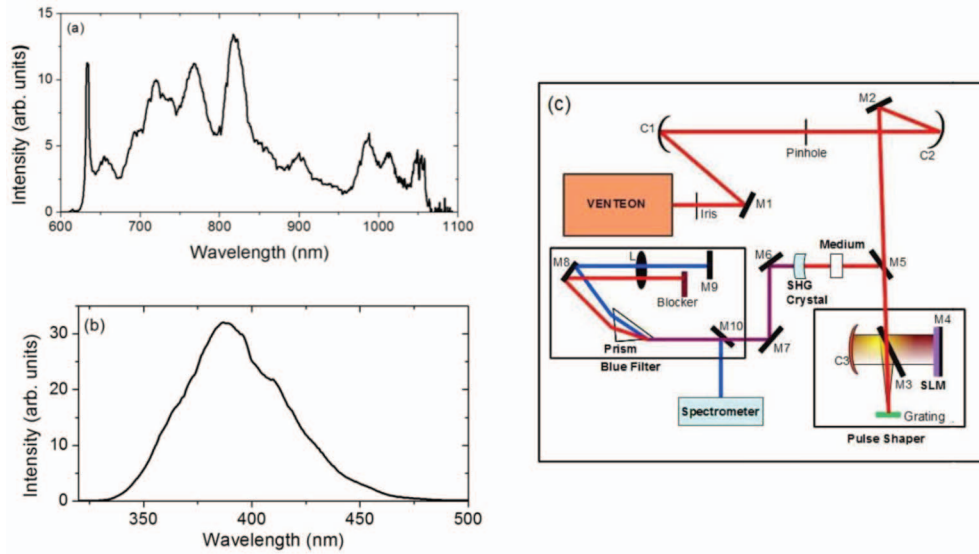


FIG. 2. (a) Spectrum of the ultrabroad-bandwidth femtosecond laser used for this work. (b) Experimental SHG spectrum after compensating the phase distortions with MIIPS. (c) Block diagram of the experimental set-up. M1-M10 are flat mirrors; C1 -C3 are curved mirrors. The rectangle with the prism is used to separate the resulting SHG.

average power of 40mW. The peak power density at the sample is estimated at  $10^5$  W/cm<sup>2</sup>, when transform limited. This is orders of magnitude below the power required for the beam to experience nonlinear optical phase distortions such as self-phase modulation or self-focusing. For measuring liquids, an empty quartz cuvette (to hold the medium) is introduced and measured to compensate the phase distortions caused by the empty cuvette. Phase distortions of the system are eliminated using MIIPS.<sup>6,7</sup> Briefly, MIIPS is a method that measures the phase of femtosecond pulses by introducing reference phases via a pulse shaper. When the reference phase introduced is linear chirp, corresponding to  $k''(\omega)=\text{constant}$ , changes in the second harmonic spectrum yield directly a measurement of  $\phi''(\omega)$ .<sup>10</sup> These measurements are self-referencing and have interferometric accuracy.<sup>7</sup> The MIIPS algorithm integrates the measured  $\phi''(\omega)$  to obtain the phase. More importantly it introduces a compensation phase  $-\phi(\omega)$ , which compensates the dispersion and determines how far the pulses are from the theoretical (Fourier transform of the laser pulse spectrum) limit. The algorithm iterates until the pulses are within 1% or better from the transform limit. Afterwards the desired medium is introduced, and its chromatic dispersion is measured using MIIPS. Given that chromatic dispersion varies linearly with the sample thickness, the second-order dispersion per unit length (mm)  $k''(\omega)$  is directly obtained.

#### IV. RESULT AND DISCUSSION

Dispersion measurements carried out for some of the most common solvents used in ultrafast laser research are presented in Fig. 3. The error bars for each liquid represent the standard deviation from six different experimental measurements, and give an estimate of the precision of our measurements. The error bars are shown only at selected wavelengths for clarity. Note the measurements are more precise within the 750-850 nm spectral region and the precision deteriorates below 700 nm and above 900 nm.

For each liquid, the experimental data (700 nm – 900 nm) is fitted to a polynomial in the frequency domain  $(\omega-\omega_0)$ , where  $\omega_0$  is taken to correspond to 800 nm. GVD ( $k''$ ) and TOD ( $k'''$ ) are extracted from the fitting coefficients. GVD measurements for seven common solvents at 23.3°C are listed in Table I. The TOD ( $k'''$ ) values at 800 nm for the same solvents are listed later in Table III. The GVD ( $k''$ ) and TOD ( $k'''$ ) values for water at 800 nm, reported in literature,<sup>5,11</sup> and derived from

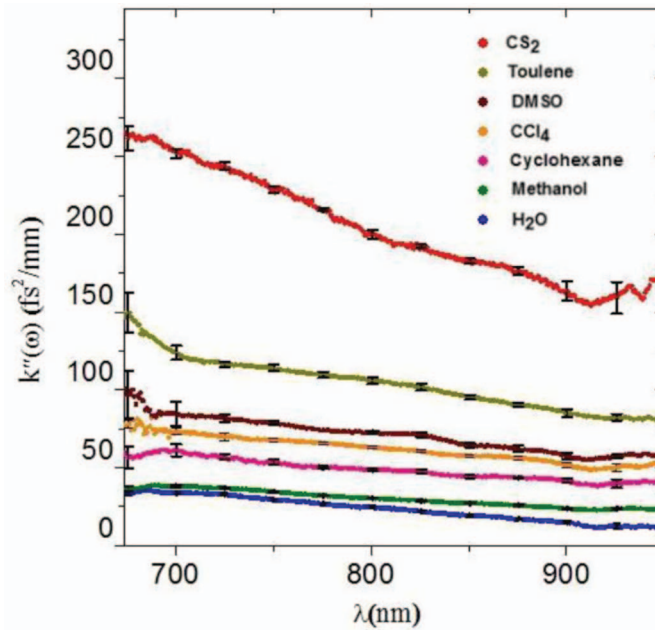


FIG. 3. GVD measurements for commonly used solvents obtained at 23.3°C. The error bars represents the standard deviation of six different experimental observations.

TABLE I. Experimental GVD ( $k''$ ) measurements of Water, Methanol, Cyclohexane,  $\text{CCl}_4$ , DMSO, Toluene and  $\text{CS}_2$  using MIIPS at 23.3°C.

Wavelength (nm)	Water ( $\text{fs}^2/\text{mm}$ )	Methanol ( $\text{fs}^2/\text{mm}$ )	Cyclohexane ( $\text{fs}^2/\text{mm}$ )	$\text{CCl}_4$ ( $\text{fs}^2/\text{mm}$ )	DMSO ( $\text{fs}^2/\text{mm}$ )	Toluene ( $\text{fs}^2/\text{mm}$ )	$\text{CS}_2$ ( $\text{fs}^2/\text{mm}$ )
700	$35.3 \pm 0.3$	$40.0 \pm 0.9$	$60 \pm 4$	$72.7 \pm 2.4$	$82.7 \pm 7.8$	$119.6 \pm 4.5$	$257.5 \pm 3$
725	$32.4 \pm 0.9$	$37.1 \pm 0.3$	$56.4 \pm 1.6$	$70.4 \pm 2.3$	$80.9 \pm 2.4$	$117.1 \pm 1.6$	$242.0 \pm 2.5$
750	$29.7 \pm 0.6$	$34.6 \pm 0.4$	$53.6 \pm 1.5$	$68.0 \pm 1.3$	$78.5 \pm 1.3$	$113.9 \pm 2.2$	$227.9 \pm 2$
775	$27.0 \pm 0.4$	$32.4 \pm 0.1$	$51.0 \pm 0.8$	$65.6 \pm 0.6$	$75.7 \pm 1.8$	$109.9 \pm 1.8$	$215.2 \pm 1$
800	$24.4 \pm 0.8$	$30.4 \pm 0.1$	$48.8 \pm 0.7$	$63.1 \pm 0.7$	$72.7 \pm 1.1$	$105.7 \pm 1.1$	$203.5 \pm 2.7$
825	$21.8 \pm 0.7$	$28.7 \pm 0.2$	$46.7 \pm 1.1$	$60.6 \pm 0.9$	$69.4 \pm 1.5$	$100.9 \pm 1.5$	$192.8 \pm 1.2$
850	$19.4 \pm 0.9$	$27.2 \pm 0.2$	$44.9 \pm 0.9$	$58.2 \pm 0.9$	$66.0 \pm 1.5$	$96.0 \pm 1.6$	$183.0 \pm 1.5$
875	$17.1 \pm 0.5$	$25.9 \pm 0.4$	$43.3 \pm 0.5$	$55.7 \pm 1$	$62.4 \pm 2$	$90.8 \pm 1.4$	$173.9 \pm 2.7$
900	$14.8 \pm 0.7$	$24.7 \pm 0.5$	$41.8 \pm 0.7$	$53.3 \pm 1.7$	$58.7 \pm 2.3$	$85.5 \pm 2.5$	$165.5 \pm 6.2$

Sellmeier's constants,<sup>12</sup> are in excellent agreement with our values (see Table II and Table III for comparison).

When  $k'''$  is plotted as a function of  $k''$ , all transparent media (solids, liquids, and gases) can be visualized within the framework of a single general model (see Theory). The values for  $k'''$  for different transparent optical media, including solids,<sup>6</sup> liquids and gases,<sup>13</sup> are plotted against the corresponding value for  $k''$  (see Fig. 4(a)). The red line shows the best fit line for all the media except (water and  $\text{CS}_2$ ). The black solid line corresponds to  $\omega_1 \rightarrow \infty$ . The slope of the best fit line is  $1.39 \pm 0.05$ . This experimentally observed ratio is useful in predicting TOD at any frequency based on a known GVD ( $\omega k''' \approx 1.4 k''$ ). The value for  $k'''$  calculated from its corresponding  $k''$  at 800 nm is listed in Table III.

The third derivative of the refractive index with respect to wavelength is plotted versus the second derivative of the refractive index with respect to wavelength for different optical media at 800 nm in Fig. 4(b). The red line shows best fit line of the experimental data. The black line represents theoretical prediction corresponding to  $\omega_1 \rightarrow \infty$ . We experimentally verify the linear relationship between different orders of refractive indices,<sup>1,14</sup> however, notice that the frequency

TABLE II. Comparison of experimentally observed  $k''$  and calculated  $k''$  from literature at 800nm.

Liquids	$k''$ , fs <sup>2</sup> /mm			
	a	b	c	d
Water	24.4 ± 0.8	24.76 ± 0.13 <sup>5</sup> 24.8 ± 0.5 <sup>11</sup>	24.9 <sup>12</sup>	47.9 <sup>12</sup>
Methanol	30.40 ± 0.1	33.56 ± 0.05 <sup>15</sup>	37.6 <sup>16</sup>	38.2 <sup>16</sup>
Cyclohexane	48.8 ± 0.7	-	51.8 <sup>16</sup>	50.2 <sup>16</sup>
CCl <sub>4</sub>	63.1 ± 0.7	-	-	-
DMSO	72.7 ± 1.1	-	75.8 <sup>16</sup>	76.5 <sup>16</sup>
Toluene	105.7 ± 1.1	-	107.9 <sup>17</sup>	106.9 <sup>17</sup>
CS <sub>2</sub>	203.5 ± 2.7	-	226.1 <sup>17</sup>	226.5 <sup>17</sup>

<sup>a</sup>Our Experiment

<sup>b</sup>Literature

<sup>c</sup>Derived from Sellmeier/Cauchy's equation

<sup>d</sup>Derived using known values of refractive indices at two different wavelengths (using optical properties). (See Supplementary Information<sup>8</sup> for actual values used for these calculations)

\*The superscript represents the reference.

TABLE III. Comparison of experimentally observed TOD ( $k'''$ ) with calculated from different models.

Liquids	$k'''$ , fs <sup>3</sup> /mm				
	a	b	c	d	E
Water	34.8 ± 0.2	34.2 <sup>5</sup> 27 ± 3 <sup>11</sup>	32.9 <sup>12</sup>	22.7 <sup>12</sup>	14.4
Methanol	24.8 ± 0.1	-	13.0 <sup>16</sup>	17.7 <sup>16</sup>	17.9
Cyclohexane	29.2 ± 0.3	-	29.4 <sup>16</sup>	23.3 <sup>16</sup>	28.8
CCl <sub>4</sub>	33.5 ± 0.2	-	-	-	37.3
DMSO	43.1 ± 0.4	-	37.8 <sup>16</sup>	36.7 <sup>16</sup>	42.9
Toluene	61.5 ± 0.2	-	58.6 <sup>17</sup>	53.2 <sup>17</sup>	62.4
CS <sub>2</sub>	151.9 ± 0.9	-	115.3 <sup>17</sup>	123.9 <sup>17</sup>	120.1

<sup>a</sup>Our Experiment

<sup>b</sup>Literature

<sup>c</sup>Derived from Sellmeier/Cauchy's equation

<sup>d</sup>Derived using known values of refractive indexes (using optical properties). (See supplementary information<sup>8</sup>)

<sup>e</sup>Derived from our experimental data (GVD).

\*The superscript represents the reference.

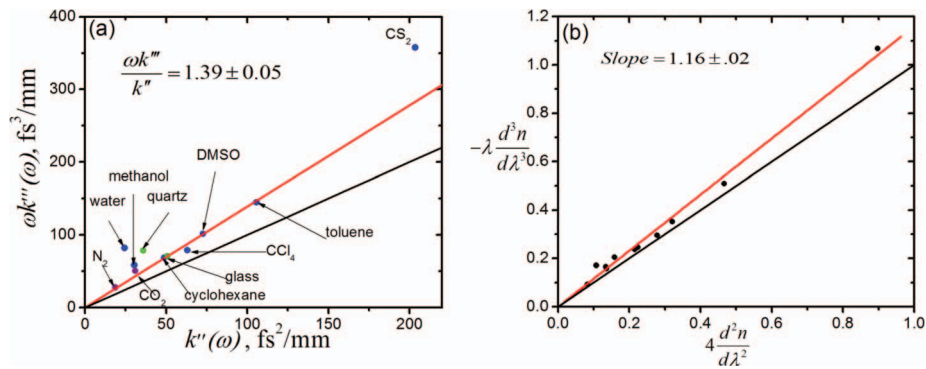


FIG. 4. (a) Third order dispersion vs. Second order dispersion of different optical media at 800nm. Dispersion for gases given per meter path length instead of per mm. Data for solid and gases (green and purple) are taken from literature.<sup>6,13</sup> The red solid line is the best fit of the experimental data. The black solid line corresponds to theoretical prediction when there is only one resonance at infinity frequency  $\omega_1 \rightarrow \infty$ , or  $\lambda_1 = 0$ . (b) The same data as (a) but presented as dependence of index of refraction in wavelength domain. The red line is the best fit, note that this plot is much less sensitive to differences between optical media and less deviates from a line with slope 1, see Supplementary Information.<sup>8</sup>



domain comparison given in Fig. 4(a) is much more sensitive than the derivatives of the index of refraction as shown in Fig. 4(b).

As mentioned earlier, it is common practice to derive  $k''$  from Sellmeier equations. We have compared our measured  $k''$  with that calculated from Sellmeier's equation/Cauchy's equation (Table II). Because the values or interest depend on second and third order derivatives, even the Sellmeier or Cauchy equations obtained using the best experimental refractive index measurements yield inaccurate second and especially third order dispersion. Using the values of the refractive indices of the medium at two different wavelengths, however, one can find the parameters  $A$  and  $\omega_1$  in Equation (2), and obtain  $n(\omega)$ . We have generated  $k''$  and  $k'''$  for each medium, using refractive indices at only two wavelengths from literature and listed them in Table II and Table III respectively. See supplementary information<sup>8</sup> Sec II for exact values used. With this approach,  $k''$  of Toluene is predicted within 1% of our experimental measurement. Table II clearly shows that given the optical properties of the medium  $A$ ,  $\omega_1$  (or refractive index at two different wavelengths),  $k''$  can be predicted with an error less than 6% for most of the media. Note that for water, methanol and CS<sub>2</sub> the deviation is greater due to known vibrational resonances in the near infrared.

TOD measurements are more difficult to perform than GVD measurements, and only few TOD measurements are reported in the literature. Our reported  $k'''$  value ( $34.8 \pm 0.2$  fs<sup>3</sup>/mm) for water, has good agreement with the literature ( $34.2$  fs<sup>3</sup>/mm<sup>5</sup> and  $27 \pm 3$  fs<sup>3</sup>/mm).<sup>11</sup> We have compared our experimentally observed  $k'''$  with  $k'''$  calculated from different models (see Table III). We used  $k''$  (from our experimental data, column (a)) to calculate  $k'''$  (column(e)) using  $\omega k''' = 1.4 k''$ . Using the refractive index at two wavelengths from the literature,<sup>16,17</sup>  $k'''$  obtained for Toluene and DMSO is within 14% and 15% respectively of the experimentally determined values. From Table III, we can clearly see that we can predict TOD with an error less than 20% for most media (except water and methanol) using their optical properties.

The proposed predictive approach based on Equation (2) (single UV resonance) is not very accurate in spectral regions that are close to optical absorption of the medium of interest. However, in the wavelength range of this study (700 nm-900nm), one can apply Equation (2) successfully provided the medium has a single absorption in the UV. In our experimental observations we see that values for water, methanol, CS<sub>2</sub>, and quartz deviate from the single UV resonance approximation. The absorption of water,<sup>18</sup> methanol<sup>19,20</sup> and CS<sub>2</sub><sup>21</sup> in the near IR explains the reason why the approximation of a single resonance fails. The OH content of quartz and the absorption of OH in the near IR<sup>22</sup> causes the deviation from the predicted value observed for quartz.

According to theory (Eq. (3)), the ratio of  $k''$  and  $k'''$  is constant. For most media, we have found  $A$  is  $1.2 \pm 0.3$  and based on a single resonance model, the optical absorption  $\omega_1$  is 100-200 nm (see supplementary information<sup>8</sup> Sec II). Typical values for  $A$  and  $\omega_1$  make the ratio almost independent of the media as clearly observed in Fig 4. The experimentally observed ratio ( $1.39 \pm 0.05$  at 800nm) is very useful since it can predict  $k'''$  only from  $k''$ . Once  $k''$  is obtained at a particular wavelength, the  $k''$  for a range of wavelengths can be calculated using,  $k'' = k''_0 + k'''_0(\omega - \omega_0)$ . For example, given  $k''_0$  at 800nm,  $k'''_0$  (at 800nm) can be predicted using the experimentally determined slope. Using these  $k''_0$  and  $k'''_0$  values, GVD values at other wavelengths (say 700 nm or 900nm) can also be calculated.

For transparent media, where  $k''' \approx 3/2 \times k''/\omega_0$ , one can estimate phase distortion far from resonance for a pulse with width  $\Delta\omega$  using a Taylor expansion up to third term

$$\Delta\phi \cong \frac{L}{2} k'' \Delta\omega^2 + \frac{L}{6} k''' \Delta\omega^3 \cong \frac{L}{2} k'' \Delta\omega^2 \left( 1 + \frac{1.5}{3} \frac{\Delta\omega}{\omega_0} \right) = \Delta\phi^{(2)} \left( 1 + \frac{\Delta\omega}{2\omega_0} \right) \quad (6)$$

If phase distortion from the SOD is  $\Delta\phi^{(2)}$  then contribution from TOD will be  $\Delta\phi^{(2)} \times \Delta\omega/2\omega_0$ . Of course this estimation is valid for media for which TOD is proportional to SOD. For water and CS<sub>2</sub> the ratio is larger than 1.4 and the effects are even larger, therefore the magnitude of  $\Delta\omega/\omega_0$  is very important.

To highlight the effect of higher order dispersion on pulse properties, we calculated the contribution of each term on pulse broadening ( $\tau/\tau_{TL}$ , where  $\tau_{TL}$  is pulse duration of the transform limited (TL) or shortest pulse supported by the available spectral bandwidth) and second harmonic spectral narrowing ( $\Delta 2\omega/\Delta 2\omega_{TL}$ , where  $\Delta 2\omega_{TL}$  is spectral width of the second harmonic generated by a TL pulse). These results are shown in Table IV. The calculations assume Gaussian pulses with

TABLE IV. Calculated Pulse Broadening ( $\tau/\tau_{TL}$ ) and Second Harmonic Spectral Narrowing ( $\Delta 2\omega/\Delta 2\omega_{TL}$ ) for ultrashort pulses with  $\Delta\omega/\omega_0=1/4$ 

	Toluene, 1cm		Water, 1 cm		Quartz, 1 cm		Air, 10 m	
	$\tau$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$	$\tau$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$	$\tau$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$	$\tau$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$
$\frac{\Delta\omega}{\omega_0} = 1/4$	$\frac{\tau}{\tau_{TL}}$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$	$\frac{\tau}{\tau_{TL}}$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$	$\frac{\tau}{\tau_{TL}}$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$	$\frac{\tau}{\tau_{TL}}$	$\frac{\Delta 2\omega}{\Delta 2\omega_{TL}}$
$k''$	133.1	1	30.6	1	45.2	1	24.9	1
$k'''$	2.4	0.11	2.0	0.19	2.0	0.19	1.5	0.46

$\Delta\omega/\omega_0=1/4$ , the carrier frequency  $\omega_0$  corresponds to 800 nm, and the pulse duration 4.7 fs. Values for  $k''$  and  $k'''$  are taken from experimental results reported in Tables II and III and from reference 6 and 13 (for quartz and air respectively). We have chosen a path-length of 10m for air and 1 cm for the rest of the optical media. The simulation results indicate a 30-130 times temporal broadening with the introduction of second order dispersion ( $k''$ ) and about 2 times temporal broadening originated from the third order dispersion ( $k'''$ ) for the dense media. Ten meter propagation in air causes a 25 times lengthening of the pulse. Odd order dispersion terms do not make the pulse significantly longer, but cause significant SHG spectral narrowing, while even order dispersion terms cause no spectral narrowing of second harmonic generation. We evaluated the changes that would be expected for fourth and fifth order dispersion. However, given the uncertainty in their estimated magnitude and their relatively small contribution we decided not to include them.

## V. CONCLUSION

In this work, we have studied high-order dispersion introduced by solvents commonly used in ultrafast laser spectroscopy. These measurements are particularly relevant given that ultrashort laser sources with spectra approaching an octave are now commercially available. The values of second and third order dispersions for water at 800 nm, reported in<sup>5,11</sup> and derived from phenomenological equations,<sup>12</sup> are in excellent agreement with our values (see Table II and Table III). For all transparent media without optical resonances close to the measured spectral region, the slope between  $\omega k'''$  and  $k''$  is found to be approximately equal to 1.4, a ratio independent of media. This experimentally found ratio should be useful in estimation of third order dispersion ( $k'''$ ) based on a known second order dispersion ( $k''$ ). We have related the slope between  $k'''$  and  $k''$  to optical properties of the media, specifically the oscillator strength and optical resonance. Given the difficulty of measuring high-order dispersion with high accuracy and precision, a general framework to estimate dispersion for all transparent optical media (solids, liquids, gases) is proposed. Based on values for the index of refraction of a medium at two wavelengths, we predicted all orders of optical dispersion values that are close to those found experimentally. The proposed methods for estimating high-order dispersion are recommended for transparent natural media. The simulation indicated that a large temporal broadening and narrowing of nonlinear spectra originated from nonlinear dispersions of the octave pulses in the common optical media. The values reported here, and the method proposed for estimating high-order dispersion for other optical media should be of importance for numerous applications of ultrashort pulses in scientific research, as well as in medicine and industry. We remark that for artificial media, such as dielectric coatings, fibers and other photonic constructs, dispersion can vary sharply as a function of frequency. In those cases, only direct measurements approaches can determine the phase introduced by the medium.<sup>23</sup>

## ACKNOWLEDGMENTS

This project has been funded by Chemical Research Instrumentation and Facilities- Instrument Development grant from the National Science Foundation CRIF:ID NSF 0923957 provided by funds from the American Recovery and Reinvestment Act of 2009. We want to thank Dmitry Pestov from BioPhotonic Solutions Inc. for initial help in experimental set up and useful suggestions. The



authors would also like to thank Daniel Parker and Andrea Dantus for their help in proof reading this manuscript.

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