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High Accuracy Molecular Spectroscopy with Combs Broadened From 1.35 to 1.7 μm

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Abstract: A coherent dual comb spectrometer spanning over 45 THz in the NIR was constructed from broadened erbium fiber lasers. Gas phase water, methane, and acetylene spectra were measured and characterized toward establishing absolute frequency references.
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Broad bandwidth comb sources garner interest for direct spectroscopic measurements because they can probe entire bands of molecules with high precision, including regions where cw lasers do not currently exist. One compelling method for comb spectroscopy is to interfere two offset combs on a detector to form a type of Fourier transform infrared spectrometer (FTIR) [1-6]. Instead of a scanning Michelson interferometer, as used in traditional FTIR, the difference in repetition rates between two mode locked lasers enables pulses from one laser to interfere with the other to produce an interferogram. Here, we demonstrate the first extension of Er fiber laser dual comb spectroscopy away from the 1550 nm Er fiber gain bandwidth to neighboring regions in the NIR, enabling detection of a wide range of molecules, including many relatively strong hydrogen stretch overtone transitions. Because the combs are rigorously referenced to absolute frequency standards, the uncertainty in molecular line centers in principle should be limited only by the absorbance signal-to-noise ratio (SNR). We confirm this accuracy to sub-MHz levels by comparison to acetylene lines previously measured through saturated absorption spectroscopy [7]. The establishing of frequency references is one potential use for the presented dual-comb system.

The experiment uses two coherent 100 MHz Er fiber ring lasers [5, 6], modified for expanded spectral coverage with novel optical fibers. The 300 mW amplified output of the femtosecond fiber lasers is compressed to 250 fs FWHM pulse duration in ~50 cm anomalous dispersion large mode area fiber (LMAF) [8]. The LMAF is followed by < 10 mm of single mode fiber and then ~15 cm of normal dispersion highly nonlinear fiber (HNLF)[9] to generate 100 mW of continuum light with a reasonably flat spectrum and very low noise extending from 1.35 to 1.7 μm. The source-comb continuum is sent through either a 30 m multipass cell filled with the sample gas or a reference path that bypasses the multipass cell, as controlled by an optical switch. The two combs are then combined, filtered by a tunable 0.2 THz grating filter, and detected. The resulting interferograms are averaged via direct summing of coherent interferograms over short times and subsequent phase correction and summing of these interferograms over longer times [5, 6]. Fig. 1 presents sample spectra of methane, acetylene, and water.
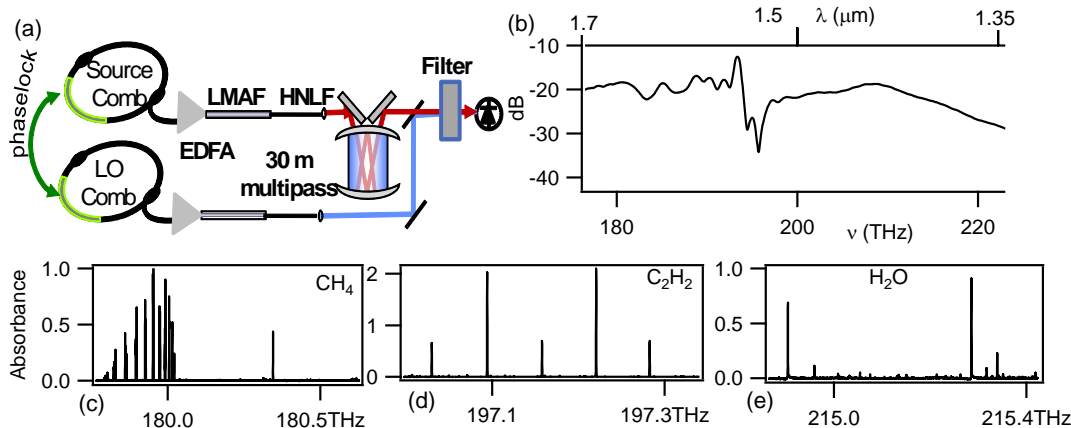

Fig. 1: (a) Schematic of the coherent dual comb setup. EDFA = Er doped fiber amplifier. (b) Representative continuum spectrum from the signal and local oscillator (LO) combs. Sufficient continuum power is generated from 1350 to 1700 nm. The use of normal dispersion HNLF insures the continuum is low-noise. (c) Sample spectrum of room temperature methane (CH_4) at a pressure of 20.5 Pa. (d) Acetylene spectrum (C_2H_2) at 3.41 Pa. (e) Water vapor (H_2O) spectrum at 1.8 Pa. At these pressures, the spectral line width is dominated by Doppler broadening.

The spectra shown in Fig. 1c–e have ~1×10^{-3} intensity noise, after 5 to 10 minutes of averaging per 0.2 THz spectral window. The stronger spectral lines then have SNR between 600 and 2000. The statistical uncertainty in the determination of the center frequency (σ_v) is approximated by $\sigma_v \approx \Delta v_D / (SNR \times \sqrt{N})$, where Δv_D is the Doppler FWHM (~600 MHz) and N is the number of resolution elements, which depends on the laser repetition rate f_{rep} via $N = \Delta v_D / f_{rep} \approx 6$. This simple calculation yields a σ_v of 0.1 to 0.4 MHz. To verify the accuracy, we have fitted several isolated lines in the acetylene and methane spectra to a Voigt line shape to find the line center (see Fig. 2). Fig 2b compares repeated measurements of the acetylene R(8) line. The first six measurements show a 1.1 MHz disagreement with the Lamb dip measurements, which were measured with 150 kHz uncertainty [7]. For the following twelve measurements the optical power was reduced by more than 50%, leading to an average value that differs from the published value by only 175 kHz and agrees within the statistical uncertainty. The cause of this systematic shift with power is still under investigation and thought to be related to detector nonlinearity causing distortions of the interferogram at high power. Similar low power measurements of nearby acetylene lines results in < 300 kHz differences with the published line center values. For the isolated methane line shown in Fig. 2c,d, we find similar scatter but a 9 to 15 MHz (8.3×10^{-8}) difference from conventional high-resolution FTIR measurements [10, 11]. This difference is outside the quoted statistical uncertainty of Ref. [10] but within systematic uncertainties [12]. Similar 7 to 20 MHz differences are seen on other isolated methane lines. These data indicate that dual-comb measurements can supply line center measurements to support broadband high-resolution FTIR at high accuracy.
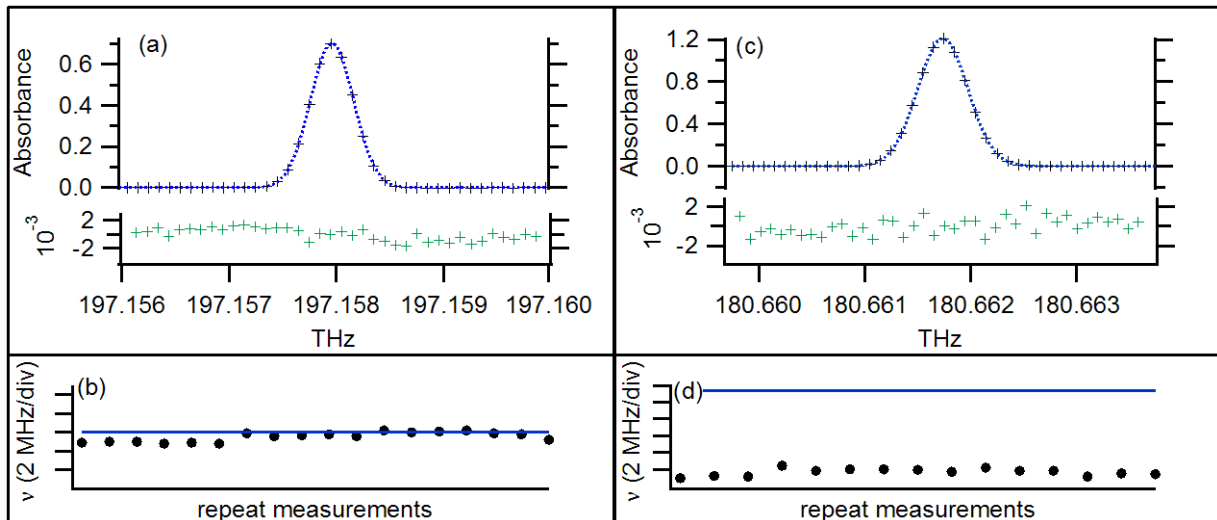

Fig. 2: (a) View of the measured line shape of a representative acetylene line ($v_1 + v_3$ $J=9\leftarrow8$) (+ markers) with Voigt fit (dotted line) and corresponding residuals (lower series of markers, expanded y-axis). (b) Fitted values of line center from repeat measurements of the line in (a). Solid line is the value reported in Ref. [7]. (c), (d) Same as (a), (b) for the methane ($2v_3$ J=2←1) line. The solid line in (d) is from Ref. [11] and differs by about 9 MHz.

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