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Feature article

Broadband molecular spectroscopy with optical frequency combs

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ABSTRACT

Over the past dozen years, optical frequency combs have evolved into valuable tools for broadband molecular spectroscopy. They have already enabled remarkable advances for the measurement of complicated molecular spectra by improving the resolution, accuracy, sensitivity, and measurement times of spectrometric approaches. In this feature article, we trace some recent developments relevant to high-resolution spectroscopy of molecules, especially in the mid-infrared spectral region. We discuss examples that harness the emerging techniques of cavity-enhanced frequency comb spectroscopy and dual-comb spectroscopy and we conclude with a perspective of forthcoming opportunities and challenges.

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1. Introduction

Since the early 2000s, laser frequency combs have been harnessed as light sources and spectrometers for molecular spectroscopy over wide spectral spans [1–8]. They now offer keys to central questions in fundamental and applied molecular physics and physical chemistry. Precise frequency measurements in simple molecules provide stringent tests of the fundamental laws of physics and of *ab initio* quantum chemistry calculations. Disentangled spectra of complex large molecules improve our understanding of molecular structure and internal dynamics. Time-resolved spectroscopy is used to investigate the kinetics of reactions and their transient intermediates. Field-deployed sensors monitor trace gases in various environments. For tackling these demanding questions and many others, frequency combs and their broad coherent spectrum of sharp laser lines facilitate groundbreaking approaches to linear and nonlinear spectroscopy that can outperform other state-of-the-art techniques with respect to resolution, accuracy, recording time, and sensitivity.

Frequency combs were initially developed for frequency metrology [9,10] and enabled absolute frequency measurements across the entire optical spectrum. A frequency comb is often produced by a laser that emits a train of ultra-short pulses at a regular repetition rate f_{rep} (Fig. 1). Dispersion in the laser cavity induces a pulse-to-pulse phase slip $\Delta\varphi_{ce}$ of the carrier wave relative to the envelope of the pulses. Both f_{rep} and $\Delta\varphi_{ce}$ can be measured and stabilized. The corresponding frequency spectrum spans a broad spectral bandwidth, inversely proportional to the pulse duration, and consists of phase-coherent laser lines, equidistantly spaced by f_{rep}. The phase slip $\Delta\varphi_{ce}$ shifts the spectrum from harmonic frequencies of f_{rep} by an amount called the carrier-envelope offset frequency $f_0 = f_{rep} \cdot \Delta\varphi_{ce}/(2\pi)$. The comb line optical frequencies may thus be written $\nu_m = m \cdot f_{rep} + f_0$, where m is an integer.

Frequency combs now find many applications that were not initially envisioned, including their use as light sources for new approaches to broadband molecular spectroscopy. In this article, we present a perspective into recent work in broadband frequency comb spectroscopy, and address some of the scientific questions that frequency combs are well-suited to tackle. We emphasize the benefits of cavity-enhanced frequency comb spectroscopy and dual-comb spectroscopy in our own studies of fundamental (ro)vibrational transitions in gas- and liquid-phase molecules, and highlight other results that we find important and promising within this personal perspective. However, we do not strive to provide a comprehensive review of this emergent and lively field, and instead refer readers to several reviews that cover various aspects of comb spectroscopy more expansively [11–19].

2. Experimental techniques

2.1. Comb sources

Powerful optical frequency comb sources emerged from the mode-locked lasers developed in the 1980s for their ultrafast

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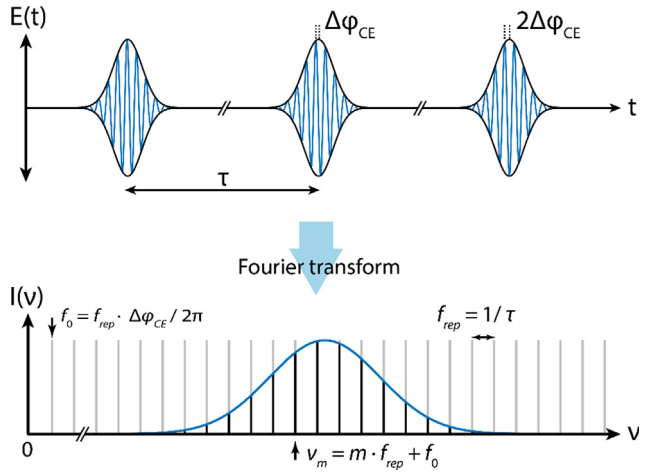

Fig. 1. Time domain representation of a mode-locked ultrafast laser pulse train and the corresponding frequency domain representation demonstrating the formation of comb teeth.

(<100 fs) pulses across the visible and near-infrared [20,21], although early demonstrations with picosecond lasers [22,23] and frequency metrology with electro-optic modulators [24] had already shown convincing potential. The most reliable and therefore most widespread comb sources were initially based on Ti:Sapphire lasers centered near 800 nm or fiber lasers [25] doped with ytterbium, erbium, or thulium, which lase near 1.0, 1.5, and 2.0 μm, respectively. With the increasingly active development of comb-based molecular spectroscopy in recent times [26,27], much work has been done to extend comb technology into the mid-infrared (mid-IR) and the terahertz (THz) regions; the following discussion will focus on these mid-IR and THz sources.

2.1.1. Difference frequency generation

While mode-locked fiber-based and solid-state lasers that emit directly in the mid-IR are in development [28,29], most mid-IR combs are generated from nonlinear frequency conversion of near-IR combs. Difference frequency generation (DFG) is one of the simplest approaches, with a single pass through a nonlinear crystal and highly convenient passive cancellation of f_0. In a typical DFG setup, light from a near-IR fiber comb is split into two arms, one of which is broadened in a nonlinear fiber and filtered to select either the shortwave or longwave component. The two arms are amplified separately and recombined in a DFG crystal to produce mid-IR light. Alternatively, intrapulse DFG achieves subtraction of the shorter and longer wavelength components within a single broadband pulse.

DFG can generate mid-IR light over a wide wavelength range, depending on the chosen pump laser, broadening scheme, and nonlinear crystal. DFG combs with average powers of up to 250 mW have been reported tunable over the 3–5 μm range using periodically poled lithium niobiate (PPLN) crystals and either erbium [30,31] or ytterbium [32] doped fiber pump lasers. Longer-wavelength combs have been generated with powers of 4 mW in GaSe at 8–14 μm [33], 1.55 mW in $AgGaS_2$ at 7.5–11.6 μm [34], and 60 mW in orientation-patterned (OP) GaP at 6–11 μm [35]. These DFG sources have typical simultaneous spectral bandwidths of several hundred cm^{-1}, while tunable over the spectral windows specified above. Highly tunable sources with relatively narrow bandwidths can be of great utility as they demonstrate increased power per comb tooth. On the other hand, intrapulse DFG sources have pushed towards broadband super-octave combs, with simultaneous bandwidths of 6.8–16.4 μm achieved with a $LiGaS_2$ crystal [36] and 4–12 μm achieved using OP-GaP [37].

2.1.2. Optical parametric oscillators

Mid-IR optical parametric oscillators (OPOs) can generate comb light with much higher power capabilities than DFG systems while maintaining a wide spectral tuning range. In the OPO process, a pump photon is converted into two lower-energy signal and idler photons in a nonlinear crystal. The conversion efficiency is dramatically improved by carrying out this process in a resonant cavity. However, additional experimental complexity is introduced: active feedback is needed to stabilize the f_0 of the resulting idler comb and the OPO cavity length must match the repetition rate of the pump laser for synchronous pumping.

A 1.5 W OPO comb at 3–5 μm based on PPLN has served as a workhorse tool for molecular spectroscopy in recent years [38–40]. Longer wavelength OPOs are also in development, though few sources have demonstrated significant power past 8 μm [41]. An OP-GaP OPO comb tunable over 5–12 μm can produce 15 mW of idler light [42] and, very recently, a $AgGaSe_2$ system was reported operating at 8–10 μm with 100 mW of idler power [43]. A broadband degenerate GaAs OPO has been designed to produce 0.5 W of light across a simultaneous 5–8 μm bandwidth [44,45]. Methods combining DFG and OPO technologies promise to extend wavelength tuning capabilities out to 20 μm [46].

2.1.3. Terahertz combs based on nonlinear frequency conversion

The terahertz (THz) domain, spanning wavelengths from 1 mm to 100 μm (10–100 cm^{-1}), is an attractive spectral window for probing molecular rotations and low-frequency, large-amplitude vibrations. When a well-chosen semiconductor is excited by the beat signal of two optical frequencies, the carrier density in the semiconductor oscillates at a THz frequency, generating an oscillating current which produces THz radiation. A broad THz frequency comb can be generated through photomixing of a near-IR frequency comb in a semiconductor-based photoconductive antenna [47–49] or via optical rectification in a nonlinear crystal, such as a lithium niobate waveguide [50]. In both cases, the optical-to-THz conversion efficiency is on the order of 10^{-3}–10^{-4}. The average power of such THz combs is therefore typically limited to a few microwatts. These intrapulse DFG methods yield THz combs with the same repetition rates as the near-IR pump combs and passively cancelled carrier-envelope offset frequencies, simplifying stabilization and control of the THz combs. The span of such combs can extend over several THz [48].

Dual-comb spectroscopy, also called asynchronous-optical sampling spectroscopy in the THz community [47–49,51–53], has been the preferred technique to harness THz combs for molecular spectroscopy. In the THz domain, the constraints on the relative timing fluctuations between pairs of pulses are much reduced compared to the optical region and the implementation of the dual-comb scheme is therefore significantly simplified.

2.1.4. Electro-optic modulators

Electro-optic modulators (EOMs) produced the first frequency combs capable of comparing optical frequencies separated by several THz [24]. Although their use in frequency metrology has been practically supplanted by octave-spanning optical frequency synthesizers based on mode-locked lasers, EOM-based frequency combs are useful in direct molecular spectroscopy where they offer an affordable and easy-to-implement alternative to pulsed ultrafast lasers.

An EOM – or a cascade of intensity and phase modulators – seeded by a narrow linewidth continuous-wave (cw) laser generates a comb with a repetition rate and a center wavelength that can be selected quickly and freely by simply dialing a knob.

Repetition rates ranging from 200 kHz (6×10^{-6} cm^{-1}) [54] to 25 GHz (0.83 cm^{-1}) [55] have been reported for spectroscopy applications. As cw lasers have become widely and quickly tunable, they enable the generation of frequency-agile combs [56]. The number of comb lines with cascaded EOMs reaches about 100 and is fundamentally limited by the multiplication of the phase noise of the synthesizer [57]. The intensity distribution of the spectral envelope may be rather flat. Techniques involving spectral broadening in a nonlinear fiber [56] or driving an EOM with chirped waveforms [54] can extend the span to 10,000 comb lines. Optical filtering by a resonant cavity in combination with spectral broadening in a nonlinear fiber can yield an octave-spanning EOM comb [58,59], though the implementation becomes significantly more complex.

2.1.5. Quantum cascade lasers

Mid-IR frequency combs based on quantum cascade lasers (QCLs) were first demonstrated in 2012 [60]. QCLs provide electrically-pumped comb sources, with repetition rates on the order of 10 GHz (0.3 cm^{-1}) and center wavelengths that can be engineered across the mid-infrared and THz [61] regions. Interband cascade lasers extend the coverage of electrically-pumped devices to wavelengths as short as 3 μm [62,63].

The direct emission of these devices in the mid-IR and THz regions makes them very attractive for spectroscopy applications. Furthermore, QCL frequency combs can produce average powers reaching 1 W in the mid-IR [64,65] and 10 mW in the THz [61], leading to an unparalleled power per comb tooth in these spectral domains. A fixed phase relationship between their equidistant comb lines has been evidenced, although they usually do not emit pulses and the physical principle for their operation may be better understood by analogy with frequency modulation mode-locking.

QCL frequency combs have fewer than a few hundred individual lines, a number which is often limited by dispersion that requires careful engineering, especially in the mid-IR. The position of the comb lines can be tuned within one free spectral range by changing the temperature or the current of the lasers [66]. Optically-pumped semiconductor-based frequency comb sources are also emerging in the near-IR [67,68].

2.1.6. Microresonators

A microresonator is a whispering gallery mode resonator inside which light is confined by total internal reflection at the air-dielectric interface. Such microresonators can combine a very high quality factor, which can exceed 10^9, and strong material nonlinearities usually of the third order. When a microresonator is pumped by a cw laser, parametric oscillation occurs and, with appropriate dispersion engineering, solitons can form. Besides the prospect of entirely integrated on-chip frequency comb sources [69], microresonator-based frequency combs feature large repetition rates, ranging from 10 GHz (0.3 cm^{-1}) to several THz (tens to hundreds of cm^{-1}), which are difficult or even impossible to reach with other technologies [70], though may not necessarily be convenient for spectroscopy. Soliton mode-locking has been reported with a number of platforms including magnesium fluoride crystals [71], silica [72], CMOS-compatible silicon nitride [73], and silicon [74] chips. Frequency comb generation has largely been reported in the telecommunication near-IR region, where optical bandwidths spanning an octave have been achieved [75]. With materials of suitable transparency, combs can also be generated in the mid-IR, with center wavelengths as long as 4.3 μm [74,76,77].

2.2. Detection methods

Various detection schemes exist to analyze the broad spectral content of a frequency comb with sufficient spectral resolution, sensitivity, and acquisition speed [16,19]. Regardless of scheme, if the spectrometer resolution is sufficient to resolve individual comb lines, the molecular spectrum is sampled by the comb repetition rate $f_{rep,}$ thus setting the resolution to f_{rep}. Ultimately, the spectral resolution may be limited by the comb tooth linewidth itself: interleaving spectra measured with discretely stepped f_{rep} or f_0 improves the resolution below the intrinsic comb line spacing.

Fourier transform spectroscopy (FTS), a widely used tool for broadband spectroscopy, is perhaps the most general readout method. In Michelson-based FTS, a scanning interferometer is used to measure the laser spectrum via the Fourier transform of its time domain interferogram [78,79]. The advantages of FTS include its compatibility with broadband and mid-IR light as well as spectral resolution down to 100 MHz achievable with a relatively compact setup. Matching the stage length of a scanning interferometer to the comb repetition rate can allow for comb-mode resolved measurements without distortion from the instrument lineshape [11,27,80]. The major shortcomings of Michelson-based FTS are the presence of moving parts and long acquisition times as the interferometer delay is mechanically scanned.

Dual-comb spectroscopy (DCS) is an FTS technique that replaces the scanning interferometer arm with a second comb [17,19]. Here, multiheterodyne detection of the comb spectrum is achieved by beating two combs with repetition rates differing by Δf_{rep}. In the time domain, the two comb pulse trains scan through one another, similar to a scanning FTS interferometer albeit much faster; the entire scan is completed in a time period of $1/\Delta f_{rep}$. In the frequency domain, the two combs beat to create a radiofrequency (RF) comb with a repetition rate of Δf_{rep}. This RF comb is recorded on a single detector and Fourier transformed to recover an RF spectrum that maps directly to the optical spectrum. DCS has become increasingly widespread as frequency comb sources have grown more diverse and compact. Some recent notable developments in this large field of work are discussed further in Section 3.2.

Electro-optic sampling (EOS) is a closely related FTS technique involving upconversion of the signal to higher optical frequencies. Though commonly used in the field of THz spectroscopy [49,53,81,82], EOS has only recently been applied for use with mid-IR combs [36,83,84]. Here, the mid-IR comb is mixed with an ultrashort near-IR pulse in a nonlinear crystal. Provided that the near-IR pulses are much shorter in time than the optical period of the mid-IR, the electric field of the mid-IR pulse can be directly sampled via ellipsometry. This method may be implemented with a delay line or a DCS detection scheme [48,49,53,81,84]. The upconversion of the mid-IR field to the near-IR allows the use of standard optical detectors with high detection bandwidths, making EOS applicable to light with wavelengths longer than 12 μm.

A different approach involves spectrally dispersing comb light onto a 2D detector array. This has been best demonstrated using a virtually imaged phased array (VIPA) etalon [6,85] in combination with a conventional grating to cross-disperse the light. The VIPA is a plane parallel solid etalon into which the laser beam is coupled at a slight angle. The beam reflections inside the VIPA interfere such that different frequencies of light leave the exit surface at distinct angles with very high angular dispersion, 30–40 times greater than a standard diffraction grating. A second grating in an orthogonal configuration separates overlapping VIPA mode orders. An image of the dispersed light is recorded with a CCD camera and read out column by column along the VIPA dispersion axis to construct a spectrum. This method allows for simultaneous broadband multichannel measurements with <1 GHz spectral resolution, time resolution down to 10 μs, and acquisition speeds typically limited by the camera frame rate. Rapid acquisition enables spectroscopy of transient species and fast image referencing for noise reduction. The recent development of high-order germanium immersion gratings promises to extend cross-dispersed comb

imaging further into the mid-IR [86,87], where the performance of VIPA etalons has not yet been demonstrated.

Vernier spectroscopy is another technique for broadband comb detection worth mentioning. Here, the comb spectrum is filtered using an optical cavity, resulting in a much larger effective repetition rate resolvable with a simple grating spectrometer. The comb f_{rep} is then swept so that new teeth come into resonance with the cavity and measurements taken throughout the sweep are interleaved to construct a complete spectrum. In one implementation, a swept mirror is used to map the sweep time axis onto the second spatial axis of a 2D detector array [7].

3. Applications to molecular spectroscopy

3.1. Cavity-enhanced direct frequency comb spectroscopy

Cavity-enhanced direct frequency comb spectroscopy (CE-DFCS) matches the evenly spaced spectral structure of a frequency comb to the resonant modes of a high-finesse optical enhancement cavity [5,11,16,88]. This method retains the advantages of direct comb spectroscopy, with (a) broadband, multiplexed detection of several species and absorption features, (b) high frequency resolution, allowing full analysis and identification of the states and species detected, and (c) fast acquisition time, both for flexibility of use and for detecting transient species in real time. The added cavity dramatically enhances the interaction length between comb and sample providing (d) high sensitivity for detection of trace transient intermediates or very weak absorptions.

Cavity-enhanced spectroscopy has been widely applied in continuous wave experiments to increase the effective pathlength of light through an intracavity sample [89]. For weakly absorbing molecules, the fractional light absorption is approximately linear with the light's pathlength through the sample, which in turn is closely related to the cavity finesse, F. The pathlength enhancement relative to a single pass measurement is proportional to the finesse; for light continuously in resonance with the cavity, this enhancement factor is $2F/\pi$.

A comb can be efficiently coupled to an optical cavity by matching the comb repetition rate f_{rep} to an integer ratio of the cavity free spectral range (FSR). The comb f_0 must also be adjusted to match an effective cavity frequency offset caused by intra-cavity dispersion. The intra-cavity dispersion additionally restricts the spectral bandwidth of the comb that can be coupled into the cavity simultaneously due to frequency walk-off between comb modes and cavity resonances. The success of cavity-comb coupling for CE-DFCS applications therefore depends heavily on the construction of a cavity with high finesse and nearly uniform FSR across the spectral window of interest, which in turn depends on the availability of low-loss and low-dispersion cavity mirrors. In the mid-IR, continuing developments in dielectric and crystalline [90] mirror coatings have facilitated CE-DFCS work at new wavelengths and with broader spectral bandwidth.

Once f_{rep} and f_0 are tuned for optimum cavity coupling, they must be actively stabilized with servo loops [91]. Both continuous transmission and swept locking schemes exist to accomplish this. A continuous transmission scheme is typically achieved with a Pound-Drever-Hall lock and has the benefit that nearly all light incident on the cavity is transmitted with a 100% duty cycle. However, the spectral bandwidth that can be simultaneously coupled may be limited and the transmitted light can suffer from frequency-to-amplitude noise conversion due to relative frequency fluctuations between the comb lines and cavity modes if the lock does not have a sufficiently large bandwidth.

In a swept lock, a frequency ramp is applied between the comb lines and cavity modes, so a burst of comb light is transmitted through the cavity at twice the sweep frequency. While this method suffers from a low duty cycle and an effective pathlength half that of the continuous transmission lock [11], it has other advantages. All cavity mode-comb line pairs need not come into resonance simultaneously, increasing the useful spectral bandwidth of the cavity beyond dispersion limitations. Additionally, light intensity noise due to comb-cavity coupling is reduced, and a relatively simple locking scheme is sufficient, using only a slow servo to keep the light transmission peak near the center of the sweep range.

In the following discussion, we highlight the capabilities of CE-DFCS for high-resolution molecular spectroscopy and kinetics measurements of transient intermediates and describe recent developments that extend this technique to sensitive noise-immune schemes and ultrafast transient absorption spectroscopy.

3.1.1. Time-resolved CE-DFCS for molecular kinetics

The broadband capability of CE-DFCS in combination with the rapid acquisition times afforded by VIPA imaging have been exploited to probe chemical reaction kinetics on microsecond timescales [39,92]. With time-resolved cavity-enhanced frequency comb spectroscopy (TR-FCS), the absorption spectra of multiple intermediates and primary products are quantitatively monitored as the reaction progresses [93].

The high sensitivity and time resolution of TR-FCS are well suited to the detection of trace transient species, making this technique apt to elucidate free radical reaction mechanisms. TR-FCS was recently used to measure the pressure-dependent reaction kinetics of the deuterated analog of the $OH + CO \rightarrow HOCO \rightarrow H + CO_2$ reaction (Fig. 2a) [39], which is the primary loss mechanism for atmospheric OH. The concentrations of OD, D_2O and *trans*-DOCO were monitored in parallel after the initiation of the reaction via flash photolysis (Fig. 2b). This represents the first observation of DOCO's formation under thermal reaction conditions. Kinetics measurements made under varying pressure conditions confirmed the mechanism for the formation of ground state DOCO through collisional stabilization of DOCO*. In subsequent work, the formation kinetics of the *cis*-DOCO isomer were also observed, yielding a thorough understanding of the isomerization and branching ratios of this system [92].

3.1.2. CE-DFCS of large, buffer gas cooled molecules

While CE-DFCS has been widely applied to high-resolution rovibrational spectroscopy of small molecules, extending this technique to larger systems brings new challenges. Molecules with as few as 10 atoms can occupy millions of vibrational and rotational states at room temperature, yielding congested spectra that are difficult to resolve, interpret, and assign. By cooling large molecules to cryogenic temperatures in the gas phase, one can take full advantage of the frequency precision afforded by comb spectroscopy.

Collisions with a cold buffer gas are a nearly universal method to achieve molecular cooling [94], and can thermalize the translational and rotational temperatures of large molecules to 10–20 K [95,96]. This leads to significantly reduced Doppler linewidths and internal partition functions. Both of these effects decrease spectral congestion and increase peak absorption cross-sections.

CE-DFCS has been integrated with a 4 K helium buffer gas cell [40,97] in the apparatus shown in Fig. 3a. The CE-DFCS spectrum of cold adamantane ($C_{10}H_{16}$) is shown in Fig. 3b, and represents the first rotationally resolved spectrum of this large molecule in the C—H stretching region. The translational temperature of adamantane is measured to be ~17 K based on Doppler linewidths. While adamantane is a spherical top, the observed rotational lines appear as dense clusters, demonstrating splittings caused by non-spherical centrifugal distortion (Fig. 3b inset).

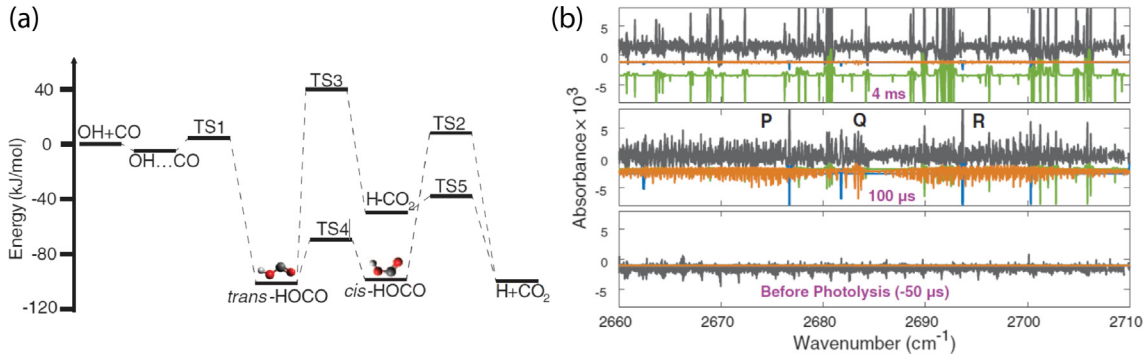

Fig. 2. (a) The potential energy surface of the OH + CO → HOCO → H + CO_2 reaction. (b) Experimental spectra of the OD + CO reaction (gray) recorded with a time resolution of 10 μs, a spectral resolution of 0.03 cm^{-1}, and a spectral bandwidth of 65 cm^{-1}. Experimental traces are shown 50 μs before (bottom panel), 100 μs after (middle panel), and 4 ms after (top panel) photolysis, and compared to the simulated line positions of OD (blue), D_2O (green), and trans-DOCO (orange). The reaction kinetics of OD + CO are followed through the temporal evolution of the concentrations of these species. Figure adapted from Ref. [39] with permission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

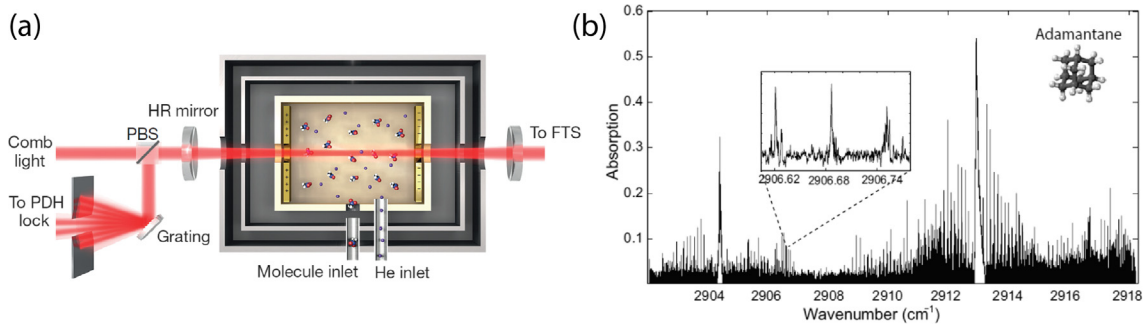

Fig. 3. (a) A schematic of the buffer gas cooling apparatus in combination with a cavity-enhanced frequency comb spectroscopy setup. (b) CE-FCS spectrum of cold adamantane ($C_{10}H_{16}$) in the C—H fundamental stretching region, where over 4000 rovibrational lines were resolved in a 90-min acquisition time. Adapted from Refs. [40,97] with permission.

A general obstacle to spectroscopy of large molecules is intramolecular vibrational energy redistribution [97], which leads to intrinsic spectral congestion and complexity. Future high-resolution CE-DFCS studies of increasingly large molecules will rely on comb sources at longer mid-IR wavelengths, probing lower internal energies where the density of background dark states is significantly reduced. Most recently, CE-DFCS has been used to make rotationally resolved measurements of the 8.5 μm vibrational band of C_{60}, which is by far the largest molecule for which such spectra have been obtained [98].

3.1.3. Noise-immune cavity-enhanced optical frequency comb spectroscopy

The tight comb-cavity lock required for readout of a comb spectrum with a Fourier transform spectrometer suffers from frequency-to-amplitude noise conversion as the comb lines jitter with respect to narrow cavity modes. While shot-noise limited measurements have been demonstrated using careful autobalanced detection of the two FTS arms, this is experimentally nontrivial to achieve [79]. An alternative method to combat frequency-to-amplitude noise is to apply a well-developed cw technique, noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS), to the field of comb spectroscopy [99,100].

NICE-OHMS is a variation of frequency modulation spectroscopy [101,102] wherein the modulation frequency is chosen to be equal to the cavity FSR, so the sidebands are transmitted through cavity modes adjacent to the carrier. Any cavity coupling noise subsequently affects the carrier and sidebands in an identical way. The sensitivity of cavity enhancement is thus preserved while the measurement remains immune to cavity noise.

NICE-OHMS has been extended to direct comb spectroscopy with a technique called noise-immune cavity-enhanced optical frequency comb spectroscopy [100]. This requires careful consideration of the cavity-comb coupling scheme. At least two empty cavity modes must remain on either side of each coupled comb tooth to accommodate the modulation sidebands. In one demonstration, an Er:fiber laser is coupled to an 80 cm cavity with a finesse of 9000, using 3 f_{rep} = 4 FSR. The modulation frequency f_m is chosen to be either 1, 3, or 5 FSR, which ensures that the sidebands of neighboring comb teeth do not beat at f_m. Spectral readout is carried out with a fast scanning FTS and the resulting interferogram is demodulated at f_m before Fourier transforming. Using this method to measure CO_2 absorption near 1.575 μm, it is possible to achieve a CO_2 concentration detection limit of 0.45 ppm $Hz^{-1/2}$ and an absorption sensitivity per spectral element of 6.4×10^{-11} cm^{-1} $Hz^{-1/2}$, which can be compared to the shot noise limited sensitivity of 3.4×10^{-11} cm^{-1} $Hz^{-1/2}$ per spectral element reported in earlier work [79].

3.1.4. Cavity-enhanced transient absorption

Cavity enhancement manifests in both pathlength and field magnitude, a feature that is fully exploited in the implementation of frequency combs in the extreme ultraviolet through intracavity high-harmonic generation [103]. Another very promising recent development in cavity-enhanced comb spectroscopy enables ultrafast transient absorption measurements in low-density molecular beam environments. Ultrafast pump-probe optical spectroscopy

is a widely used technique across chemistry, physics, and materials science. However, its application in the gas phase is limited, as many transient molecules and clusters can be prepared only with prohibitively low number densities. Ultrafast work in molecular beam environments has thus far been limited to action spectroscopies, the results of which are difficult to compare to condensed phase measurements.

Cavity-enhanced transient absorption spectroscopy (CE-TAS) harnesses the pulsed temporal structure of a frequency comb to make transient absorption measurements that are both ultrafast and highly sensitive [104]. An experimental schematic is shown in Fig. 4. A single comb is split into two arms to form the pump and probe beams, whose relative delay is set with a translation stage. The pump and probe are resonantly coupled into two bow-tie ring cavities, which overlap at the expansion of a molecular beam. The pump and probe pulses circulate in their respective cavities, making many passes through the sample at a repetition rate equal to the cavity FSR. For each repetition, the pump and probe arrive at the same relative time delay, creating an identical excitation. The fractional absorption of the probe light, and thus in principle the transient absorption signal, is amplified by the product of the pump and probe cavity finesses.

One challenge is that the repetition rate of the measurement is higher than the inverse of the transit time of the molecular beam through the laser interaction region, leading to a persistent bleach signal. In order to combat this problem, a counter-propagating reference beam is introduced to the probe cavity, delayed by 6 ns from the pump beam, so that the persistent bleach is sampled rather than the ultrafast transients of interest. An autobalanced differential measurement is then made between the probe and reference pulses, which has the added benefit of removing common mode light intensity noise. In practice, the pump power is also modulated and data in the differential probe-reference signal is recorded with a lock-in amplifier as the pump-probe delay is scanned.

The capabilities of CE-TAS have been demonstrated with a study of the ultrafast dynamics of I_2, using a frequency doubled Yb:fiber comb centered at 529 nm. The pump and probe arms are coupled into cavities with finesses of 200 and 270 respectively. The resulting transient absorption signal shows an ultrafast oscillation corresponding to the beating of a vibrational wavepacket on the I_2 $B^3\Pi^+_{0u}$ surface. These measurements are reported with a 120 fs time resolution and the sensitivity to measure changes in optical density of $1 \times 10^{-9}\,\mathrm{Hz}^{-1/2}$. This represents an improvement in sensitivity of over 3 orders of magnitude from the previous best transient absorption measurements. This method could be extended to ultrafast studies across the IR and the UV, as well as to nonlinear multidimensional measurements, as described in Section 3.3.

3.2. Dual-comb spectroscopy

Dual-comb spectroscopy currently attracts the interest of dozens of research groups. In principle, a DCS spectrometer allows measurements with broad spectral spans limited only by the emission bandwidth of the laser source and resolution limited only by the comb repetition rate f_{rep}, using a single photo-detector and no moving parts. As with other detection schemes, the resolution may be improved down to the width of the comb lines by spectral interleaving [105]. Unlike other detection schemes that make use of well-understood and widely-used spectrometers, dual-comb interferometry was developed rather recently and requires challenging instrumentation. Nevertheless, noteworthy results in molecular spectroscopy have already been reported and we discuss a selection of these in the following sections.

3.2.1. Laboratory linear absorption spectroscopy

Broadband comb spectroscopy faces many instrumental and experimental challenges, which can be overcome with continued technological advances and creativity. A challenge specific to DCS is the need to keep the two combs mutually coherent during the measurement time. In DCS, the signal-to-noise ratio is roughly inversely proportional to the number of spectral elements. Thus, high signal-to-noise (>1000) broadband spectra require measurement times of several tens of minutes or hours, and it has been a major goal to access such measurement times while fully preserving the accuracy, precision, and consistency of the dual-comb spectrum. If this is not achieved, spectral artifacts and degraded resolution prevent quantitative spectroscopic studies. Several solutions have been successfully implemented in the near-infrared enabling maintenance [106,107] or reconstruction [108–110] of the coherence between the two combs. Near-infrared dual-comb spectra were demonstrated with a record experimental mutual coherence of 2000 s, while requiring no electronic or digital correction [107].

In the mid-infrared, the situation is more complex: mid-IR comb sources often involve nonlinear frequency conversion, which adds noise, and photonics instrumentation for direct stabilization of the mid-infrared combs is not straightforwardly available. Remarkable progress has nevertheless been achieved for improving the quality of mid-IR spectra measured with optical parametric oscillators [45] and with difference-frequency generation systems [37]. Real-time digital correction techniques have been extended to stabilized mid-IR DFG dual-comb systems and they successfully account for remaining subtle, yet harmful, phase fluctuations [31]. Recently, using feed-forward relative control of the carrier-envelope offset frequency, high-accuracy mid-IR spectra have been reported without any evidence of instrumental artifacts at a comb-

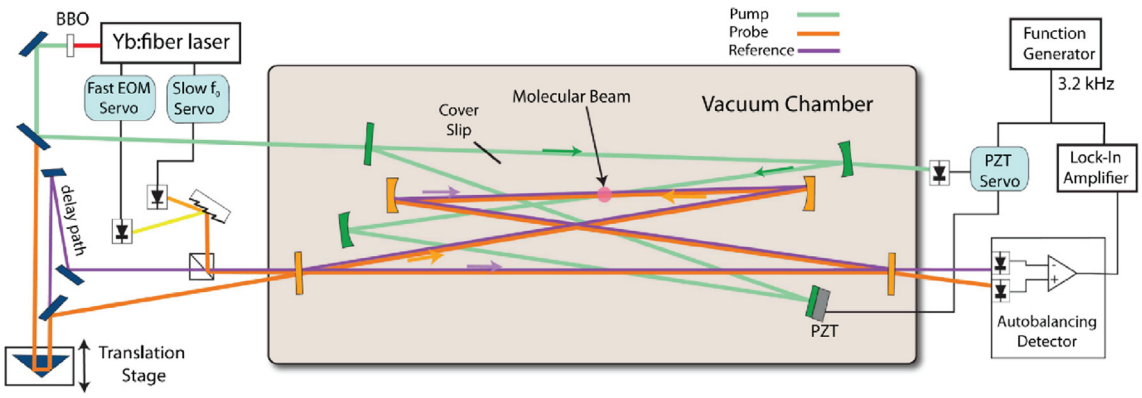

Fig. 4. Schematic of the cavity-enhanced transient absorption spectroscopy apparatus. Reproduced from Ref. [104] with permission.

mode-resolved resolution of 100 MHz [111]. The averaging times, under mutual coherence, reach an unparalleled 30 min and no corrections are required, thus opening favourable opportunities for precision spectroscopy.

Dual-comb spectroscopy is usually harnessed for linear absorption measurements. One of the combs interrogates the sample while the other serves as a local oscillator. The two combs are combined and beat on a fast photo-detector. The time domain interference signal is Fourier transformed to reveal the spectrum. Using this optical layout, transmission and phase spectra are acquired simultaneously, giving access to both the absorption and dispersion of the sample. Measuring a broadband phase spectrum in such a straightforward manner is a new feature enabled by DCS, which is particularly promising for the accurate determination of the optical properties of solids [112,113]. The setup is similar to that of a dispersive scanning interferometer [114], which is demanding to implement but nevertheless provides valuable results in the far-infrared.

Most DCS results have been obtained with mode-locked erbium-doped fiber lasers on near-infrared rovibrational overtone transitions of small gas-phase molecules. The main features of such spectra are illustrated in Fig. 5, which displays a dual-comb spectrum of acetylene with resolved comb lines, recorded with the instrument described in Ref. [107]. The 670 cm^{-1} span is determined by the spectral bandwidth of the erbium fiber laser oscillators. Two hundred thousand comb lines, spaced by 3.3×10^{-3} cm^{-1} (100 MHz), are resolved. The Doppler profiles of the rovibrational lines, with a full width at half-maximum of $\sim 1.5 \times 10^{-2}$ cm^{-1}, are sufficiently sampled by the discrete comb lines (Fig. 5a). Importantly, the instrumental line shape and the optical lines of the comb that interrogates the sample are very narrow compared to the Doppler profiles. Their contribution to the observed profiles may therefore be neglected. The wavenumber scale of the spectrum is directly calibrated against a RF clock through a self-referenced frequency comb.

In practice, the complete resolution of comb lines as shown in Fig. 5a is not required. An equivalent procedure is to Fourier transform the interferogram with a resolution of exactly the comb line spacing, so that spectral samples correspond to the position of the comb lines, as demonstrated for the amplitude and phase spec-

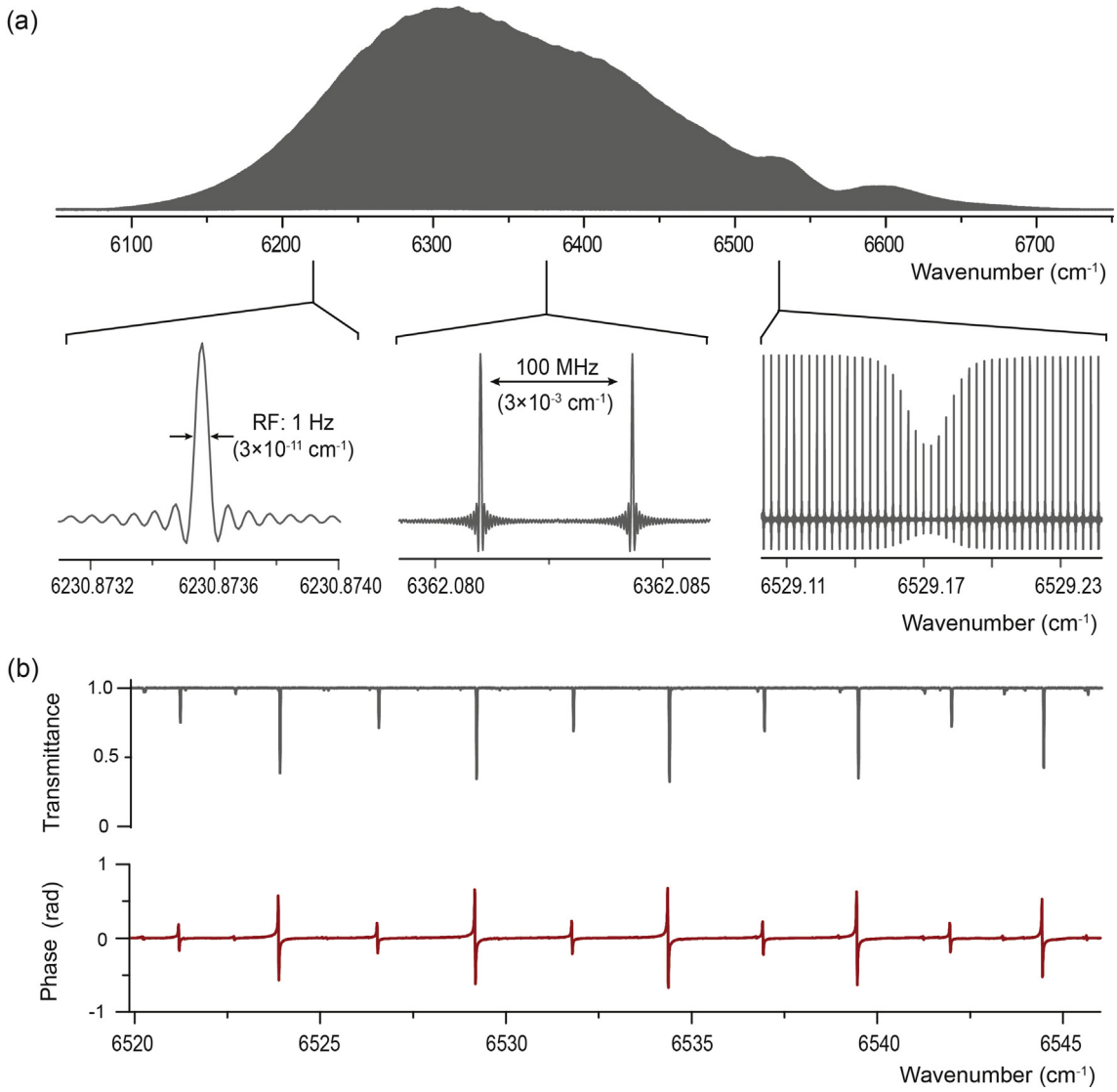

Fig. 5. (a) Experimental dual-comb spectrum with resolved comb lines of the $\nu_1 + \nu_3$ band of $^{12}C_2H_2$ around 6400 cm^{-1}. The spectrum is shown apodized over the full span and unapodized in the three insets. The measurement time is 1000 s, divided among 1000 interferograms of 1 s. The radio-frequency beat notes show comb lines of a width of 1 Hz, convolved by the expected cardinal sine instrumental line-shape. (b) The interferogram leading to the spectrum shown in (a) can also be transformed to sample the spectrum at exactly the comb line positions, as shown with a portion of the resulting simultaneously-acquired transmittance and dispersion spectra.

tra in Fig. 5b. When the conditions are met to average the interferograms in the time domain, this procedure is advantageous as it avoids storing very large data files.

As with any Fourier transform spectroscopy technique, detector nonlinearities induce subtle yet systematic effects in the spectra and distort the measurements of the line parameters such as positions and intensities. Accurate line position measurements have been reported with methane [115,116] and acetylene [107,116], where the relative uncertainty is essentially limited by the width of the Doppler profiles to 10^{-9}. The study of spectral line shapes is also emerging; the determination of speed-dependent Voigt line-shape parameters in high-temperature spectra of water is one noteworthy example [117]. In the mid-IR, the first broadband high-resolution spectra with a high signal-to-noise ratio and careful control of systematic effects have only recently been reported [31,111]. We expect that precise mid-IR DCS studies of molecular systems will appear in the near future as well.

While DCS studies have predominantly harnessed near-IR mode-locked fiber lasers, other frequency comb generators can enable more efficient performance with different spectroscopic schemes. EOMs are well suited for gas-phase spectroscopy over moderate, but rapidly tunable, spectral spans. They have been harnessed in dual-comb spectrometers [56,118] and self-heterodyne spectrometers [54,110] mostly in the near-IR around 1550 nm and 800 nm. These frequency-agile comb generators achieve unprecedented refresh rates (80 kHz) and tuning speeds ($40\ cm^{-1}\ s^{-1}$) with high signal-to-noise ratios in the telecommunication region for spans that extend over a few tens of cm^{-1} [56]. Precise line positions and intensities may be retrieved with relative accuracies of 10^{-8} and 2%, respectively, from spectra measured on the millisecond time scale. Doppler-broadened transitions in molecules [56,118–120] and Doppler-free resonances in alkali atoms [54,110] have been investigated. The sensitivity to weak absorptions has been enhanced with high-finesse resonators [121] and long hollow-core fibers [56]. The limited spectral span of EOM combs allows for rapid DCS measurements, a feature that has been exploited for the time-resolved investigation of the kinetics of spectral hole burning under transient pump excitation in cesium atomic transitions [110]. The technique of frequency-agile DCS has recently been extended to the mid-IR, around 3 μm, via DFG [119,120]. As EOM instrumentation is simpler than that involving mode-locked lasers, frequency-agile combs have potential applications as portable gas sensors for rapid *in situ* diagnostics.

With direct emission in the mid-IR or THz range and electrical pumping, quantum and interband cascade lasers are another class of emerging powerful devices of high compactness, with a potential for compact sensors. They have been harnessed for demonstrations of gas-phase spectroscopy [63,66] over narrow spectral spans and, when combined with synchronous detection techniques, they can provide noise-equivalent absorption down to $5 \times 10^{-4}\ Hz^{-1/2}$ near 8 μm [122]. Nonrepetitive events on the scale of a microsecond may also be investigated using dual-comb spectroscopy with QCLs, through time-resolved monitoring of vibrational fingerprints, as recently demonstrated with a first study of the kinetics of the bacteriorhodopsin photocycle, a reaction of biological relevance [123]. As QCL devices also work as detectors, integrated compact comb-based long-wavelength spectrometers may be envisioned [124].

All frequency comb spectroscopy techniques benefit from comb sources with repetition rates of the same order of magnitude as the desired spectral resolution. This is particularly true in DCS, as measurement times are optimized concurrently. Microresonator-based frequency combs usually exhibit a line spacing larger than 100 GHz ($3\ cm^{-1}$), which places them in a peculiar regime for spectroscopy applications. In the first proof-of-concept of microresonator-based DCS, performed on the gas-phase $2\nu_3$ band of $H^{13}CN$ in the telecommunication region [125], the comb line spacing was insufficient to properly sample the pressure-broadened resonances. This inconvenience has been overcome in experiments of mid-IR Michelson-based Fourier transform spectroscopy where the frequency of the cw laser pumping the microresonator and the microresonator resonance are simultaneously swept, achieving a resolution of 80 MHz ($0.002\ cm^{-1}$) [126]. Nevertheless, the most interesting domain of application for DCS with microresonator-based combs is perhaps vibrational spectroscopy in the condensed phase, as demonstrated with silicon and silicon nitride platforms [127,128]. Here microresonators present the exciting prospect of spectrometers able to measure a broad spectral bandwidth with a cycling time of hundreds of nanoseconds, which would permit time-resolved spectroscopy of non-repetitive single events.

3.2.2. Nonlinear dual-comb spectroscopy

Since frequency combs are often ultrafast lasers, they can be harnessed to study nonlinear interactions. Nonlinear dual-comb spectroscopy is a novel approach to broadband spectroscopy, with applications as diverse as hyperspectral microscopic imaging and precision spectroscopy. The first implementations involved Raman effects [129,130] and two-photon excitation [131,132]. Recent demonstrations expand the available toolbox to four-wave mixing phenomena other than coherent Raman effects [133] and to time-resolved pump-probe investigations [134].

Alongside the methods of Raman spectroscopy [135] and imaging [136], coherent anti-Stokes Raman dual-comb spectroscopy is a powerful way to access vibrational transitions without the need for mid-IR combs, and also has applications in spectro-imaging [130]. Here, the femtosecond pulses of one comb periodically excite low-lying vibrational levels in a two-photon Raman process. After each pump excitation, the pulse of a second comb probes the sample at a linearly increasing time delay, generating an alternately blue- and red-shifted beam. Measuring the intensity modulation of the blue-shifted light behind a spectral filter yields a radio-frequency signal encoding the excited vibrational frequencies. The Fourier transform of this time-domain interferogram (Fig. 6a) reveals the Raman spectrum. All spectral elements are simultaneously measured on a single photo-detector within a few tens of microseconds. The spectral span is determined by the bandwidth of the ultrafast laser and the resolution is limited by the few cm^{-1} intrinsic width of the vibrational bands of the condensed-phase sample. As an example, Fig. 6b shows a spectrum of a mixture of toluene and dimethyl sulfoxide at a resolution of $5\ cm^{-1}$. Raman spectra, recorded within 80 μs, span the entire fingerprint region, covering more than $3200\ cm^{-1}$ [137]. Such capabilities have been extended to spectro-imaging with an acquisition rate of 50 pixels/s [130]. These experiments were initially performed with 100 MHz repetition rate Ti:Sapphire lasers, leading to poor cycling times [130]. The extension of this technique to lasers with higher repetition rates [138,139] and fiber-based lasers [140] makes it more versatile. Although the sensitivity requirements are particularly challenging, there remain intriguing prospects for spectrally resolved microscopy and spectro-imaging.

Two-photon excitation dual-comb spectroscopy also has great potential. Two-photon excitation spectroscopy with a single comb [1,22,23] has been used in precision spectroscopy of simple atoms. The technique is easy to implement, as it does not require a spectrometer. However, it is only suitable for spectra composed of very few transitions, as the free spectral range is equal to the line spacing of the frequency comb. The new technique of dual-comb two-photon spectroscopy [131,132] identifies each transition uniquely by the modulation imparted by interfering excitations. Here, sub-Doppler resolution is combined with a free spectral range limited only by the spectral bandwidth of the laser frequency combs; a proof-of-principle demonstration has been achieved with

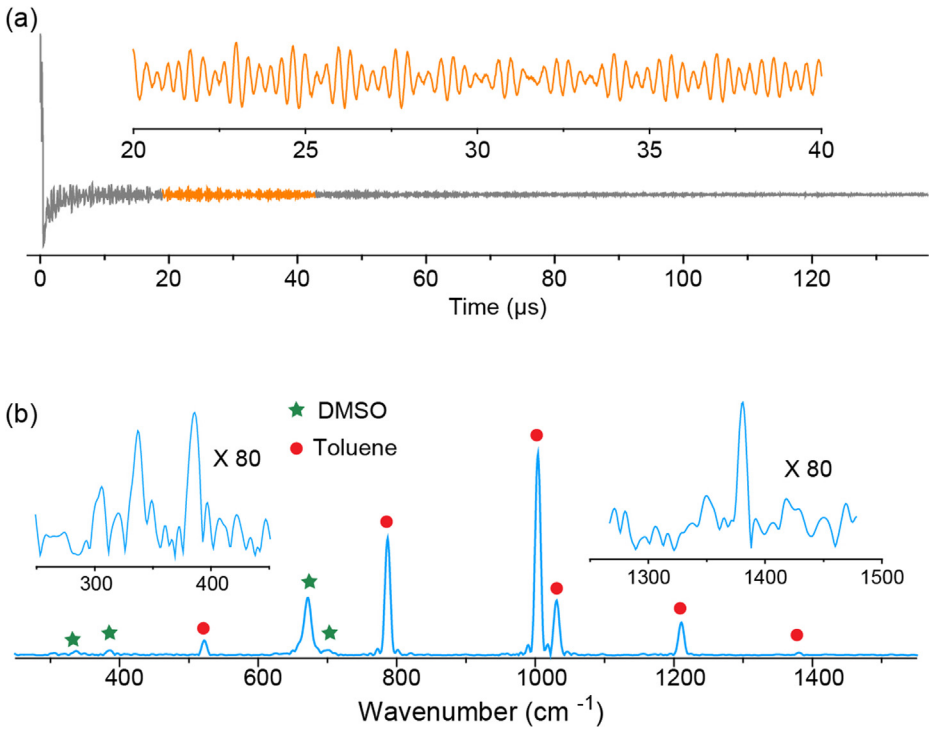

Fig. 6. (a) Dual-comb CARS interferogram of a mixture of toluene and dimethyl sulfoxide (DMSO) in a 1:1 mixing ratio showing the interferometric modulation of the vibrational transitions shown in (b). (b) Dual-comb CARS spectrum. The span of 1400 cm^{-1} is determined by the pulse duration of the frequency combs, of about 15 fs. The measurement time is 120 μs; the apodized resolution is 5 cm^{-1}, narrower than the width of the molecular bands.

the 5S-5D two-photon transitions of rubidium [132]. Such a multiplexed technique with sub-Doppler resolution may enable broadband spectroscopy with unprecedented precision.

3.2.3. Dual-comb spectroscopy in combination with other sampling techniques

Like Fourier transform spectroscopy in general, dual-comb spectroscopy is versatile and likely to enable powerful multimodal tools. For the interrogation of gases, dual-comb spectrometers have been used with multipass cells [116] and enhancement cavities [141], and have also enabled broadband evanescent sensing [142]. Polarization analysis, accomplished with ellipsometry, characterizes the optical properties of birefringent materials and thin films [143]. Combined with imaging techniques, DCS can be used to map the spectral behaviour of spatially-inhomogeneous samples, as shown with Raman spectro-imaging [130]. The broad spectrum of a frequency comb can also be used for space-to-wavelength conversion and is thus beneficial for scanless confocal imaging of microscopic standing culture fixed cells [144].

3.3. Multidimensional dual-comb spectroscopy

Recent work has pushed beyond dual-comb spectroscopy to acquire multidimensional nonlinear coherent spectra with frequency combs [133,145]. Multidimensional coherent spectroscopy (MCS) is a well-developed technique for studying structure and ultrafast dynamics in molecules and materials [146]. Among the many advantages of MCS are that it can decouple homogeneous and inhomogeneous line broadening, elucidate couplings between states, and determine which spectral features arise from a common absorber in a mixture of analytes. However, the applications of MCS are limited by a spectral resolution of >10 GHz (>0.3 cm^{-1}) and long acquisition times due to scanning mechanical delay stages. The combination of dual-comb techniques with MCS overcomes these limitations, allowing rapid acquisition times and the best-yet reported spectral resolution for multidimensional spectra (300 MHz, 0.01 cm^{-1}).

In one implementation of dual-comb MCS, a photon echo excitation sequence is used: the sample is excited with two pulses from two combs with different f_0, using two arms of the same source comb in combination with an acousto-optic modulator [133]. The sample subsequently radiates a four-wave-mixing (FWM) signal, which is measured via DCS with a second local oscillator comb. A 2D spectrum is constructed by calculating the Fourier transform of the FWM signal with respect to both the emission time and the delay between the two excitation pulses. Using this method, 2D spectra of the hyperfine structure of ^{87}Rb and ^{85}Rb were reported, allowing differentiation of lines arising from each isotope and the observation of couplings between transitions sharing an initial or final state [145]. A double-quantum excitation scheme was subsequently used to isolate a FWM signal arising from collective hyperfine resonances induced by dipole-dipole interactions between rubidium atoms [147].

A recent proposal aims to extend multidimensional comb spectroscopy to enhancement cavities for the study of species in molecular beams with low optical densities [148]. Multiple combs with the same f_{rep} but distinct f_0 could be effectively coupled into different spatial modes of the same cavity, making use of the fact that the cavity Gouy phase depends on the spatial mode order. This would lead to an enhancement of the FWM signal by a factor of the cavity finesse squared, potentially allowing for unprecedented multidimensional studies of the dynamics of cold, gas-phase molecules and clusters.

3.4. In-situ and remote sensing

Broadband frequency comb spectroscopy also demonstrates an interesting potential for spectroscopic diagnostics and sensing. Laser beams enable both local sensing at very high sensitivity, particularly in combination with enhancement cavities, as well as

integration over columns of kilometers of open path. The broad spectral bandwidth enables simultaneous interrogation of several species and transitions, improving the consistency and reliability of measurements. When comb lines are resolved, the contribution of the instrument to the experimental line profiles can be negligible.

The first proof-of-concept demonstrations of broadband frequency comb spectroscopy for sensing applications already highlight this potential. A free-running mid-IR dual-comb spectrometer achieved open-path monitoring of the ν_2 band of ammonia from 22 m away, with a recording time as short as 70 μs and a cycling time of 1 ms [4]. A near-ultraviolet cavity-enhanced dispersive spectrometer located at a station in East Antarctica measures the concentration of radicals involved in the atmospheric chemistry of the marine boundary layer such as BrO, IO, and NO_2 on minute timescales and with detection limits better than 10 pptv [149]. The first open-path comb-based mid-IR measurements using spectral readout with a VIPA etalon achieved detection of atmospheric CH_4 and H_2O on millisecond timescales [150], while mid-infrared detection of methane in the ambient laboratory air was demonstrated with a detection limit of 60 ppbv using dual-comb spectroscopy [151].

Recently, dual-comb spectroscopy with resolved comb lines interrogated atmospheric trace gases with high sensitivity over a 2-km open-air path [152]. Soon after, two independent self-referenced dual-comb spectrometers retrieved path-integrated concentrations of several greenhouse gases with remarkable consistency across the two measurements, agreeing to within better than 0.5% [153]. With continued progress in fiber laser technology, such dual-comb spectrometers have become transportable. Field-deployed instruments have been successfully used to make measurements in an industrial gas turbine [154] and identify and quantify leaks from methane sources over multiple-square-kilometer regions at emission rates three orders of magnitude lower than conventional approaches [155].

These promising approaches provide the first landmarks for the next generation of spectroscopic sensing instruments. Transportable and even portable mid-IR spectrometers will offer enhanced detection limits and increased numbers of detectable species. Furthermore, other sampling techniques may diversify the tools for spectroscopic diagnostics. For instance, a recent report of the combination of laser-induced breakdown spectroscopy and dual-comb spectroscopy [156] lays the groundwork for *in situ* analysis of soils, rocks and minerals.

4. Conclusions and outlook

In this perspective, we have highlighted broadband frequency comb spectroscopy as a powerful tool for molecular spectroscopy, with emphasis on cavity-enhanced and dual-comb methods. The combination of high brightness, broad bandwidth, high spectral resolution, and fast readout afforded by comb spectroscopy has already been applied to a wide range of gas- and condensed-phase systems. Comb spectroscopy in the mid-infrared is coming to the fore, allowing unprecedented study of the fingerprint vibrations of transient molecular species and cold molecules [39,40]. The ultrafast pulse structure of frequency combs generated from mode-locked lasers is beginning to be harnessed for nonlinear spectroscopies [129,145], spectro-imaging [130], and pump-probe measurements of weakly absorbing samples [104]. Combs are also being used for precision metrology in small molecules towards tests of quantum electrodynamics [157].

Ongoing technical developments, including extensive work in laser sources and detection schemes, represent progress towards realizing the full potential of frequency comb spectroscopy. While many new and creative comb spectroscopy schemes are still in the proof-of-principle stage, we expect that they will be deployed towards problems of great scientific interest in the near future. Recent developments in phase stabilization of dual-comb spectrometers [107] extend the interferometer coherence time and may drastically improve the achievable sensitivity and resolution for trace measurements. Chip-based microresonator combs could find widespread use in physical and analytical chemistry once they become a more mature technology [69,70], and, more generally, compact, field-deployable comb-based spectrometers [155] will enable new capabilities in remote sensing, atmospheric chemistry, and medical diagnostics. The combination of mid-IR comb and microscopy technologies could have important applications in imaging of biological specimens, materials, and nanostructures. With the extension of comb sources to new frequency ranges, we envision further applications in molecular reaction dynamics, ultracold molecules and chemistry, and quantum state resolved measurements of increasingly complex systems.

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