Mid-infrared frequency combs

Albert Schliesser1,2, Nathalie Picqué2,3,4* and Theodor W. Hänsch2,3

Laser frequency combs are coherent light sources that emit a broad spectrum of discrete, evenly spaced narrow lines whose absolute frequency can be measured to within the accuracy of an atomic clock. Their development in the near-infrared and visible domains has revolutionized frequency metrology while also providing numerous unexpected opportunities in other fields such as astronomy and attosecond science. Researchers are now exploring how to extend frequency comb techniques to the mid-infrared spectral region. Versatile mid-infrared frequency comb generators based on novel laser gain media, nonlinear frequency conversion or microresonators promise to significantly expand the applications of frequency combs. In particular, novel approaches to molecular spectroscopy in the ‘fingerprint region’, with dramatically improved precision, sensitivity, recording time and/or spectral bandwidth may lead to new discoveries in the various fields relevant to molecular science.

The mid-infrared spectral region of 2–20 μm (500–5,000 cm⁻¹) is a domain of interest to many areas of science and technology. A large number of molecules undergo strong characteristic vibrational transitions in this domain (Fig. 1a), thus making mid-infrared spectroscopy a univocal way to identify and quantify molecular species, including isotopologues, in a given environment. Mid-infrared spectroscopy provides not only a powerful tool for understanding the structure of molecular matter and its governing physical laws, but also for performing non-intrusive diagnostics of composite systems of physical, chemical or biological interest, in the gas, liquid or solid phase. The mid-infrared region also contains two important windows (3–5 μm and 8–13 μm) in which the Earth’s atmosphere is relatively transparent. These regions can be exploited to detect small traces of environmental and toxic vapours down to sensitivities of parts-per-billion in a variety of atmospheric, security and industrial applications. The low Rayleigh scattering losses in the mid-infrared region benefit tomography and imaging in turbid media.

Since their introduction in the late 1990s, laser frequency combs have revolutionized 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 equal to the pulse repetition frequency. Optical frequency combs in the visible and near-infrared domains have enabled the development of new ultra precise optical atomic clocks, and commercially available combs have quickly matured to become standard instruments of precision spectroscopy. Frequency combs are now becoming enabling tools for an increasing number of applications, ranging from the calibration of astronomical spectrographs to molecular spectroscopy. The extension of frequency comb techniques to new spectral regions from terahertz frequencies to the extreme-ultraviolet is likely to trigger many future applications — including novel laser gain media, nonlinear frequency conversion or microresonators — that are of primary interest for physics and applications. We focus explicitly on mid-infrared sources, whose comb structure has been established, even though major achievements have also been reported in the development and exploitation of other broadband mid-infrared coherent sources. Although mid-infrared lasers and photonic technologies have been studied for over five decades, technical challenges have slowed down the development of convenient instrumentation in this spectral region. Over the past few years, in contrast, remarkable progress has been made in efficient mid-infrared frequency comb generators. A variety of innovative solutions — including novel laser gain media, nonlinear frequency conversion and Kerr comb generators — offer a wide choice of comb sources covering vast ranges of repetition frequency and spectral span. Compelling demonstrations in precision spectroscopy and direct frequency comb spectroscopy of molecules in the mid-infrared add enhanced capabilities to spectroscopy and provide new uses for frequency comb generators.

Several new avenues of research are being opened by the introduction of the mid-infrared frequency comb.

Frequency comb generators in the mid-infrared

The characteristics of a frequency comb. A frequency comb is traditionally generated by means of a mode-locked laser: every time the pulse circulating in the laser cavity reaches the output coupler, a fraction of its energy is coupled out of the laser. The emitted pulse train therefore has a strictly periodic envelope function with a repetition frequency (fₚₑ slander) given by the inverse round-trip time of the pulse in the laser cavity fₚₑ slander = νₑ / L, where νₑ is the group velocity of the light in the cavity and L is the round-trip length of the cavity. However, due to dispersion in the laser resonator, the carrier wave of the pulse propagates at a phase velocity νₚₑ slander which is generally different from νₑ. Therefore, the electric field of the outcoupled pulses is shifted with respect to the pulse envelope by a constant amount Δφ from pulse to pulse. This means that the electric field is not strictly periodic in time. Nevertheless, the Fourier spectrum of the electric field is composed of a discrete set of equidistantly spaced, sharp frequency components νₑ slander that obey the simple relation νₑ slander = n νₚₑ slander + fₚₑ slander in which the carrier–envelope offset frequency is given by fₚₑ slander = Δφ fₚₑ slander / 2π and n is a large integer (Fig. 1b).

Mode-locked lasers. Mid-infrared radiation with such spectral properties can be generated through several techniques. Mode-locked lasers in the mid-infrared are similar to established sources

**FOCUS**

The mid-infrared spectral region of 2–20 μm (500–5,000 cm⁻¹) is a domain of interest to many areas of science and technology. A large number of molecules undergo strong characteristic vibrational transitions in this domain (Fig. 1a), thus making mid-infrared spectroscopy a univocal way to identify and quantify molecular species, including isotopologues, in a given environment. Mid-infrared spectroscopy provides not only a powerful tool for understanding the structure of molecular matter and its governing physical laws, but also for performing non-intrusive diagnostics of composite systems of physical, chemical or biological interest, in the gas, liquid or solid phase. The mid-infrared region also contains two important windows (3–5 μm and 8–13 μm) in which the Earth’s atmosphere is relatively transparent. These regions can be exploited to detect small traces of environmental and toxic vapours down to sensitivities of parts-per-billion in a variety of atmospheric, security and industrial applications. The low Rayleigh scattering losses in the mid-infrared region benefit tomography and imaging in turbid media.

Since their introduction in the late 1990s, laser frequency combs have revolutionized 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 equal to the pulse repetition frequency. Optical frequency combs in the visible and near-infrared domains have enabled the development of new ultra precise optical atomic clocks, and commercially available combs have quickly matured to become standard instruments of precision spectroscopy. Frequency combs are now becoming enabling tools for an increasing number of applications, ranging from the calibration of astronomical spectrographs to molecular spectroscopy. The extension of frequency comb techniques to new spectral regions from terahertz frequencies to the extreme-ultraviolet is likely to trigger many future applications — including novel laser gain media, nonlinear frequency conversion or microresonators — that are of primary interest for physics and applications. We focus explicitly on mid-infrared sources, whose comb structure has been established, even though major achievements have also been reported in the development and exploitation of other broadband mid-infrared coherent sources. Although mid-infrared lasers and photonic technologies have been studied for over five decades, technical challenges have slowed down the development of convenient instrumentation in this spectral region. Over the past few years, in contrast, remarkable progress has been made in efficient mid-infrared frequency comb generators. A variety of innovative solutions — including novel laser gain media, nonlinear frequency conversion and Kerr comb generators — offer a wide choice of comb sources covering vast ranges of repetition frequency and spectral span. Compelling demonstrations in precision spectroscopy and direct frequency comb spectroscopy of molecules in the mid-infrared add enhanced capabilities to spectroscopy and provide new uses for frequency comb generators. Several new avenues of research are being opened by the introduction of the mid-infrared frequency comb.

Frequency comb generators in the mid-infrared

The characteristics of a frequency comb. A frequency comb is traditionally generated by means of a mode-locked laser: every time the pulse circulating in the laser cavity reaches the output coupler, a fraction of its energy is coupled out of the laser. The emitted pulse train therefore has a strictly periodic envelope function with a repetition frequency (fₚₑ slander) given by the inverse round-trip time of the pulse in the laser cavity fₚₑ slander = νₑ / L, where νₑ is the group velocity of the light in the cavity and L is the round-trip length of the cavity. However, due to dispersion in the laser resonator, the carrier wave of the pulse propagates at a phase velocity νₚₑ slander which is generally different from νₑ. Therefore, the electric field of the outcoupled pulses is shifted with respect to the pulse envelope by a constant amount Δφ from pulse to pulse. This means that the electric field is not strictly periodic in time. Nevertheless, the Fourier spectrum of the electric field is composed of a discrete set of equidistantly spaced, sharp frequency components νₑ slander that obey the simple relation νₑ slander = n νₚₑ slander + fₚₑ slander in which the carrier–envelope offset frequency is given by fₚₑ slander = Δφ fₚₑ slander / 2π and n is a large integer (Fig. 1b).

Mode-locked lasers. Mid-infrared radiation with such spectral properties can be generated through several techniques. Mode-locked lasers in the mid-infrared are similar to established sources

© 2012 Macmillan Publishers Limited. All rights reserved.
in the near-infrared (Fig. 2a). Transition metals such as chromium or iron provide a broad gain bandwidth in the mid-infrared region if doped into crystals of group ii–vi compounds. Electronic transitions in these laser-active metals are strongly coupled to phonons in the lattice of the host crystal, which leads to significant homogeneous broadening — often more than 30% of the centre frequency. Chalcogenide hosts such as ZnSe and ZnS are particularly well-suited to this process because they support this ‘vibronic’ coupling, while sufficiently suppressing undesirable non-radiative multiphonon relaxation — even at room temperature — due to their low maximum phonon energy.

Using semiconductor saturable absorber mirrors or the Kerr lens effect, researchers have demonstrated modelocked operation at repetition rates of around 100 MHz in Cr:ZnSe crystals (refs 11–13) and Cr:ZnS lasers (ref. 14) lasers, emitting relatively wide (>300 cm⁻¹) spectra around a wavelength of 2.5 μm and with powers of the order of 10 μW per mode (Figs 3, 4a). The comb structure of these lasers has been indirectly established by their successful application to dual-comb spectroscopy (see below). Further engineering could give access to the full ~2,000 cm⁻¹-wide gain bandwidth of chromium ions at 2.5 μm. Within the 4–5 μm region, tunable lasing has been demonstrated in Fe⁺⁺:doped crystals. Such lasers, if mode-locked, could provide frequency comb sources deep in the mid-infrared. Thulium, holmium and erbium ions also have several gain bands in the mid-infrared region (Fig. 3b). Thulium-doped silica fibre lasers emit at around 1.9 μm, and mode-locking has been achieved through the power of these combs to the watt level, thus facilitating their application to dual-comb spectroscopy, while sufficiently suppressing undesirable non-radiative multiphonon relaxation — even at room temperature — due to their low maximum phonon energy.

**Difference-frequency generators.** Laser sources have remained scarce at wavelengths beyond 3 μm. Quantum cascade lasers can be tailored to operate at nearly arbitrary wavelengths, and recent experiments indicate that mode-locking is possible in principle. However, the comb properties of these rather narrow (<50 cm⁻¹) emission spectra have not yet been tested. In most cases, a different route is taken to access the spectral region beyond 3 μm, in which nonlinear optical effects are harnessed to transfer electromagnetic energy from the visible or near-infrared domain into the mid-infrared (Fig. 2b,c).

For example, all modes of a near-infrared frequency comb can simultaneously be subjected to difference-frequency generation (DFG). When mixed with a continuous-wave (CW) laser of frequency ν_CW, the modes of a comb with frequencies ν_n = ν_rep + f_n can correspondingly be transferred to ν_n^DFG = ν_n - ν_CW, which can lie in the mid-infrared for an appropriately chosen ν_CW. The efficiency of this process depends not only on the strength of the optical nonlinearity, but also on the ability to achieve phase-matching — that is, constructive interference of the radiation generated at different depths in the nonlinear crystal — over the wide necessary bandwidth. For broadband conversion, a common approach is to use periodically poled crystals, in which the sign of the nonlinear coefficient is reversed just at the depth where the generated waves would start to oscillate out of phase. This ensures that the difference-frequency builds up coherently all along the crystal. However, even in this case, imperfect phase-matching is often the limiting factor for the achieved bandwidth because the poling period is optimized for only part of the comb spectrum. This approach typically achieves a spectral width of 200 cm⁻¹ and powers of the order of nanowatts per mode (Fig. 3). DFG between two synchronized combs has so far been marginally investigated, owing to its complexity and cost. Alternatively, difference-frequencies can be generated between the different teeth of a single comb. In this case ν_CW = |n - m| f_rep, where both n and m are integers. The comb’s carrier–envelope offset frequency is fixed to zero, which simplifies control over the modes’ absolute frequency. Using periodically poled lithium niobate (PPLN) as a nonlinear medium, researchers have generated spectra that span 3–5 μm with a width of more than 500 cm⁻¹ and powers of up to 10 nW per comb mode. At a wavelength of around 5 μm, absorption in lithium niobate sets a limit on how far this approach can be pushed into the mid-infrared. Other materials must be used to access longer wavelengths (Fig. 3b). For example, 300-cm⁻¹-wide spectra tunable in the range of 3–17 μm have been generated in gallium selenide, with powers of up to 50 nW per comb tooth.

**Optical parametric oscillators.** A key challenge in sources based on nonlinear optics is the efficiency of the desired photon-conversion process. This metric often remains well below 1%, even in the best...
Recently, researchers have demonstrated wide (>100 cm⁻¹) mid-infrared combs pumped by compact solid-state laser, many longitudinal ‘signal’ modes of the resonator in an optical microresonator comprises a toroidal ring of sub-millimetre diameter that provides access to longer wavelengths. Another noteworthy route is the use of orientation-patterned GaAs as the nonlinear medium, as its transparency in the deep mid-infrared provides access to longer wavelengths.

**Microresonator-based Kerr combs.** Recently, researchers have reported that a special form of parametric oscillation (sometimes referred to as hyper-parametric oscillation) can be used to generate a frequency comb in an optical microresonator (Fig. 2d). The resonator comprises a toroidal ring of sub-millimetre diameter that
Although, the coherence of the resulting spectra is not destroyed by competing nonlinearities.

Resonators made from crystalline materials such as calcium and magnesium fluoride support ultrahigh-Q whispering-gallery modes deep in the mid-infrared (λ < 7 μm) and simultaneously exhibit the anomalous dispersion required for efficient and low-noise comb generation\(^{62,63}\). Researchers have employed pumping at 2.45 μm to demonstrate a Kerr comb covering the range of 2.35–2.5 μm (at around −60 dB)\(^{64}\) (Fig. 4d). The combination of a powerful pump source and a large mode spacing of 107 GHz (corresponding to the round-trip along the resonator’s perimeter) enables milliwatt powers per mode (Figs. 3, 4d). This novel approach enables the generation of simple and compact mid-infrared combs with yet unexplored opportunities for different resonator materials (Si, Ge and InP) or pump sources. Finally, the large mode spacing could be beneficial for a number of emerging applications in spectroscopy and metrology, as described below.

Applications

The first applications of mid-infrared frequency combs concentrated on the precision spectroscopy of molecules. Recent experiments have demonstrated an intriguing potential for the rapid and sensitive acquisition of molecular spectra over a vast spectral span. Foreseen applications might push the frontiers of spectroscopy and dynamics even further by employing coherent control or nonlinear phenomena.

Frequency combs as spectroscopic calibration tools. Although frequency combs were initially conceived for precision spectroscopy of the hydrogen atom, they are now commonly used for precise frequency measurements of atomic resonances and molecular rovibrational transitions throughout the visible and near-infrared spectral regions. The mid-infrared spectral region offers additional opportunities due to the presence of strong rovibrational transitions in a number of molecules (Fig. 1a). Accurate frequency measurements in the mid-infrared provide an in-depth understanding of a molecule’s energy levels. Because frequency combs can conveniently link optical and microwave frequencies, they provide the long-living mechanism needed to realize an optical clock. In the mid-infrared region, frequency combs have enabled the demonstration of molecular optical clocks, using, for example, the hyperfine \(^{2}\)F\(_{2}\) optical transition\(^{35,37}\) of the P(7) line of the \(\nu_3\) band in methane as a pendulum with a fractional instability of 1.2 × 10\(^{-14}\). This allows the comparison between a mid-infrared clock and other optical clocks.

Comb-enabled accurate frequency measurements (Fig. 5a) in the mid-infrared also allow new tests of fundamental physical laws and improvements in the determination of fundamental constants, as well as sensitive limits for their possible slow variation. For instance, the frequency comparison of a rovibrational transition in SF\(_6\) (Fig. 5b) around 10 μm — accessed through spatial two-photon Ramsey fringes — to a caesium microwave atomic clock by means of a frequency comb and an optical link\(^{40}\) has set an upper limit on a possible small variation of the proton-to-electron mass ratio\(^{40}\). These model-free results are derived from an absolute frequency measurement within an impressive fractional uncertainty of 2.8 × 10\(^{-14}\). Such data are complementary to those retrieved from astronomical observations, where measurements are effectively separated in time by several billion years.

Precise measurements of the Boltzmann constant have so far been performed using acoustical gas thermometry, with an inaccuracy of 1.7 × 10\(^{-4}\). In recent years, researchers have accurately measured\(^{47}\) the Doppler profile of a well-isolated absorption line of a molecular gas as a potential way to determine the Boltzmann constant by optical means. This requires, in addition to in-depth

---

**Figure 3** | Spectral coverage of different approaches and materials. **a.** Overview of the spectral regions and power range accessible with mid-infrared femtosecond lasers (blue), DFG (red), OPOs (green) and microresonator-based Kerr combs (yellow). Black and white bars represent a selection of realized comb sources, with citations shown in brackets. The width of each bar represents the spectral span over which the respective comb has at least the power per mode indicated by its position on the ordinate. Note that many of the sources shown here are also wavelength-tunable (not shown). **b.** Potential spectral coverage of selected materials if employed in mid-infrared combs (generation approaches are colour-coded as in a and Fig. 2). Note that the range indicated for the rare-earth ions covers different transition bands in each of the ions.

---

**Figure 3** | Spectral coverage of different approaches and materials. **a.** Overview of the spectral regions and power range accessible with mid-infrared femtosecond lasers (blue), DFG (red), OPOs (green) and microresonator-based Kerr combs (yellow). Black and white bars represent a selection of realized comb sources, with citations shown in brackets. The width of each bar represents the spectral span over which the respective comb has at least the power per mode indicated by its position on the ordinate. Note that many of the sources shown here are also wavelength-tunable (not shown). **b.** Potential spectral coverage of selected materials if employed in mid-infrared combs (generation approaches are colour-coded as in a and Fig. 2). Note that the range indicated for the rare-earth ions covers different transition bands in each of the ions.
line-shape modelling and control over systematic effects, accurate control of the frequency of the laser that probes the absorption profile. As a last example, measuring small differences between the infrared transition frequencies of the two enantiomers of a chiral molecule might provide evidence on parity violation due to the weak interaction. However, the latest predictions estimate such relative differences to be as small as $8 \times 10^{-17}$ for the CHFClBr molecule, and of the order of $10^{-13}$–$10^{-14}$ for oxorhenium complexes around $10 \mu m$ in size. The latter sensitivity, although technically challenging for such complex molecules, might be soon within reach using a state-of-the-art ultrahigh-resolution set-up.

Precision spectroscopy in the mid-infrared uses the frequency comb as a frequency ruler (Fig. 5a), similar to the way it is used in the near-infrared or visible regions. The unknown absolute frequency $\nu_i$ of a CW laser is determined by creating a beat note $f_c$, thus giving $\nu_i = n f_{rep} + f_{c} \pm f_c$. The correct sign of $f_c$ is determined by a small change in either of the frequencies, and the mode number $n$ is determined by a coarse measurement of $\nu_i$, for example, with a wavemeter. Although researchers have successfully referenced a CW laser to a mid-infrared frequency ruler, such experiments have not yet reached the performance of their visible counterparts. Frequency combs have been produced by DFG for the direct referencing of methane-stabilized HeNe lasers at 3.39 $\mu m$ or DFG CW sources at 3 $\mu m$. The main drawback of this approach is that both the comb and the probing laser emit in the mid-infrared region, where low-noise high-speed detectors — and more generally advanced photonics technology — are lacking. Upconversion of the infrared light from the CW laser is therefore a preferred alternative. Sum-frequency generation between the CW laser and the near-infrared comb produces a frequency-shifted comb that may still overlap the initial comb. The resulting phase-coherent beat signal can be used to determine the frequency of the CW laser independently of the comb’s carrier–envelope offset frequency. Such an approach has been implemented in, for example, Doppler-free two-photon spectroscopy of SF$_6$ and saturated-absorption spectroscopy of formic acid with CO$_2$ lasers around 9–10 $\mu m$ (refs 70, 71) and Doppler-limited spectroscopy of CO$_2$, with quantum cascade lasers at 4.3 $\mu m$ (ref. 72). The metrological link to a near-infrared frequency comb could also be realized by sum-frequency generation between two CW lasers, as demonstrated, for example, by mixing a 4.4 $\mu m$ quantum cascade laser and a 1.064 $\mu m$ Nd:YAG laser. Alternatively, when the infrared radiation of the CW probing laser is produced by the nonlinear frequency downconversion of near-infrared lasers, the near-infrared CW laser may be referenced to a near-infrared frequency comb, as already implemented in schemes involving DFG (Fig. 5c) and optical parametric conversion.

**Direct frequency comb spectroscopy.** Direct frequency comb spectroscopy, a denomination that first appeared in 2004, was the first application of frequency combs. In the mid-1970s, researchers showed that picosecond mode-locked dye lasers can produce a stable phase-coherent pulse train, and then used it to achieve direct excitation of atomic vapours. Direct frequency comb spectroscopy of atomic resonances by Ramsey-like excitation with a coherent train of multiple light pulses and Doppler-free two-photon excitation therefore has a long history in the visible and ultraviolet regions. This technique involves monitoring the fluorescence from an excited sample while tuning either the repetition frequency or the carrier–envelope offset. The comb can then be used in a manner similar to a CW laser, with the added advantage that the high peak intensity of pulsed lasers facilitates efficient nonlinear conversion into frequency regions where CW lasers are not yet available.

In recent years, novel techniques have been developed in which the comb directly interrogates a vast number of transitions of an absorbing sample. Direct frequency comb absorption spectroscopy of molecules in the gas phase has so far been the most prominent application of mid-infrared frequency combs. In the mid-infrared domain, with its strong molecular fingerprints, attracts considerable interest. Direct absorption frequency comb spectroscopy can provide short measurement times, high sensitivity and high accuracy over a broad spectral bandwidth. The spectrum of the comb is frequency-selectively attenuated and phase-shifted by the molecular resonances, and is analysed using a spectrometer. So far, the preferred spectrometric approach has been Fourier transform spectroscopy because the dispersers associated with detector arrays are neither efficient nor conveniently available in the mid-infrared. Fourier spectrometers record the spectroscopic signal on a single photodetector and therefore overcome dispersive-related issues. Two different implementations of Fourier transform spectrometers have been reported: Michelson-based Fourier transform spectroscopy, and dual-comb spectroscopy. Each presents its own distinct advantages, but both rely on the same physical principle (Fig. 6a,b). Because the frequencies of the mid-infrared comb are too high (15–150 THz) to be counted directly, these techniques downconvert the signal to a lower frequency region where it can be manipulated through digital signal processing. Frequency comb Fourier transform spectroscopy is

![Figure 4 | Typical mid-infrared spectra obtained through different approaches.](image)
Optical frequency measurements are often used to determine the absolute frequency of an atomic or molecular transition interrogated by a single-frequency CW laser. By heterodyning the CW laser against a nearby optical frequency comb — or any broadband coherent source — as the light source for a Michelson-based Fourier transform spectrometer, the two radiofrequencies can be measured. The resulting frequency comb — or any broadband coherent source — as the light source for a Michelson-based Fourier transform spectrometer can then be counted with standard radiofrequency equipment.

Michelson-based Fourier transform spectroscopy has been mastered for more than 40 years, so replacing the traditional incoherent light source with a frequency comb does not present major difficulties. Dual-comb spectroscopy, in contrast, is in its infancy and thus its full potential is yet to be fully realized.

In dual-comb spectroscopy (Fig. 6e), two frequency combs with slightly different line spacings are heterodyned after passing through the cell, yielding a downconverted radiofrequency comb that contains information on the absorption experienced by both combs. Other implementations allow a single comb to interrogate the sample and also to measure the dispersion induced by the sample. The static scheme of dual-comb spectroscopy overcomes the shortcomings induced by the moving mirror of the Michelson interferometer. Its resolution is limited only by the measurement time and the line spacing of the combs. Interleaving several spectra may improve the measurement down to the comb intrinsic linewidth. Moreover, the entire radiofrequency domain up to $f_{rep}/2$ can be covered, and is restricted only by aliasing. Recording times in dual-comb spectroscopy may be much less than those of Michelson-based Fourier transform spectroscopy.

Low-resolution, proof-of-principle demonstrations of dual-comb spectroscopy with difference-frequency generators have a time-domain technique in which the pulse train of a comb is interferometrically sampled — akin to an optical sampling oscilloscope — by a second pulse train of different repetition frequency, which may be produced either by the varying optical delay of a Michelson interferometer or by a second frequency comb source.

In Michelson-based frequency comb Fourier transform spectroscopy (Fig. 6c), the pulse train of a frequency comb with a pulse repetition frequency $f_{rep}$ is analysed by a Michelson interferometer that records interference versus path difference $2vt$, where $t$ is time and $v$ is the constant velocity of the moving mirror. The comb travelling along the fixed mirror arm keeps its native line-spacing $f_{rep}$. The comb in the moving arm of the interferometer has a Doppler-shifted repetition frequency of $f_{rep}(1 - 2vt/c)$. The two interfering frequency combs exiting the interferometer interrogate the absorbing sample and beat on a photodetector. Due to the limited speed of the moving mirror, the optical frequencies are down-converted to the acoustic range of <100 kHz. Using a mid-infrared frequency comb — or any broadband coherent source — as the light source for a Michelson-based Fourier transform spectrometer dramatically reduces the measurement time (or improves the signal-to-noise ratio) owing to the high spectral radiance of the coherent source. This concept has been demonstrated using a Cr:ZnSe mode-locked laser [1] with a wavelength of around 2.4 μm and an OPO-based frequency comb [2] that is tunable in the range of 2.8–4.8 μm and has a width of 50–400 cm$^{-1}$. Sensitivity to weak absorption may be greatly enhanced when the effective absorption pathlength is increased using a multipass cell or a high-finesse resonator, in which the optical cavity is matched to the laser resonator so that it is simultaneously resonant for many comb lines. This scheme therefore requires dispersion-managed cavity mirrors, control over the two degrees of freedom of the comb for coherent addition of the pulses circulating inside the resonator, and tight locking of the comb to the cavity to avoid frequency-to-amplitude noise conversion. The strong intensity of the rovibrational mid-infrared lines associated with a sensitivity enhancement in the cavity of several thousand provides [3] detection levels as low as one part per billion for H$_2$O$_2$ at a wavelength of around 3.75 μm (Fig. 6d).

Another intriguing application explores the potential of broadband near-field microscopy with a frequency comb produced by DFG around 1,000 cm$^{-1}$ to map interferograms of the near-field interaction between a metal tip and polar materials within a few seconds per tip-illuminated spot [4].
been carried out at wavelengths of around 10 μm since 2004, probing gaseous and solid-state samples. Although limited in terms of optical power and comb stability, these demonstrations highlighted one promising characteristic of dual-comb spectroscopy: the very short measurement times enabled by the absence of moving parts. Frequency-comb-based scanning near-field optical microscopy has also been explored. The lack of efficient mid-infrared frequency comb sources and the difficulty associated with synchronizing the pulse trains of two combs with interferometric precision have hindered the development of mid-infrared
dual-comb spectroscopy, and most reports have therefore been in the near-infrared domain. Stimulated Raman dual-comb spectroscopy is an alternative technique for accessing fundamental transitions with near-infrared combs. However, a recent proof-of-principle demonstration using unstabilized Cr:ZnSe mode-locked lasers around 2.4 μm enabled the rovibrational spectrum of acetylene in the range of 3.960–4.220 cm⁻¹ to be recorded within 10 ps at a resolution of 12 GHz. DFG dual-comb experiments at around 3.4 μm have exhibited (Fig. 6f) a high accuracy of 10⁻⁵ cm⁻¹ when measuring the line positions of the Doppler-broadened transitions of the ν₁ band of methane. Simplification of the laser systems for dual-comb spectroscopy is also highly desirable; an intriguing option is offered by a 3.3 μm femtosecond OPO emitting two asynchronous trains of pulses, with no significant nonlinear coupling between the two channels.

Michelson-based frequency comb Fourier transform spectroscopy and dual-comb spectroscopy share a number of advantages over traditional spectrometric instruments: as with any Fourier transform spectrometer, the spectral span is limited only by the spectral bandwidths of the source and detector. The multiplex advantage grants overall consistency of the simultaneously measured spectral elements, which may prove crucial when, for example, investigating transient phenomena. The spatial directionality of laser sources permits remote measurements and microscopic focusing. The high spectral radiance of frequency comb sources provides high signal-to-noise ratios and reduced measurement times. The comb structure of the spectrum dramatically improves the detection sensitivity through the optimal use of cavity-enhanced techniques. Moreover, resolving the comb lines allows for self-calibration of the frequency scale of the spectra. Analyzing the comb light with a Michelson interferometer results in a robust, fast and sensitive multiplex spectrometer, and the already high quality of the achievements guarantees immediate opportunities for many applications, such as in the trace gas detection of multiple species. Dual-comb spectroscopy is more technically challenging than Michelson-based spectroscopy and still requires considerable work to explore its full potential. However, the ability to record Doppler-limited 300 cm⁻¹ mid-infrared spectra within 100 μs is clearly within reach — as are resolutions limited only by the comb linewidth. The absence of moving parts in dual-comb spectroscopy overcomes the speed and resolution limitations of the Michelson-based approach, and may lead to compact high-resolution instruments. One may even envision a chip-size dual-comb spectrometer based on microresonators for real-time spectroscopy in the liquid phase.

Combining frequency combs with other advanced tools in the fields of laser science, nonlinear optics and electronic signal processing may vastly enhance the range and capabilities of molecular laser spectroscopy. However, molecular physics with laser frequency combs is still in its early stages of development. Both Michelson-based frequency comb Fourier transform spectroscopy and dual-comb spectroscopy can be combined with, for example, Doppler-free measurement schemes, hyperspectral imaging, microscopy, temporal resolution or selective molecular detection techniques, while maintaining their already demonstrated capabilities. More interestingly, because laser frequency combs involve intense ultrashort laser pulses, nonlinear interactions can additionally be harnessed and, by controlling the phase of the electric field of ultrashort laser pulses and employing line-by-line pulse shaping, the combination of coherent control over quantum-mechanical processes and high-sensitivity broadband frequency comb spectroscopy techniques can be envisioned. Frequency comb Fourier transform spectroscopy might establish the basis of ground-breaking spectroscopic tools and open up new insights into the understanding of the structure of matter, as well as new horizons in advanced diagnostic instruments in chemistry and biomedicine.

**Future applications.** Beyond enabling advances in molecular spectroscopy, mid-infrared frequency combs are expected not only to add tremendous value to existing applications, but also to have a strong impact on emerging or unexpected fields throughout many areas of research. For instance, the line-by-line pulse shaping of mid-infrared frequency combs would allow for the coherent control over molecular vibrational excitation in the electronic ground state or elementary excitations in condensed matter systems. Traditional shaping devices are either not transparent or exhibit very low diffraction efficiency in this wavelength region, which obstructs the direct modulation of the electric field transients. One approach may be to shape the signal beam of an OPO-based frequency comb.

Frequency combs in the near-infrared and visible regions have recently enabled great improvements in the calibration of ground-based astronomical spectrographs. The atmospheric ‘windows’ in the mid-infrared are beneficial to the radial velocity technique for detecting high red-shift galaxies and exoplanets, as well as the spectroscopic characterization of their atmospheres. Several existing or planned mid-infrared cross-dispersed echelle spectrographs at large telescope facilities, such as the CRYogenic high-resolution InfraRed Echelle Spectrograph at the Very Large Telescope, may benefit from calibration using a mid-infrared frequency comb with a large mode spacing.

Mid-infrared frequency combs can serve as pump sources for extending the spectral territories covered by frequency comb techniques. Femtosecond thulium fibre lasers are already used for synchronously pumping OPOs that span the 3–6 μm range. Access to mid-infrared wavelengths also extends the cut-off energy in high-harmonic generation, which provides intriguing prospects for ultrafast phenomena, the generation of attosecond pulses and the extension of precision spectroscopy into the extreme ultraviolet region. Moreover, as sources of phase-stabilized femtosecond pulses, frequency combs have made an essential contribution to the production of attosecond pulses and the complete recovery of electric field transients. Intense few-cycle long-wavelength laser systems with carrier–envelope phase stabilization may therefore benefit high-field physics applications.

Many other applications might also emerge in the near future, such as dual-comb static optical coherence tomography of tissues with low water content, or the dual-comb calibration of rapidly swept CW mid-infrared lasers.

**Conclusion**

Over the past decade, near-infrared and visible frequency combs have revolutionized optical frequency metrology and optical frequency synthesis. The rapidly evolving developments of frequency comb generator technology in the mid-infrared spectral region suggest that nature and turn-key sources will soon become available, which will stimulate much interest in novel applications. However, fundamental and technological progress in several key areas is still yet to be achieved. Direct laser emission of few-cycle phase coherent pulses across the mid-infrared range, improved materials for efficient nonlinear frequency conversion over a broad spectral bandwidth beyond 6 μm and octave-spanning low-phase noise microresonator-based frequency combs centred deeper in the mid-infrared are among the most important goals of the field. Current applications, mostly benefiting the spectroscopy of molecules, have opened up intriguing prospects in frequency metrology and trace-gas detection. As the performance frontiers of these photonic tools are advanced, we hope to see the development of unforeseen groundbreaking measurement techniques and unexpected scientific discoveries.
References
1. Udem, T., Holzwarth, R. & Hänsch, T. W. Optical frequency metrology. *Nature* **416**, 239–247 (2002).
2. Cundiff, S. T. & Ye, J. Colloquium: Femtosecond optical frequency combs. *Rev. Mod. Phys.* **75**, 325–342 (2003).
3. Ye, J. & Cundiff, S. T. (eds) *Femtosecond Optical Frequency Comb: Principle, Operation and Applications* (Springer, 2005).
4. Hall, J. L. Nobel Lecture: Defining and measuring optical frequencies. *Rev. Mod. Phys.* **78**, 1279–1295 (2006).
5. Hänsch, T. W. Nobel Lecture: Passion for precision. *Rev. Mod. Phys.* **78**, 1297–1309 (2006).
6. Diddams, S. A. The evolving optical frequency comb. *J. Opt. Soc. Am. B* **27**, B51–B62 (2010).
7. Page, R. H. et al. Cr$^{2+}$-doped zinc chalcogenides as efficient, widely tunable mid-infrared lasers. *IEEE J. Quant. Electron.* **33**, 609–619 (1997).
8. Sorokin, I. T. Crystalline mid-infrared lasers. *Top. Appl. Phys.* **89**, 255–349 (2003).
9. Sorokin, E., Naumov, S. & Sorokina, I. T. Ultrabroadband infrared solid-state lasers. *IEEE J. Sel. Top. Quant. Electron.* **16**, 903–917 (2010).
10. Mirov, S. B. et al. Progress in mid-IR Cr$^{2+}$ and Fe$^{2+}$ doped n-ir materials and lasers Invited. *Opt. Mater. Express* **1**, 898–910 (2011).
11. Sorokin, E., Sorokina, I. T., Mandon, J., Guelachvili, G. & Picqué, N. Sensitive multiple spectroscopy in the molecular fingerprint 2.4 μm region with a Cr$^{2+}$:ZnSe femtosecond laser. *Opt. Express* **15**, 16540–16545 (2007).
12. Cizmekcian, M. N., Cankaya, H., Kurt, A. & Sennaroglu, A. Kerr-lens mode-locked femtosecond Cr$^{2+}$:ZnSe laser at 2420 nm. *Opt. Lett.** **34**, 3056–3058 (2009).
13. Slobodchikov, E. & Moulton, P. Progress in ultrafast Cr:ZnSe lasers in Sources, and Related Photonics Devices paper AWA5.4 (OSA, 2012).
14. Sorokin, E., Toluk, N. & Sorokina, I. Kerr-lens mode-locked Cr:ZnSe laser in Lasers, Sources, and Related Photonics Devices paper AWA5.4 (OSA, 2012).
15. Bernhardt, B. et al. Mid-infrared dual-comb spectroscopy with 2.4 μm Cr$^{2+}$:ZnSe femtosecond lasers. *Appl. Phys. B** **100**, 3–8 (2010).
16. Fedorov, V. V. et al. 3.77–5.05 μm tunable solid-state lasers based on Fe$^{2+}$:ZnSe crystals operating at low and room temperatures. *IEEE J. Quant. Electron.* **42**, 907–917 (2006).
17. Frolow, M. P. et al. Laser radiation tunable within the range of 4.35–5.45 μm in a ZnSe crystal doped with Fe$^{2+}$ ions. *J. Russ. Laser. Res.** **32**, 528–536 (2011).
18. Kozlovsky, V. I. et al. Pulsed Fe$^{2+}$:ZnSe laser continuously tunable in the wavelength range of 3.94–4.65 μm. *Quantum Electron.* **41**, 1–3 (2011).
19. Pollnau, M. & Jackson, S. D. In *Topics in Applied Physics* Vol. 89 (eds Sorokina, I. & Vodopyanov, K.), 219–225 (Springer, 2003).
20. Nelson, L. E., Ippen, E. P. & Haus, H. A. Broadly tunable sub-500 fs pulses from an additive-pulse mode-locked thulium-doped fiber laser ring laser. *Appl. Phys. Lett.* **67**, 21–9195 (1995).
21. Solodyanykin, M. A. et al. Mode-locked 1.93 μm thulium fiber laser with a carbon nanotube absorber. *Opt. Lett.** **33**, 1336–1338 (2008).
22. Kieu, K. & Wise, W. Solliton thulium-doped fiber laser with carbon nanotube saturable absorber. *IEEE Photon. Techn. Lett.* **21**, 128–130 (2009).
23. Hassen, F., Wandt, D., Morgner, U., Neumann, J. & Kracht, D. Pulse characteristics of a passively mode-locked thulium fiber laser with positive and negative cavity dispersion. *Opt. Express** **18**, 18891–18898 (2010).
24. Wang, Q., Geng, J. H., Jiang, Z., Luo, T. & Jiang, S. B. Mode-locked Ti:Ho-codoped fiber laser at 2.06 μm. *IEEE Photon. Techn. Lett.* **23**, 682–684 (2011).
25. Phillips, C. R. et al. Supercontinuum generation in quasi-phase-matched LiNbO$_3$ waveguide pumped by a Tm-doped fiber laser system. *Opt. Lett.** **36**, 3912–3914 (2011).
26. Adler, F. & Diddams, S. A. High-power, hybrid Er:Yb/Tm:Er fiber frequency comb source in the 2 μm wavelength region. *Opt. Lett.** **37**, 1400–1402 (2012).
27. Galusceli, N. et al. 1.6-W self-referenced frequency comb at 2.06 μm using a Ho:YLF multipass amplifier. *Opt. Lett.** **36**, 2299–2301 (2011).
28. Hofstetter, D. & Faist, J. High performance quantum cascade lasers and their applications. *Top. Appl. Phys.* **89**, 61–96 (2003).
29. Paella, R. et al. Self-mode-locking of quantum cascade lasers with giant ultrafast optical nonlinearities. *Science** **290**, 1739–1742 (2000).
30. Wang, C. Y. et al. Mode-locked pulses from mid-infrared quantum cascade lasers. *Opt. Express** **17**, 12929–12943 (2009).
31. Fischer, C. & Sigrist, M. W. Mid-IR difference frequency generation. *Top. Appl. Phys.* **89**, 97–140 (2003).
32. Maddaloni, P., Malaria, P., Gagliardi, G. & De Natale, P. Mid-infrared fiber-based optical comb. *New J. Phys.* **8**, 262 (2006).
33. Baumann, E. et al. Spectroscopy of the methane v$_3$ band with an accurate midinfrared coherent dual-comb spectrometer. *Phys. Rev. A** **84**, 062513 (2011).
64. Wang, C. Y. et al. Mid-infrared frequency combs based on microresonators. Preprint at http://arxiv.org/abs/1109.2716 (2011).
65. Dousse, C. et al. Long-distance frequency dissemination with a resolution of 10^{-17}. Phys. Rev. Lett. 94, 203904 (2005).
66. Shelkovnikov, A., Butcher, R. J., Chardonnet, C. & Amy-Klein, A. Stability of the proton-to-electron mass ratio. Phys. Rev. Lett. 100, 150801 (2012).
67. Lemarchand, C. et al. Progress towards an accurate determination of the Boltzmann constant by Doppler spectroscopy. New J. Phys. 13, 073028 (2011).
68. Darquié, B. et al. Progress toward the first observation of parity violation in chiral molecules by high-resolution laser spectroscopy. Chirality 22, 870–884 (2010).
69. Mala, P., Maddaloni, P., Gagliardi, G. & De Natale, P. Absolute frequency measurement of molecular transitions by a direct link to a comb generated around 3 μm. Opt. Express 16, 8242–8249 (2008).
70. Amy-Klein, A. et al. Absolute frequency measurement of a SF6 two-photon line by use of a femtosecond optical comb and sum-frequency generation. Opt. Lett. 30, 3320–3322 (2005).
71. Bielsa, F. et al. HCOOH high-resolution spectroscopy in the 9.18 μm region. J. Mol. Spectrosc. 247, 41–46 (2008).
72. Gatti, D. et al. High-precision molecular interrogation by direct referencing of a quantum-cascade-laser to a near-infrared frequency comb. Opt. Express 19, 17520–17527 (2011).
73. Bartalini, S. et al. Frequency-comb-referenced quantum-cascade laser at 4.4 μm. Opt. Lett. 32, 988–990 (2007).
74. Giussfredi, G. et al. Saturated-absorption cavity ring-down spectroscopy. Phys. Rev. Lett. 104, 110801 (2010).
75. Okubo, S., Nakayama, H., Iwakuni, K., Inaba, H. & Sasada, H. Absolute frequency list of the ν1 transitions of methane at a relative uncertainty level of 10^{-15}. Opt. Express 19, 23878–23888 (2011).
76. Vainio, M., Merimaa, M. & Halonen, L. Frequency-comb-referenced molecular spectroscopy in mid-infrared region. Opt. Lett. 36, 4122–4124 (2011).
77. Marian, A., Stowe, M. C., Lawall, J. R., Felinto, D. & Ye, J. United time–frequency spectroscopy for dynamics and global structure. Science 306, 2063–2068 (2004).
78. Teets, R., Eckstein, J. & Hänsch, T. W. Coherent two-photon excitation by multiple light pulses. Phys. Rev. Lett. 38, 760–764 (1977).
79. Eckstein, J. N., Ferguson, A. I. & Hänsch, T. W. High-resolution two-photon spectroscopy with picosecond light pulses. Phys. Rev. Lett. 40, 847–850 (1978).
80. Diddams, S. A., Hollberg, L. & Mbele, V. Molecular fingerprinting with the resolved modes of a femtosecond laser frequency comb. Nature 445, 627–630 (2007).
81. Mandon, J., Guelachvili, G. & Picqué, N. Fourier transform spectroscopy with a laser frequency comb. Nature Photon. 4, 55–57 (2009).
82. Bernhardt, B. et al. Cavity-enhanced dual-comb spectroscopy. Nature Photon. 4, 55–57 (2010).
83. Thorpe, M. I. & Ye, J. Cavity-enhanced direct frequency comb spectroscopy. Appl. Phys. B 91, 397–414 (2008).
84. Adler, F. et al. Cavity-enhanced direct frequency comb spectroscopy: technology and applications. Ann. Rev. Anal. Chem. 3, 175–205 (2010).
85. Thorpe, M. I. et al. Broadband cavity ringdown spectroscopy for sensitive and rapid molecular detection. Science 311, 1595–1599 (2006).
86. Griffiths, P. R. & De Haseth, J. A. Fourier Transform Infrared Spectroscopy 2nd edn, 1–656 (Wiley, 2007).
87. Adler, F. et al. Mid-infrared Fourier transform spectroscopy with a broadband frequency comb. Opt. Express 18, 21861–21872 (2010).
88. Foltynowicz, A., Malowski, P., Fleisher, A. J., Bjork, B. & Ye, J. Cavity-enhanced optical frequency comb spectroscopy in the mid-infrared — application to trace detection of H2O2. Preprint at http://arxiv.org/abs/1202.1216 (2012).
89. Amarie, S. & Keilmann, F. Broadband-infrared assessment of phonon resonance in scattering-type near-field microscopy. Phys. Rev. B 83, 045404 (2011).
90. Ganz, T., Brehm, M., von Ribbeck, H. G., van der Weide, D. W. & Keilmann, F. Vector frequency-comb Fourier-transform spectroscopy for characterizing metamaterials. New J. Phys. 10, 123007 (2008).
91. Brehm, M., Schlässer, A. & Keilmann, F. Spectroscopic near-field microscopy using frequency combs in the mid-infrared. Opt. Express 14, 11222–11233 (2006).
92. Coddington, I., Swan, W. C. & Newbury, N. R. Coherent multiheterodyne spectroscopy using stabilized optical frequency combs. Phys. Rev. Lett. 100, 013902 (2007).
93. Zolot, A. M. et al. Direct-comb molecular spectroscopy with accurate, resolved comb teeth over 43 THz. Opt. Lett. 37, 638–640 (2012).
94. Ideguchi, T., Poisson, A., Guelachvili, G., Picqué, N. & Hänsch, T. W. Adaptive real-time dual-comb spectroscopy. Preprint at http://arxiv.org/abs/1201.4177 (2012).
95. Ideguchi, T., Bernhardt, B., Guelachvili, G., Hänsch, T. W. & Picqué, N. Femtosecond stimulated raman dual-comb spectroscopy in CLEO: Applications and Technology paper CThC5.6 (OSA, 2012).
96. Zhang, Z. et al. Asynchronous midinfrared ultrafast optical parametric oscillator for dual-comb spectroscopy. Opt. Lett. 37, 187–189 (2012).
97. Cundiff, S. T. & Weiner, A. M. Optical arbitrary waveform generation. Nature Photon. 4, 760–766 (2010).
98. Steinmetz, T. et al. Laser frequency combs for astronomical observations. Science 233, 1335–1337 (2008).
99. Li, C.-H. et al. A laser frequency comb that enables radial velocity measurements with a precision of 1 cm s^{-1}. Nature 452, 610–612 (2008).
100. Mayor, M. & Queloz, D. A Jupiter-mass companion to a solar-type star. Nature 378, 353–359 (1995).
101. Figueira, P. et al. Radial velocities with CRIRES. Pushing precision down to 5–10 m/s. Astron. Astrophys. 511, A55 (2010).
102. Sheehy, B. et al. High harmonic generation at long wavelengths. Phys. Rev. Lett. 83, 5270–5273 (1999).
103. Krause, J. L., Schafer, K. J. & Kulander, K. C. High-order harmonic generation from atoms and ions in the high intensity regime. Phys. Rev. Lett. 68, 3535–3538 (1992).
104. Silva, F., Bates, P. K., Esteban-Martin, A., Ebrahim-Zadeh, M. & Biegert, J. High-average-power, carrier–envelope phase-stable, few-cycle pulses at 2.1 μm from a collinear BiB3 optical parametric amplifier. Opt. Lett. 37, 933–935 (2012).
105. Lee, S. J., Widyatmoko, B., Kourogi, M. & Ohtsu, M. Ultrahigh scanning speed optical coherence tomography using optical frequency comb generators. Ipn J. Appl. Phys. 40, L878–L880 (2001).
106. Giorgetta, F. R., Coddington, I., Baumann, E., Swann, W. C. & Newbury, N. R. Fast high-resolution spectroscopy of dynamic continuous-wave laser sources. Nature Photon. 4, 853–857 (2010).
107. Rothman, L. S. et al. The HITRAN 2008 molecular spectroscopic database. J. Quant. Spectrosc. Ra. 110, 533–572 (2009).

Acknowledgements
T.W.H. and N.P. acknowledge support by the European Associated Laboratory ‘European Laboratory for Frequency Comb Spectroscopy’ and the Max Planck Foundation. A.S. acknowledges support from a Marie Curie IAPP programme and the Swiss National Science Foundation. A. Amy-Klein, E. Baumann, B. Darquié, P. de Natale, A. Foltynowicz-Matsyba, F. Keilmann, T.J. Kippenberg, D. Mazzotti, N.R. Newbury, K. Vodopyanov, C.Y. Wang and J Ye are gratefully acknowledged for providing comments, data and figures.

Additional information
Correspondence and requests for materials should be addressed to N.P.