

# Mid-infrared dual comb spectroscopy with 2.4 $\mu\text{m}$ $\text{Cr}^{2+}:\text{ZnSe}$ femtosecond lasers

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**Abstract:** The mid-infrared part of the electromagnetic spectrum is the so-called molecular fingerprint region because gases have tell-tale absorption features associated with molecular rovibrations. This region can be for instance exploited to detect small traces of environmental and toxic vapours in atmospheric and industrial applications. Novel Fourier transform spectroscopy without moving parts, based on time-domain interferences between two comb sources, can in particular benefit optical diagnostics and precision spectroscopy. To date, high-resolution and -sensitivity proof-of-principle experiments have only been reported in the near-infrared region where frequency comb oscillators are conveniently available. However, as most of molecular transitions in this region are due to weak overtone bands, such techniques are not ideal for sensitive and rapid detection. Here we present a proof-of-principle experiment of frequency comb Fourier transform spectroscopy with two  $\text{Cr}^{2+}:\text{ZnSe}$  femtosecond oscillators directly emitting in the 2.4  $\mu\text{m}$  mid-infrared region. The acetylene absorption spectra in the region of the  $\nu_1+\nu_5^1$  band, extending from 2370 to 2525 nm, could be recorded within a 10  $\mu\text{s}$  acquisition time without averaging with 12 GHz resolution.

## 1. Introduction

Introduced in the late 1990s, laser frequency combs have revolutionized [1,2] precise measurements of frequency and time. The regular pulse train of a mode-locked femtosecond laser can give rise to a regular comb spectrum of millions of laser modes, with a spacing precisely equal to the pulse repetition frequency. Commercially available laser frequency combs are now becoming routine tools for precise optical spectroscopy, and they are being harnessed for the synthesis of arbitrary optical waveforms. Laser frequency combs have enabled the development of new ultra-precise optical atomic clocks, and they have become a key to attosecond science by permitting control of the phase of the electric field of ultrashort laser pulses. The calibration of astronomical spectrographs with laser frequency combs will permit sensitive searches for earth-like planets, and precise interferometric distance measurements might allow new space missions with highly controlled formations of space vehicles. Extensions of frequency comb techniques to new spectral regions from THz frequencies to the extreme ultraviolet are now under exploration.

Dramatic advances in molecular science are now foreseen for new spectroscopic methods based on frequency combs [3-18]. Recent experiments [3,4] of multi-heterodyne frequency comb Fourier transform spectroscopy (also called dual-comb spectroscopy) have demonstrated that the precisely spaced spectral lines of a laser frequency comb can in particular be harnessed for the rapid and sensitive acquisition of highly multiplexed spectra of molecules. Motionless Fourier interferometers based on two laser frequency combs [3-11] with slightly mismatched repetition frequencies may open new opportunities in physics, chemistry, biology and industry. The spectral structure of sharp comb lines can be very useful even in the recording of broadband spectra without extremely sharp features, as they are e.g. encountered for molecular gases or in the liquid phase. A first frequency comb then interrogates the absorbing sample, while a second frequency comb of different line spacing permits the generation of a comb of radio frequency beat notes, which effectively map the optical spectrum into the radio frequency regime, so that it can be recorded with a single fast photodetector, followed by digital signal analysis. It provides simultaneous and accurate access to a broad spectral bandwidth within a short measurement time and can physically be equally understood in terms of time domain interferences, multi-heterodyne detection, optical free induction decay, linear optical sampling or cross-correlation between two electric fields. Spectra with GHz resolution and reasonable signal-to-noise ratio may be recorded [4,10]

within a few tens of microseconds. The early proof-of-principle demonstrations of this promising technique have been carried out in the 10  $\mu\text{m}$  region [5,6], where the femtosecond comb radiation was produced by optical rectification that hardly leads to optical powers in excess of few microwatts. Consequently, spectra exhibiting high resolution and sensitivity have only been obtained in the near-infrared region [3,4,10,11] where frequency comb oscillators are conveniently available. However, the region is unsuitable to sensitive diagnostic, as most of molecular transitions are due to weak overtone bands.

Most of the strong fundamental molecular vibration frequencies are indeed located in the mid-infrared spectral region (2 - 20 $\mu\text{m}$ ), which is referred to as the fingerprint region. Mid-infrared spectroscopy proves an efficient tool for the determination of the structure of molecules, the quantitative analysis of complex mixtures, the investigation of dynamic systems, biomedical spectroscopy, micro-spectroscopy and hyperspectral imaging, and the study of many types of interfacial phenomena. A mid-infrared spectrometer can be deployed in a large number of roles, such as minimally invasive medical diagnostics, environmental and workplace monitoring, industrial real-time process control and even security applications. To date, the overriding broad-spectral-bandwidth analytic spectroscopic instrument in the infrared with applications throughout the physical, chemical, and biological sciences has been the Michelson-based Fourier transform spectrometer. Starting in the early seventies [19], Fourier-transform spectroscopy has dramatically improved the quality of infrared spectra and minimized the time required to obtain data. In addition, with constant improvements to computers, infrared spectroscopy has made further great strides. However, the design of scanning Michelson-based Fourier transform interferometers has hardly evolved since and the instrument no longer meets some of the demanding capabilities of modern physics and sensing. In particular, the use of incoherent light sources limits the sensitivity, the resolution is set by the excursion of a mechanical moving mirror and the moving-mirror displacement speed determines the recording time, which ranges between seconds and hours depending on the desired resolution. Developing mid-infrared dual-comb Fourier transform spectroscopy is therefore a demanding but highly desirable task.

In this article, we report on a proof-of-principle demonstration of dual-comb Fourier transform spectroscopy with ceramic  $\text{Cr}^{2+}:\text{ZnSe}$  femtosecond oscillators that are directly emitting in the 2.45  $\mu\text{m}$  region. Ultrabroadband solid-state infrared lasers should have a strong potential to compete with the available techniques of nonlinear frequency conversion, as they might be more convenient to operate, more environmentally stable, more efficient,

simpler, and more compact in design. Due to the broadest gain among all solid-state laser materials, Cr<sup>2+</sup>-based lasers [20] hold promise for the generation of ultra-short infrared pulses down to a few optical cycles. In particular, sub-100 fs mode-locked operation of Cr<sup>2+</sup>:ZnSe lasers has been reported recently [21-23] and the potential of such lasers for high-brightness spectroscopic sources has already been demonstrated [24] with a Michelson-based Fourier transform interferometer.

## 2. Experimental set-up and results

The experimental set-up for dual-comb spectroscopy is schematized in Figure 1. Two similar prismless laser oscillators based on 2-mm thick Brewster-cut Cr<sup>2+</sup>:ZnSe polycrystalline active media (Cr concentration  $5 \cdot 10^{18} \text{ cm}^{-3}$ ) are pumped by the same 1607 nm erbium-doped fiber laser. The ceramics are edge-mounted without active cooling and absorb about 65% of pump radiation. The astigmatically compensated X-fold cavities consist of 76-mm and 50-mm radius-of-curvature dichroic mirrors, a 45-mm radius of curvature mirror focusing the light onto an InAs/GaSb semiconductor saturable absorber mirror (SESAM), and an output coupler with transmission of 2 % at 2.4  $\mu\text{m}$ . Dispersion compensation is provided by a single 3-mm thick sapphire plate and self-starting mode-locking is ensured by the SESAM. The laser repetition frequencies and carrier-envelope offsets are not actively stabilized. The lasers are typically operated at ambient atmosphere at 1.8-2.1 W of pump power, although the lasers could be modelocked in the 0.9 - 2.2 W pump power range, delivering 45 to 120 mW of average output power at 215 MHz repetition frequency. Fig. 2 provides a low resolution (100 GHz) spectrum and an interferometric autocorrelation trace of the pulses from one of the two lasers, measured by a collinear autocorrelator using two-photon absorption in an InGaAs photodiode. The full width at half maximum (FWHM) of the trace is 190 fs, which leads to a pulse width of the order of 100 fs, consistent with the 70 nm autocorrelation measured FWHM of the corresponding spectrum. The spectrum also contains continuous-wave components that could be removed by lowering the pump power, at the expense of the stability of the mode-locked operation. For dual-comb spectroscopy, one of the lasers interrogates a single pass 70-cm long cell, which is filled with 230 hPa of acetylene in natural abundance. The information encoded by this interrogating comb is then retrieved by heterodyning it with a second femtosecond oscillator, which serves as a reference. The interrogating comb is superimposed on the second femtosecond laser with slightly different repetition frequency (about 400Hz) with a beam mixer. A single 60-MHz bandwidth

extended InGaAs photodiode then produces an output signal with a comb of radio frequencies due to the interference between pairs of optical comb lines. In the frequency domain, the optical spectrum is thus effectively mapped into the 0-27 MHz radio frequency region. In the time domain, the pulse train of the interrogating comb excites the absorbing sample at regular time intervals of 4.6 ns. The second pulse train of slightly different repetition frequency interferometrically samples, at an experimental scan rate of 215 MHz, every effective 8.6 fs the transient response or “free induction decay” of the medium, akin to an optical sampling oscilloscope, where the correlation between the electric field of the interrogating comb and the reference comb is measured. The electric interferometric time-domain signal from the photodiode is sampled by a high-resolution 16 bits digitizer with 65-MHz-bandwidth at a rate of 180 MSamples/s. A fast Fourier transform is performed to reveal the spectrum.

Figure 3 displays an experimental interferogram resulting from the interferences between the two femtosecond oscillators as retrieved from the experimental set-up of Figure 1. Due to the fixed mismatch between the repetition frequencies of the pulses of the two combs, the interferogram is expected to repeat itself at a period, which is the inverse of the difference in the repetition frequencies of the two lasers. Therefore, strong bursts occur when pulses from the two lasers overlap. In the present experiment, one of the mode-locked lasers operates in a double-pulse regime. Consequently, the interferogram shown in Fig. 3 exhibits a doubly-periodic structure, with two series of bursts with a period of 2.53 ms in the experimental time frame and separated from each other by 1.08 ms. This double-pulse regime could not be evidenced from the autocorrelation and spectral measurements presented in Figure 2, as the two pulses are effectively separated by 2.0 ns, which represents an optical delay of about 60 cm. The regime is not troublesome to the interferometric measurement reported here: the modulation due to the molecular transitions is only occurring on one side of the burst as only one laser beam interacts with the molecular sample and two successive bursts are still well further apart so that one interferogram does not spread on the other. Achieving stable multiple-pulse operation of the femtosecond lasers may actually be a passive method to increase the occurrence rate of the bursts with reasonable laser cavity lengths and might present interest for the acquisition of time-resolved sequences of broadband spectra reporting the evolution of dynamic single-events.

As a first demonstration of the capabilities of the spectrometer for broadband absorption spectroscopy, the rovibrational spectra of acetylene has been recorded around 2450 nm. Figure 4 gives an illustration of the C<sub>2</sub>H<sub>2</sub> spectrum, in the region of the  $\nu_1 + \nu_5^1$  band [25]

where the  $P$ ,  $Q$  and  $R$  branches can be easily distinguished. The intensity alternation is obvious in the upper left inset of Figure 4 showing a zoom in the  $R$ -branch. This spectrum is retrieved from the Fourier transform of a 10  $\mu\text{s}$  sequence of the interferogram, without averaging several interferogram sequences. The dual-comb spectrum extends from 2370 to 2525 nm, with 12 GHz unapodized resolution. Numerical apodisation is performed on the spectrum displayed on Figure 4, with a Blackman Harris function. The number of spectral elements  $M$  ( $=$  spectral span / resolution ) is equal to 500. With the recording time  $T=10 \mu\text{s}$ , we benefit from an uppermost signal-to-noise ratio of about 50. In this spectrum, the noise equivalent absorption coefficient (NEA) reaches  $3 \times 10^{-4} \text{ cm}^{-1}$ . The NEA at one second averaging per spectral element is  $(L \times \text{SNR})^{-1} \times (T/M)^{1/2} = 4 \times 10^{-8} \text{ cm}^{-1} \cdot \text{Hz}^{-1/2}$ , where  $L$  is the absorption path length. In the present spectral region, this level of sensitivity allows for the high resolution detection of 17 parts per million by volume (ppmv) of  $\text{C}_2\text{H}_2$  at 1 s of integration time per spectral element. This detection limit value is relatively high, first because the absorption path and signal-to-noise ratio of the present demonstration still require improvements, second because the combination bands of  $\text{C}_2\text{H}_2$  in this region are weak: their intensity, of the order of  $10^{-21} \text{ cm} \cdot \text{molecule}^{-1}$ , is not higher than in the 1.5  $\mu\text{m}$  region. For hydrogen fluoride HF (1-0 band, with intensity of the  $R(2)$  line at 2454 nm equal to  $2.3 \cdot 10^{-18} \text{ cm} \cdot \text{molecule}^{-1}$  [26]), the corresponding detection level is 14 parts per billion by volume (ppbv) in the 2.4  $\mu\text{m}$  spectral region.

### 3. Discussion

Further improvements to the present proof-of-principle experiment are to be implemented. The stability of the mode-locked operation of the ceramic  $\text{Cr}^{2+}:\text{ZnSe}$  lasers still remains an issue. This currently represents the main sensitivity and reliability limitations in our experiment. Consequently the instrumental resolution in the computation of the spectra is chosen as a compromise between signal-to-noise ratio and resolution of the individual rovibrational profiles. Yet, single-crystal  $\text{Cr}^{2+}:\text{ZnSe}$  active medium provide much longer-term hands-free stable operation. However, one of the most interesting promise of  $\text{Cr}:\text{ZnSe}$  is the availability of technologically developed and low-cost polycrystalline material. The existing technologies of producing ceramic ZnSe, such as chemical vapor deposition or hot pressing of powders result in low-cost substrates of arbitrary size and potential for scaling output power by producing large ceramic active elements of arbitrary shape. In the future, combined with diode-pumping,  $\text{Cr}^{2+}:\text{ZnSe}$  ceramic gain media might hold promise to become the most practical, compact and cost-effective femtosecond lasers in the mid-infrared. Once this is

achieved, the resolution of dual-comb spectroscopy can easily be improved up to a formal limit only due to the width of the comb lines by increasing the interferogram measurement time. It would also be desirable to significantly increase the measured spectral domain. The enormous gain bandwidth of the  $\text{Cr}^{2+}:\text{ZnSe}$  laser (850 nm FWHM) should indeed allow for coverage of a much broader spectral region, either by tuning, or more interestingly by construction of a few-cycle laser source to observe hundreds of nm simultaneously. As a continuous wave tuning range from 2000 to 3100 nm has already been demonstrated [27], coverage of the entire 2-3  $\mu\text{m}$  region might be feasible in an optimized Kerr-lens mode-locked configuration. Generation of a mid-infrared spectrally broadened comb with highly nonlinear fibers also looks compelling, as chalcogenide [28] and ZBLAN [29] microstructured fiber design is a rapidly evolving field. Non-linear frequency conversion processes, already demonstrated with an optical parametric oscillator [30] spanning simultaneously up to 300 nm in the 2.8-4.8  $\mu\text{m}$  range or with difference frequency generation in the 2.9 to 3.5  $\mu\text{m}$  region (in 180 nm wide spans) from mixing [31] a near-infrared erbium-doped fiber comb and a tunable continuous-wave laser, also provide interesting alternatives. Sensitivity improvement can benefit from absorption path length enhancement either by use of a classical multipass cell [32] or by injection of all the modes of the interrogating frequency comb in a resonant high finesse cavity [4], or from efficient averaging of interferograms, then at the expense of the measurement time [33].

For molecular science research, reaching the mid-infrared region is a crucial objective, as the strength of the fundamental molecular lines drastically enhances the detection sensitivity. As dual-comb Fourier spectroscopy only needs a single photodetector, it does not encounter spectral domain limitations. It can therefore be envisioned that this technique, which is still at its infancy, has the potential to vastly enhance the range and capabilities of molecular physics, similarly to the way Michelson-based Fourier transform spectroscopy revolutionized Doppler-limited molecular spectroscopy in the seventies. Instruments providing simultaneously high resolution, ultra-sensitivity, broad spectral bandwidth, high accuracy and very short measurement times would indeed meet the challenging objectives set by applications that range from detection of explosives or biologically hazardous materials to an improved experimental determination of the electron's electric dipole moment. More interestingly, such unprecedented capabilities may spark off totally new discoveries or insights in the various fields relevant to molecular sciences.

## 4. Conclusion

Summarizing, we have reported on the first implementation of dual-comb spectroscopy in the 2-7  $\mu\text{m}$  mid-infrared region. A simple experimental setup based on two  $\text{Cr}^{2+}:\text{ZnSe}$  femtosecond oscillators emitting in the 2.4 $\mu\text{m}$  region already measures spectra spanning 150 nm within 10  $\mu\text{s}$  and with 12 GHz resolution. Although stable mode-locked operation of ceramic  $\text{Cr}^{2+}:\text{ZnSe}$  lasers remains challenging, these results demonstrate a conceptually simple and robust instrumentation that is capable of mid-infrared real-time broadband absorption measurements.

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## Figure captions:

**Figure 1 Experimental set-up.** Two similar Cr<sup>2+</sup>:ZnSe femtosecond oscillators are pumped by the same 1.61  $\mu\text{m}$  continuous-wave Er-doped fiber laser. They have slightly different line spacing. One of the oscillators interrogates a single pass cell, which contains the acetylene sample under study and is heterodyned against the second oscillator on a single fast photodetector, yielding a down-converted radio-frequency comb containing information on the absorption losses experienced by each line of the interrogating fs laser. The electrical signal is digitized and is Fourier-transformed using a fast Fourier transform (FFT) algorithm.

**Figure 2.** (a) Spectrum (FWHM: 70 nm) and (b) interferometric autocorrelation of a 100-fs pulse of the Cr<sup>2+</sup>:ZnSe mode-locked laser. Pump power: 1.9 W, output power: 50 mW, repetition rate 215 MHz.

**Figure 3. Time-domain interferogram.** A interferogram sequence of 12 ms is displayed. The Fourier transform of a 10  $\mu\text{s}$  unweighted interferogram leads to a spectrum with 12 GHz unapodized resolution. The interferogram is expected to repeat itself at a period of 2.53 ms, which is the inverse of the difference in the repetition frequencies of the two combs. The bursts correspond to the overlap of two femtosecond pulses. As one of the femtosecond oscillators is running in double-pulse mode, the interferogram exhibits a double periodic sequence of bursts enlightened in blue and red.

**Figure 4 Mid-infrared dual-comb spectrum of acetylene.** The  $\nu_1 + \nu_5^1$  combination band of C<sub>2</sub>H<sub>2</sub> recorded within 10  $\mu\text{s}$  is plotted on a linear intensity scale. The 70-cm long single-pass cell is filled with 230 hPa of acetylene in natural abundance. The laser spectrum extends from 2370 to 2525 nm, with 12 GHz unapodized resolution. Signatures seen in the upper left inset around 2430 nm belong to the *R*-branch (from *R*(17e) to *R*(5e)).

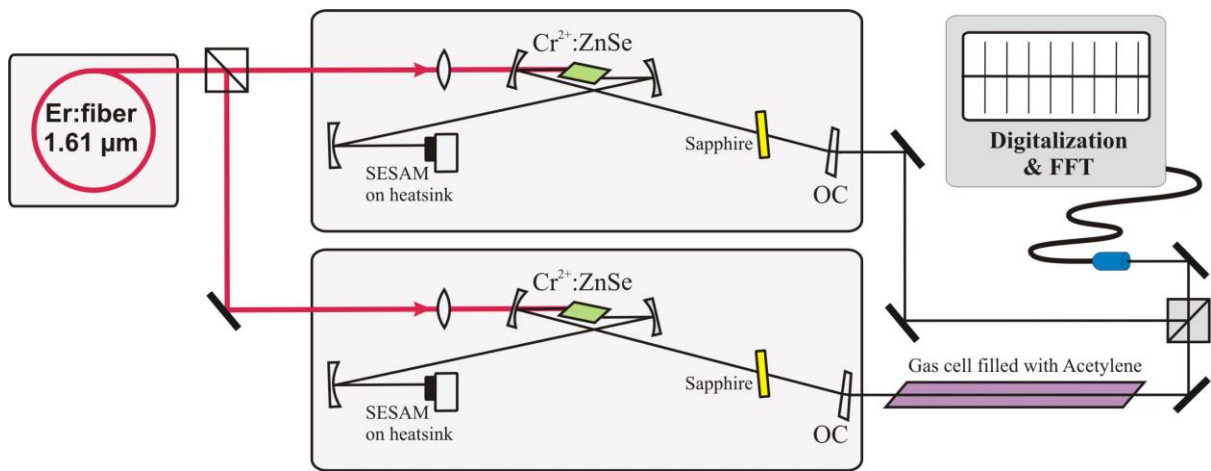


Figure 1

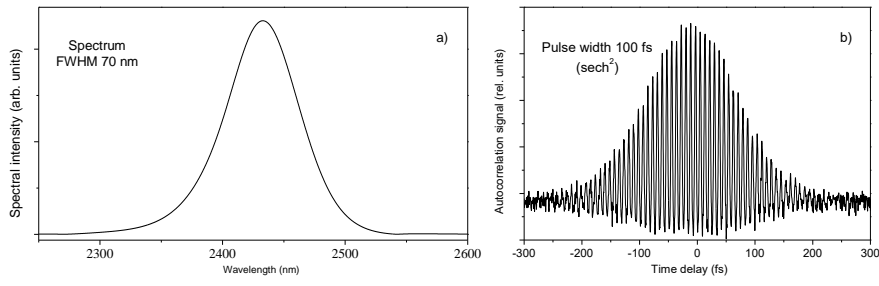


Figure 2

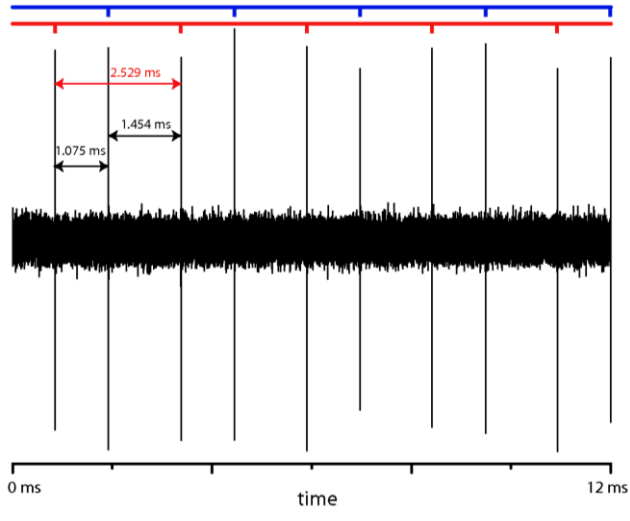


Figure 3

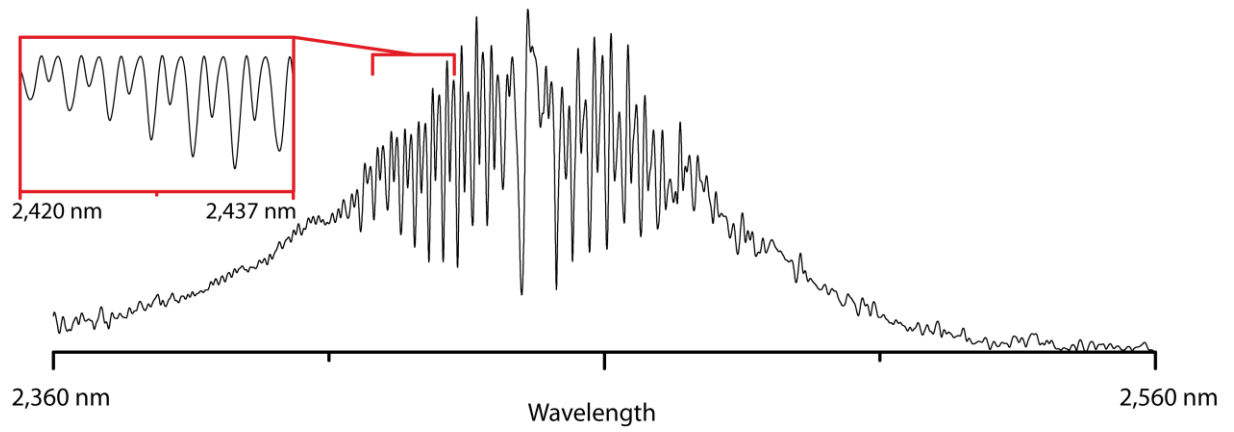


Figure 4