Frequency-comb-based absolute frequency measurements in the mid-infrared with a difference-frequency spectrometer

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We demonstrate the possibility of extending the well-established metrological performance of optical frequency-comb synthesizers to the mid-IR region by phase locking the pump and signal lasers of a difference-frequency source to two near-IR teeth of an optical comb. An uncertainty of $800 \times 10^{-11}$ in the absolute frequencies of CO$_2$ transitions near 4.2 $\mu$m has been measured by cavity-enhanced saturated-absorption spectroscopy. Prospects for the creation of a new dense set of high-quality molecular frequency standards in the IR are discussed. © 2005 Optical Society of America

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Since the first demonstration of femtosecond-laser-based optical frequency combs as powerful metrological tools for the visible–near-IR region, scientists have been working on possible extensions of their spectral coverage (see Ref. 4 for a comprehensive review). The use of mode-locked femtosecond fiber lasers has already succeeded in extending combs to 2.3-$\mu$m wavelength in the IR. A different approach consists in direct generation of IR combs by difference-frequency generation (DFG) in nonlinear crystals, as was recently demonstrated experimentally. A DFG comb benefits from being offset free, because of the perfect cancellation of any carrier-envelope phase offset that may be present in the original frequency comb. Such a DFG comb, however, has an intrinsically multimode spectrum, with the total power shared among the many modes; therefore its application as a source for high-resolution spectroscopy can be nontrivial.

We propose a technique that overcomes this disadvantage while it maintains the offset-free nature of DFG combs. The basic idea is to generate DFG radiation in the mid-IR and to phase lock it to a near-IR comb. The experimental setup is shown in Fig. 1. The pump laser source for the $\chi^{(2)}$ nonlinear process is a pair of semiconductor lasers at 850 nm, with a low-power (25-mW) external-cavity diode laser (master) optically injecting a more powerful (130-mW) bare Fabry–Perot laser (slave). The signal laser source is a monolithic-cavity Nd:YAG laser at 1064 nm seeding an Yb fiber amplifier (5-W maximum power). The nonlinear mixing process that takes place in a 40-mm-long periodically poled LiNbO$_3$ crystal generates as much as 170 $\mu$W of idler radiation at 4.2 $\mu$m in a single-pass scheme.

The optical frequency synthesizer (OFS; Model FC8003 from Menlo Systems) covers an octave in the visible–near-IR (500–1100 nm) region. The reference oscillator to lock the OFS’s repetition rate, $\nu_r = 1$ GHz, is made from high-stability Global Positioning Satellite– (GPS-) disciplined 10-MHz quartz (Model 8600 from Oscilloquartz). The measured stability of this quartz against a Cs-fountain-disciplined H maser limits the OFS’s precision to $6 \times 10^{-13}$ at 1 s and its accuracy to $5 \times 10^{-12}$. After nonlinear mixing, rf beat notes are generated between both the pump and the signal beams and their associated closest tooth of the comb, with frequencies $\Delta \nu_p$ and $\Delta \nu_s$, respectively. These rf beat notes are phase locked to local oscillators by feedback of appropriate frequency corrections to the piezoelectric transducer (PZT) of the Nd:YAG laser and to the PZT of the master diode laser cavity as well as to the drive current of the master laser. With these locks, the frequency of the generated IR radiation is given by

![Fig. 1. Schematic of the experimental setup: DMs, dichroic mirrors; PPLN, periodically poled LiNbO$_3$ crystal; PD1, PD2, InSb photodiodes; $\lambda/4$, quarter-wave plate; PLL1, PLL2, phase-locked loops; APD1, APD2, avalanche photodiodes; TMP, turbomolecular pump; PG, pressure gauge; PI, proportional-integrating.](image-url)
\[ \nu_i = (N_p - N_s) \nu_s + \Delta \nu_p + \Delta \nu_s. \] (1)

The diode OFS phase-locked-loop electronics makes use of a hybrid digital–analog design with two mutually exclusive operation modes, thus taking advantage of both the wide locking range of a digital mode and the fast response of an analog mode. Instead, only a digital design is used for the Nd:YAG OFS mode because of the low phase noise of the signal laser. We measured phase-locked bandwidths of \( \sim 1.5 \) MHz for the diode OFS lock and of \( \sim 30 \) kHz for the Nd:YAG OFS lock. In the former case, phase delay in the phase-locked loop limited the bandwidth; the PZT actuator was the limiting factor in the latter case. We verified that these bandwidths were wide enough to produce an IR frequency stability limited by the OFS. In fact, we measured the Allan deviation of the rf beat notes when the lasers were locked to the OFS, obtaining \( 1.2 \tau^{-1/2} \) Hz and \( 0.6 \tau^{-1/2} \) Hz with \( 0.5 \text{s} < \tau < 100 \text{s} \) for the diode and the Nd:YAG lasers, respectively. Although a measurable Allan deviation means that some cycle slips are present, these values confirm that the contribution of the laser locks to the IR stability is less than the OFS stability at the frequencies of operation \([\approx (N_p - N_s) \nu_s]\).

The IR radiation generated is used for saturated-absorption spectroscopy by coupling to a confocal Fabry–Perot cavity with a free spectral range of \( \sim 1.3 \) GHz and a finesse of \( \sim 550 \). The reflection and transmission signals are detected by a pair of twin liquid-N\(_2\)-cooled InSb photodiodes. We perform IR frequency scans by sweeping the beat-note frequency of the pump or the signal laser with the OFS. With this procedure a maximum scan width of 500 MHz can be achieved, limited by the 1-GHz OFS repetition rate. One can make wider scans by scanning the OFS repetition rate instead. During a scan, the cavity mode must be kept resonant with the IR frequency by control of its length with a PZT. First-derivative Lamb-dip recordings are made by modulation of the Nd:YAG laser frequency at a rate of a few kilohertz.

We tested the performance of this setup by measuring the absolute frequency of the \((0^0 1–0^0 00) R(60)\) CO\(_2\) transition at 2384.994 cm\(^{-1}\). An example of a recorded spectrum for the \(R(56)\) line is shown in Fig. 2. For these measurements we made the 10-MHz IR scan by changing the Nd:YAG frequency. The total acquisition time to record 100 data points, with a 300-ms lock-in time constant, was 200 s. We averaged data from two opposite sweeps (forward and backward) to compensate for possible distortions caused by the lock-in integration process. Simultaneously, the beat-note frequencies \(\Delta \nu_p\) and \(\Delta \nu_s\) for each data point of the spectrum were recorded to yield an absolute frequency scale following Eq. (1). We measured the line center absolute frequency by fitting the experimental line shapes to a theoretical model, taking into account several parameters of the observed Lamb dips: transit time (Gaussian) and pressure-broadening (Lorentzian) widths, saturation parameter, total absorption level, and line shape of the filled cavity mode. We followed this procedure 67 times over a 2-month period. The fit results are plotted in Fig. 3. The weighted-average value has an uncertainty of 800 Hz. Although errors in single line center values are even less than 1 kHz, this final uncertainty is limited by the reproducibility of \( \sim 10 \) kHz; this value includes several components, such as the quartz–GPS accuracy of the OFS, day-to-day gas pressure variations, and other experimental conditions that may vary. It is worth noting that an estimation of the actual accuracy requires a careful analysis of all systematic contributions to the uncertainty. A precision of 800 Hz (\(1.1 \times 10^{-11}\)) for frequency measurements of CO\(_2\) transitions near 4.2 \(\mu\)m with the present experimental apparatus is thus demonstrated.

Molecular transitions that belong to fundamental rovibrational bands can become a dense natural comb of high-quality IR frequency standards. To this purpose, one should reduce the observed linewidth \(\Delta \nu\) close to the natural value, to increase the quality factor, \(Q = \nu/\Delta \nu\). We summarize the contributions to this linewidth in Table 1. This table also contains the analytical expressions for the various contributions. Apart from the multiplicative factors that are due to the saturation physical process and the modulation technique, the main contributions to
broadening come from transit time (~400 kHz) and collisions (~90 kHz). To overcome this limitation we designed a new 1-m-long Fabry–Perot cavity with a larger mode waist and a higher finesse (~6000) that should allow the transit-time broadening to be reduced by at least a factor of 5. Also, a reduction in collisional broadening of more than 100 times is expected, even for weak transitions that involve high-J levels. For actual linewidth reduction the IR jitter needs to be controlled. Because $\Gamma_c$ is limited by the quartz jitter and by the high order number of each OFS tooth, a new reference oscillator in the visible for locking the OFS repetition rate could help to reduce the OFS linewidth below the 1-kHz limit. Alternatively, appropriate beat-note combinations between the pump–signal lasers and the OFS can be used to cancel the contribution of the OFS linewidth to the IR jitter.\(^{15}\)

Summarizing, we have developed a DFG-based IR coherent source with a frequency directly traceable to the primary frequency standard by an OFS. This source is used for high-precision molecular spectroscopy in the mid-IR. The ultimate precision in these frequency measurements will be limited by the OFS's stability. For this purpose we are now implementing a GPS-disciplined Rb clock to better control the quartz frequency on longer time scales (>100 s). This improvement, combined with a cavity with a larger finesse and a larger waist, could be used to build a comb of secondary frequency standards by measuring molecular transitions resonant with the laser source. Tunable IR laser sources, such as quantum cascade lasers, will directly benefit from the creation of a dense comb of high-quality frequency standards. Furthermore, the unprecedented combination of high precision for absolute frequency measurements and a wide IR spectral coverage can facilitate precise testing of theories\(^{16}\) and boost observation of tiny effects in molecules. Such newly measured IR standards will find application in astrophysics as well as in environmental investigations.

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### Table 1. Broadening Contributions to the Saturated-Absorption Line Shape of the CO$_2$ Line Shown in Fig. 2

<table>
<thead>
<tr>
<th>Source</th>
<th>Expression$^a$</th>
<th>Actual Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural lifetime</td>
<td>$k^3\mu^2 / 3\pi\epsilon_0\hbar$</td>
<td>0.2 kHz</td>
</tr>
<tr>
<td>Collisions</td>
<td>$c_P P$</td>
<td>90 kHz</td>
</tr>
<tr>
<td>Transit time</td>
<td>$\sqrt{\ln 2 / \pi k_B T / m 1 / w}$</td>
<td>400 kHz</td>
</tr>
<tr>
<td>IR jitter</td>
<td>$[1 - (v_p / v_p')]\Gamma_c$</td>
<td>&lt;50 kHz</td>
</tr>
<tr>
<td>Power</td>
<td>$1 + (I/I_s)$ $\times 1.4$ ([I/I_s]=1)</td>
<td></td>
</tr>
<tr>
<td>Modulation</td>
<td>$\times 1.3$ ($\beta=1$)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Notation: $k$, wave number; $\mu$, electric dipole matrix element of the transition; $c_P$, pressure-broadening coefficient; $P$, pressure; $T$, temperature; $m$, molecular mass; $w$, cavity mode waist; $v_p$, $v_c$, pump and signal frequencies, respectively; $\Gamma_c$, linewidth of the OFS mode near $v_p$; $I$, intracavity intensity; $I_s$, saturation intensity; $\beta$, modulation index.