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Measurements of the GVD of water and methanol and laser pulse characterization using direct imaging methods

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Abstract. We report experimental values of the group velocity dispersion (GVD) of water and methanol at 800 nm. We find $GVD_{800}^{water} = (25.71 \pm 0.5)\,fs^2\,mm^{-1}$ and $GVD_{800}^{methanol} = (33.56 \pm 0.5)\,fs^2\,mm^{-1}$. These were measured by sending 50 fs, 800 nm pulses with various amounts of chirp through a glass cell filled with a solution of fluorescein in these solvents and recording the production of visible light from the side using a commercial digital camera. This simple setup also gives quantitative information on the duration of our pulses and lets us check independently the correct operation of our grating-based pulse compressor. Results are compared to FROG measurements.

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1. Introduction

The broad bandwidth of femtosecond pulses makes them very sensitive to the dispersive qualities of the media through which they propagate. The increasingly broad range of applications for femtosecond laser systems has magnified the need for measuring the dispersive qualities of a wide variety of media. In particular, the group velocity dispersion (GVD) of a medium, which causes a pulse to stretch or compress in time, is of great importance.

The ability to control the pulse duration of an optical system while propagating through a medium has significance in a broad range of applications. Femtosecond lasers are used in LASIK techniques and ocular surgeries to treat corneal damage and retinal lesions. Knowledge of the GVD of the components of the eye can allow the surgeon to achieve the shortest pulse duration directly at the target. As a result, less power is needed, reducing the risk of damage to surrounding tissue. Because of the range of applications of ultrashort pulses to surgeries in the eye, [1] measured experimentally the GVD of water, seawater and ocular components in 2007. The GVD of some transparent solvents are also of interest for a variety of reasons. Liquids such as water, methanol and ethanol are often used as a solvent in organic dye laser systems. Knowledge of the GVD of such liquids could be very useful in aligning and optimizing such laser systems.

While the knowledge of the ability to stretch and compress ultrashort laser pulses is important, so is the ability to quantitatively measure the temporal profile of such a pulse. The frequency-resolved optical gating (FROG) technique [2] allows very precise measurement of both spatial and temporal aspects of ultrashort pulses. Such technology is commercially available; however, it is quite expensive. Alternative methods to measure the phase and/or spatio-temporal profile [3]–[5] of a femtosecond laser pulse have shown some success.

Current methods to measure the GVD such as the method in [1] can be very complicated, requiring the use of a pulse shaper, second-harmonic generation crystal and a feedback loop. We present a method that allows us to very directly measure the GVD of transparent liquids using only our existing laser system, a glass cell filled with the desired liquid and a commercial digital camera. This is achieved by dissolving a small amount of a dye into the solution and using the known dispersive qualities of our grating-based pulse compressor to send in pulses with different amounts of temporal dispersion. The visible signal from the dye is then measured, and allows

us to measure the GVD of the solvent. Additionally, we obtain temporal information about our laser pulses.

2. Theory

2.1. The mathematics of linear dispersion

The (linear) dispersion of an optical medium has two well-known effects on short pulses. Firstly, the group velocity is different from the phase velocity. Secondly, depending on the initial conditions and the medium, incoming pulses may get compressed or stretched in time. All these phenomena are described by the dispersion function $k(\omega)$, in which k is the wavenumber and ω the angular frequency. The second derivative $k_0'' = (\partial^2 k / \partial \omega^2)_{\omega=\omega_0}$ governs pulse stretching/compression (ω_0 is the carrier frequency). Such stretching/compression is the result of a change in the chirp of the pulse.

To mathematically study pulse stretching/compression in dispersive media in detail, we will make use of Gaussian electric field pulses (with chirp) given by

$$\mathcal{E}(t) = \sqrt[4]{\frac{2a}{\pi}} \exp(-\Gamma t^2 - \mathrm{i}\omega_0 t) \text{ with } \Gamma = a + \mathrm{i}b. \tag{1}$$

The complex-valued parameter Γ is called the *complex beam parameter* [6]. The parameter $a = \mathrm{Re}[\Gamma]$ determines the pulse duration[2] of the intensity profile

$$\Delta t = \sqrt{\frac{2 \ln 2}{a}}. \tag{2}$$

The parameter $b = \mathrm{Im}[\Gamma]$ determines the rate of change of its instantaneous frequency, known as the chirp of the pulse. The instantaneous phase is given by $\phi(t) = bt^2 + \omega_0 t$, so that the instantaneous frequency is $\omega(t) = \mathrm{d}\phi(t)/\mathrm{d}t = \omega_0 + 2bt$. When b vanishes, there is no chirp; the pulse then has a constant carrier frequency. When $b > 0$, the instantaneous frequency increases over time, and we say there is positive chirp. When $b < 0$, the instantaneous frequency decreases over time, which is called negative chirp [7].

In our experimental setup, we have two components that change the complex beam parameter Γ: the pulse compressor in our Ti : sapphire laser amplifier and a glass cell capped with calcium fluoride windows and filled with transparent liquid, such as water or methanol. The compressor is the final component in our amplifier's chirped pulse amplification scheme, and is designed as a double-folded version of the scheme in [8]. Its job is to compress incoming amplified (but still stretched) pulses to strong and ultrashort pulses by modifying the complex beam parameter. Writing $\Gamma_0 = a_0 + \mathrm{i}b_0$ for the complex beam parameter of the stretched pulses entering the compressor, and $\Gamma_{\mathrm{out}} = a_{\mathrm{out}} + \mathrm{i}b_{\mathrm{out}}$ for the beam parameter of pulses leaving it, we have

$$\frac{1}{\Gamma_{\mathrm{out}}(u)} = \frac{1}{\Gamma_0} + 2\mathrm{i}Gu, \tag{3}$$

in which G is a negative constant (unit $\mathrm{s}^2\,\mathrm{m}^{-1}$) fixed by the geometry of the compressor that serves as an effective GVD, and u an adjustable distance between two elements in the

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[2] All widths and durations are full-width at half-maximum (FWHM), unless noted otherwise.

compressor. It can be shown that the pulse with no chirp ($u = u_{\text{opt}}$) is also the shortest pulse, with the pulse duration given by

$$\Delta t(u) = \Delta t_{\text{opt}} \sqrt{1 + 4a_{\text{opt}}^2 G^2 (u - u_{\text{opt}})^2}, \tag{4}$$

where we define $\Delta t_{\text{opt}} = \Delta t(u_{\text{opt}}) = \sqrt{2 \ln 2 / a_{\text{opt}}}$ and $a_{\text{opt}} = \frac{a_0^2 + b_0^2}{a_0}$.

In our experiments, we send the pulses coming out of the compressor through a cell containing a transparent liquid (water or methanol). The atmospheric air path (length ℓ), the calcium fluoride entrance window of the cell (thickness of window $= d$), and the liquid inside the cell all modify the pulse. In the liquid, at a distance z away from the inner face of the entrance window, the complex beam parameter $\Gamma(u, z)$ is determined by

$$\frac{1}{\Gamma(u, z)} = \frac{1}{\Gamma_0} + 2iGu + 2iK_{\text{air}}\ell + 2iK_{\text{CaF}_2}d + 2iKz, \tag{5}$$

in which K_{air}, K_{CaF_2}, and K are the GVD of air, the window CaF_2 and the liquid, respectively, for the carrier frequency ω_0 of the pulse. In our experiments, all of these three GVD values are positive. The constant air and quartz terms can be dealt with by redefining u_{opt} as

$$u_{\text{opt}} = \frac{1}{2G} \left(\frac{b_0}{a_0^2 + b_0^2} + 2K_{\text{air}}\ell + 2K_{\text{CaF}_2}d \right), \tag{6}$$

this new u_{opt} is the setting of the compressor that produces prechirped pulses such that they are transform-limited at the location where they enter the liquid. If we adjust the compressor such that $u > u_{\text{opt}}$ pulses with a negative chirp enter the liquid, which will start to compress them. The length of liquid needed to obtain a transform-limited pulse is

$$z = z_{\text{opt}}(u) \equiv \frac{(-G)(u - u_{\text{opt}})}{K}. \tag{7}$$

If $u < u_{\text{opt}}$, then $b(u) > 0$, so pulses enter the liquid with positive chirp. The liquid will then only further stretch such pulses, and there is no location in the liquid for which the pulse is transform-limited. In general, for a given fixed u, the GVD of the liquid changes the temporal profile of the pulse such that

$$\Delta t(z) = \Delta t_{\text{opt}} \sqrt{1 + 16(\ln 2)^2 K^2 (z - z_{\text{opt}})^2 / \Delta t_{\text{opt}}^4} \tag{8}$$

is the pulse duration at a given position inside the liquid.

2.2. Visualizing the position-dependent pulse duration using a dye

If we assume that no energy is lost during the dispersive processes described here, the peak intensity of the pulse must be proportional to the inverse pulse duration:

$$I_{\text{peak}}(z) = \frac{I_{\text{peak}}(z_{\text{opt}})}{\sqrt{1 + 16(\ln 2)^2 K^2 (z - z_{\text{opt}})^2 / \Delta t_{\text{opt}}^4}}. \tag{9}$$

In our experiments, we measure the intensity distribution (equivalently, the pulse duration) by dissolving a dye into the liquid under investigation. The dye fluoresces in the visible after two-photon absorption of light from the laser beam. We assume for now that the dye concentration is so small that we can ignore absorption loss in the laser beam. The light pulses from the laser

propagate inside the liquid with the group velocity v_g, while their duration and chirp constantly change.

From the known cross sections for two-photon excitation of our dye molecules [9], we conclude that the total production of fluorescence light at any position inside the liquid is proportional to the local time-integrated intensity-squared. This visible signal $S(z)$ (ignoring proportionality factors) is thus given by

$$S(z) \propto \int\limits_{-\infty}^{\infty} I^2(t,z)\,\mathrm{d}t = I_{\mathrm{peak}}^2(z)\sqrt{\frac{\pi}{4}}\frac{\Delta t(z)}{\sqrt{2\ln 2}} \propto \frac{1}{\Delta t(z)}. \tag{10}$$

Thus, by recording the visible fluorescence light produced in the cell when ultrashort pulses propagate through the liquid inside it, we can visualize and study the dispersion (stretching/compression) of these light pulses. Doing so, we measure two quantities: the GVD of the liquid, and the transform-limited pulse duration of our pulses. The GVD of the liquid is found by studying the change in the position of z_{opt} (the location at which $S(z)$ is largest) as a function of the setting u of the compressor: from equation (7) we see that $\mathrm{d}z_{\mathrm{opt}}(u)/\mathrm{d}u = -G/K$, so that knowing G we can determine K experimentally. Once this quantity is known, we can use the relation

$$\Delta z_{1/2} = \frac{\sqrt{3}}{2\ln 2}\frac{\Delta t_{\mathrm{opt}}^2}{K}, \tag{11}$$

in which $\Delta z_{1/2}$ is the width of the visible signal in the cell to determine the transform-limited pulse duration simply by measuring the width of $S(z)$.

3. Experimental setup

In our experiments, we sent 800 nm laser pulses from a Ti : sapphire Spitfire laser system through a liquid contained in a glass cell. The laser system had a 1 kHz repetition rate, and the pulse duration ranged from 50 to 600 fs, depending on the amount of initial chirp. Two glass cells were used: a Hellma 120 QS cylindrical cell with a 100 mm internal light path, and a Technical Glass Products ST14 rectangular cell (14 mm by 14 mm cross section) with a 305 mm internal light path. Through the redefinition of u_{opt} used in equation (6), the transmission windows and external path length become arbitrary.

To record the visible signal from the dye solution, we used a commercial digital camera, Canon EOS 20D, equipped with a Canon EF-S 18-55/3/5-5.6 objective mounted about 65 cm away from the cell, as seen in figure 1. To ensure the absence of nonlinear effects in the solution, the average beam power was attenuated to $\sim$20 mW so that the visible signal was very small. To compensate for this small signal, a two-second shutter time was used for each image.

To measure fluorescent light intensities, we took pictures in Canon's native CR2 'raw' format, so that unprocessed values as recorded by the pixel sensors are stored without loss in a file. To access these recorded individual pixel values we decrypted the *.CR2 files (unfortunately CR2 is an encrypted format) using the freely-available, open source converter 'dcraw', which we adapted slightly for our purposes. After decryption of the raw data we used the G channel of the RGB color image for image analysis since fluorescein fluoresces at 521 nm. The results of this image analysis can be seen in figure 2.
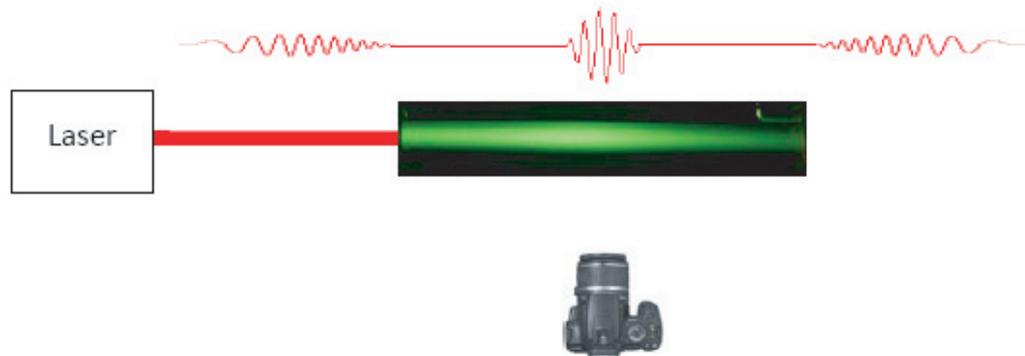
Figure 1. Diagram of experimental setup. 800 nm femtosecond laser radiation was emitted from a Spitfire system and propagated through a glass cell filled with a solution of fluorescein in the desired solvent. The intensity-dependent visible signal produced by the fluorescein dye was recorded by a commercial Canon EOS 20D digital camera for image processing.
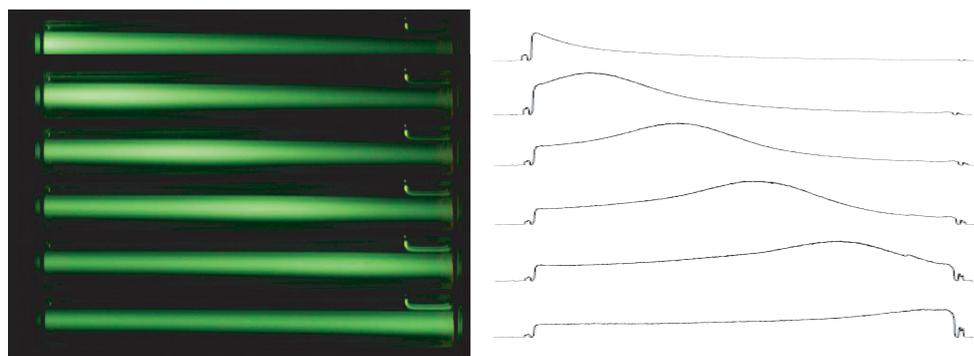

Figure 2. Pictures of 305 mm cell with solution of fluorescein in methanol (left) and integrated visible signals (right). Images show (from top to bottom) increasing amounts of negative chirp in the incoming pulse, such that it takes a greater amount of liquid to compress the pulse.

4. Experimental results and discussion

Before conducting the experiments, studies were conducted to ensure that absorption effects (namely, the loss of power through fluorescence in the liquid) would not skew the experimental results. It was found that, for solutions less than 0.01 M for water or methanol, these effects could be neglected. All data shown were taken with solutions less than 0.002 M.

4.1. Measuring the GVD of water and methanol

As seen in equation (7), plotting the position of maximum intensity in the cell z_{opt} against the position of the compressor's reflector u will result in a line with slope $-G/K$, where G is the effective GVD of the compressor, and is known through a geometrical analysis. So by the slope of the function $z_{opt}(u)$ we can directly measure the GVD of the liquid.
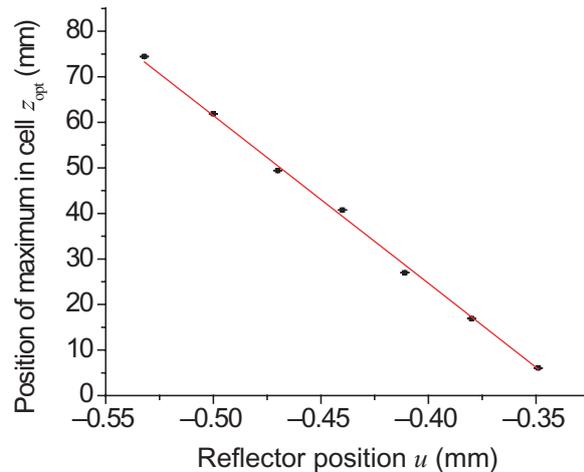
Figure 3. Plot of the position of maximum intensity inside a 0.002 M solution of fluorescein in water as a function of the position of the compressor's retroreflector mirror.

To test the method, we used a 0.002 M solution of water in a 100 mm cylindrical cell. Inserting our known value of G, we find

$$\mathrm{GVD}_{800}^{\mathrm{water}} = (25.71 \pm 0.5)\,\mathrm{fs}^2\,\mathrm{mm}^{-1}\,(\text{experimental from figure 3}),$$

where the experimental error is almost entirely contained within the precise measurement of angles in the geometry of the compressor. In principle, this could be measured to much higher accuracy.

Recently Cuello *et al* [1] measured experimentally the GVD of water using a multiphoton intrapulse interference phase scan. Additionally, Huibers [10] reviews a large number of publications on the index of refraction of water, and concludes that the curves in [11, 12] are the most accurate models. Assuming a temperature of 25 °C, we find the following predicted values for the GVD of water at 800 nm:

$$\mathrm{GVD}_{800}^{\mathrm{water}} = (24.76 \pm 0.13)\,\mathrm{fs}^2\,\mathrm{mm}^{-1}\,(\text{experimental from [1]}),$$

$$\mathrm{GVD}_{800}^{\mathrm{water}} = 35.66\,\mathrm{fs}^2\,\mathrm{mm}^{-1}\,(\text{derived by us from curve in [11]}),$$

$$\mathrm{GVD}_{800}^{\mathrm{water}} = 24.27\,\mathrm{fs}^2\,\mathrm{mm}^{-1}\,(\text{derived by us from curve in [12]}).$$

The curve presented in [12] is also recommended by the International Association for the Properties of water and steam in their most recent release on the refractive index of water [13]. Because our result matches closely with both [1] and [12], we conclude that our method does provide an accurate representation of the GVD.

To find the GVD of methanol, the same method was used with some slight changes. To allow more accurate measurement, a 305 mm cell was used so that 25 data points could be measured (as opposed to 7 for the water solution). The cell was filled with a 0.0013 M solution.

This results in an experimental value of

$$\mathrm{GVD}_{800}^{\mathrm{methanol}} = (33.56 \pm 0.5)\,\mathrm{fs}^2\,\mathrm{mm}^{-1}\,(\text{experimental from figure 4}),$$

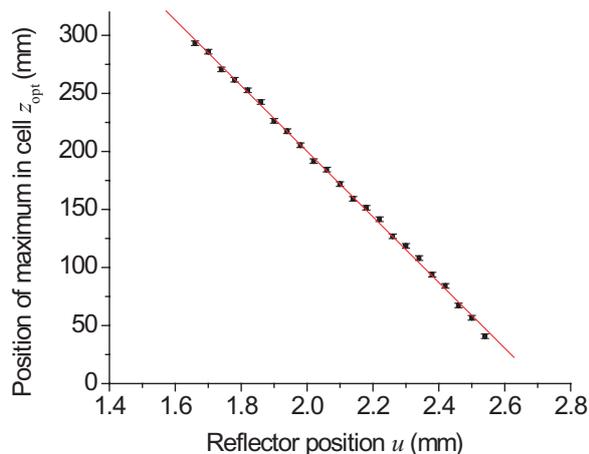**IOP** Institute of Physics Φ DEUTSCHE PHYSIKALISCHE GESELLSCHAFT

Figure 4. Plot of the position of maximum intensity in a 0.0013 M solution of fluorescein in methanol as a function of the position of the compressor's retroreflector mirror.

where the experimental error is again dominated by the measurement of angles in the compressor.

Refractive index curves for methanol are found in [14, 15]; however, because these curves are the result of extrapolations from only a few data points in the visible and UV, they do not even agree on the value of n at 800 nm. As correctly noted in [15], the 'extrapolation of refractive-index data outside the measured wavelength range with a dispersion formula can lead to serious errors—a well-known, however, in practice, often ignored fact'. Not surprisingly, the values of the GVD at 800 nm derived from the two curves also differ substantially:

$$GVD_{800}^{methanol} = 52.77 \, fs^2 \, mm^{-1} \, (derived \, by \, us \, from \, curve \, in \, [14]),$$

$$GVD_{800}^{methanol} = 38.79 \, fs^2 \, mm^{-1} \, (derived \, by \, us \, from \, curve \, in \, [15]).$$

Given that our GVD value of water agreed well with previous results (both theoretical and experimental), we are confident that our value of the GVD of methanol is accurate in spite of its disagreement with the theoretical predictions since these are, as mentioned above, unreliable.

4.2. Temporal pulse characterization

In addition to giving information about the dispersive qualities of the solvent, this method can be used to quantitatively characterize the laser pulse. Once a value for the GVD of the solvent has been measured, the transform-limited pulse duration is easily calculated based on the spatial width of the visible signal from equation (11). Further, equations (4) or (8) can be used to determine the pulse duration at any setting of the compressor or position within the liquid cell, respectively. This is a broader adaptation of the method in [5] used to determine the transform-limited pulse duration.

Figure 5 shows the pulse duration as determined from the visible signal overlaid with FROG (Newport UPM-8-20) measurements. The visible signal was measured in a 305 mm cell and converted to a pulse duration using equation (11) to find Δt_{opt}. Equation (8) was then used
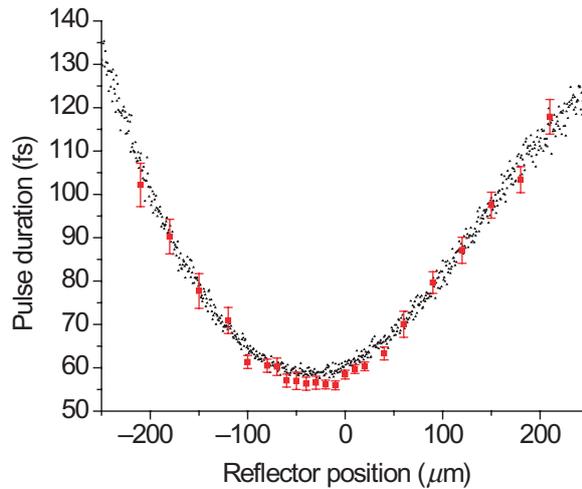
Figure 5. Plot of pulse duration extrapolated from the visible signal (black) as a function of the position of the compressor's retroreflector mirror as determined by equation (8) overlaid with actual FROG data (red) taken at actual positions of the retroreflector.

to convert the signal into a pulse duration, and equation (7) was used to map the pulse duration onto the same axis as the FROG data.

This gives an independent check on the operation of the compressor while giving quantitative information about the pulse duration at each position. Additionally, this method can be used to identify small misalignments in the laser system. The noticeable asymmetry in the data in figure 5 is consistent with a cubic phase term in the pulse [2]. In principle, any misalignment that affects the temporal profile of the pulse as it propagates could be identified through this method.

5. Conclusion

We have introduced a simple and inexpensive method to accurately measure the GVD of transparent solvents, and we report experimental values for methanol and water. In addition, the same method is used to quantitatively characterize the temporal distribution of our laser pulses. We extract temporal information on the pulses output by our grating-based pulse compressor, and find it in excellent agreement with FROG measurements. This study also provides an independent check of our compressor.

Acknowledgments

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