Coherent multidimensional spectroscopy is an analogue of two-dimensional (2D) NMR and is a powerful technique to resolve couplings between different chromophores [1–2]. Optical 2D spectroscopy evolved over years from using limited wavelength ranges accessible using stable oscillators [3] and infrared sources [4,5], into the visible regime using optical parametric amplifiers (OPA) [7,8], and more recently, the ultraviolet (UV) [9–11]. These experiments had in common the use of noncollinear OPA (NOPA) systems to generate the excitation pulses that are limited in bandwidth to several tens of nanometers. Studying complex systems requires addressing several electronic states simultaneously, and this often requires large spectral bandwidth spanning tens to hundreds of nanometers not accessible by NOPAs. The recent advancement of light sources generating continua in inert gases [12,13] allows for the realization of ultra-broadband 2D setups [14]. Here we present a compact passively phase-stabilized ultra-broadband 2D setup using only conventional optics in a boxcar geometry that can perform measurements using near Fourier-limit ultra-broadband pulses in the visible range as well as in the UV with minimal modifications.

A cryogenically cooled TiAlO3 regenerative amplifier tunable from 3 to 15 kHz provides 800-nm, sub-50-fs pulses of 1–3 mJ. The laser output is used to pump a 1.1-m long 260-μm diameter hollow core fiber (Imperial Consultants) filled with 3 bars differential pressure of argon. A pressure gradient along the fiber is produced by pumping the fiber entrance with a scroll pump, achieving a base pressure of ~5E-1 mbar while at the fiber exit 3 bar of argon is applied. This pressure gradient allows the decreasing intensity profile along the fiber to be matched with and increase gas pressure, thus allowing a higher transmission before plasma formation in the gas produces instabilities in the output.

Part of the laser output (~0.5 mJ) is coupled into the fiber using a 75-cm concave mirror, causing self-phase modulation and spectral broadening due to high intensity coupling through a confined mode. By tuning the coupled intensity, pressure, and the pulse duration, the generated continuum can span from 420 to 900 nm (Fig. 1), while pumping the fiber with the second harmonic of the laser gives us access to the 360–450-nm spectral range [15]. The advantages of the hollow core fiber, compared to conventionally used NOPA, resides in a flatter spectrum over a large spectral range, a TEM00 spatial mode, and high output intensity simplifying the use of pulse shapers. In comparison to the light continuum generated by filamentation in a gas cell, the output of the hollow-core fiber has higher inherent pointing stability and is spectrally smoother output [12,13,16]. Furthermore, the ability to differentially pump hollow core fibers increases transmission for a set broadening as compared to a filament.

A home-built deformable mirror (DM) based pulse shaper is used to compress the output of the fiber to near Fourier-limit pulses using the geometry (Fig. 2(b)) proposed by Vdovin et al. [17]. A 3.3-cm-long DM (OKO tech) is positioned in the Fourier plane of a folded 4f zero dispersion stretcher. The stretcher consists of a 300 grooves/mm grating blazed for 550 nm and a 27 cm focal length. The stretcher, comprising a 3.3-cm-long DM (OKO tech) is positioned in the Fourier plane of a folded 4f zero dispersion stretcher. The stretcher consists of a 300 grooves/mm grating blazed for 550 nm and a 27 cm focal length.

Fig. 1. Accessible spectrum of the hollow core fiber pumped 0.5 mJ, 55-fs pulses centered at 790 nm. (b) shows a TG-FROG autocorrelation trace of the selected spectrum from 480 to 685 nm with a flat spectral phase.
length mirror allowing to fill the whole DM surface with a spectral range of about 300 nm visible light. After spectral recombination, the beam is sent downward toward the optical table into BS1 splitting it into two identical parts (beam 1/2 and 3/4) as shown in Fig. 2(a). A delay stage DS1 is used to move BS1 and M1 at 45° angle (along the vector direction in Fig. 2) with respect to the incoming beam creating a path difference between the beam pairs B1 and B2. Another set of metallic BSs (BS2) are used to split B1 and B2 into 4 identical beams, such that we can use the first three as excitation pulses (red) and the fourth as a local oscillator (black) as shown in Fig. 2(c). Mirrors M4 and M6 are mounted on DS2 moving at 45° angle creating the time difference between the pulse pairs 1/2 and 3/4. Glass plates of the same thickness as the BSs are added in the path of the beams reflected off the BS to compensate for the delay due to its substrate, and more importantly for the dispersion, which is crucial for broadband pulses. The compensation plates (CP) are set at a specific angle adjusted to minimize the spectral phase difference between the three beams, which is measured by spectral interferometry.

In order to create the desired pulse sequence [Fig. 2(d)], combination of movement of DS1 and DS2 is needed. A standard spherical mirror \( f = 40 \text{ cm} \) focuses the four beams onto the sample via a folding mirror and with a focal spot of 80 \( \mu \text{m} \) in diameter. The spectral interferograms of pulses 1 and 2 for different positions of DS2 and pulses 1 and 3 for different positions of DS1 are sent via a single-mode fiber to a 0.5-m imaging spectrograph and a cooled \( 400 \times 1600 \) CCD camera. The FFT analysis of the interferograms gives a direct relationship between time delay and motor position.

With the boxcar geometry used, the generated photon echo is emitted in the same direction as beam 4, due to the phase matching condition \( k_s = -k_1 + k_2 + k_3 \). A 2-mm-thick variable density filter is placed in the path of the local oscillator to attenuate its intensity, and to delay it by about \( \tau_4 = 3.2 \text{ ps} \). As seen in Fig. 3, the resulting interference fringes are well resolved. The filter is positioned between the spherical mirror and the sample to displace the focal spot on the sample, thus avoiding overlap with pulses 1 to 3, while the beam remains parallel to its original path. This is required to prevent the local oscillator from containing any undesired pump–probe signals [2].

Optimum pulse compression at the sample position is obtained using the standard MATLAB genetic-algorithm...
For determining a complete four-wave mixing signal for a specific population time \( T \), both delays are used to scan the time difference between pulses 1 and 2 by steps of 0.2 fs between the signal field and the local oscillator recording spectral interferograms at every step. High interferometric phase stability is required since the signal phase depends directly on the timing of arrival of the three excitation pulses. Additionally, the fringe pattern also depends on the local oscillator phase as shown in the following relationship \([7]\):

\[
\varphi_{ai} = \varphi_{Lo} - \varphi_s = \varphi_{Lo} - i\omega_0(-t_1 + t_2 + t_3).
\]  

(1)

The geometry of our setup uses the same technique as Selig et al. \([8]\) where pulses are paired such that no individual pulse hits an individual mirror. As shown in Fig. 2, mirrors and BS2 for beam pairs 1/3, and 2/4 are mounted on the same metallic holders. Any path variation of beams 1 or 2 causing a change in their arrival time \( \Delta t_1 \) or \( \Delta t_2 \), will cause an opposite variation to its pair 3 or 4, respectively, changing the arrival time by \( -\Delta t_1 \) or \( -\Delta t_2 \). Therefore, the total phase variation of the four beams cancels out:

\[
\omega_0(\Delta t_1 - \Delta t_3 + \Delta t_2 - \Delta t_4) = 0.
\]  

(2)

and the recorded spectral fringes are stable except from negligible air drifts that may affect the beams independently. To enhance the phase stability, the geometry used to split the beams and introducing delays at the same time makes the set-up very compact with minimal optical components. The absolute time and phase between the local oscillator and the signal are adjusted by comparing the sum of the absorptive 2D data along the probe axis with the pump–probe (PP) data (projection slice theorem) recorded on the same actual setup \([2]\). Automated beam shutters are set in the path of the three pump beams and used to remove scattering terms \([7]\).

In order to assess the stability of the setup, a photon echo signal is generated by placing a 100-μm glass plate in the sample position and setting the coherence and population time to zero. Spectral interference between the nonlinear signal and LO is recorded every second for more than 13 h. The mean phase deviation was calculated using inverse Fourier transform. Figure 3(a) shows that over the 13 h of measurements, we obtain a shot-to-shot (0.2 s accumulation per shot) stability of \( \lambda / 60 \) at 540 nm, while there was no noticeable long-term drift. This long-term stability allows for the systematic phasing correction of the 2D data spectra taken over multiple hours.

To test the accuracy of the setup, 2D measurements were performed on a test system, Rhodamine 101 in ethanol in a 0.1-mm flow cell, which has been intensely studied previously and is known to exhibit vibrational coherences that could be triggered with such short pulses \([19,20]\). Pulses with 90-nm bandwidth centered at 550 nm were compressed to 7 fs and used for excitation to perform 2D measurements, as well as transient absorption measurements. Interferograms were taken at a specific time delay from every 2D scan and compared to each other. The phase was highly stable even though the stages were repeatedly moving for hours as shown in Fig. 3(b). An example of a 2D spectrum at 100-fs population time is shown in Fig. 4(a). The signal is a positive peak along the diagonal axis caused by ground state bleach, with a pronounced elongation indicative of spectral inhomogeneity. Analysis of the 2D spectra and integrating over a 10 nm window around the peak (570 nm) shows an oscillation of 150-fs period decaying within the first picosecond (Fig. 5). The same oscillations were also observed in the pump–probe measurements performed
on the 2D setup and on an independent setup using sub-30-fs pump pulses centered around 580 nm (Fig. 5) [20].

In summary, a hollow core fiber was used to generate an ultra-broadband pulse for a passively phase-stabilized 2D visible spectroscopy using all conventional optics. Pulses were compressed to near Fourier limit using a deformable mirror based pulse shaper yielding 7-fs FWHM pulses. Short- and long-term phase stability was achieved allowing for measurements over long time periods.

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References