



Mid-infrared feed-forward dual-comb spectroscopy

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Mid-infrared high-resolution spectroscopy has proven an invaluable tool for the study of the structure and dynamics of molecules in the gas phase. The advent of frequency combs advances the frontiers of precise molecular spectroscopy. Here we demonstrate, in the important 3- μm spectral region of the fundamental CH stretch in molecules, dual-comb spectroscopy with experimental coherence times between the combs that exceed half an hour. Mid-infrared Fourier transform spectroscopy using two frequency combs with self-calibration of the frequency scale, negligible contribution of the instrumental line shape to the spectral profiles, high signal-to-noise ratio, and broad spectral bandwidth opens up opportunities for precision spectroscopy of small molecules. Highly multiplexed metrology of line shapes may be envisioned.

frequency comb | laser spectroscopy | mid-infrared | molecular spectroscopy

Mid-infrared frequency combs with unprecedented mutual coherence times open the important spectral region around 3 μm to broad-spectral-bandwidth gas-phase molecular spectroscopy with high precision and negligible instrumental linewidth. A frequency comb (1) is a spectrum that spans a broad bandwidth and that is made up of phase-coherent evenly spaced narrow laser lines, the frequency of which may be known within the accuracy of an atomic clock. Frequency combs find numerous new applications. In spectroscopy over broad spectral bandwidths, they are used to directly interrogate the transitions of atomic and molecular species. One of the techniques of broadband frequency comb spectroscopy, dual-comb spectroscopy (2), currently attracts significant interest. Dual-comb spectroscopy is a technique of linear (3–6) and nonlinear (7, 8) Fourier transform spectroscopy without moving parts. In most implementations of linear spectroscopy (Fig. 1A), a frequency comb interrogates an absorbing sample and is heterodyned against a second comb of slightly different line spacing, at a single fast photodetector. The measured time-domain interference leads to a spectrum through the harmonic analysis provided by Fourier transformation. Dual-comb interferometers hold promise for efficient spectrometers that would offer a unique combination of distinguishing features: (i) absence of geometric limitations, unlike Michelson-based or grating spectrometers, theoretically leading to unlimited spans and resolutions; (ii) absence of moving parts; (iii) multiplexed recording (in other words: all of the spectral elements are simultaneously measured on a single photodetector), like other interferential spectrometers, granting excellent overall consistency of the spectral measurements and applicability in any spectral regions; (iv) interrogation of the sample by laser lines of narrow width providing a negligible contribution of the instrumental line shape; (v) calibration of the frequency scale within the accuracy of an atomic clock; (vi) short measurement times; (vii) use of laser beams of high brightness.

The development of dual-comb spectroscopy in the regions of interest to molecular spectroscopy, such as the mid-infrared range where most molecules have strong vibrational transitions, turns out to be rather challenging for several reasons.

Novel laser technology is still emerging and many different approaches to mid-infrared frequency comb generation (9) have been and are being explored. They include quantum cascade (10)

and interband cascade (11) lasers, microresonators (12, 13), novel solid-state (14) or doped-fiber (15) gain media, improved approaches to nonlinear frequency conversion (16) benefiting optical parametric oscillation, difference frequency generation, and spectral broadening in nonlinear waveguides (17, 18).

Furthermore, the technical requirements for a dual-comb spectrometer are more challenging than those for a metrological frequency comb. A dual-comb interferometer requires that the optical delay between the pairs of interfering pulses is controlled, from pulse pair to pulse pair, within interferometric accuracy. Timing fluctuations in the attosecond range can be detrimental. In the near-infrared domain, coherence between the two combs at most reached the order of 1 s in different experimental realizations (19–21). The measurement time can be extended to several minutes or hours by more or less complex techniques of phase correction, that are implemented through analog (22), digital (23), or a posteriori computer (24) treatment. Maintaining coherence in the mid-infrared domain is even more difficult than in the near-infrared region, because, e.g., of the more complex laser systems and of the difficulty to design continuous-wave mid-infrared lasers with a hertz linewidth, that could serve as optical references for the combs.

Finally, experimenting in the mid-infrared region is generally more demanding than in the visible and near-infrared range, because the optics technology is not as advanced.

Consequently many reports of mid-infrared dual-comb spectroscopy, although pointing to an intriguing potential, have remained at a stage of promising proofs of principle. Many laser systems developed lately have led to a variety of implementations (14, 25–30). For instance, the first demonstrations with frequency combs of large line spacing, such as microresonators (31) and quantum cascade lasers (32), highlight novel opportunities in

Significance

Each molecule leaves characteristic absorptions, which enable one to unambiguously identify and quantify it, and to understand its structure and dynamics. Such fingerprints, strong in the mid-infrared region of the electromagnetic spectrum, can be accessed by measuring the intensity of light transmitted through a medium as a function of its frequency. Here, we describe a spectrometer for mid-infrared spectroscopy based on two frequency comb generators, light sources emitting narrow evenly spaced laser lines over a broad spectral bandwidth. Our instrument without moving parts simultaneously measures broad high-resolution spectra with calibration of the frequency scale directly to an atomic clock and precise spectral line shapes. These features are obtained from the experimental data without any need for corrective processing.

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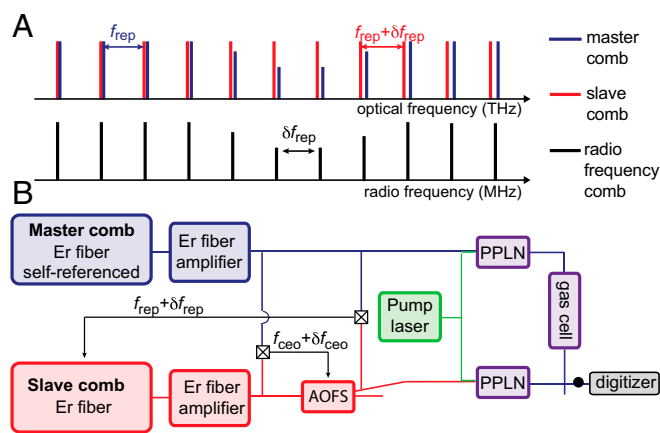


Fig. 1. (A) Frequency-domain principle of dual-comb spectroscopy. Beat notes between pairs of lines of two optical combs, with a spacing of f_{rep} and $f_{\text{rep}} + \delta f_{\text{rep}}$, respectively, generate a radio-frequency comb of line spacing δf_{rep} . The radio-frequency comb can be digitally processed. (B) Experimental setup for mid-infrared broadband dual-comb spectroscopy using feed-forward control of the relative CEO frequency. AOFS, acousto-optic frequency shifter.

time-resolved spectroscopy for physical chemistry in the condensed phase. Nevertheless, quantum cascade (33) and inter-band (34) cascade lasers, difference-frequency generation using erbium-doped fiber lasers (3), and electro-optic modulators (6) have produced, over narrow spectral bandwidths, high-quality spectra with resolved comb lines. Recently, the control of degenerate optical parametric oscillators has also been remarkably advanced (35), while a combination of difference-frequency comb generators stabilized in the near-infrared and of real-time digital correction proved successful in producing (4) spectra with resolved comb lines over a broad spectral bandwidth.

Not long ago, we devised (5) a scheme of dual-comb interferometry that reports coherence times more than three orders of magnitude longer than the state of the art. The initial demonstration has been performed in the near-infrared region with erbium-doped fiber oscillators spectrally broadened in nonlinear fibers. The near-infrared interferometer, based on feed-forward stabilization of the relative carrier-envelope offset frequency, does not require any type of phase correction for continuous averaging of interferograms up to half an hour, resulting in greater experimental simplicity and reduction of possible artifacts. Here we explore the extension of our scheme to broadband highly accurate dual-comb spectroscopy in the mid-infrared 3- μm range, where the fundamental CH, NH, OH stretches in molecules are found.

Experimental Setup

Our 3- μm dual-comb laser system (Fig. 1B) is based on difference-frequency generation of near-infrared femtosecond erbium-doped fiber lasers.

The near-infrared dual-comb system has already been described in ref. 5. We summarize here its main features for the clarity of the description. Two amplified mode-locked erbium-doped fiber laser systems emit trains of pulses at a repetition frequency of about 100 MHz. Their spectrum is centered at an optical frequency of about 190 THz and it spans more than 20 THz. The repetition frequency f_{rep} and the carrier-envelope offset (CEO) frequency f_{CEO} of the first fiber laser system (called master comb) are stabilized against the radio-frequency clock signal of a hydrogen maser, and all electronic instruments in our setup are synchronized to this clock signal. In the experiments described below, we choose $f_{\text{rep}} = 100.00$ MHz and $f_{\text{CEO}} = 20.0$ MHz and both radio frequencies are counted during the recording of the interferograms. The second fiber laser system,

called slave comb, has a slightly different repetition frequency $f_{\text{rep}} + \delta f_{\text{rep}}$ (with $\delta f_{\text{rep}} \ll f_{\text{rep}}$) and a different CEO frequency $f_{\text{CEO}} + \delta f_{\text{CEO}}$. Here, we set $|\delta f_{\text{rep}}| = 130$ Hz, which leads to an optical free spectral range of 38 THz. For interferometry measurements, the optical retardation between pairs of interfering pulses must be accurately controlled during the duration of the measurement. Our technique is based on feed-forward control of the relative CEO frequency: an acousto-optic frequency shifter, at the output of the slave laser system, keeps δf_{CEO} constant over arbitrary times by frequency translating, with a fast response time (about 550 ns), all of the comb lines of the slave comb. A slow feedback loop (<1-kHz bandwidth) adjusts the length of the cavity of the slave comb to maintain a fixed difference in repetition frequencies δf_{rep} . The signals that enable one to monitor the relative fluctuations between the combs are two beat notes between two pairs of optical comb lines, one from each comb. Two continuous-wave lasers, emitting at 189 and 195 THz, respectively, serve as intermediate oscillators to produce the two beat notes. For the spectroscopy setup, the output of the master comb and that of the first-order diffracted beam of the acousto-optic frequency shifter of the slave comb have an available average power of about 250 mW each.

Each near-infrared signal comb is converted to a mid-infrared idler comb by difference-frequency generation in a periodically poled lithium-niobate (PPLN) crystal of a length of 3 mm and with seven poling periods of about 30 μm . The pump beam is provided by a continuous-wave laser that emits at $f_{\text{pump}} \sim 281.8$ THz (1,063.8 nm) and that is phase-locked to a line of the master comb. Its free-running linewidth at 100 μs is specified to be 50 kHz. For frequency calibration of the spectra, we count the absolute frequency of the pump laser f_{pump} , that of the 189-THz continuous-wave intermediate-oscillator laser, and the radio-frequency parameters of the two signal combs during the measurement of the interferograms. The pump is split into two beams. For each, an average power of 2 W is combined with 250 mW of signal beam by means of a dichroic mirror and each superimposed beam is focused onto a mixing PPLN crystal. We generate an idler comb spanning up to 8.2 THz—a span limited by the phase-matching bandwidth of the PPLN crystal—with an average power up to 90 μW . Such a technique of difference-frequency comb generation has already been harnessed in dual-comb spectroscopy with erbium fiber lasers (3) and with electro-optic modulators (6). Mixing a continuous-wave laser and an ultrashort pulse is a fairly inefficient process; the simplicity of its implementation and the fact that, due to detector nonlinearities, we do not require high mid-infrared powers, justifies though that we retained this scheme. The efficiency could be much increased with a build-up cavity for the pump beam and by introducing a pulse-stretching chirp for the pulses of the near-infrared signal combs. The repetition frequency of the idler comb is the same as that of the signal comb. The CEO frequency of the idler comb is shifted by an amount $f_{\text{pump}} [\text{modulo } f_{\text{rep}}]$. As the same pump laser is used for the generation of the two idler combs, the two CEO frequencies are shifted by the same amount and their difference remains δf_{CEO} . The center frequency of the idler comb is adjustable between 82 and 100 THz by changing the temperature and the poling period of the PPLN crystal. After each PPLN crystal, an optical long-wavelength-pass filter filters out the residual pump and signal beams. The master idler comb beam passes through a single-pass absorption cell of a length of 70 cm. The master and slave idler beams are combined on a pellicle beamsplitter. One of the outputs of the beamsplitter is focused onto a fast thermoelectrically cooled HgCdTe photodetector. To avoid detector nonlinearities that generate distortions and systematic effects in the spectra, the total average power at the detector is kept weaker than 40 μW . The electric signal is amplified and filtered. It is sampled synchronously to the master comb repetition frequency, $f_{\text{rep}} = 100$ MHz, by a fast digitizer. To keep the individual interferograms in phase and enable their averaging in the time domain,

we set $\delta f_{\text{CEO}} = 0$ [modulo δf_{rep}]. The time-domain interference signal is Fourier transformed to reveal the spectrum. Integration times of several minutes are required to get good signal-to-noise ratios over a broad spectral bandwidth. We average the raw interferograms in the time domain by simply adding them up. We do not perform any numerical corrections (like phase correction) to the interferograms or to the spectra. The displayed transmission spectra are the amplitude of the complex Fourier transform of the averaged interferograms while the dispersion spectra are their phase.

Results

Fig. 2A displays a transmission spectrum with 82,000 resolved comb lines, resulting from an interferogram averaged during 29 min (1,742 s). For illustrating the resolved comb lines, interferometric sequences of 0.146 s including 19 individual interferograms are time averaged and the resulting interferogram is Fourier transformed. In Fig. 2A, the spectrum is shown over the entire useful spectral span of 8.2 THz, from 88 to 96.2 THz, with triangular apodization of the interferogram. Fig. 2B shows an expanded view of the unapodized spectrum, illustrating that the rovibrational transitions of the absorbing sample, here ethylene C_2H_4 in natural abundance, with a Doppler full width at half maximum of 215 MHz at 296 K are satisfactorily sampled by the comb lines of 100-MHz spacing. The ethylene pressure is 147 Pa and the absorption path length is 70 cm. The individual comb lines (Fig. 2C) have the expected line shape, a cardinal sine due

to the finite measurement time, which convolves the comb beat notes of negligible width. The full width at half maximum of the observed comb lines is 6.8 Hz in the radio-frequency domain, which corresponds to the Fourier transform limit. The measurement time is similar to that in our recent near-infrared spectra (5) that use the same feed-forward technique and we observe no degradations in the retrieved instrumental line shapes due to the operation in the mid-infrared region.

The spectrum sampled at exactly the comb-line positions reveals (Fig. 3A) the absorption by ethylene. Ethylene C_2H_4 is a near-prolate planar asymmetric top molecule. Our span covers the region of the ν_9, ν_{11} -stretching dyad of $^{12}\text{C}_2\text{H}_4$, which includes the $\nu_2 + \nu_{12}$, $2\nu_{10} + \nu_{12}$, and $\nu_9 + \nu_{10}$ cold bands. Fig. 3B and C illustrates details of the transmission and dispersion spectra. The signal-to-noise ratio at 92.3 THz peaks at 1,275 for a measurement time of 1,742 s, corresponding to $30.5 \text{ s}^{-1/2}$. The average signal-to-noise ratio is 570 (or $13.6 \text{ s}^{-1/2}$) across the full span of 8.2 THz, and the corresponding figure of merit, which is given by the product of the average signal-to-noise ratio per unit square root of measurement time and the number of spectral elements 82,000, is $1.1 \times 10^6 \text{ s}^{-1/2}$. Such a figure of merit is comparable to those reported in the same spectral region for other experiments of narrowband (3, 6) or digitally corrected broadband (4) dual-comb spectroscopy. When the interferograms are averaged in the time domain, the average signal-to-noise increases (Fig. 4) as the square root of the measurement time: the experimentally

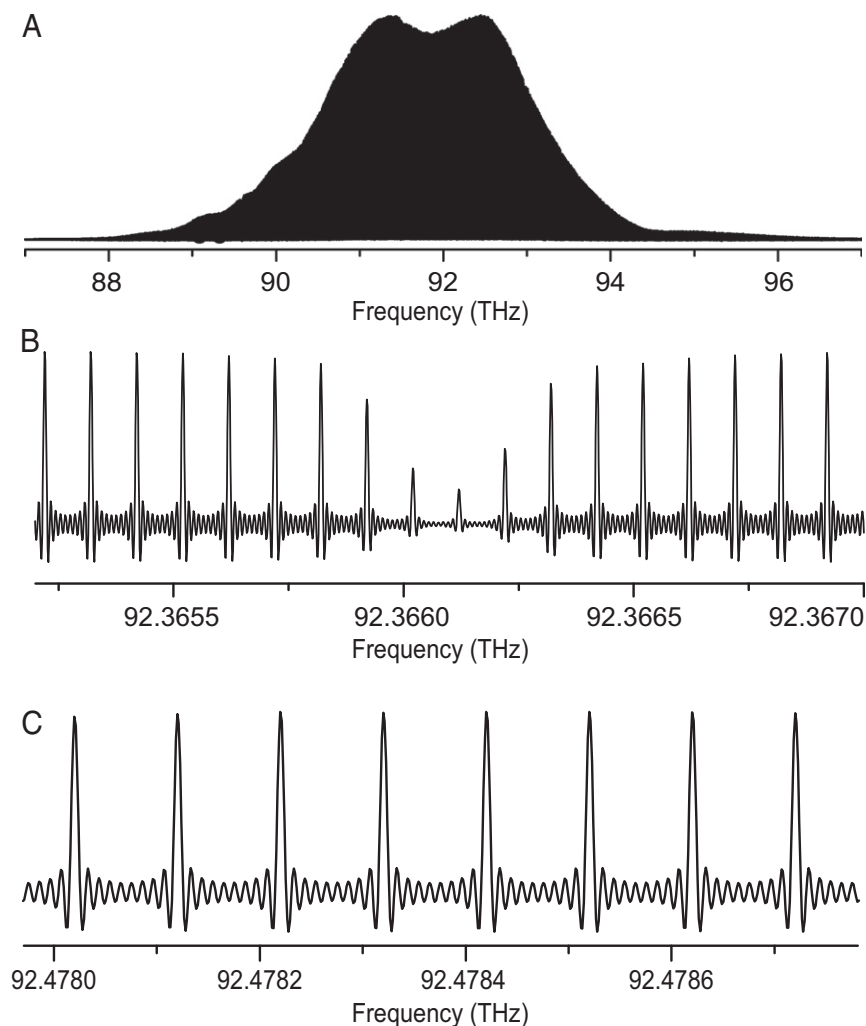


Fig. 2. Experimental dual-comb spectrum with resolved comb lines, recorded within 1,742 s. (A) Entire apodized spectrum: 82,000 individual comb lines spanning 8.2 THz are resolved. (B) Detail of the unapodized representation of A showing the ($J' = 13, K_a' = 1, K_c' = 13$)-($J'' = 14, K_a'' = 0, K_c'' = 14$) line in a P branch of the ν_9 band of $^{12}\text{C}_2\text{H}_4$ sampled by the comb lines of 100-MHz spacing. (C) Magnified unapodized representation of A showing eight individual comb lines with their cardinal sine instrumental line shape. The frequency scale is converted to the optical scale, thus the transform-limited width of 6.8 Hz of the radio-frequency comb lines appears as 5.3 MHz in the optical domain.

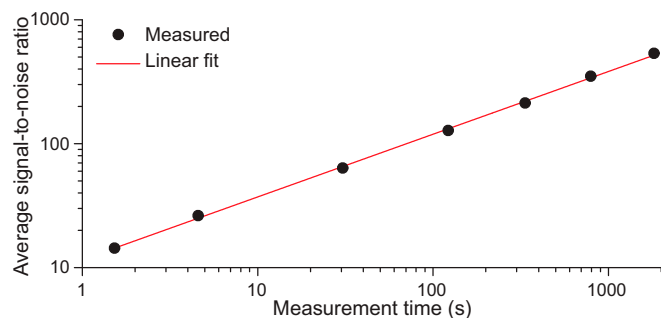


Fig. 4. Evolution of the average signal-to-noise ratio with the measurement time in an ethylene spectrum. The fit of a line to the experimental data shows a slope of 0.506 (5) indicating that the signal-to-noise ratio shows dependence with the square root of the measurement time. The spectrum corresponding to a measurement time of 1,742 s is shown in Figs. 2 and 3.

compare the positions of about 250 selected isolated lines of $^{12}\text{C}_2\text{H}_4$ to those available in the literature. The retrieved positions in our line selection present an average statistical uncertainty of 0.8 MHz with a standard deviation of 0.4 MHz. An extensive linelist is available in the 2016 HITRAN database (38), which reproduces the report (39). In the report (39), the precision of the line-position measurements is given to ± 20 MHz and the accuracy is said to be “slightly worse.” The average value of the difference between the positions in ref. 39 and ours is 0.3 MHz and the standard deviation is 1 MHz. About 60 of our selected lines, in the ν_{11} band, were also measured in ref. 40 with an accuracy of ± 18 MHz. The average value of the difference between the positions in ref. 40 and ours is 1.0 MHz and the standard deviation is 3.2 MHz. This indicates that precise position measurements of Doppler-broadened transitions may be achieved with our setup. The accuracy of the frequency scale is granted by the direct calibration to the hydrogen maser. Special care was also taken to operate the photodetector within its linearity range to avoid systematic shifts due to detector nonlinearities. However, biases at the sample, such as pressure shifts, have not been evaluated yet and will be the object of future investigations.

Discussion

Here, we demonstrate self-referenced broadband mid-infrared dual-comb spectroscopy, with resolved comb lines and negligible contribution of the instrumental line shape, which does not require any type of phase correction. We experimentally achieve mutual coherence times that far exceed the state of the art. Meanwhile the instrumental setup for coherence control is relatively simple. The implementation of real-time phase-correction algorithms, that reconstruct the coherence, requires complex computer hardware and programming. Compared with these, our technique is straightforward. In contrast to locking the combs to optical references, our technique does not require reference cavities (nor other means of achieving a continuous-wave laser with a linewidth of a hertz or below). As already discussed in ref. 5, phase correction is not always implementable and it may otherwise induce subtle artifacts detrimental to precision measurements. Thus, an instrument that does not require any data corrections will be useful to broadband precision spectroscopy and it will help ascertaining the precision frontiers and identifying tiny systematic instrumental effects.

Our spectrometer provides self-calibration of the frequency scale directly within the accuracy of an atomic clock, as well as a negligible contribution of the instrumental line shape to the experimental profile. As the achieved mutual coherence is excellent, the strongest contribution to the instrumental profiles comes from the optical comb lines of the self-referenced master

comb that interrogate the sample. Their width is about 100 kHz at an integration time of 1 min, thus three orders of magnitude narrower than the Doppler width. Therefore, the intrinsic molecular line shape can directly fit the line profile. Even for spectroscopy of Doppler-broadened profiles at room temperature, improved line parameters—not limited to positions and shifts—may be determined. To date, most of the precise spectroscopic individual line parameters retrieved from high-resolution infrared spectra have derived from Michelson-based Fourier transform spectroscopy (FTS) with an incoherent light source, where the wavenumber-scale calibration relies on the presence of molecular lines, accurately measured by other means, which can serve as wavenumber standards in the spectra. The instrumental line shape in Michelson-based FTS has a width generally of the same order of magnitude as the intrinsic width of the observed lines and has to be included in the fits. The use of an incoherent light source in Michelson-based FTS enables recordings over extended spectral bandwidths that are still out of reach with frequency-comb spectroscopy. Over limited bandwidths, which are commonly used in Michelson-based FTS for signal-to-noise ratio improvement, coherent light sources of high brightness represent (41, 42) a significant increase in signal-to-noise ratio (or decrease in measurement time). Our system benefits from this high brightness and adds the advantages of the accuracy of the frequency scale, of the precision of the line-profile determination, and of the absence of moving parts.

A limitation of the present dual-comb system is the low average power ($90 \mu\text{W}$) of each mid-infrared comb. For spectroscopy in a single-pass cell or in a multipass cell with a small number of reflections, the achieved average power is appropriate, as the total power on the detector needs to be kept lower than 30–40 μW to avoid detector nonlinearities. For laboratory spectroscopy over long paths in a multipass cell or in a high-finesse cavity (43), the

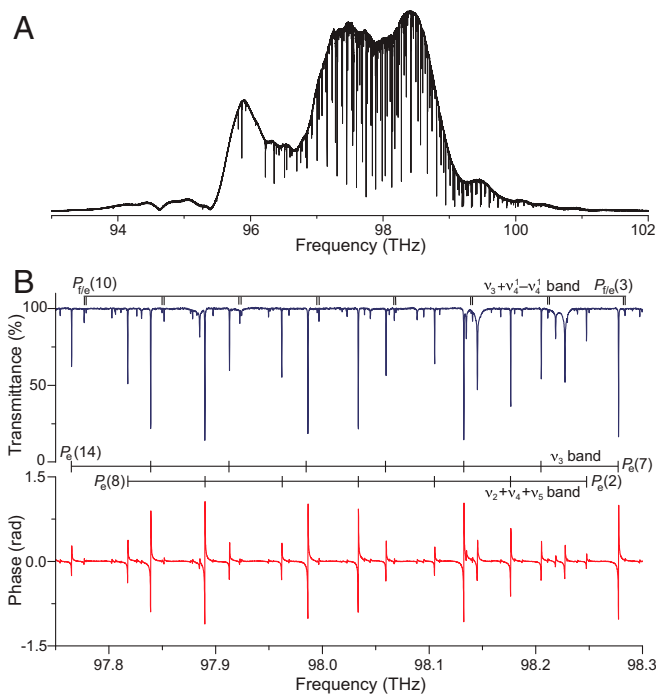


Fig. 5. Experimental spectrum of acetylene in the region of the ν_3 band with a resolution of 100 MHz. (A) The entire spectrum is measured within 2,050.2 s. (B) Transmittance and dispersion spectra in the region of the P branch of the ν_3 band of $^{12}\text{C}_2\text{H}_2$. The assignments for a selection of strong and weak lines are provided (36). The lines with a broader pedestal are due to atmospheric water vapor, outside the cell, in the beam path.

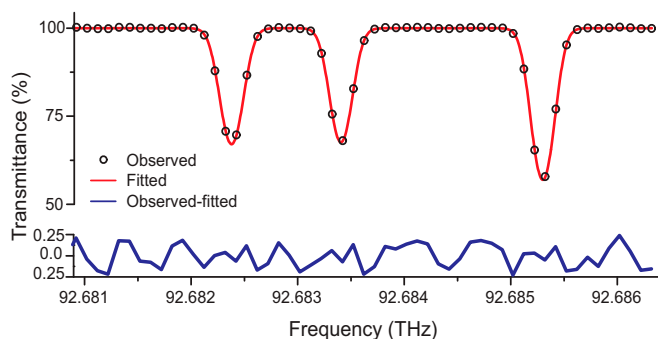


Fig. 6. Portion of the transmittance spectrum of $^{12}\text{C}_2\text{H}_4$ (black open dots, labeled observed), magnifying three rovibrational lines. The transmittance y scale in the spectrum stops at 50%. The experimental profile is satisfactorily fitted by a Doppler line shape (red line, labeled fitted). The standard deviation of the residuals ("observed-fitted") is at the noise level. The y scale of the residuals is magnified compared with that of the top.

power would likely be too low. In our configuration though, the pump photons from the continuous-wave laser are entirely depleted. By chirping the signal pulses to several picoseconds, we increase the conversion efficiency and the average power by one order of magnitude, which would be sufficient for multipass cells.

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For experiments requiring significantly higher power, other comb sources, such as optical parametric oscillators (35) or systems based on difference-frequency generation between ultrashort pulses (4, 26, 44, 45), would have to be harnessed. The feed-forward relative control could be implemented on the mid-infrared beams. This still has to be experimentally demonstrated, but is technically achievable. With our setup, the span currently covers 81–106 THz (2.8–3.7 μm). Broader tunability over the entire 60–100-THz (3–5- μm) atmospheric window could readily be achieved with the same setup, by spectrally broadening the output of the erbium oscillators in nonlinear waveguides. Lower frequency ranges, and particularly the atmospheric window spanning 21–37 THz (8–14 μm), would require a tunable continuous-wave laser as the pump in the difference-frequency generation or, more interestingly, intrapulse difference-frequency generation in a semiconductor (9), such as orientation-patterned gallium phosphide (16, 27).

The 3- μm region is rich in strong molecular transitions, belonging, e.g., to fundamental bands of many small and large organic, nitrogen-containing, and oxygen-containing molecules, of relevance to fundamental and applied spectroscopy. Future work will exploit our feed-forward dual-comb spectrometer for precise spectroscopy of molecular line shapes.

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