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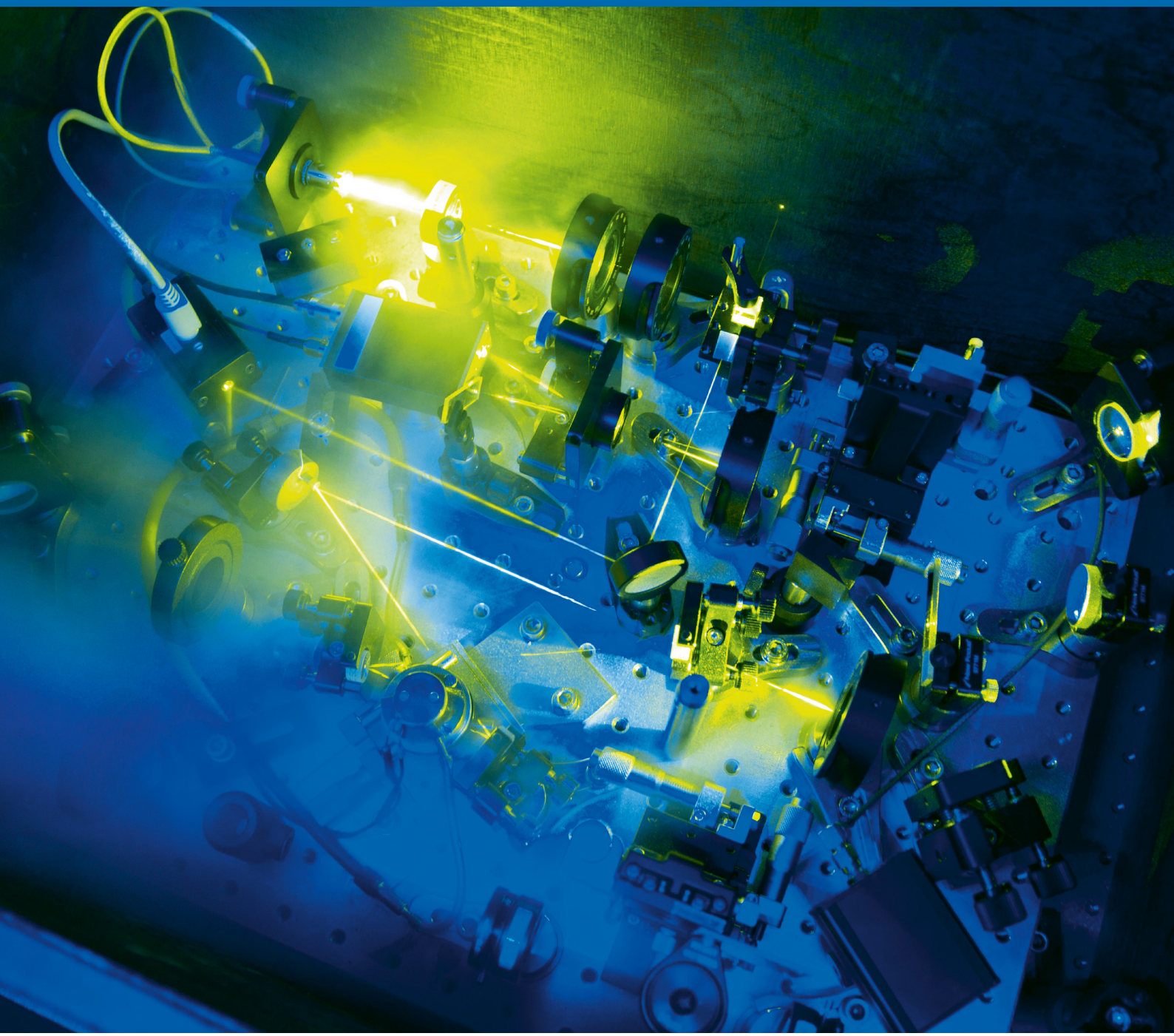


Compact Sub-50 fs Lasers for Time-Domain Kerr-Effect Spectroscopy

Time-domain spectroscopies based on the optical Kerr effect can provide a glimpse into the ultrafast processes that dictate fundamental properties of material and biological samples. Such experiments can provide insights into molecular interactions and energy transfer processes that could facilitate improved solar cell efficiencies, better pharmaceuticals, and new photonics devices.

Until recently, this established and rather complex technique has been confined to academic research labs due to the limited availability of compact and robust laser sources with sub-50 fs pulse durations. In this white paper, a compact, commercially available fiber-based femtosecond laser displaying a 34 fs pulse duration was used to verify the capability of such laser sources for both optical Kerr effect (OKE) spectroscopy and Raman-induced Kerr effect spectroscopy (RIKES), thus opening new possibilities and opportunities for commercial systems based on these techniques.

Authors

Prof. Marcus T. Cicerone is professor in Chemistry at Georgia Institute of Technology, Atlanta. His research uses light, neutrons, and molecular dynamics simulation to probe intramolecular and intermolecular motion on timescales ranging from MHz to PHz.

Dr Oliver Prochnow is CEO of VALO Innovations GmbH, now a part of HÜBNER Photonics, as well as Product Manager for the VALO Femtosecond Series lasers. He has more than 15 years of experience in the field of ultrafast fiber lasers and amplifiers including a PhD from Laser Zentrum Hannover e.V. from the “Ultrafast Photonics Group”.

Background

Time-domain spectroscopies based on the optical Kerr effect can provide useful information about material and biological samples. Approaches such as optical Kerr effect (OKE) spectroscopy are exquisitely sensitive to the picosecond-timescale relaxation processes in liquids and amorphous solids 1 that control the chemical and physical stability of products such as biopharmaceuticals. Another approach, Raman-induced Kerr effect spectroscopy (RIKES), can be combined with microscopy to provide label-free chemically specific sample mapping at sub-micron spatial resolution for applications ranging from microelectronic wafer inspection to cell phenotype mapping in histology.

Despite their many potential applications, time-domain Kerr-effect spectroscopies are used almost exclusively in academic-style research laboratories, partly because they require very short (sub 50 fs) laser pulses that are compressible with a very low pedestal, at average powers of at least 1 to 2 W. Historically, such pulses have been available only from large, rather complex, and expensive Ti:Al_2O_3 lasers. A fiber laser that could provide such pulses in a user-friendly, turnkey way, with only air cooling, would make these powerful spectroscopies available to a much broader user base.

Creating the Time-Domain Signal

The Kerr effect describes a change in the refractive index of a material due to an electric field. When the field is strong enough to slightly change the binding potential felt by the electrons, the electrons interact more strongly with passing photons, increasing the refractive index. In the optical Kerr effect, the light itself provides the electric field needed to change the refractive index according to:

$$\Delta n = I\, n_2$$

where Δn is the refractive index change, I is the irradiance in W/m^2, and n_2 is the nonlinear refractive index with units of m^2/W; n_2 is proportional to the nonlinear susceptibility. With optical fields strong enough to perturb bound electrons, the light can induce tiny forces on molecules in the sample, introducing a transient non-equilibrium state. Thus, an optical "pump" pulse can perturb the system, which can then be monitored through the time-dependent refractive index changes as it re-equilibrates to equilibrium. In rotational OKE, an optical torque is induced due to anisotropy in the nonlinear susceptibility tensor of the molecule. In RIKES, two components of the optical pump field oscillate at frequencies that differ by an amount equal to the resonant frequency of a chemical bond of interest. These bonds in the sample are excited through the Raman effect, which induces some degree of vibrational coherence in the sample. In both cases, the motion of the molecular nuclei (rotation or vibration) caused by the pump pulse creates time-dependent refractive index changes. However, in each case, the forces on the nuclei are indirect and mediated by the direct interaction of the electrons with the pump field, so the electronic motion induces a far greater refractive index change than the nuclear motion of interest.

Reading the Time-Domain Signal

The pump-induced dynamics are read out by measuring the time-dependent refractive index changes in the sample. Typically, Δn is on the order of 10^{-5}, necessitating differential detection, comparing the phase of two weak light pulses that interact with the perturbed refractive index differently. The signal of interest can change on timescales of 10s of fs and is accompanied by a 100X stronger but less informative signal from electron motion. Thus, the pump and read pulses must be short (< 50 fs) with a pedestal < 10^{-3}.

Figure 1 shows a RIKES signal induced and read by pulses from a VALO Tidal. Using only the built-in pulse compression, we can excite vibrations up to 800 cm^{-1}. The pulses have a sufficiently low pedestal (<10^{-4}) that weak atomic vibrations are easily observed; no post-pulse pump light interferes with our signal.

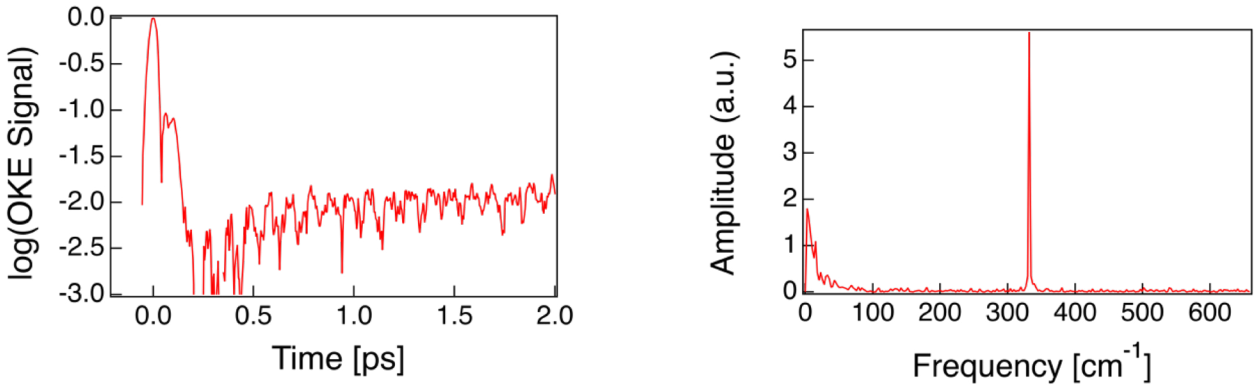


Figure 1:

Top: The first 2 ps of a 13 ps OKE signal from CF_2 using a VALO Tidal. The laser pulse FWHM is 34 fs and the pulse pedestal is below 10^{-4}. Bottom: The spectrum of the data in the top graph. The peak at 319 cm^{-1} is due to CaF_2 lattice vibrations. The spectral resolution is 2.5 cm^{-1}.

Continuum Generation

We are often interested in exciting and reading molecular vibrations at frequencies up to 3200 cm^{-1}. Broadening the laser pulse, typically in a photonic crystal fiber, is necessary in these cases. Here, the input pulse must be ultrashort and highly compressible to generate continuum light of sufficient bandwidth without excessive phase oscillations. Figure 2 shows the spectrum of a continuum pulse generated by passing 1.6 W of light from the VALO Tidal through a short segment of photonic crystal fiber. The experimental result compares favorably with a simulated result using split-step integration of the nonlinear Schrödinger equation with the Python package pyNLO.

The simulated and measured continuum profiles agree well and suggest that this arrangement will allow us to achieve > 3000 cm^{-1} of impulsive excitation bandwidth.

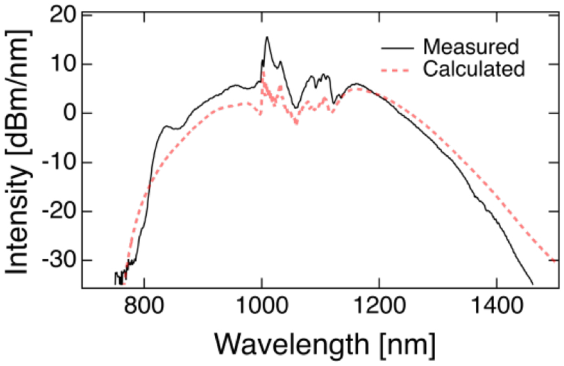


Figure 2:

The spectral resolution is 2.5 cm^{-1}.

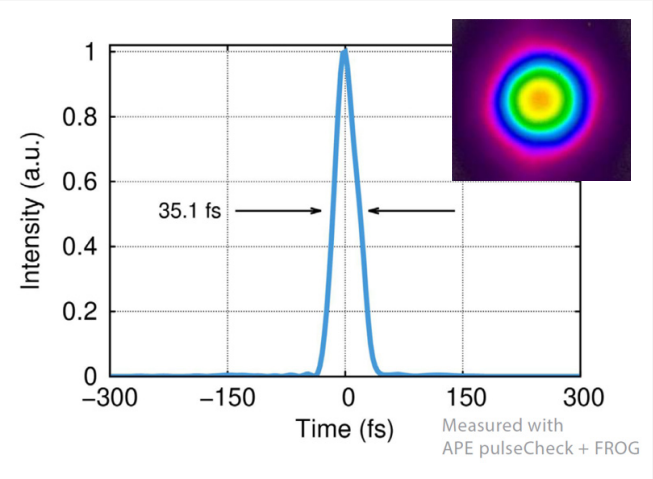
Why VALO Femtosecond Fiber Lasers?

For applications such as RIKES, the advantage of a clean, sub-50 fs pulse is simple: exceptional experimental flexibility. The ultrashort pulses provided by VALO femtosecond lasers facilitate differential detection in the 10s of fs regime, while the inherently low pedestal permits the excitation and reading of molecular vibrations over a wide range of frequencies.

The compact and robust nature of the VALO femtosecond series also plays a significant role in experimental flexibility. The small laser head footprint (214mm x 370mm) – which is passively cooled and does not require additional chillers or fans – can be easily integrated onto optical tables or into existing experimental applications. Lasers producing sub-50 fs pulses are both spatially and financially feasible.

The compact VALO Aalto and VALO Tidal lasers deliver sub-50 fs pulses (typically < 40 fs) at a repetition rate of 30 MHz with pulse energies of 6.6 nJ and 66 nJ, and average powers of 200 mW and 2 W, respectively. They produce an alignment-free high-quality beam profile (typical M^2<1.1 for Aalto and M^2<1.2 for Tidal) and integrated dispersion pre-compensation capabilities.

The average output power of the VALO femtosecond lasers is actively stabilized, resulting in more than 24 hours of uninterrupted performance stability typically better than 0.05% for Aalto and 0.1% for Tidal. An example of a typical temporal pulse profile and beam profile from the VALO Series lasers is shown in Figure 3a) along with an example of the broad optical spectrum 3b) and a picture of the laser 3c).



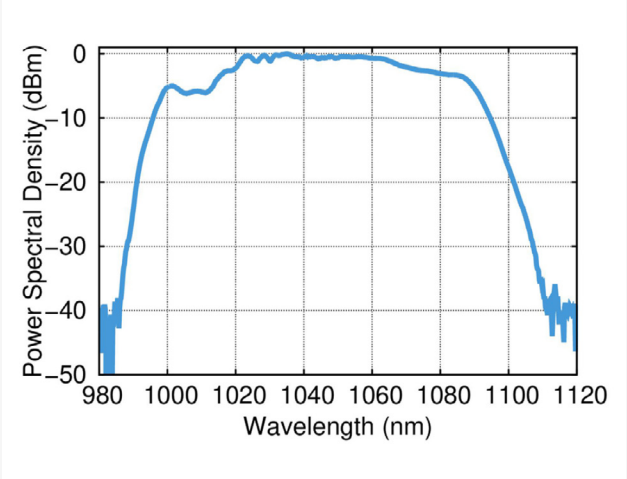


Figure 3:

a) Typical temporal pulse profile highlighting the sub 50 fs pulse duration with very low pulse pedestal and inset showing the typical beam profile, b) typical optical spectrum of c) HÜBNER Photonics VALO Femtosecond Series lasers.

Outlook

As femtosecond laser technology improves, Time-domain spectroscopies based on the optical Kerr effect are becoming increasingly practical for probing molecular structures and their interactions. Until recently, commercially available lasers that provide high peak powers and ultrashort pulses have been cumbersome and unstable. The rise of the fiber laser has changed this reality. Using compact fiber lasers with 34 fs pulses, both OKE and RIKES have now been demonstrated, thereby launching the possibility of commercial systems based on such spectroscopic techniques.

References

[1] Bender, J. S., Zhi, M. & Cicerone, M. T. The polarizability response of a glass-forming liquid reveals intrabasin motion and interbasin transitions on a potential energy landscape. Soft Matter 16, 5588–5598 (2020).

Acknowledgment

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About HÜBNER Photonics

HÜBNER Photonics is committed to supplying high performance and innovative lasers that meet or exceed the market´s expectation concerning quality, reliability and robustness.

HÜBNER Photonics offers the full range of high performance Cobolt lasers, C-WAVE cw tunable lasers, VALO femtosecond lasers, Ampheia fiber amplifiers along with a full selection of C-FLEX laser combiners. HÜBNER Photonics supply lasers to major instrument manufacturers and leading research labs for cutting-edge applications in the areas of fluorescence microscopy, multiphoton microscopy, flow cytometry, Raman spectroscopy, metrology, holography, nanophononics and quantum research.