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Broad-band frequency references in the near-infrared: Accurate dual comb spectroscopy of methane and acetylene

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The Doppler-limited spectra of methane between 176 THz and 184 THz (5870–6130 cm^{-1}) and acetylene between 193 THz and 199 THz (6430–6630 cm^{-1}) are acquired via comb-tooth resolved dual comb spectroscopy with frequency accuracy traceable to atomic standards. A least squares analysis of the measured absorbance and phase line shapes provides line center frequencies with absolute accuracy of 0.2 MHz, or less than one thousandth of the room temperature Doppler width. This accuracy is verified through comparison with previous saturated absorption spectroscopy of 37 strong isolated lines of acetylene. For the methane spectrum, the center frequencies of 46 well-isolated strong lines are determined with similar high accuracy, along with the center frequencies for 1107 non-isolated lines at lower accuracy. The measured methane line-center frequencies have an uncertainty comparable to the few available laser heterodyne measurements in this region but span a much larger optical bandwidth, marking the first broad-band measurements of the methane $2\nu_3$ region directly referenced to atomic frequency standards. This study demonstrates the promise of dual comb spectroscopy to obtain high resolution broadband spectra that are comparable to state-of-the-art Fourier-transform spectrometer measurements but with much improved frequency accuracy.

1. Introduction

Atomic and molecular spectra have long been used as frequency references, and emerging applications present the need for reference lines of even higher accuracy. For instance, precisely calibrated hydrogen cyanide and acetylene spectra near 1550 nm provide optical frequency references for fiber-optics communication [1,2], active sensing of atmospheric greenhouse gases requires the precise positioning of laser probes [3], and extrasolar planets are detected by precise monitoring of Doppler line-shifts of stars orbiting the star-planet center of mass [4]. For these and other applications, traceable reference spectra facilitate agreement among researchers working around the globe. As absolute frequency accuracy becomes more important, the limitations of traditional wavelength-based spectroscopy become noticeable, motivating spectral investigations with highly accurate optical frequency comb methods.

There is an important distinction between frequency and wavelength metrology. Most spectroscopic systems fundamentally measure absorption versus wavelength, which is determined via the spatial interference of light waves. These wavelength measurements depend ultimately on precisely constructed mechanical objects, such as the translating mirror in Michelson Fourier-transform spectroscopy (FTS), the distance between mirrors in an etalon, or calibrated groove spacing and tilt angle in grating spectrometers. Conversion to true frequency (or vacuum wavenumber) requires correction for the wavelength-dependent index of refraction, instrument alignment, and

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path-length effects; even for perfect alignment in an evacuated spectrometer, diffraction ultimately limits the accuracy of wavelength measurements. Corrections are usually applied by comparison of the measured spectra to accurate frequency references from standardized reference spectra [5]. Such an approach has enabled high-precision wavelength-based techniques, and particularly FTS and etalon-calibrated laser spectrometers, to be adopted as workhorse tools underpinning the vast progress into fundamental and applied spectroscopy for several decades. However, other than in the telecommunication band near 1550 nm (6450 cm^{-1}) [1,2], there is a scarcity of high accuracy frequency references in the near infrared [5]. Indeed, the 2008 version of the HITRAN database [6] retains methane frequencies in the $2\nu_3$ region from a study performed in the late 1980s [7] that continues to be used as a calibration standard in this region [8].

Frequency combs provide a new tool for high-accuracy spectroscopy across broad spectral bandwidths [9–12]. As a light source, the advantages of combs include high brightness, excellent spatial beam quality for long interrogation paths, and broad bandwidth on par with the typical bandwidth an FTS can measure at one time. Frequency combs also uniquely provide a large number of perfectly spaced, ultra-narrow optical frequency lines or "comb teeth" (see Fig. 1) that have exceptional implications for frequency-accurate spectroscopy. With appropriate phase-locking, the absolute frequency of each of these teeth may be referenced to an atomic reference. By passing a comb through a gas and recording the response on a comb-tooth-by-comb-tooth basis, one can retrieve the absorbance (or phase) spectrum versus absolute optical frequency. The challenge to broadband comb spectroscopy is to separately resolve each of the 10^5–10^6 comb teeth, often only separated by 100 MHz (0.003 cm^{-1}).

Coherent dual comb spectroscopy (DCS) presents a unique method for making comb-tooth-resolved measurements [13–28]. It can be thought of as a novel variation on FTS, where the role of the delay arm is played by a second comb with differing repetition rate. As in FTS, the signal originates from optical interference on a single photoreceiver. DCS has been demonstrated over a range of wavelengths, and with widely varying accuracies, precision and resolution. In some cases, speed and simplicity are emphasized over accuracy or comb-tooth resolution. Here, we use a coherent dual comb spectrometer that relies on stabilized, calibrated optical frequency combs to resolve individual teeth that are also referenced to atomic standards [16,17,25,26]. This configuration, referred to as fully resolved and accurate DCS, results in a frequency accuracy that is higher than that of FTS, a point spacing on par with the resolution of state-of-the-art FTS systems, and a resolution potentially as low as 1 Hz. Whereas point spacing and resolution are generally equal to each other in FTS, in this system the point spacing is equal to the separation of the comb teeth while the resolution is limited only by the linewidth of the comb teeth (generally 1 kHz). This resolution may be excessive for most applications, but it does imply a negligible instrument response function making DCS a promising technique for high fidelity line-shape measurements.

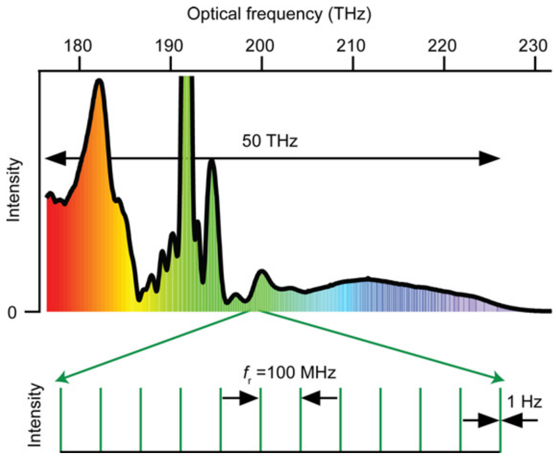

Fig. 1. Intensity spectrum (linear scale) of the optical frequency comb used in this experiment. The spectrum has been optimized for power over the 180 THz methane band and therefore does not span a full octave, as it would for a "self-referenced" comb. The spectrum is composed of discrete comb-lines, or "teeth," as shown. The linewidth of each tooth is determined by the reciprocal of the coherence period and can be on the order of 1 Hz.

Following Ref. [25], we use fully resolved and accurate DCS to acquire accurate spectra across 43 THz of bandwidth. We report the Doppler-limited spectra of the acetylene ($^{12}C_2H_2$) $\nu_1+\nu_3$ band centered at 1525 nm and the methane ($^{12}CH_4$) $2\nu_3$ (tetradecad [29]) region near 1660 nm. Acetylene line-center frequencies have been previously measured with very high precision and accuracies below 10 kHz by use of sub-Doppler techniques [2,30]. By comparison with these measurements, we establish the frequency accuracy of our DCS system to be about 0.2 MHz. An identical analysis of the methane spectrum provides accurate line-center frequencies for 46 well-isolated, intense methane lines. The sub-megahertz uncertainty is comparable to the best available references [31], and 42 of the 46 line-center frequencies are measured at this high accuracy for the first time. Analysis of the entire methane spectrum retrieves center frequencies for an additional 1107 lines with coarser accuracy. Although state-of-the-art sub-Doppler techniques can produce uncertainties more than 10 times lower, DCS still yields low uncertainties and, in contrast to sub-Doppler techniques, does not require high optical powers for saturation, provides larger spectral coverage, and is not constrained to low gas pressures where collisional broadening is less than the Rabi frequency.

The following section provides an introduction to optical frequency comb sources, DCS, the experimental apparatus, and the data-acquisition method. Section 3.1 describes the analysis of the Doppler-limited acetylene absorbance and phase spectra. Section 3.2 describes an identical analysis across well-isolated, Doppler-limited lines in the methane spectra. Section 3.3 provides a broader analysis of the methane spectrum over 1153 lines. The paper concludes in Section 4 with a summary of the results and prospects for future applications of the DCS technique.

2. Experiment

All spectra are recorded with the coherent dual-comb spectrometer at NIST in Boulder, Colorado [16,17,25]. This