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► **To cite this version:**

Julien Mandon, Guy Guelachvili, Nathalie Picqué. Molecular fingerprinting with femtosecond lasers. 2008. hal-00261710v1

HAL Id: hal-00261710

<https://hal.science/hal-00261710v1>

Preprint submitted on 8 Mar 2008 (v1), last revised 20 Aug 2008 (v2)

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Efficient Two-Comb Fourier Spectroscopy

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Molecular fingerprinting through absorption spectroscopy is a powerful analytical method. Light is sent through the analysed medium and its chromatic absorption provides the required information.

Fundamental and applied domains benefit from absorption spectroscopy essentially based on laser and Fourier transform spectroscopies. Wide spectral ranges are explored with Doppler-limited resolution. Fast data acquisition, accurate measurements of frequency, intensity, and line shape; time-resolved, selective spectra are achieved with excellent sensitivities.

However, presently spectrometers are unable to provide all these features at once.

Here we show with experimental evidence that, based on frequency comb lasers, a spectrometer may overcome this difficulty.

We have recorded two series of spectra with a 1.5 μm home-made Cr^{4+} YAG femtosecond frequency comb. In the first series, we propose to use the comb structure to considerably improve the recording time and signal to noise ratio of Doppler-resolved spectra, which are Fourier transform of the beating signatures of two combs issued from the same initial laser. The second series demonstrates that under very simple experimental conditions, Fourier transform spectroscopists may record much more sensitive spectra, thanks to the brightness of the comb replacing the usual incoherent white light source.

Our results show that femtosecond frequency comb spectroscopy is able to provide in a single experiment, multiple species spectra covering at once more than 165 nm with an unapodized resolution equal to 185 MHz. A new detection scheme based on the beating of neighbouring comb lines is proposed to improve the signal to noise ratio. Additionally in a single experiment absorption and dispersion line shapes are measured at once.

The final improvement is to reach recording time and resolution at the limit with Fourier spectroscopy based on two independent frequency combs.

High resolution spectroscopy is a well established powerful tool for a great variety of fundamental and applied domains, from the quantum description of matter to non-intrusive diagnostics of various media. It is also presently the subject of a recent intense research activity in instrumental methodology for solving basic and applied issues at the forefront limits. Intent is to implement new instruments gifted for fast and sensitive acquisition of accurate and well resolved data over large spectral bandwidth.

Currently these characteristics are not available from a single instrument. Each experimental set-up is a trade-off against the predominant scientific requirements. For instance, tunable lasers provide rapid, resolved and sensitive answer on narrow spectral ranges. On the other hand, Fourier transform (FT) spectrometers are the most efficient instruments to get high resolution spectra over extended spectral ranges, often recorded during hours with limited sensitivity.

New strategies for the next generation of spectroscopic instruments aim at implementing devices gathering together all virtues separately found in various spectrometers. Femtosecond frequency combs¹ made of equidistant narrow lines with stable and accurate individual positions are very attractive new laser sources to achieve this objective.

Papers^{2,3,4,5,6} based on the formal approach of Schiller⁷ have reported spectroscopic results with femtosecond frequency combs. Two combs with slightly different repetition rates probe the sample and beat with each other. The spectrum is provided by the Fourier transform analysis of the harmonic beat signatures. Experimental results have also been given on the same principle with one unequally spaced cw frequency comb⁸. Another efficient spectroscopic advance with combs rests on two dimensional measurements^{9,10,11,12,13,14,15} with grating and array detectors, together with cavity-based sensitivity enhancement^{9,10,11,12}. None manage to analyse the whole light available from the comb in a single experiment and the best resolution¹⁰ with gratings is 800 MHz. Presently, all these methods have fast acquisition times but only narrow spectral ranges are recorded. As stated in¹²: "...recording the full bandwidth in a single measurement proved challenging".

In this contribution, we present a versatile approach to frequency comb spectroscopy which, unlike previous reports, provides in a single measurement, with no spectral range restriction, instrumental resolution better than the width of the Doppler-broadened profiles (a few hundreds of MHz in the infrared).

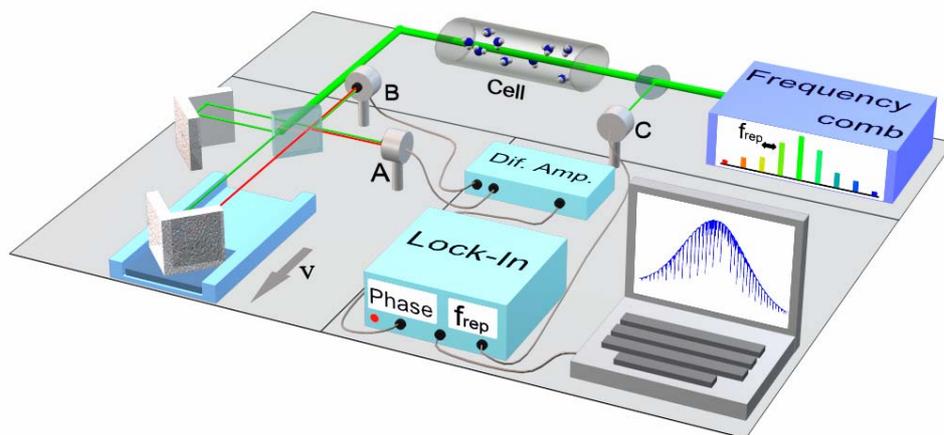


Figure 1. Two-comb experiment principle.

After interacting with a sample, the comb of the comb with a repetition rate f_{rep} enters the Michelson FT interferometer with a moving mirror assembly at velocity v . Fast detectors A, B measure the beating of two different laser combs. The comb traveling along the fixed mirror arm keeps the original f_{rep} . The other one has a Doppler-shifted repetition rate equal to $f_{rep}(1 - 2v/c)$ with c speed of light. The component of the interferogram which is unmodulated by path difference is removed by the differential amplifier to improve the dynamics of the

measurements. The path-difference-modulated component is synchronously detected at f_{rep} by the lock-in amplifier. The reference signal is provided by the detector C receiving about 10% of the initial comb light. Absorption and dispersion spectra are essentially respective Fourier transforms of the in-phase and in-quadrature signals from the lock-in amplifier.

The experiment principle is schematized on Figure 1. Ultra-short pulses, periodically emitted by a mode-locked laser with a pulse repetition frequency f_{rep} , interact with an atomic/molecular sample enclosed in a single or multipass cell, or in a high finesse cavity. The laser beam is sent to an FT interferometer recording the data versus the path difference $2vt$ (t : time, v : constant velocity of the moving mirror assembly). Two interfering frequency combs with f_{rep} and $f_{\text{rep}}(1 - 2v/c)$ respective frequency rates exit from the Michelson interferometer. c is the speed of light. The signal measured by two receivers, A and B, is synchronously detected at f_{rep} . Since f_{rep} can be in the radio frequency (rf) range 0.1-5 GHz, our time-domain method reduces considerably the technical noise when compared to the presently best commercial interferometers detecting interferograms at audio frequencies around 20 kHz. Additionally absorption and dispersion parameters are given at once from the FT of the in-phase and in-quadrature rf signals detected by the lock-in amplifier. Our method is similar to frequency-modulation spectroscopy with tunable lasers¹⁶. It has the additional benefits of broadband coverage, no need of external modulation and optimal modulation index.

Two distinct demonstrative experimental results, recorded with a home-made high resolution Connes-type FT interferometer, are presented. Both make use of a home-made frequency comb based on 20-mm-long Brewster-cut Cr^{4+} :YAG crystal pumped by a 1064 nm Nd:YVO₄ laser. With a semiconductor saturable absorber mirror for mode-locking and chirped mirrors for dispersion compensation, the laser generates pulses of approximately 40 fs, in the 1.5 μm region, with a repetition rate of 140 MHz and about 50 mW average output power. The oscillator operates under primary vacuum to reduce atmospheric absorption.

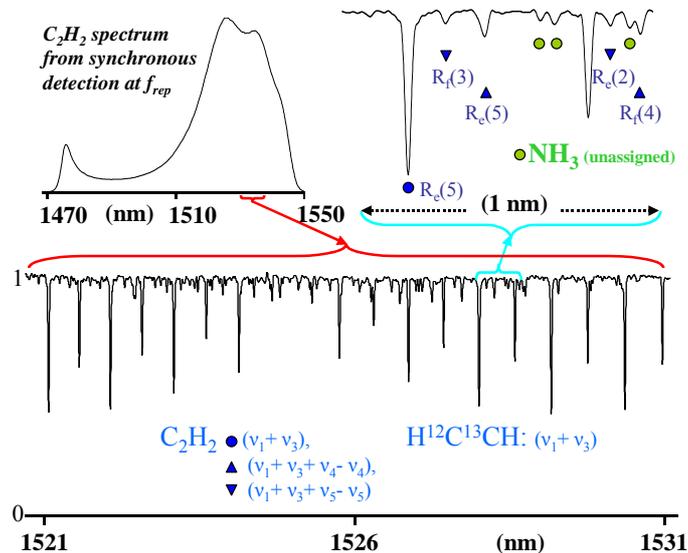


Figure 2. In-phase rf detected spectrum of C_2H_2 probed by a Cr^{4+} : YAG comb

FT spectrum of overtone bands of C_2H_2 recorded according to the principle described in Figure 1. A 70-cm long cell is filled with 12 hPa of acetylene in natural abundance. The left upper part is the full spectrum at extremely low resolution, Fourier transform of a very restricted first portion of the interferogram beginning at path difference zero. The spectrum extends from 1470 to 1550 nm ($6800\text{-}6450\text{ cm}^{-1}$). A 10 nm fully resolved portion around 1526 nm, reveals the rotational fine structure of the bands. The Doppler line shapes are made obvious on the upper right part of the figure. Unexpected traces of NH_3 in the cell are detected.

The first results are recorded according to the principle described in Figure 1 and explained in the Method section. The interferometer is equipped with fast InGaAs detectors. Synchronous detection at 140 MHz frequency is performed by a commercial lock-in amplifier, unable to reconstitute the demanding dynamics of the interferogram. A ratio of more than 10^6 may indeed exist between the most intense and the weakest interferogram samples. Even so, the recorded spectra, shown on Figure 2 and Figure 3, are satisfactory. They will be drastically improved after the ongoing installation of a recording solution similar to an already well tested one that we developed for time resolved spectroscopy¹⁷. Data storage and computation are performed on personal computers. Figure 2 depicts the in-phase detected spectrum of overtone vibrational bands of acetylene. Unapodized resolution is 1.5 GHz ($50 \cdot 10^{-3} \text{ cm}^{-1}$). Even under poor dynamics conditions, the signal to noise ratio (SNR) is about 500, the recording time 280 s for 7200 spectral elements and the noise equivalent absorption coefficient (NEA) at 1-s averaging, with a 70 cm absorption path, is $5 \cdot 10^{-6} \text{ cm}^{-1} \cdot \text{Hz}^{-1/2}$ per spectral element. Figure 3 demonstrates the agreement between experimental and simulated data, on both the absorption and the dispersion signatures.

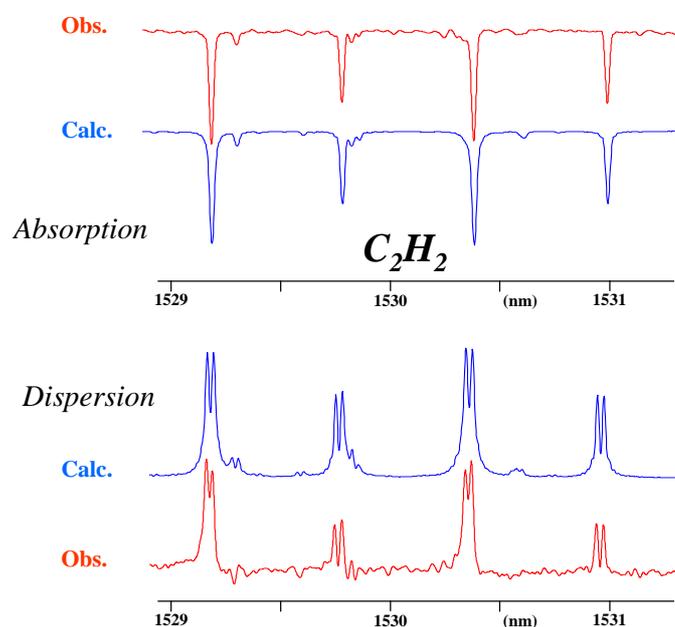


Figure 3. Comparison between observed and simulated spectra

Portions of the C_2H_2 spectrum shown on Figure 2. The calculations are performed according to Equation 2 in the Method section. All the experimental profiles are well reproduced by the simulation.

The second results are recorded according to the description given by Figure 1 without the C detector and the rf lock-in amplifier. This is the classical FT absorption configuration, with the usual incoherent white light source replaced by the frequency comb. The modulation of the interferogram is now in the audio frequency range and standard InGaAs detectors are suitable. The rf modulation rewards on the noise reduction and the access to absorption and dispersion parameters are absent. Nevertheless we still benefit from the brightness of the frequency comb. The spectrum shown on Figure 4 covers more than 165 nm (695 cm^{-1}). The NEA at 1-s averaging, with a 40 m absorption path, equals $3.9 \cdot 10^{-8} \text{ cm}^{-1} \cdot \text{Hz}^{-1/2}$. About 112 000 individual spectral elements are simultaneously recorded with 185 MHz ($6.2 \cdot 10^{-3} \text{ cm}^{-1}$) instrumental resolution and a SNR at best equal to 1000. The rotationally resolved structures of complete vibrational bands belonging to five different molecules shown on Figure 4 illustrate the excellent efficiency of the molecular fingerprinting approach given by this conceptually very simple experiment.

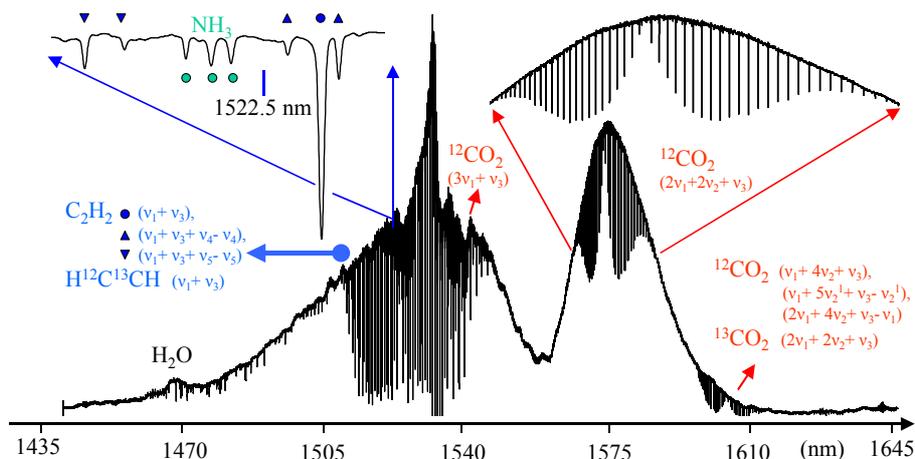


Figure 4. Absorption spectrum of C_2H_2 and CO_2 recorded with a Cr^{4+} : YAG comb source by traditional Fourier spectroscopy.

The instrumental set-up may still be described by Figure 1, provided the C detector and the rf lock-in amplifier are removed from the figure. The spectrum is obtained with a White-type multiple pass cell adjusted to 40-m absorption path and filled up with 8 hPa of CO_2 (Doppler width: 350 MHz) and 0.17 hPa of C_2H_2 (Doppler width: 475 MHz). It is recorded in 45 minutes in a single experiment, and extends over more than 165 nm, from 1460 to 1625 nm (6849 to 6154 cm^{-1}). The laser emission is broader than on Figure 2, thanks to a Kerr lens more effective contribution. The unapodized instrumental resolution is 185 MHz ($6.2 \cdot 10^{-3}$ cm^{-1}).

The two-comb spectroscopy results shown in Figure 2, Figure 3, and in Figure 4 illustrate the following unprecedented advantages. All the spectral elements are measured simultaneously with one detector in a single experiment covering the whole comb extension. The resolution is better than the Doppler width of the molecules at low pressure observed in the near infrared. Actually it is limited by f_{rep} . The overall consistency of the intensity and frequency scales is granted by the FT approach. Absorption and dispersion parameters are measured simultaneously. Grating dispersers, concatenation of sequentially recorded spectral portions, array detectors are not needed.

Our Michelson-based two-comb spectroscopy exploits one single initial comb. Its carrier envelop offset and frequency rate fluctuations are similarly reported on the two interfering combs. This practically eliminates related degrading effects on the measurements. The present results may be obtained by a multitude of Michelson-based FT spectrometers. The simplest procedure would be to replace their white lamp by the frequency comb. Low resolution spectra have already been obtained from mode-locked lasers^{18,19} and optical parametric oscillators²⁰. In particular, at GHz resolution, a recording time reduction by more than 2 orders of magnitude in the 1.5 and 2.5 μm regions^{18,19}, due only to the comb brightness, was demonstrated. The adaptation of the data recording system of the existing FT spectrometers to our rf approach, according to the principle shown on Figure 1, would be more demanding but worthwhile. It would bring an additional SNR improvement ability of at least four orders of magnitude. Nevertheless, Michelson-based two-comb Fourier spectroscopy, even with renewed designs of faster interferometers, is faced, for mechanical reasons, to redhibitory limitations on spectral resolution (~ 5 MHz) and recording time (~ 5 s).

We have shown the importance of the well established FT spectroscopic approach for two-comb spectroscopy. For the first time, high resolution and simultaneous observation absorption and dispersion over the whole comb extension are obtained from a single detector

which is the only spectral range limitation. Practically we validate powerful multiplex spectroscopy from the beating of two different frequency combs. Recent excellent spectra⁴, recorded in about 1 s, on 2 nm segments with a resolution of 100 kHz support this statement. Clearly, path is open to the implementation of two-comb Fourier spectrometry gathering all dreamed qualities: acquisition time at the limit, extreme sensitivity, low to very high resolution, extreme accuracies, absorption and dispersion, instrument compactness, spectral extension from THz to VUV. The domains of relevance include biology, chemistry, environment, industry, medicine, and physics. All the well tested tools and the experience of traditional FT spectroscopy can straightforwardly be taken advantage of: hyperspectral imaging, microscopy, spatial resolution, time resolution, selectivity (vibrational circular dichroism, ions, paramagnetic species, short-lived radicals), attenuated total reflection. Systematic acquisition of excellent dispersion profiles may boost interest in fields left aside for experimental complexity reasons. The applications include solid, liquid, gas states characterization, industrial process control, fundamental spectroscopy and dynamics, fundamental tests and variation of fundamental constants, rarefied samples characterization (cold atoms and molecules), trace gas detection (pollution, risk management), real time spectroscopy.

Method

The electric field at the output of a mode-locked laser having a pulse envelope $\mathbf{A}(t)$ of $1/f_{\text{rep}}$ periodicity and a carrier pulsation ω_c may be written as

$$E_1(t) = \mathbf{A}(t) \exp(i\omega_c t) + \text{c.c.} = \sum_n A_n \exp [i(\omega_c + n\omega_{\text{rep}})t] + \text{c.c.} \quad (1)$$

where A_n are Fourier components of $\mathbf{A}(t)$, n is an integer and $\omega_{\text{rep}} = 2\pi f_{\text{rep}}$ and c.c. stands for the conjugate complex of the preceding expression in Eq. 1. When interacting with the gas, each pulsation component of the electric field experiences attenuation and phase-shift due to absorption and dispersion. Following the notations in¹⁶, this interaction may be written as $\exp [-\delta(\omega) - i\phi(\omega)]$ where δ is the amplitude attenuation and ϕ the phase shift. Consequently, at the output of the cell, the electric field E_2 is:

$$E_2(t) = \sum_n A_n \exp[-\delta(\omega_c + n\omega_{\text{rep}}) - i\phi(\omega_c + n\omega_{\text{rep}})] \exp i[(\omega_c + n\omega_{\text{rep}})t] + \text{c.c.}$$

This radiation is then analyzed by the interferometer. The electric field E_3 at its output port A may be written as a function of path difference Δ :

$$E_3(\Delta, t) = \frac{1}{2} E_2(t) + \frac{1}{2} \sum_n A_n \exp [-\delta(\omega_c + n\omega_{\text{rep}}) - i\phi(\omega_c + n\omega_{\text{rep}})] \exp \{i[(\omega_c + n\omega_{\text{rep}})t - (\omega_c + n\omega_{\text{rep}})\Delta/c]\}$$

where c is the velocity of light.

For the sake of simplicity, the following notations are adopted: $\delta_n = \delta(\omega_c + n\omega_{\text{rep}})$ and $\phi_n = \phi(\omega_c + n\omega_{\text{rep}})$. Detected by a fast photodetector the interferogram $I(\Delta, t)$ is proportional to $E_3 E_3^*$ which contains a term $I_{\text{frép}}(\Delta, t)$ oscillating at the constant f_{rep} frequency and carrying spectral information of the absorption and dispersion parameters of the lines interacting with the comb. With the assumption that, whatever n , $A_n = A$, $I_{\text{frép}}(\Delta, t)$ is proportional to:

$$\begin{aligned} I_{\text{frép}}(\Delta, t) \propto & \sum_n \frac{1}{4} A A^* \cos(\omega_{\text{rep}} t) \times \left\{ \cos[(\omega_c + n\omega_{\text{rep}})\Delta/c] \times [\cos(\phi_{n-1} - \phi_n) \exp(-\delta_{n-1} - \delta_n) + \right. \\ & \left. \cos(\phi_n - \phi_{n+1}) \exp(-\delta_n - \delta_{n+1})] \right. \\ & \left. + \sin[(\omega_c + n\omega_{\text{rep}})\Delta/c] \times [\sin(\phi_{n-1} - \phi_n) \exp(-\delta_{n-1} - \delta_n) - \right. \\ & \left. \sin(\phi_n - \phi_{n+1}) \exp(-\delta_n - \delta_{n+1})] \right\} \\ + & \sum_n \frac{1}{4} A A^* \sin(\omega_{\text{rep}} t) \times \left\{ -\cos[(\omega_c + n\omega_{\text{rep}})\Delta/c] \times [\sin(\phi_{n-1} - \phi_n) \exp(-\delta_{n-1} - \delta_n) + \right. \\ & \left. \sin(\phi_n - \phi_{n+1}) \exp(-\delta_n - \delta_{n+1})] \right. \\ & \left. + \sin[(\omega_c + n\omega_{\text{rep}})\Delta/c] \times [\cos(\phi_{n-1} - \phi_n) \exp(-\delta_{n-1} - \delta_n) - \right. \\ & \left. \cos(\phi_n - \phi_{n+1}) \exp(-\delta_n - \delta_{n+1})] \right\} \quad (2) \end{aligned}$$

Equation 2 gives the in-phase and in-quadrature intensity-modulated parts of the recorded interferogram. The modulation at f_{rep} in the radio-frequency range provides very high sensitivities with rapid signal recovery. The absorption of the lineshapes is the preponderant factor in the in-phase detected signal. The in-quadrature detected interferogram carries essentially the dispersion contribution.

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