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Ultrabroadband mid-IR frequency combs show promise for standoff chemical sensing

Konstantin Vodopyanov

Frequency combs produced in a near-degenerate optical parametric oscillator pumped by an ultrafast fiber laser enable massively parallel real-time molecular detection and standoff chemical sensing.

Some 20 years ago, optical frequency combs emerged as a radically new laser technology[1] that culminated in the 2005 Nobel Prize in Physics. Frequency combs, which can be generated in phase-stabilized mode-locked lasers, possess unique properties in both the spectral and time domains. In the spectral domain, they correspond to a manifold of several hundred thousand equally spaced narrow spectral 'comb' lines. In time, they relate to a periodic train of pulses with an extremely stable repetition rate and carrier-envelope phase. These combs hold much promise for high-resolution spectroscopy and spectroscopic detection. A laser comb can directly interrogate a vast number of molecular transitions, resulting in an immense parallelism of spectral measurements, thereby enabling quick measurements of a variety of chemicals.[2,3] Frequency combs combined with Fourier transform spectroscopy (FTS) are especially advantageous because one can retain massive parallelism of spectral measurements, as well as high accuracy and sensitivity, using just one optical detector. FTS can be performed using a single comb source combined with a Michelson interferometer,[4] or two mutually phase-locked frequency combs with a small offset in their pulse repetition rate.[5] In the latter case (so-called dual-comb spectroscopy), an enormous advantage in data acquisition speed may be achieved due to the absence of moving parts.

Broad spectral coverage is another important benefit provided by frequency combs. The instantaneous spectrum produced in the visible range (e.g., in a titanium-sapphire laser) can span over an octave (and several 1000s of cm^{-1}) in frequency. However, their counterparts in the 'fingerprint' mid-IR region—a region of fundamental absorption molecular resonances (broadly speaking 3–12μm) best suited for ultrasensitive trace chemical detection—suffers from much narrower instantaneous spectral coverage, typically 100–300cm^{-1}.[6,7]

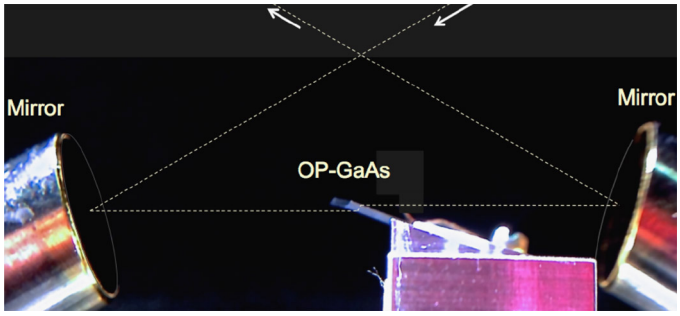

Figure 1. *The 'engine' of the subharmonic optical parametric oscillator (OPO) comb source based on orientation-patterned gallium arsenide (GaAs).*

We have implemented a new technique that enables the use of octave-wide frequency combs to be extended into the highly desirable, yet challenging, mid-IR fingerprint spectral range, leading to the development of ultrabroadband mid-IR combs. We used a short (few-100μm) second-order nonlinear crystal as the gain element in a synchronously pumped optical parametric oscillator (OPO) that operates very close to its degeneracy, where gain bandwidth is very broad and hence enables a very broad instantaneous spectrum to be obtained in the output. The role of the OPO is to rigorously both down-convert and augment the spectrum of a pump frequency comb, such that the laser comb spectrum is transferred to half of its central frequency and dramatically broadened.

To prove the viability of this technique, we used a variety of OPO gain materials in combination with ultrafast pump lasers. Broadband (>1000nm) instantaneous outputs were reported in three setups: an erbium-fiber laser-pumped periodically poled lithium niobate subharmonic OPO with a center

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frequency near 3μm,[8] a thulium-fiber-laser-pumped orientation-patterned gallium arsenide (OP-GaAs) OPO with center frequency ~4μm[9] (see Figure 1), and a chromium-doped zinc-selenide-laser-pumped OP-GaAs OPO with center frequency ~5μm.[10] In addition to the low pump threshold (<10mW) associated with their doubly resonant nature, these OPOs have the important property of preserving pump laser coherence.[11,12] The latter characteristic is extremely important for performing dual-comb spectroscopy.

We recently achieved frequency combs with an unprecedented instantaneous bandwidth spanning from 2.5 to 7.5μm (1.5 octaves in frequency) using a thulium-fiber-laser-pumped GaAs OPO system[13] (see Figure 2). Using Fourier transform spectroscopy, we were also able to demonstrate trace detection of a number of chemicals (methane, carbon dioxide, isotopic carbon dioxide, carbon monoxide, ethylene, acetylene, and formaldehyde), achieving part-per-billion sensitivity levels for methane and isotopic carbon dioxide.[14] A large comb bandwidth enables the simultaneous detection of several species in a mixture.

Figure 3 represents simultaneous detection, via spectral signatures, of trace amounts (ppm level) of methane and acetylene gases mixed in the same container. The measurement time for acquiring 1200 spectral data points, with averaging, was 60s and the obtained spectral shapes are in excellent agreement with theory.

Our new mid-IR comb technology could have a major impact in a wide range of applications based on real-time spectroscopic molecular detection. These span from trace explosive and chemical/biological hazard detection to many industrial and commercial applications in areas including environmental monitoring, medicine, planetary exploration, and analytical chemistry. In future work, we hope to develop a frequency comb with an instantaneous bandwidth of two octaves (2.5–10μm) by using special 'chirped' dielectric mirrors in the OPO resonator, enabling compensation of group velocity variation over the whole spectrum. We also intend to build a 'twin' OPO system, based on a pair of phase-locked fiber lasers, for dual-comb spectroscopy. This system will provide an enormous advantage in terms of the sensitivity and data acquisition speed of standoff chemical sensing.

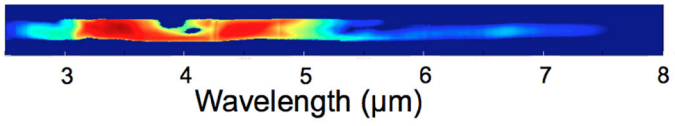

Figure 2. *The spectrum of a thulium-fiber-pumped GaAs OPO reaching 1.5 octaves in the mid-IR.*

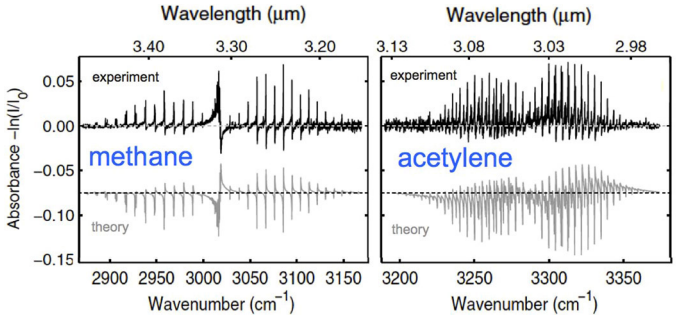

Figure 3. *Absorption spectra showing simultaneous detection of methane and acetylene at part-per-million-level concentration. Theoretical spectra (gray) are inverted and offset for clarity.*

Author Information

Konstantin Vodopyanov
The Center for Research and Education in Optics and Lasers (CREOL)
University of Central Florida
Orlando, Florida

Konstantin L. Vodopyanov obtained his MSc from Moscow Institute of Physics and Technology, Russia. He completed his PhD and DSc (Habilitation) in the Oscillations Laboratory of the Lebedev Physical Institute, Russia, led by Nobel Prize winner Alexander Prohorov. He was an assistant professor at Moscow Institute of Physics and Technology (1985–1990), Alexander von Humboldt Fellow at the University of Bayreuth, Germany (1990–1992), and a Royal Society postdoctoral fellow and lecturer at Imperial College, UK (1992–1998). In 1998, he moved to the US and became head of the laser group at Inrad Inc., NJ (1998–2000), and later director of mid-IR systems at Picarro Inc., CA (2000–2003). His other industry experience includes co-founding and providing technical guidance for several US and European companies. In 2003, he returned to academia (Stanford, CA, 2003–2013) and is now a 21st Century Scholar Chair & Professor of Optics at CREOL.

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