Rapid-scan nonlinear time-resolved spectroscopy over arbitrary delay intervals

T. Flöry1,*, V. Stummer1, J. Pupeikis2, B. Willenberg2, A. Nussbaum-Lapping2, F. V. A. Camargo3, M. Barkauskas4, C. R. Phillips2, U. Keller2, G. Cerullo3,5, A. Pugžlys1,6, A. Baltuška1,6

1Photonics Institute, TU Wien, Vienna, Austria
2Institute for Quantum Electronics, ETH Zurich, Zurich, Switzerland
3Istituto di Fotonica e Nanotecnologie-CNR, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
4Light Conversion Ltd., Vilnius, Lithuania
5Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
6Institute for Quantum Electronics, ETH Zürich, Zürich, Switzerland

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Femtosecond comb lasers have revolutionized linear Fourier-domain spectroscopy by offering a rapid motion-free, precise and accurate measurement mode with easy registration of the combs beat note in the RF domain. Extensions of this technique found already application for nonlinear time-resolved spectroscopy within the energy limit available from sources operating at the full oscillator repetition rate. Here, we present a technique based on time filtering of femtosecond frequency combs by pulse gating in a laser amplifier. This gives the required boost to the pulse energy and provides the flexibility to engineer pairs of arbitrarily delayed wavelength-tunable pulses for pump-probe techniques. Using a dual-channel millijoule amplifier, we demonstrate programmable generation of both extremely short, fs, and extremely long (>ns) interpulse delays. A predetermined arbitrarily chosen interpulse delay can be directly realized in each successive amplifier shot, eliminating the massive waiting time required to alter the delay setting by means of an optomechanical line or an asynchronous scan of two free-running oscillators. We confirm the versatility of this delay generation method by showing \( \chi^{(3)} \) cross-correlation and \( \chi^{(3)} \) multicomponent population recovery kinetics. © 2022 Optica Publishing Group under the terms of the Optica Open Access Publishing Agreement

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Ultrafast pump-probe spectroscopy is a very powerful technique to investigate the dynamics of photinduced processes in a variety of systems; from (bio)-molecules to solids. It is typically performed in a stroboscopic fashion, whereby at first a pump pulse excites the system and its photoinduced absorption/reflection change is monitored by a time-delayed probe pulse. Typically, the pump and probe pulses are derived from the same laser source, often using nonlinear optical frequency conversion to obtain photon energies matching the energy levels of the samples and a mechanical delay line to control their timing up to a delay of a few nanoseconds \([1]\). However, many processes, such as ligand rebinding in proteins \([2]\) and charge recombination in photovoltaic devices \([3]\), occur over a multitude of timescales, from fs to µs, which cannot be accessed by mechanical delays. In addition, delay lines require careful alignment to avoid lateral beam drifts and may suffer from spurious signal variations due to a change of the focused beam diameter induced by divergence. For these reasons, there is a high demand for sources of synchronized, high-energy pulses whose delay can be electronically controlled over a wide range without moving optical arms.

Femtosecond dual-comb sources operating at MHz to GHz repetition rate have revolutionized frequency metrology and linear Fourier-domain spectroscopy by offering an interpulse delay scanning mode, known as equivalent time sampling and in specific configurations ASynchronous Optical Sampling (ASOPS) \([4,5]\), both without the need for a mechanically steered optical delay line and its associated shortcomings for large (>ns) interpulse delays \([6,7]\).

While a powerful technique, ASOPS is not suitable for generating a sufficient dynamic range for time-resolved spectroscopy on a broad class of higher order nonlinear susceptibilities. Firstly, the interpulse delay increment is fixed, which does not allow for efficient sampling of complex dynamics extending over multiple timescales. Furthermore, the pulse energy is limited since amplifying a laser oscillator at its full repetition rate implies a high average power (with corresponding technical challenges on the laser source and thermal damage on the sample). The short inter-pulse spacing also limits the scan range, and the measurements are susceptible to the accumulation of long-lived components, e.g. population of triplet states \([9]\); such artifacts are a typical challenge of 3rd and higher-order nonlinear spectroscopies. Importantly for our further discussion, even if the single-pulse energy at a full oscillator repetition rate is boosted to a level sufficient for parametric frequency conversion and/or for pump-
probe signal generation, there will remain numerous problems with the acquisition of kinetics. One prominent problem being the inability to average the nonlinear signal at a fixed delay point and a substantial waiting time before the same delay point can be revisited again. The waiting time grows inversely proportion to the time-resolution step determined by the detuning of the two cavities.

Dividing up the MHz repetition rate of a master oscillator by capturing a selected pulse in a kHz multipass or regenerative amplifier (RA) allows for the generation of fully electronically tunable interpulse delays, as shown in several published schemes [10–12]. The most intuitive approach is to seed two RA cavities from a common oscillator; by either selecting different oscillator pulses or by using different lengths of the amplification window, pulse spacings in the order of the oscillator repetition period can be generated [13]. This method allows the generation of arbitrarily long interpulse delays at the expense of nanosecond resolution. Fully electronically tunable delays over a broad range were demonstrated by Bredenbeck et al. [10], using two electronically synchronized mode-locked oscillators seeding two individually controlled RAs. However, the time resolution was limited to 1.8 ps due to synchronization jitter between the oscillators.

Another interesting development is the (kHz-) Arbitrary Detuning – ASOPS (AD-ASOPS) technique [14–16]. Instead of relying on two synchronized oscillators, two deliberately strongly detuned oscillators with a correspondingly short beat period are used to seed two RAs. The instantaneous frequency of the two oscillators together with a coincidence event are continuously monitored and evaluated. Notably, it is also possible to recover shorter time-delays on a sub-ps scale by post-calibrating the measured results, for example by evaluating the spectral interference fringes of the amplified pulses. The inconvenience, ultimately translated into significantly longer acquisition times, is that the appearance of a particular delay setting within an expected delay range becomes statistical. [10–12]

Here we report a method capable of a deterministic control of time delay scans from fs to ms with femtosecond accuracy, which overcomes most problems arising in both opto-mechanical delay generation and in earlier attempts at electronic delay control and recovery. Our method is enabled by the use of a low-noise, spatially multiplexed, single-cavity, femtosecond, dual-comb oscillator similar to the one presented in [17]. While this can also be accomplished by two synchronized oscillators [18,19], the intrinsic lower noise and experimental setup simplicity of the single-cavity dual-comb enabled us to achieve sub-100-fs jitter at arbitrary delays between the amplified pulses.

Figure 1 shows the conceptual scheme of the system. A dual-comb oscillator (Yb:CaF$_2$, $\lambda = 1050$ nm) delivers two femtosecond pulse trains with 2.0 W average power each at a repetition rate $f_{\text{rep1,2}} \cong 80$ MHz and a repetition-rate detuning of $\Delta f_{\text{rep}} \cong 500$ Hz. This results in a time delay increment between consecutive pulses $\Delta t = 1/f_{\text{rep1}} - 1/f_{\text{rep2}} \cong 80$ fs. A fraction of the oscillator output is directed towards a cross-correlation setup used to detect the temporal overlap of the pulse trains by generating the sum-frequency signal in a $\beta$-barium borate (BBO) nonlinear crystal in type I phase matching configuration.

This signal is detected (PDA10A2, 150 MHz bandwidth) to obtain a trigger “start” signal for the timing electronics. The pulses are stretched in a common grating-based stretcher and amplified in two RA cavities [Yb:CaF$_2$, $\sim 600$ fs pulse duration, 1 mJ pulse

 energies; further details in supplementary) built as a monolithic block pumped by a single laser diode. The amplified pulses are then recompressed in a compressor employing a single transmission diffraction grating but two separated beam paths. The RAs employ Pockels cells in order to select single oscillator pulses and control the amplification window. A fresh amplification cycle is started with a certain waiting period to select a pulse pair with the desired delay, every time a pulse overlap is detected by the cross-correlation setup. Therefore, the RAs operate at a repetition rate corresponding to the oscillator detuning frequency $f_{\text{os}} = \Delta f_{\text{rep}} = 500$ Hz.

![Fig. 1. System setup. MHz-X: cross correlation of the two pulse trains at the full repetition rate for zero overlap detection. Timing: Timing electronics for the RAs.](image1)

![Fig. 2. Operating principle: top trace shows pulses from OSC1, middle trace are the pulses from OSC2, bottom: cross correlation between OSC1 and OSC2. Shaded areas indicate pulses selected for amplification for two cases: gray: $\Delta t < 1/f_{\text{rep2}}$, hatched gray: $\Delta t > 1/f_{\text{rep2}}$.](image2)
correlation signal and firing the regenerative amplifiers at a fixed repetition rate ($f_{0A}$). Details for this mode can be found in the supplementary.

Single-cavity dual-comb lasers can provide few-femtosecond relative timing jitter [17]. However, at long time scales the relative timing is subject to drifts due to thermal variation in the environment. In our case we have used a single-cavity dual-comb laser for which the repetition rate difference $\Delta f_{0A}$ was stabilized [17]. This stabilization could be avoided by live tracking of the repetition rate difference and recalculating the time delay on a shot-to-shot basis. Using equation 12 from [20] one can estimate the period jitter for the used oscillator to be in the order of 4 fs, which is the determining uncertainty for any pulse pair selected within a 2 ms ($=1/f_{0A}=1/\Delta f_{0A}$) time window.

As a proof-of-principle demonstration, a cross-correlation measurement of the amplified output pulses was performed. For this measurement the amplified pulses were focused and overlapped, using a single lens, into a BBO crystal and the sum-frequency output signal was recorded using a biased photodiode (Thorlabs DET10A, 350 MHz bandwidth). To suppress scattered light from the fundamental beams, an aperture and optical short-pass filters were installed before the photodiode.

Figure 3 shows the result of the cross-correlation measurements with ~80 fs step size. Panel a) shows the direct result while for panel b) the pulse compressor parameters for one of the channels was changed, by adjusting the optical path length, resulting in a longer output pulse in the corresponding channel and reduced peak intensity.

The excellent match between individual scans in Fig. 3 shows the reproducibility of the technique. Furthermore, one can choose for how many cycles the delay value is kept. This allows for example to dwell at a certain delay step for a given number of shots to increase the signal to noise ratio by averaging.

Figure 4a shows the case where for each delay 400 shots were accumulated. In Fig. 4b the intensity distribution for four selected delay values corresponding to the steepest slope of the cross-correlation signal are plotted. Fig 4c shows the corresponding timing jitter as obtained by the slope of the signal from Fig. 4a. Most jitter originates from a uncertainty of the trigger signal which is in the order of one step size ($\Delta t = 80$ fs). More details on the trigger uncertainty are supplied in the supplementary.

To demonstrate the versatility and flexibility of the presented technique, transient absorption measurements of a perovskite sample (polycrystalline thin film of CH$_3$NH$_3$PbI$_3$) were performed using a two color pump-probe setup, which is shown schematically in Fig. 5. Probe pulses with a bandwidth of 15 nm were generated in a non-collinear optical parametric amplifier (NOPA), tuned to 760 nm near the bandgap of the material. The pump pulses at 525 nm were obtained by frequency doubling the fundamental output of the other RA, providing more than 780 meV of excess energy above the bandgap.

In conclusion, we have demonstrated a versatile scheme for the flexible generation of amplified femtosecond pulse pairs with rapidly variable, electronically tunable delays ranging from femtosecond to milliseconds with femtosecond precision, enabled by a low-noise, spatially multiplexed, single-cavity, femtosecond, dual-comb solid-state oscillator in combination with a twin amplifier. In the demonstrated implementation the timing
uncertainty between two arbitrarily delayed amplifier pulses is limited to the delay step \( \Delta t = \frac{\Delta f_{rep}}{(f_{rep})^2} \) which in our case was 80 fs at \( \Delta f_{rep} = 500 \) Hz rate. However, by pairing such system with a single-cavity dual-comb oscillator at 1 GHz repetition rate [25], 1 fs timing uncertainty at 1 kHz amplifier rate can be achieved.

The presented approach allows the recording of dynamics in nonlinear transient absorption spectroscopies ranging over orders of magnitude, from femtoseconds to milliseconds. We envisage, that, besides the present use in ultrafast spectroscopy, the presented method will also enable several new applications in nonlinear beam steering and time / frequency space mapping by utilizing presented rapid delay control for time-gating intense chirped pulses.

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**Supplemental document.** See Supplement 1 for supporting content.

**References**

1. M. Maiuri, M. Garavelli, and G. Cerullo, "Ultrafast Spectroscopy: State of the Art and Open Challenges," J Am Chem Soc 142, 3–15 (2020).
2. J. Bredenbeck, J. Helbing, A. Sieg, T. Schrader, W. Zinth, C. Renner, R. Behrendt, L. Moroder, J. Wachtveitl, and P. Hamm, "Picosecond conformational transition and equilibration of a cyclic peptide," Proceedings of the National Academy of Sciences 100, 6452–6457 (2003).
3. Z. Guo, Y. Wan, M. Yang, J. Snader, K. Zhu, and L. Huang, "Long-range hot-carrier transport in hybrid perovskites visualized by ultrafast microscopy," Science (1979) 356, 59–62 (2017).
4. K. J. Weingarten, M. J. W. Rodwell, H. K. Heinrich, B. H. Kolner, and D. M. Bloom, "Direct electro-optic sampling of GaAs integrated circuits," Electron Lett 21, 765 (1985).
5. P. A. Elzinga, R. J. Kneisler, F. E. Lytle, Y. Jiang, G. B. King, and N. M. Laurendeau, "Pump/probe method for fast analysis of visible spectral signatures utilizing asynchronous optical sampling," Appl Opt 26, 4303 (1987).
6. N. Picquè and T. W. Hänsch, "Frequency comb spectroscopy," Nat Photonics 13, 146–157 (2019).
7. I. Coddington, N. Newbury, and W. Swann, "Dual-comb spectroscopy," Optica 3, 414 (2016).
8. T. Ideguchi, S. Holzner, B. Bernhardt, G. Guelachvili, N. Picquè, and T. W. Hänsch, "Coherent Raman spectro-imaging with laser frequency combs," Nature 502, 355–358 (2013).
9. W. P. de Boeij and D. A. Wiersma, "Ultrafast solvation dynamics explored by nonlinear optical spectroscopy," (1997).
10. J. Bredenbeck, J. Helbing, and P. Hamm, "Continuous scanning from picoseconds to microseconds in time resolved linear and nonlinear spectroscopy," Review of Scientific Instruments 75, 4462–4466 (2004).
11. D. J. Jones, E. O. Potma, J. Cheng, B. Burfeindt, Y. Pang, J. Ye, and X. S. Xie, "Synchronization of two passively mode-locked, picosecond lasers within 20 fs for coherent anti-Stokes Raman scattering microscopy," Review of Scientific Instruments 73, 2843–2848 (2002).
12. J. T. Fourkas, L. Dhar, K. A. Nelson, and R. Trebino, "Spatially encoded, single-shot ultrafast spectroscopies," Journal of the Optical Society of America B 12, 155 (1995).
13. G. M. Greetham, P. M. Donaldson, C. Nation, I. v. Szanovics, I. P. Clark, D. J. Shaw, A. W. Parker, and M. Townie, "A 100 kHz Time-Resolved Multiple-Probe Femtosecond to Second Infrared Absorption Spectrometer," Appl Spectrosc 70, 645–653 (2016).
14. L. Antonucci, X. Solinas, A. Bonvalet, and M. Joffre, "Asynchronous optical sampling with arbitrary detuning between laser repetition rates," Opt Express 20, 17928 (2012).
15. L. Antonucci, A. Bonvalet, X. Solinas, L. Daniault, and M. Joffre, "Arbitrary-detuning asynchronous optical sampling with amplified laser systems," Opt Express 23, 27931 (2015).
16. X. Solinas, L. Antonucci, A. Bonvalet, and M. Joffre, "Multiscale control and rapid scanning of time delays ranging from picosecond to millisecond," Opt Express 25, 17811 (2017).
17. J. Pupeikis, B. Willenberg, S. L. Camenzind, A. Benayad, P. Camy, C. R. Phillips, and U. Keller, "Spatially multiplexed single-cavity dual-comb laser," Optica 9, 713 (2022).
18. R. Shelton, L.-S. Ma, H. Kapteyn, M. Murnane, J. Hall, and J. Ye, "Active synchronization and carrier phase locking of two separate mode-locked femtosecond lasers," J Mod Opt 49, 401–409 (2002).
19. R. Gsbs, G. Klatt, C. Janke, T. Dekorsy, and A. Bartels, "High-speed asynchronous optical sampling with sub-50fs time resolution," Opt Express 18, 5974 (2010).
20. S. L. Camenzind, D. Koenen, B. Willenberg, J. Pupeikis, C. R. Phillips, and U. Keller, "Timing jitter characterization of free-running dual-comb laser with sub-attosecond resolution using optical heterodyne detection," Opt Express 30, 5075 (2022).
21. J. M. Richter, F. Branchi, F. Valduga de Almeida Camargo, B. Zhao, R. H. Friend, G. Cerullo, and F. Deschler, "Ultrafast carrier thermalization in lead iodide perovskite probed with two-dimensional electronic spectroscopy," Nat Commun 8, 376 (2017).
22. T. Ghosh, S. Aharon, L. Etgar, and S. Ruhman, "Free Carrier Emergence and Onset of Electron–Phonon Coupling in Methylammonium Lead Halide Perovskite Films," J Am Chem Soc 139, 18262–18270 (2017).
23. L. M. Herz, "Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites," Annu Rev Phys Chem 67, 65–89 (2016).
24. L. M. Fazous-Ottoun, T. P. Xiao, and E. Yablonovitch, "Fundamental Efficiency Limit of Lead Iodide Perovskite Solar Cells," J Phys Chem Lett 9, 1703–1711 (2018).
25. B. Willenberg, J. Pupeikis, C. R. Phillips, and U. Keller, "SESAM-mode-locked gigahertz solid-state dual-comb oscillator with flexible repetition rate difference," in Solid State Lasers XXXI: Technology and Devices, W. A. Clarkson and R. K. Shori, eds. (SPIE, 2022), p. 8.