

Frequency-comb infrared spectrometer for rapid, remote chemical sensing

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Abstract: We demonstrate real-time recording of chemical vapor fluctuations from 22m away with a fast Fourier-transform infrared (FTIR) spectrometer that uses a laser-like infrared probing beam generated from two 10-fs Ti:sapphire lasers. The FTIR's broad 9 – 12 μm spectrum in the "molecular fingerprint" region is dispersed by fast heterodyne self-scanning, enabling spectra at 2 cm^{-1} resolution to be recorded in 70 μs snapshots. We achieve continuous acquisition at a rate of 950 IR spectra per second by actively manipulating the repetition rate of one laser. Potential applications include video-rate chemical imaging and transient spectroscopy of e.g. gas plumes, flames and plasmas, and generally non-repetitive phenomena such as those found in protein folding dynamics and pulsed magnetic fields research.

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1. Introduction

Distinguishing among chemical species is commonly done by spectroscopy of molecular vibrations arising from intramolecular forces. The frequencies of vibrational "fingerprints" range from approximately 10 to 100 THz (or 300 to 3000 cm^{-1}), and are measured typically either by Raman scattering or by direct absorption with Fourier-transform infrared (FTIR) spectrometers [1]. While FTIR spectroscopy is a standard tool in many chemical and biological laboratories, its application is limited to the investigation of relatively slow phenomena as it relies on mechanically scanned mirrors to record the interferogram, placing speed limits on the acquisition of spectra. This limitation can be overcome in the case of externally triggered, repeatable processes by the step-scan method which allows time resolution in the nanosecond range [2]. For the general case, however, 200 spectra/s is the fastest acquisition rate reported for a mechanically-scanned FTIR [3]. Another drawback of conventional FTIR spectrometers is their weak and—more important—incoherent blackbody source which severely limits the attainable focus size in infrared microscopy, and also the stand-off distance in remote sensing applications. Infrared lasers provide a solution in some cases, but do not allow fast broadband sensing as their wavelengths are either fixed or can be tuned within a relatively narrow frequency range only.

Recently we introduced a new type of frequency-comb FTIR (c-FTIR) that overcomes these limitations and demonstrated its feasibility in a preliminary experiment [4]. c-FTIR uses femtosecond laser-based broadband IR sources [5] and disperses the spectrum in time, at virtually unlimited speed because it uses no moving parts. Here we present measurements demonstrating the high quality and resolution attainable. For the first time, we acquire IR spectra several orders of magnitude faster compared to a commercial FTIR spectrometer by manipulating the femtosecond-laser cavity. Furthermore, the spatially coherent beam of c-FTIR with its dramatically improved brightness allows us to sense chemical content and fluctuations at considerable distances. By providing the fastest-reported time-resolved open-path FTIR for remote sensing by probing the absorption spectra of fluctuating NH_3 vapor 22 m away from the spectrometer, this new development opens the way for many more applications.

2. Multi-heterodyne spectroscopy with frequency combs

When two electromagnetic waves of slightly different frequency superimpose and interfere on a power detector the output signal contains a modulation (“beat”) at the difference frequency. In many measurement situations this frequency is placed in a convenient radio-frequency (rf) range, and the registration of the beat amplitude (and phase) is referred to as the heterodyne measurement of the waves’ amplitude (and phase). We have extended this principle to frequency combs (evenly spaced spectral lines) and thus introduced a broadband, quasi-continuous, coherent spectroscopy [6]. Multi-heterodyne spectroscopy uses the superposition of two slightly detuned, harmonic frequency combs, i.e. two series of waves with harmonically related frequencies nf_r and $n(f_r + \Delta)$, respectively, where $n = M, M + 1, \dots, N$ and $\Delta \ll f_r$. Pairwise interference of waves with identical harmonic order n generates a detector signal modulation at a series of harmonically related beat frequencies $n\Delta$. This beat-frequency comb enables a multi-heterodyne, simultaneous determination of all harmonic waves’ amplitudes (and phases), and thus of a broadband complex-valued spectrum (Fig. 1). We have earlier realized the concept of a frequency-comb spectrometer in the far-infrared region below 2 THz, by generating up to about $N = 300$ harmonics from microwave sources at $f_r = 6$ GHz [7].

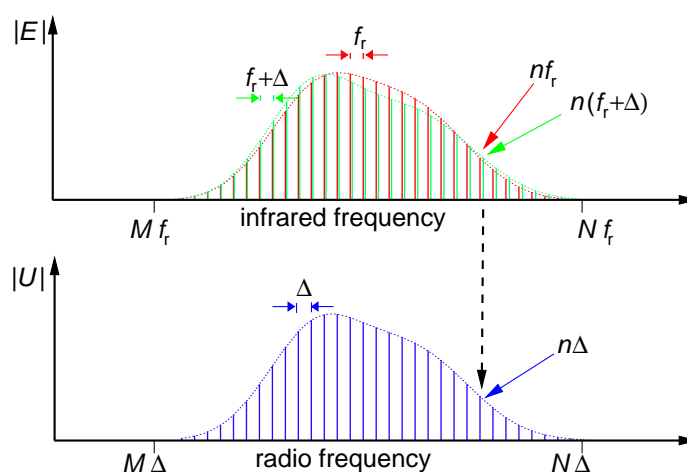


Fig. 1. Principle of quasi-continuous, broadband spectroscopy using multi-heterodyne detection. The evenly spaced narrow lines of the infrared spectrum to be measured (red) constitute a frequency comb. Pairwise interference with a slightly detuned reference comb (green) generates a comb spectrum of much lower “beat” frequencies (blue) that carries amplitude and phase information of the infrared spectrum.

Multi-heterodyne infrared spectroscopy with frequency combs (c-FTIR) [4] requires the steps of (i) producing a coherent, dual IR beam with two superimposed harmonic combs of frequencies nf_r and $n(f_r + \Delta)$, respectively, (ii) probing a sample with this beam, (iii) recording a transient detector signal that repeats at rate Δ and contains an rf harmonic comb of beat frequencies $n\Delta$, (iv) Fourier-transforming this signal to determine the rf spectrum, and (v) scaling the frequency axis by f_r/Δ to recover the IR spectrum.

3. Mid-infrared coherent frequency-comb spectrometer

We derive a harmonic frequency comb in the mid-IR fingerprint region from the optical frequency comb emitted by a mode-locked Ti:sapphire laser [8–10]. For this purpose, we subject the train of near-visible femtosecond pulses emitted by the laser to difference-frequency gener-

ation in a GaSe crystal (Fig. 2) [11, 12]. With the chosen phase-matching parameters [13], the quasi-continuous infrared spectrum extends from 25 THz to 34 THz (835 cm^{-1} to 1135 cm^{-1}), and thus its field

$$E(t) = \sum_{n=M}^N E_n \cos(2\pi n f_r t + \phi_n) \quad (1)$$

contains about 70,000 spectral lines that are harmonics of $f_r \approx 125.130 \text{ MHz}$ with order numbers n between $M = 200,000$ and $N = 270,000$. In order to provide a self-scanning c-FTIR spectrometer, a second such beam is produced from a similar system generating a field

$$E'(t) = \sum_{n=M}^N E'_n \cos(2\pi n (f_r + \Delta)t + \phi'_n). \quad (2)$$

Both beams are superimposed using a beam combiner, and the resulting, dual beam power is detected (Fig. 2). The output signal $U(t) \propto \langle (E(t) + E'(t))^2 \rangle$ contains two d.c. terms which are suppressed by a high-pass filter, and several series of a.c. terms. We choose $\Delta < f_r/2N \approx 230 \text{ Hz}$ so that only one series, namely

$$\sum_{n=M}^N E_n E'_n \cos(2\pi n \Delta t + \phi'_n - \phi_n), \quad (3)$$

lies in the frequency range $< f_r/2$ and becomes selected by a 60 MHz low-pass filter. Its rf spectrum represents a unique replica of the mid-IR spectrum [14], downscaled on the frequency axis by the factor f_r/Δ (Fig. 1).

In the time domain, the rf beats appear as a periodic, transient waveform that repeats at rate Δ . The time of its appearance is determined by the coincidence of pulses of both IR beams at the beam combiner. Due to the difference in repetition rates the pulses in one IR beam are continuously shifted against those of the other, akin to the conventional FTIR [1] or THz [15] spectrometers, where a scanning mirror delays one partial wave against the other. The observed transients at period $1/\Delta$ are therefore equivalent to interferograms in FTIR spectrometers.

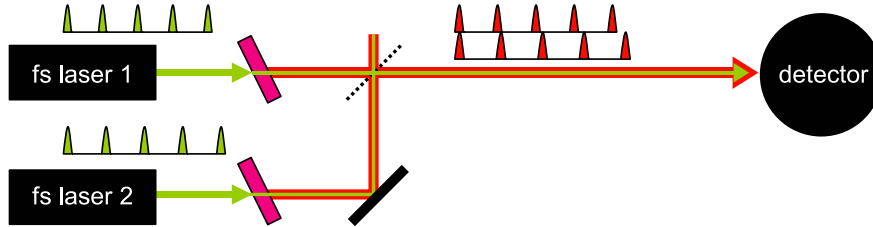


Fig. 2. Comb-FTIR spectrometer consisting of two independent, mode-locked Ti:sapphire lasers (green beams) to produce mid-IR comb spectra (red beams) in GaSe, a beam combiner to launch the probing dual beam, and a HgCdTe detector.

Our instrument uses two 5W-laser-pumped Ti:sapphire lasers (FemtoSource Compact Pro, FemtoLasers) emitting 10 fs pulses with a 100 nm-broad (FWHM) spectrum centered at 800 nm and a 500 mW average power. One laser contains a movable mirror to fine-tune the repetition rate. After warming up in our laboratory, which is thermally stabilized to $\pm 1^\circ \text{ C}$, we find that the repetition rates of $\sim 125.130 \text{ MHz}$ drift by less than 1 Hz over several seconds. This allows us to perform c-FTIR without active stabilization of the repetition rate difference Δ of the lasers. We use $f = 25 \text{ mm}$ parabolic mirrors for focusing and recollimating each beam and place $200 \mu\text{m}$ thick GaSe crystals at 55° incidence in each focus. The $\sim 10 \mu\text{W}$ mid-IR output beams closely

track the visible pump beam transmitted through each crystal, simplifying the alignment of, e.g., remote retroreflective mirrors used for open-path FTIR spectroscopy. For a beam combiner we use an uncoated ZnSe surface at 45° incidence. The combined mid-IR dual beam is passed through the sample to be characterized and then focused on a $200\ \mu\text{m}$ diameter LN_2 -cooled HgCdTe detector (Kolmar Technologies). The signal is continuously sampled by a fast digitizing card (Interactive Circuits and Systems) and processed online with self-implemented software.

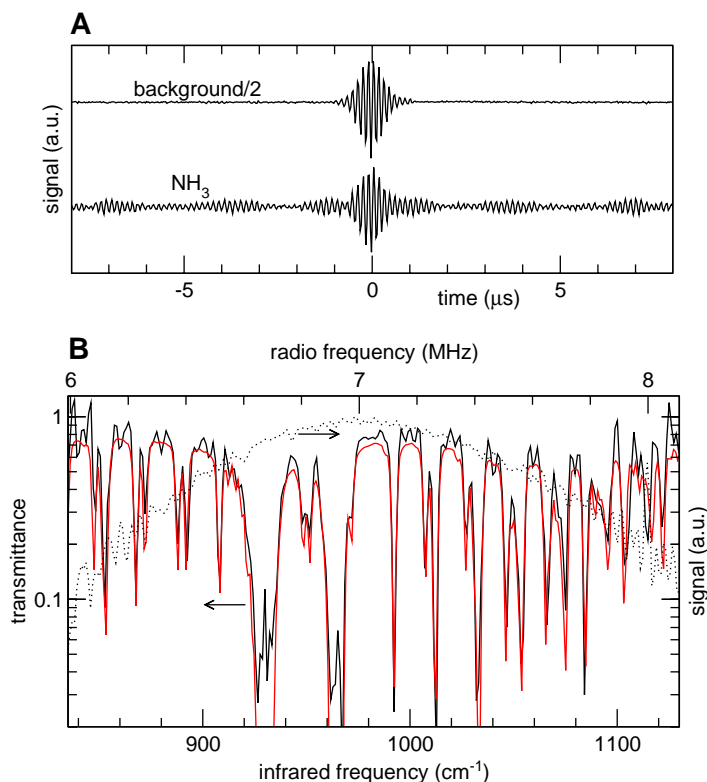


Fig. 3. (A) Single interferograms with $70\ \mu\text{s}$ acquisition time window each ($16\ \mu\text{s}$ displayed, $t = 0$ arbitrarily chosen at window center), without (background) and with a gas absorption cell (NH_3); (B) IR spectra calculated from (A) by Fourier transformation, vs. both radio frequency and IR frequency scales; background spectrum with maximum normalized to 1 (dotted), NH_3 cell transmittance (full black). For comparison we give the transmittance of conventional FTIR obtained at $2\ \text{cm}^{-1}$ resolution and 60 s acquisition time (32 spectra averaged, red trace).

The function of c-FTIR is experimentally demonstrated by single detector transients and their Fourier transforms displayed in Fig. 3, with Δ set to 29.93 Hz. For Fourier transformation we use a $70\ \mu\text{s}$ time window to achieve an instrumental broadening of $1/70\ \mu\text{s} = 14\ \text{kHz}$ (no apodisation). The transient or interferogram is a 7 MHz pulse that lasts only about $2\ \mu\text{s}$ when no sample is in the beam. Its spectrum (dotted in Fig. 3(B)) follows a smooth curve between 6 and 8 MHz. The lower, infrared frequency scale is derived from the upper, rf scale by multiplication with $f_r/\Delta = 4,181,000$. With a 45 mm long gas cell containing a few drops of NH_4OH solution and closed by $25\ \mu\text{m}$ thick polyethylene windows, the interferogram exhibits a much longer signature (Fig. 3(A)), owing to sharp spectral features of NH_3 absorption. A quantitative

transmittance spectrum of the cell is obtained by computing the ratio of sample and background spectra derived from the traces in Fig. 3(A). Note the infrared instrumental broadening can be computed by multiplying 14kHz with f_r/Δ to amount to 2 cm^{-1} . For a comparison we measured the cell also in a conventional FTIR spectrometer (Nexus, Thermo Nicolet) operating at 2 cm^{-1} resolution. The excellent agreement of both spectra verifies the calibration and resolution of c-FTIR, and suggests its use for quantitative analysis.

4. Rapid IR spectroscopy of non-repetitive phenomena

With an instantaneous puff of NH_3 applied by a piston into a 10cm long, windowless tube placed before the detector, Fig. 4 shows the result of 180 consecutive c-FTIR beam spectra assembled in a total time of 4.1 s, with Δ set to 44Hz. The Fourier transformation extended over a $24\mu\text{s}$ time window, to achieve an instrumental broadening of 4 cm^{-1} . The sudden onset of gas absorption is clearly expressed in the depth of the two prominent and also of the weaker absorption lines that were already seen in Fig. 3(B). The onset of absorption happens between two consecutive spectra, that is, within the time interval of $1/\Delta = 0.023\text{ s}$ that lies between two spectral “snapshots” lasting $24\mu\text{s}$ each.

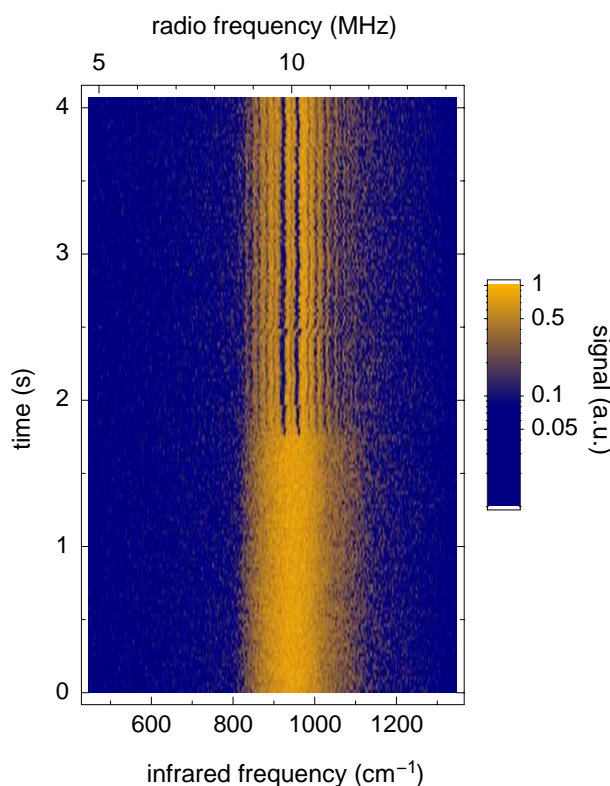


Fig. 4. c-FTIR raw beam spectra with color coding for beam intensity, monitoring a suddenly applied NH_3 puff (at about 1.8s) at 44 spectra/s—a direct demonstration of real-time sensing applications.

Evidently the absorption lines' spectral position is not perfectly stable but oscillates at low frequencies in the range of 10 to 40Hz, and possibly higher. The rms excursion of the 10MHz line is about 30kHz, that is 0.3%. Since all lines vary in proportion, the effect is likely due to a

0.3% oscillation of Δ , that is 0.14 Hz, caused by pump fluctuations and/or mechanical oscillations of the mirrors defining the Ti:sapphire laser resonators. Three consequences are noteworthy. First, the similarities of shapes of consecutive spectral snapshots proves that the observed oscillations are not significant *during* each recording time window of 24 μ s. A correction procedure could therefore align individual spectra, e.g. by recording simultaneous reference spectra of a known sample in the conjugate output beam emerging from the beam combiner (Fig. 2). Secondly, if one were to choose averaging over consecutive, uncorrected spectra taken with free running lasers, the oscillation effect would contribute an extra broadening amounting to 0.3% with $\Delta = 44$ Hz, that is 3 cm^{-1} at 1000 cm^{-1} , or proportionally less if a higher value were chosen for Δ . Finally, by stabilizing Δ with a feedback loop the oscillation effect would be rendered negligible; frequency-locking to available standards [8] could achieve extremely high resolution performance far exceeding that of the classical, incoherent FTIR.

5. Accelerated spectrum repetition by laser manipulation

The experimental c-FTIR system described so far affords relative long waiting times between successive interferogram recordings. For this reason the inherent potential regarding spectrum repetition rate and signal-to-noise ratio is not yet fully exploited. Increasing f_r by a large factor would make higher values of Δ possible, but the IR generation efficiency would be significantly reduced given the average laser power stayed constant.

We introduce and demonstrate here a different way to acquire spectral recordings at arbitrarily short waiting times, so that for any spectral resolution desired, maximum spectrum repetition rate is achieved. The basic idea is to change the value of Δ immediately after an interferogram recording, by active manipulation of one of the Ti:sapphire lasers' pulse repetition rate. We recall that the point in time for an interferogram to appear is determined by the coincidence of pulses of both IR beams. Two versions are illustrated in Fig. 5: either Δ is increased by a given factor to shorten the waiting time by the same factor, or the sign of Δ is flipped to cut the waiting time to zero by alternating between a forward or backward scan of pulse delay, respectively.

We use a step-wise piezoelectric translation of one laser mirror to induce a rapid change of Δ . Typically a few Volts suffice for a submicrometer step that produces a 100 Hz shift. Care was taken to tailor the step waveform to avoid mechanical overshoot oscillation, and to minimize hysteresis. The IR detector transients were used for triggering. A variable delay was used to initiate the step after the end of the desired interferogram recording window. The length and height of the essentially rectangular manipulation pulse were varied to set the desired waiting time. An example of the operation of c-FTIR in a manner as depicted in Fig. 5(C) will be given below. We note that our manipulation method bears resemblance with a known strategy to shorten the experimental "dead time" encountered in self-scanned asynchronous optical sampling for ultrafast pump-probe studies [16]. However, our method avoids any of the complex stabilization methods for setting f_r and Δ as required in [16]; it represents a simple, flexible, self-triggered manipulation that is easily installed.

6. Remote comb-FTIR spectroscopy

The c-FTIR dual beam's propagation properties are clearly governed by the primary qualities of the pump beams and of the GaSe crystals, but detrimental distortions could also come from multiple internal reflections, phase mismatch, and from nonlinear absorption as well as thermal lensing in GaSe. A measurement of each beam's profile just after its recollimating mirror exhibits a smooth distribution similar to a Gaussian fundamental mode with $2w = 15$ mm that expands to about 27 mm after propagating through a 20 m air path. We conclude that the IR beams are nearly diffraction limited, and that even with their $\sim 15\%$ spectral bandwidth they propagate approximately as a Gaussian beam with $10 \mu\text{m}$ wavelength. Clearly this is very bene-

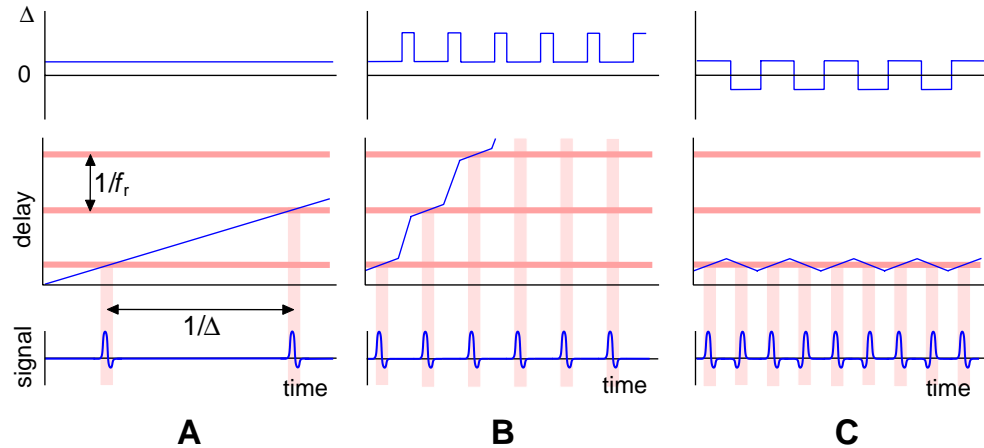


Fig. 5. Pulse coincidence between two pulse trains with repetition rates f_r and $f_r + \Delta$, respectively. (A) Free running pulse trains have a constant Δ (upper graph) and exhibit self-scanned pulse coincidences (red bands in middle graph) at a period of $1/\Delta$, which results in the observation of repeated interferograms (lower graph). Note the long waiting time between interferograms. (B) Triggered increase of Δ —e.g. by shortening one laser cavity—shortens the time between coincidences, but resets Δ just before the coincidences, and thus, before the occurrence of interferograms. (C) Triggered flipping of the sign of Δ provides continuous coincidence scans with alternating directions.

ficial for spectral microscopy, ellipsometry and near-field-microscopy [17, 18] applications that all require a diffraction-limited focus.

We conducted an experiment where the collimated dual IR beam travelled 22m to a point 7m outside the laboratory where a 30m radius concave mirror reflected the beam back to the detector on the laboratory table. With a low temperature outside, 10°C , the reflected beam's position (as indicated by the co-propagating visible beam) fluctuated by several mm due to air turbulence. The detected power was half of the emitted power and did not fluctuate with air turbulence since a sufficiently large diameter lens was used for focusing. Interferograms and broadband spectra appeared without noticeable distortion, at a signal strength reduced only by the power loss. Thus no effect due a loss of coherence was observed, as to be expected, because propagation-phase fluctuations that are certainly present do not affect the detected signal since both IR beams experience identical paths. A remote recording is shown in Fig. 6 that at the same time can be taken as demonstration of the high quality spectra attainable with the accelerated spectrum repetition method.

In this recording we used a setting of $\Delta = 14\text{Hz}$, and accelerated the spectrum repetition by method (C) of Fig. 5, i.e., we applied the manipulation pulse such that it reduced the repetition frequency of the faster repeating laser. The waiting time could thus be significantly reduced, and a spectrum repetition up to 950 spectra/s was attained. Since the delay direction alternates between consecutive interferograms, a slight drift of the lasers lead to unequal delay scan speeds of $\Delta = 14.1\text{Hz}$, for the forward, but only $\Delta = -13.6\text{Hz}$ for the backward interferograms. To correct off-line for this imbalance we normalized the data such that the average spectrum of all 1500 forward spectra, and likewise that of all 1500 backward spectra, had its prominent absorption dips at the proper IR frequencies. The resulting absorption spectra (Fig. 6), and hence the NH_3 chemical concentration of the convective cloud could be easily monitored as it changed with a slight breeze. Again the oscillations of the spectral line positions are seen in Fig. 6 as before in Fig. 4, with similar amplitudes. Since the spectrum repetition frequency is

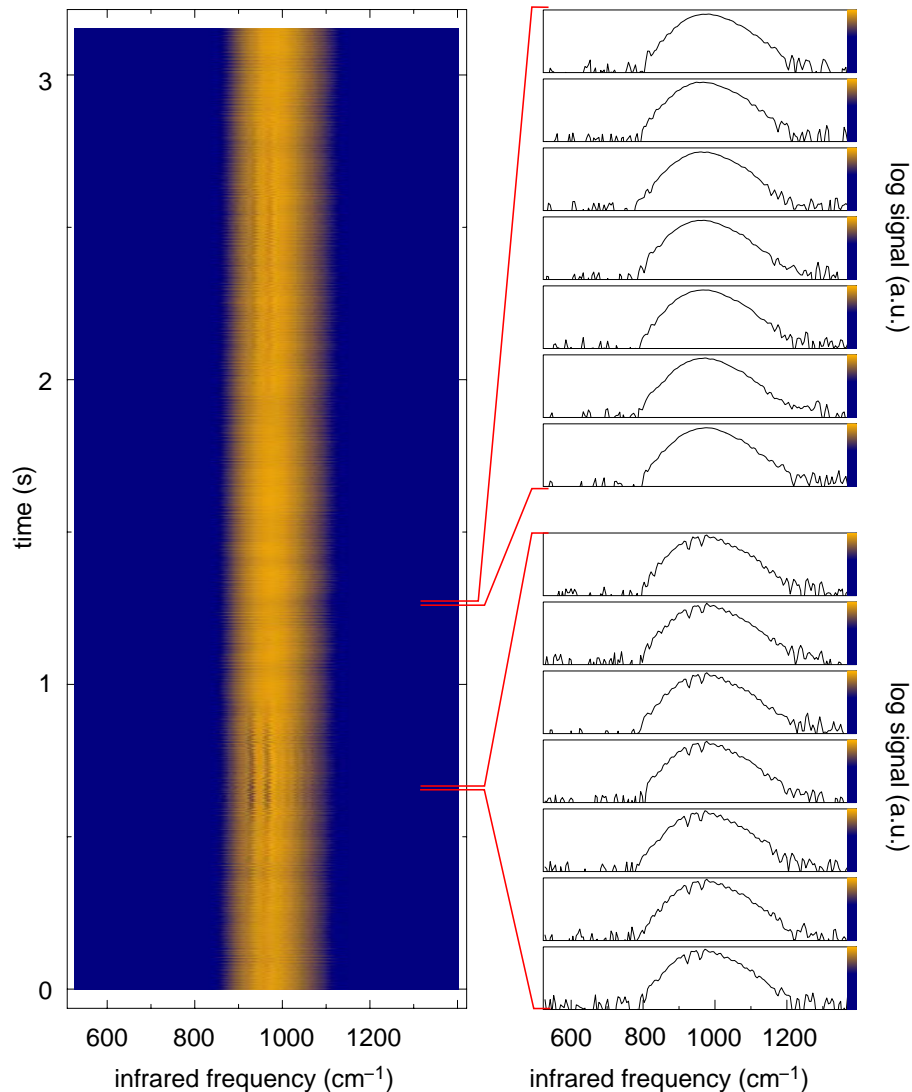


Fig. 6. Rapid remote c-FTIR recording of 3000 IR spectra in a total time of 3.15 s, over a path of 44 m length (left panel). Near a retroreflector outside the laboratory an open NH_4OH bottle had been placed just below the infrared beam path, so small emanating NH_3 clouds are sensed in real time. The right panels display, for two instances, seven consecutive spectra separated by 1 ms.

22 times faster, 950 Hz, we can now see that the oscillations contain no sizable components at frequencies above about 200 Hz.

7. Outlook and applications

We expect that c-FTIR atmospheric chemical sensing can be done over much longer distances. The rapid sequence of spectra would readily be applicable for mapping a scene with a scanned beam. Although a stable setup is required between the lasers and the beam combiner, the detector can operate at a remote and unstable platform, such as a swinging tower, a moving satellite-

lite, or even an active volcano, because the signal does not depend on propagation phase or mild beam deviation by turbulence as long as the beam stays within the receiver's aperture. Furthermore, because of its rapid response, stand-off chemical sensing of transient, non-repeatable phenomena like combustion, plasmas and explosions—all in environments inhospitable to conventional instrumentation—now becomes possible. The method is expandable to wider frequency ranges, such as the THz [15] region, and to both higher beam power and faster rate. In the laboratory, c-FTIR enables important new applications in chemical imaging where high rates of spectral acquisition are needed to scan a large number of pixels. An intriguing prospect is chemical recognition by infrared microscopy in biological [19] and medical [20] applications, and even more so, ultra-resolved chemical recognition by near-field microscopy, employing infrared fingerprint resonance to reveal chemical composition at the nanometer scale [18], performing localized spectroscopy of nanocomposites and molecules.

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