

Fourier transform spectroscopy with a laser frequency comb

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Molecular fingerprinting using absorption spectroscopy is a powerful analytical method, particularly in the infrared, the region of intense spectral signatures. Fourier transform spectroscopy—the widely used and essential tool for broadband spectroscopy—enables the recording of multi-octave-spanning spectra, exhibiting 100 MHz resolution with an accuracy of 1×10^{-9} and 1×10^{-2} in wavenumber and intensity determination, respectively. Typically, 1×10^6 independent spectral elements may be measured simultaneously within a few hours, with only average sensitivity. Here, we show that by using laser frequency combs as the light source of Fourier transform spectroscopy it is possible to record well-resolved broadband absorption and dispersion spectra in a single experiment, from the beating signatures of neighbouring comb lines in the interferogram. The sensitivity is thus expected to increase by several orders of magnitude. Experimental proof of principle is here carried out on the 1.5- μm overtone bands of acetylene, spanning 80 nm with a resolution of 1.5 GHz. Consequently, without any optical modification, the performance of Fourier spectrometers may be drastically boosted.

Gas-phase spectroscopy is a well-established and powerful tool for use in a great variety of fundamental and applied domains, from the quantum description of matter to non-intrusive diagnostics of various media. Related intense research in instrumental methodology is presently being undertaken to develop and implement new spectrometers with the advantages of fast and sensitive acquisition of accurate and well-resolved data over a large spectral bandwidth. Currently, these characteristics are not available from a single instrument. Each experimental set-up is a tradeoff against the predominant scientific requirements. For instance, Fourier transform spectrometers are most efficient in obtaining well-resolved spectra over extended spectral ranges, these often being recorded over several hours with only average sensitivity. Conversely, tunable lasers provide rapid, highly resolved and sensitive answers, but over restricted spectral ranges.

Femtosecond frequency combs¹ (FCs) made of equidistant narrow lines with stable and accurate individual positions are very attractive laser sources used recently to develop new strategies for improved spectrometers. Other researchers^{2–7} have reported spectroscopic results with FCs based on the formal approach of Schiller⁸. Two combs with slightly different repetition rates probe the sample by beating with each other. The spectrum is provided by harmonic analysis of the beating signatures. One unequally spaced c.w. frequency comb⁹ may be used in a similar manner. Another efficient spectroscopic advance with combs relies on two-dimensional measurements^{10–17} using grating and array detectors, together with cavity-based sensitivity enhancement^{10–15,17}. None manages to analyse the whole light available from the comb in a single high-resolution experiment. These comb spectroscopies rarely resolve the individual comb modes, but take advantage of different aspects of the comb structure.

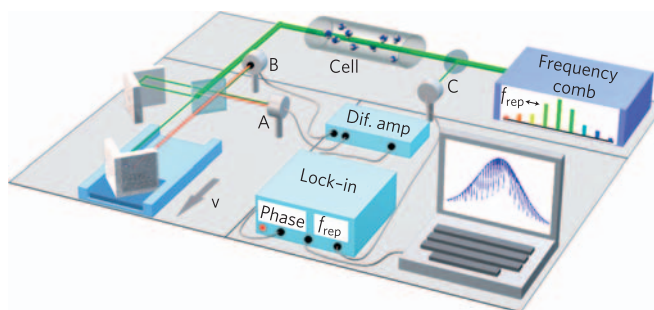


Figure 1 | Principle of the FC-FTS experiment. After interacting with a sample, the beam of the comb, with a repetition rate f_{rep} , enters the FT interferometer. Fast detectors A and B measure the interferogram as a function of the difference between the optical path in each arm of the interferometer. Their signals are synchronously detected at f_{rep} by the lock-in amplifier. The reference is provided by the detector C, receiving about 10% of the initial comb light. Absorption and dispersion spectra are essentially Fourier transforms of the in-phase and in-quadrature signals from the lock-in amplifier, respectively.

In this contribution, we present an original method combining FCs with Fourier transform spectroscopy (FTS). It aims to provide, in a single experiment, wide spectral ranges only limited by the comb spectral extension, instrumental resolutions from very low (a few hundreds of GHz) to high enough (a few hundreds of MHz) for a full description of the Doppler profiles, and a large reduction in the traditional recording times of FTS. We report two experiments. The first, FC-FTS, enables the measurement of absorption and dispersion sensitive spectra simultaneously and requires the interferometer electronics to be modified. Although less powerful, the second experiment increases the sensitivity of traditional absorption FTS with the use of commercially available devices only.

The FC-FTS first experiment principle is presented in Fig. 1. Ultrashort pulses, periodically emitted by a mode-locked laser with a repetition frequency f_{rep} , interact with an atomic/molecular sample in a single or multipass cell, or in a high-finesse cavity. The comb beam is sent to a FT interferometer. The interferogram is synchronously detected at f_{rep} by two receivers. Because f_{rep} is in the range 0.1–5 GHz, FC-FTS is expected to reduce the $1/f$ technical noise by three to five orders of magnitude when compared with the best interferometer measurements to date performed at an upper modulation frequency of 50 kHz. Moreover, a single measurement provides absorption and dispersion parameters from in-phase and in-quadrature detection by the lock-in amplifier. FC-FTS (explained in the Supplementary Information, Methods) is similar to frequency-modulation laser spectroscopy¹⁸, but with the additional benefits of broadband coverage, no need for external modulation, and an optimal modulation index.

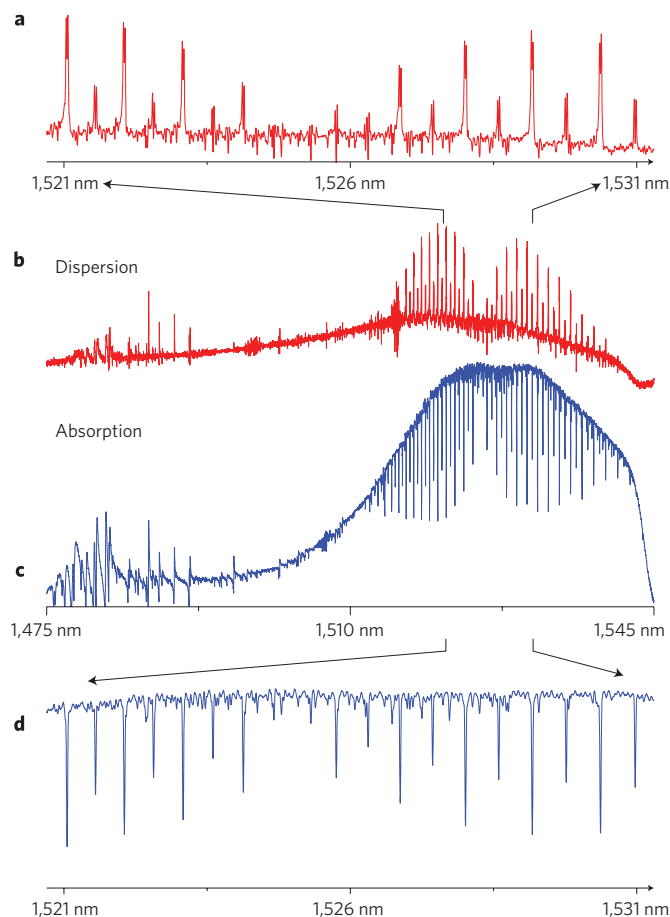


Figure 2 | In-quadrature and in-phase FC-FTS spectra of C_2H_2 probed by a Cr^{4+} :YAG comb. **a–d**, The overtone bands of C_2H_2 recorded according to the FC-FTS principle illustrated in Fig. 1 are plotted with a linear intensity scale. The cell is filled with 12 hPa of C_2H_2 in natural abundance. The laser spectrum extends from 1,470 to 1,550 nm. In-quadrature and in-phase detections provide, respectively, dispersion and absorption from the same experiment. Dispersion (**b**) and absorption (**c**) spectra of the full recorded range on the same frequency scale. **a** and **d** show zoomed sections of spectra **b** and **c**. Both dispersion and absorption spectra report the C_2H_2 intensity alternation of the intense $\nu_1 + \nu_3$ vibrational band centred at 1,525.2 nm. Signatures seen on **b** and **c** around 1,485 nm are dispersion profiles induced by residual atmospheric water inside the laser cavity (see in ref. 26). Within the same recording time, a laser span as wide as 1,000 nm could have been recorded with the interferometer.

Proof-of-principle spectra of the first experiment with the FC-FTS method were recorded with our Connes-type¹⁹ two-output stepping-mode interferometer equipped with fast InGaAs detectors (Figs 2 and 3). The laser frequency comb source generated pulses of ~ 40 fs with ~ 50 mW average output power in the 1.5 μm region, with f_{rep} set to 140 MHz. Its cavity included a Cr^{4+} :YAG crystal pumped by a 1,064 nm Nd:YVO₄ laser, a semiconductor saturable absorber mirror for mode-locking, and chirped mirrors for dispersion compensation. Synchronous detection was performed using a commercial lock-in amplifier. Data storage and computation were performed on personal computers.

Figure 2 depicts absorption and dispersion spectra of overtone vibrational bands of acetylene (C_2H_2) in a single path cell. The absorption path length L is 70 cm. The resolution is 1.5 GHz, the signal-to-noise ratio (SNR) in the spectral domain for the most intense line is ~ 500 and the recording time $T = 280$ s for $M = 7,200$ spectral elements (SE) ($M = \text{span}/\text{resolution}$).

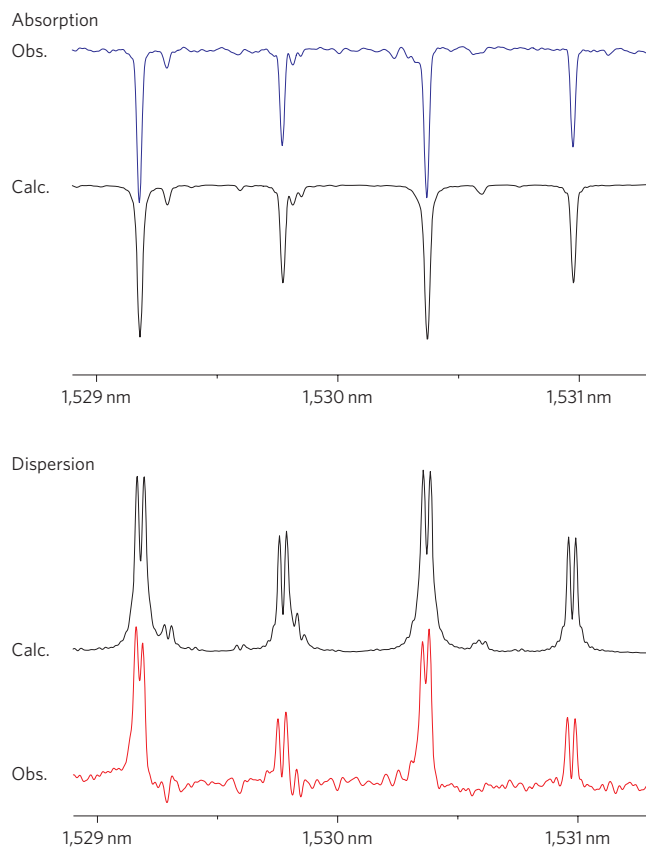


Figure 3 | Comparison between observed and simulated spectra. Portions of the C_2H_2 spectrum shown in Fig. 2 are plotted with a linear intensity scale. (The *ab initio* calculations are performed according to equation (2) in the Supplementary Information, Methods.) All the experimental profiles are well reproduced by the simulation.

To account for the FC-FTS multiplex nature, the noise equivalent absorption coefficient (NEA) at 1 s time averaging per SE is defined as $(L \times \text{SNR})^{-1} \times (T/M)^{1/2}$. Indeed, although tunable lasers may achieve higher sensitivities than our system for single spectral features, our approach is less time-consuming in achieving good sensitivity across an extended span. Here, the NEA is $5 \times 10^{-6} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per SE. The present limitation arises only from the restricted dynamic range of the commercial lock-in amplifier. It presently restricts the SNR and resolution of the recorded spectra. Future work will include the development of dedicated electronics, based on well-tested methodological solutions²⁰. Nevertheless, as shown in Fig. 3, experimental spectra are well reproduced by the calculated simulation. Moreover, the data show a sixfold improvement in NEA when compared with a spectrum that we recorded with a tungsten lamp under similar experimental conditions (recording time, gas pressure absorption path, and so on). Another check of the quality of the spectra is made by assessing their frequency accuracy by comparing the measured frequencies of 34 $^{12}C_2H_2$ absorption lines to excellent references²¹. The resulting standard deviation equal to 29 MHz is quite consistent with the expected line position uncertainties related to SNR and linewidth.

The advantage of FC-FTS arising from the brightness of the femtosecond laser replacing the usual source in absorption FTS is actually available in all spectral approaches^{22–24} making use of broadband lasers. We have already demonstrated, at 6 GHz resolution, a factor of 150 reduction in recording times²³, even with a reduced laser flux to avoid detector saturation. In the second experiment we show, at 185 MHz resolution and with a high-resolution

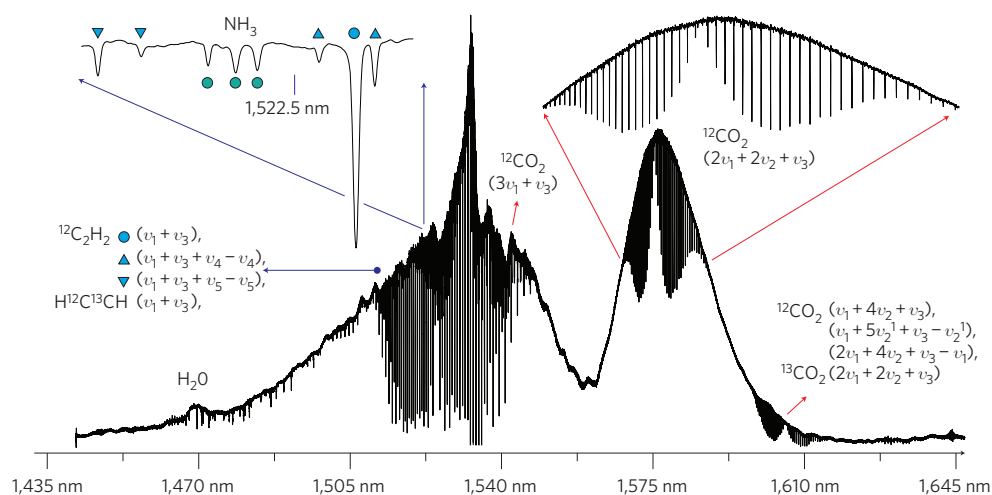


Figure 4 | Absorption spectrum of C_2H_2 and CO_2 recorded with a Cr^{4+} :YAG comb source by traditional Fourier spectroscopy. The instrumental set-up may still be described by Fig. 1 without detector C and the RF lock-in amplifier. The spectrum, plotted with a linear intensity scale, is obtained with a White-type multiple-pass cell filled with 8 hPa of CO_2 (Doppler width: 350 MHz) and 0.17 hPa of C_2H_2 (Doppler width: 475 MHz). It was recorded in a single experiment, and extends over more than 165 nm, from 1,460 to 1,625 nm. The laser emission is broader than that of Fig. 2, thanks to a more effective Kerr lens contribution.

interferometer¹⁹, that using excess light power to increase the absorption path to $L = 40$ m gives access to sensitive NEA. Indeed, an FT spectrum, as shown in Fig. 4, comprising 112,000 spectral elements covering 165 nm, recorded in 45 min with a SNR in the spectral domain at best equal to 1,000, has a NEA equal to $3.9 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per SE. With a white lamp and identical experimental conditions, the SNR is degraded by a factor of 13. To obtain identical results, the recording time would have had to have been 169 times longer. By comparing 35 $^{12}CO_2$ line frequencies of the $2\nu_1 + 2\nu_2 + \nu_3$ vibrational band to accurate wavenumbers²⁵ we find a standard deviation of the measurements equal to 3.3 MHz. The frequency accuracy is, as expected, better than with the above proof-of-principle FC-FTS spectrum.

The current FC-FTS results present the following unprecedented advantages. Absorption and dispersion spectra are measured simultaneously in a single experiment limited only by the comb spectral extension. The resolution ($\geq f_{\text{rep}}$) is of the order of the Doppler width of the low-pressure molecules in the near-infrared. Excellent consistency of the intensity and frequency scales is provided by FTS (ref. 19). Grating dispersers, concatenation of sequentially recorded spectral portions and array detectors are not needed. FC-FTS is transferable to any FT spectrometers without structural modifications. Because it makes use of a single frequency comb, no sophisticated phase-locking electronics to control the carrier-envelope offset and repetition rate are needed, whereas these are crucial in two-comb Fourier spectroscopy⁴. It is expected that the current set-up will improve, by more than five orders of magnitude, the sensitivity of classical absorption FTS. This results first from the interferogram being detected at the RF comb repetition rate (140 MHz) instead of the audio range (10 kHz), which provides potentially four orders of magnitude $1/f$ noise reduction, and second, from the laser frequency comb that is used instead of the traditional white lamp, bringing one order of magnitude improvement. All Fourier spectrometers, whatever their resolution, may benefit from this approach. Although less promising, simply coupling a comb to a multipass cell easily increases sensitivity and is straightforward to apply with commercial devices. Furthermore, FC cavity-enhanced spectroscopy has recently demonstrated spectacular sensitivities¹¹, and it could benefit from the ability of FC-FTS to handle a huge amount of spectral data.

The interferometer records the interference pattern between two combs with slightly different f_{rep} because the light reflected by the moving mirror of the interferometer is Doppler shifted. This has strong similarities with the recent promising spectroscopy making use of two different combs⁴. Our method is, for mechanical reasons, limited to achieving a highest spectral resolution of ~ 5 MHz in ~ 5 s recording time. Commercial interferometers are already available with 15 MHz resolution. With renewed designs, it is possible to multipass the interferometer, as demonstrated in ref. 27. High-frequency detection enables faster scanning of the fringes, and furthermore, the small étendue of laser beams enables a compact instrument. Our method is particularly well suited for Doppler-limited spectroscopy. The domains of relevance include biology, chemistry, the environment, industry, medicine and physics. All the well-tested tools of traditional FTS can be taken advantage of easily, including hyperspectral imaging, microscopy, time resolution, selectivity and attenuated total reflection. Systematic acquisition of excellent dispersion profiles may boost interest in fields neglected because of experimental complexity. Applications include solid, liquid and gas states characterization, industrial process control, spectroscopy and dynamics, rarefied sample characterization, trace gas detection and real-time spectroscopy.

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Additional information

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