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Mid-infrared laser phase-locking to a remote near-infrared frequency reference for high-precision molecular spectroscopy

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Abstract. We present a method for accurate mid-infrared frequency measurements and stabilization to a near-infrared ultra-stable frequency reference, transmitted with a long-distance fibre link and continuously monitored against state-of-the-art atomic fountain clocks. As a first application, we measure the frequency of an OsO_4 rovibrational molecular line around $10\,\mu m$ with an uncertainty of 8×10^{-13}. We also demonstrate the frequency stabilization of a mid-infrared laser with fractional stability better than 4×10^{-14} at 1 s averaging time and a linewidth below 17 Hz. This new stabilization scheme gives us the ability to transfer frequency stability in the range of 10^{-15} or even better, currently accessible in the near infrared or in the visible, to mid-infrared lasers in a wide frequency range.

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Contents

1. Introduction

With their rich internal structure, molecules can play a decisive role in precision tests of fundamental physics. They are, for example, now being used to test fundamental symmetries [1–3] and to measure either absolute values of fundamental constants [4] or their temporal variation [5–6]. Most of those experiments can be cast as the measurement of molecular frequencies. Ultra-stable and accurate sources in the mid-infrared (MIR) spectral region, the so-called molecular fingerprint region that hosts many intense rovibrational signatures, are thus highly desirable. MIR laser frequency stabilization has been performed for a long time using molecular references such as CH_4 or OsO_4 (see for instance [7–10]). However obtained stability is at least one order of magnitude below those of visible or near-infrared lasers stabilized to an ultra-stable cavity. Moreover, only a few molecular lines can be used when ultra-high accuracy is needed.

In this paper we present a method for accurate MIR laser frequency stabilization. The frequency reference is a near-infrared cavity-stabilized laser continuously monitored against primary standards, and the coherent frequency link between near-infrared and MIR frequencies is obtained by using an optical frequency comb. Moreover, we demonstrate this stabilization scheme with a remote near-infrared frequency reference transferred via an optical fibre link from a national metrological institute (NMI). This technique is thus accessible to any laboratory that can be connected to such an NMI with a fibre optical link [11].

Optical frequency combs have proven to be essential for laser frequency measurement and stabilization from the infrared to ultraviolet domain (see for instance [12]). Fractional accuracy and stability (at 1 day averaging time) down to a few 10^{-16} are potentially reachable when the frequency reference is provided by advanced primary standards. Extension to the MIR spectral domain has been demonstrated by comparing the MIR laser frequency with a very high harmonic of the comb repetition rate using sum-frequency generation (SFG) or difference-frequency generation [13–20]. Efforts have also been made towards the development of MIR frequency combs [10, 21–26].

In this paper we first describe the setup for coherent frequency stability transfer between near-infrared and MIR frequencies around $10\,\mu$m. Then we demonstrate absolute frequency measurement of a MIR frequency with a fractional resolution of at least 4×10^{-14}. We also report a first application to high-resolution molecular spectroscopy with a fractional uncertainty of 8×10^{-13} on the line centre. Finally, we present the MIR laser frequency stabilization against the near-infrared frequency reference.

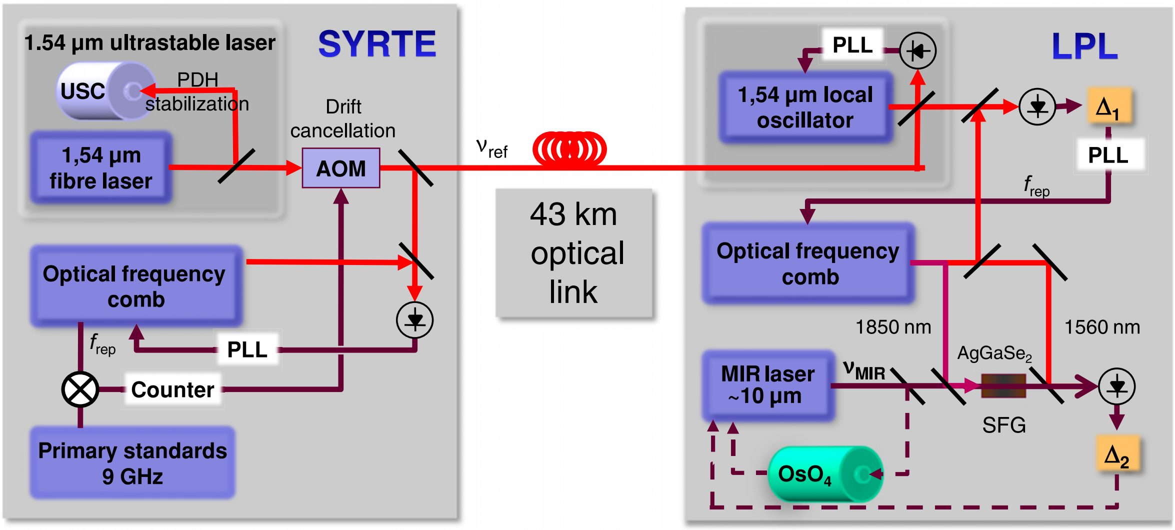

Figure 1. Experimental setup. The MIR laser frequency can be controlled with either the beat-note Δ_2 or the OsO_4 absorption signal. PLL: phase-lock loop; PDH: Pound–Drever–Hall stabilization; SFG: sum-frequency generation; AOM: acousto-optic modulator; USC: ultra-stable cavity.

2. Experimental setup

The experimental setup is shown in figure 1. The ultra-stable optical reference located at LNE-SYRTE is a 1.54 μm fibre laser locked to a high-finesse cavity. Its fractional frequency instability was measured to be lower than 2×10^{-15} at 1 s and 10^{-14} at 100 s (after a 0.3 Hz s^{-1} drift was removed) [27]. Its frequency is measured using a fibre fs laser centred around 1.55 μm. The laser repetition rate is phase-locked to the optical reference frequency after removal of the comb frequency offset f_0. Fast corrections are applied to an intra-cavity electro-optic modulator (bandwidth >400 kHz) and slower corrections to a piezo-electric transducer (PZT) controlling the laser cavity length (bandwidth ~10 kHz) [28]. The absolute frequency of the comb repetition rate 36th harmonic (9 GHz) is continuously measured against the LNE-SYRTE frequency references, which includes an H-maser, a cryogenic oscillator and Cs fountains [29–30]. It enables real-time measurement of the ultra-stable laser frequency drift and its correction by applying to the driving frequency of an acousto-optic modulator an opposite linear drift (with a step every ms) updated every 100 s. This makes up an ultra-stable near-infrared reference, the frequency of which is currently traceable to primary standards with a 10^{-14} uncertainty after 100 s.

This optical reference signal is transmitted to Laboratoire de Physique des Lasers (LPL) through a 43 km long optical link [27]. The free-running link exhibits a propagation instability of 2×10^{-14} at 1 s and around 10^{-15} between 100 s and 1 day. When compensated, the link instability has been measured to be roughly $10^{-15}\,\tau^{-1}$ and to reach around 10^{-18} after 10^3 s (see figure 3) [27]. The frequency stability and accuracy of the reference signal are thus preserved at the LPL optical link end.

At LPL, a low-noise laser diode (free-running linewidth below 10 kHz) is phase-locked to the incoming signal with a bandwidth of 100 kHz and constitutes the local optical frequency

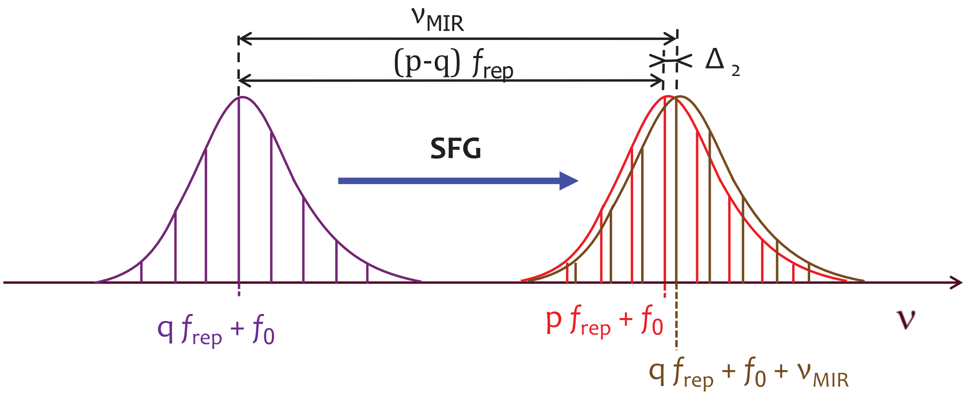

Figure 2. Sum-frequency of a comb output centred at 1850 nm (purple comb), of mode frequencies $qf_{rep} + f_0$ with q an integer, and the MIR laser (of frequency ν_{MIR} around 10 μm) results in a shifted comb (brown comb) centred at 1550 nm of mode frequencies $qf_{rep} + f_0 + \nu_{MIR}$. The beat-note of this shifted comb with the comb main output centred at 1550 nm (red comb), of mode frequencies $pf_{rep} + f_0$ with p an integer, can be written as $\Delta_2 = \pm((qf_{rep} + f_0 + \nu_{MIR}) - (pf_{rep} + f_0))$, which results in $\Delta_2 = \pm(\nu_{MIR} - (p - q) f_{rep})$. SFG: sum-frequency generation.

reference ν_{ref}. The repetition rate f_{rep} of a 1.55 μm fibre fs laser is phase-locked to ν_{ref}. To that purpose, the beat-note Δ_1 between ν_{ref} and the Nth comb mode ($N \sim 780\,000$) is used, after removal of the comb frequency offset f_0:

$$\nu_{ref} - N\, f_{rep} = \pm\, \Delta_1. \tag{1}$$

Fast and slow corrections are applied to an intra-cavity electro-optic modulator and a PZT, respectively, as performed at LNE-SYRTE [28]. A second beat-note Δ_2 compares the MIR laser frequency ν_{MIR} around 10 μm and the nth harmonic of the repetition rate with $n \approx 120\,000$:

$$\nu_{MIR} - n\, f_{rep} = \pm\, \Delta_2. \tag{2}$$

This signal is generated using SFG of the MIR light and an additional comb output centred on 1.85 μm, generated in a nonlinear fibre (figure 2) [14]. This comb output (~25 mW) and the MIR laser beam (~100 mW) are focused in a 10 mm long crystal of $AgGaSe_2$ for type-I SFG. The measured efficiency is around 0.4 mW/W^2 and the phase-matching bandwidth (for the 1.85 μm comb) is about 30 nm (~3 THz). The resulting shifted comb, centred on 1.55 μm, is combined with the 1.55 μm fs laser output. An adjustable delay line enables us to control the overlapping of the pulses in the time domain. About 10^4 mode pairs generate the beat-note Δ_2 which shows a signal-to-noise ratio of about 30 dB in a 100 kHz bandwidth. An RF tracking oscillator is phase-locked to this beat-note. As a result of the frequency difference between two modes of the same comb, Δ_2 is independent of the comb offset f_0.

Combining (1) and (2), the MIR laser frequency ν_{MIR} is finally obtained as

$$\nu_{MIR} = \pm\, \Delta_2 + \frac{n}{N}\, (\nu_{ref} \mp\, \Delta_1) \tag{3}$$

with n/N roughly equal to 0.15. The MIR frequency is thus directly linked to the near-infrared frequency reference, once the integers n and N and the signs have been determined.

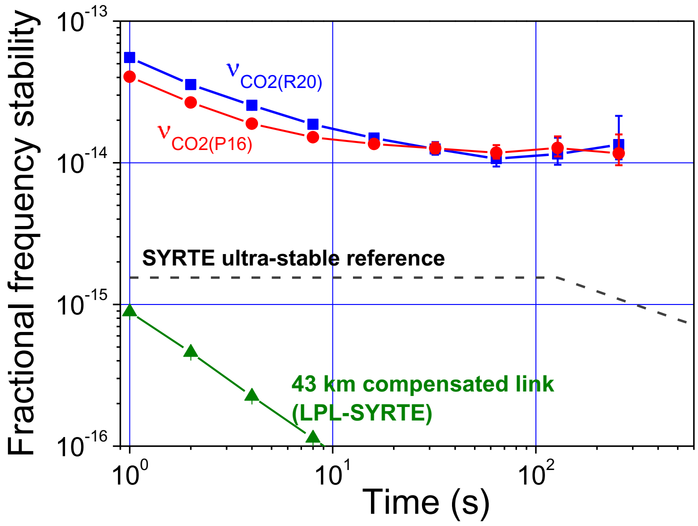

Figure 3. Frequency stability of a CO_2 laser locked on two different OsO_4 saturated absorption lines: the P(55) line of $^{190}OsO_4$ near the 10.55 μm P(16) CO_2 laser line (red circles ●) and the R(67) line of $^{192}OsO_4$ near the 10.25 μm R(20) CO_2 laser line (blue squares ■). The propagation instability of the compensated LPL-SYRTE fibre link (green up-triangles ▲) and the stability of the SYRTE frequency reference that is made of a combination of an H-maser, a cryogenic oscillator and Cs fountains [29] (dashed line) are shown for comparison.

3. Mid-infrared frequency measurement and stabilization

To characterize the phase-coherent link between the near-infrared frequency reference and the MIR frequency, we used this setup to measure the absolute frequency of a CO_2 laser stabilized onto an OsO_4-saturated absorption line. Such an OsO_4-stabilized CO_2 laser constitutes the current state-of-the-art MIR secondary reference standard [7, 8]. In this work, the CO_2 laser was locked either to the P(55) line of $^{190}OsO_4$ near the 10.55 μm P(16) CO_2 laser line or to the R(67) line of $^{192}OsO_4$ near the 10.25 μm R(20) CO_2 laser line. Corrections are applied to a PZT controlling the laser cavity length with a stabilization bandwidth of about 400 Hz limited by the PZT actuator. The obtained fractional frequency stability, shown in figure 3 (red circles and blue squares), is 4×10^{-14} at 1 s, reaches 10^{-14} after 100 s of integration, and degrades at longer times due to a frequency drift of the CO_2/OsO_4 frequency reference. We checked that this stability was limited by the CO_2/OsO_4 reference since changing the CO_2 laser locking parameters induced a variation of the obtained stability. This stability is consistent with previous measurements obtained by comparing either two identical stabilized CO_2 lasers [7–8] or one of such lasers to a titanium–sapphire (Ti:Sa) frequency comb referenced to a microwave frequency [13]. This demonstrates the capability of the system to measure the stability of the best MIR frequency sources to date without any degradation. We expect the optical link and the frequency comb to contribute a few 10^{-15} at 1 s to the frequency instability [27–28].

The relationship of equation (3) between the frequency of the 1.54 μm LNE-SYRTE reference laser and that of the MIR laser is ensured by means of coherent phase-lock loops.

Thus the accuracy of the MIR frequency measurement only depends on the uncertainty of the near-infrared frequency reference. The latter is known with an uncertainty of about 10^{-14} after 100 s averaging time, when only steered with the H-maser which is sufficient for this experiment. The 3×10^{-16} Cs fountain accuracy [30] can ultimately be reached and then transferred from the optical reference to the MIR frequency.

As a first application to high-precision spectroscopy, we determined the absolute frequency of the P(55) line of $^{190}OsO_4$ by measuring the OsO_4-stabilized CO_2 laser frequency. Eleven measurements were performed between December 2011 and April 2012. The beat-note Δ_2, the repetition rate f_{rep} and the frequency ν_{ref} were counted with a gate time of 1 s. Δ_2 and ν_{ref} were combined using equation (3) to calculate the CO_2/OsO_4 frequency. Signs in equation (3) and values of n and N were unambiguously deduced from f_{rep} and the value $\nu_{OsO_4/1999} = 28\,412\,648\,819\,596\,(45)$ Hz of the CO_2/OsO_4 frequency obtained by combining two independent measurements reported in the literature [31, 32]. The mean value over 600 measurements of 1 s of the CO_2/OsO_4 frequency gives one data point. For each data point, we correct the frequency of the LNE-SYRTE H-maser using the data published by Bureau International des Poids et Mesures[5]. Between each measurement the OsO_4 absorption cell was pumped and filled again or the whole experiment was switched off and on. We obtained $\nu_{OsO_4/2012} = 28\,412\,648\,819\,588(24)$ Hz where the uncertainty is the weighted $1-\sigma$ deviation of the data points. It is -8 Hz from the value $\nu_{OsO_4/1999}$ and +8 Hz from another measurement performed in 2004 with a microwave-referenced Ti:Sa frequency comb with an uncertainty of 58 Hz [13]. Within $1-\sigma$ error bars the present result agrees with the previous measurements and confirms the very high accuracy of the measurement setup. The factor of 2 improvement of the uncertainty obtained in the measurement reported here, still limited by the molecular reference, is due to a better control of the OsO_4 pressure and optimization of the CO_2 laser locking parameters.

From the previous results, we conclude that the coherent frequency chain is a viable and potentially much better alternative to an OsO_4 molecular transition for frequency stabilization of a MIR source. This was investigated by locking the CO_2 laser frequency to the optical comb: the beat-note of the free-running CO_2 laser with the comb repetition rate nth harmonic, Δ_2, was phase-locked onto a stable frequency synthesizer with a 400 Hz bandwidth. The obtained CO_2 laser frequency stability is characterized by measuring the beat-note Δ_3 with a second independent CO_2 laser stabilized onto OsO_4. Figure 4 displays this beat-note signal, fitted with a Lorentzian of linewidth 17 Hz (full-width at half-maximum). In the case of a Lorentzian lineshape, the contribution of each laser linewidth adds [33] and we deduce a linewidth between 8.5 and 17 Hz for each laser, the state of the art for a CO_2 laser [7]. Figure 5 displays Δ_3's frequency noise power spectral density (PSD) (red trace). Using the beat-note Δ_2 with the local frequency comb, the frequency noise PSD of the OsO_4-stabilized CO_2 laser was also measured (figure 5, blue trace). The two PSDs almost perfectly overlap as expected from efficient phase stabilization. Together with the above results, it shows that the comb-stabilized MIR laser frequency noise is at least as low as that of the OsO_4-stabilized laser. The former is most probably much lower, potentially compatible with the frequency noise of the optical frequency reference of which the inferred PSD (including noise added by the link) is displayed in figure 5 (dotted black line). This noise level is the lowest reachable with our stabilization scheme.

[5] See publication of the clocks' rates relative to TAI on ftp://ftp2.bipm.org/pub/tai/publication/.

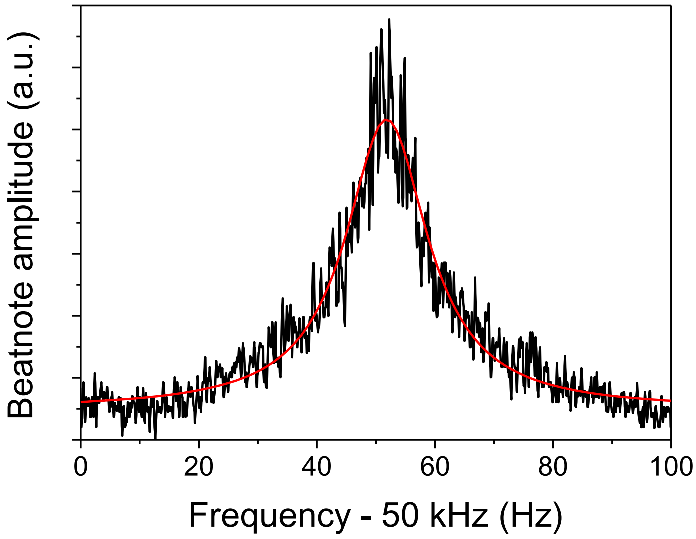

Figure 4. Down-converted beat-note of two independent CO_2 lasers, one stabilized on an OsO_4 resonance line, the other phase-locked to a comb repetition rate high-harmonic; the red line is a Lorentzian fit of linewidth 17 Hz.

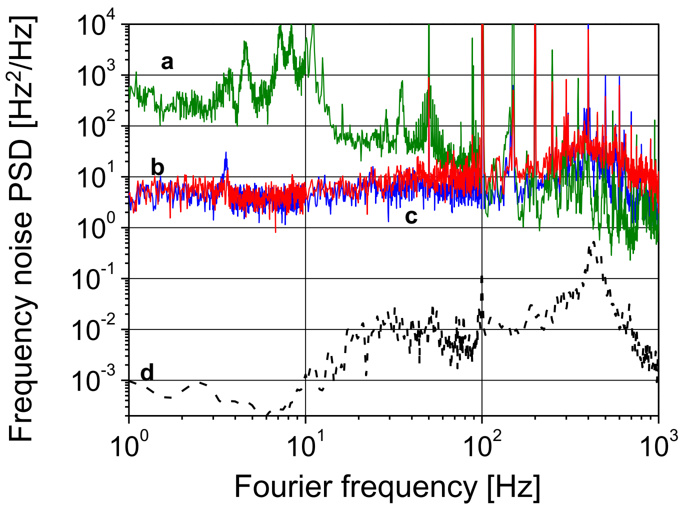

Figure 5. Frequency noise PSD of (a) the free-running CO_2 laser (green trace), (b) the beat-note between the CO_2 laser stabilized onto the frequency comb and an independent OsO_4-stabilized CO_2 laser (red trace), (c) the OsO_4-stabilized CO_2 laser measured with the comb (blue trace) and (d) the optical reference (dotted black line). The free-running CO_2 laser PSD has been measured using the beat-note Δ_2 with the local frequency comb and is given for comparison.

4. Conclusion

We have demonstrated a coherent frequency chain linking a remote ultra-stable 1.54 μm frequency reference and a MIR source, leading to the control of the absolute MIR frequency.

It uses reliable commercially available fibre-based frequency combs and an optical reference potentially available to any laboratory connected to a fibre network [11]. Stability below 4×10^{-14} at 1 s was demonstrated, and we expect it to be in the 10^{-15} range. Using a state-of-the-art near-infrared ultra-stable laser [34] may reduce this value even further. The 3×10^{-16} accuracy of the LNE-SYRTE Cs fountains is potentially within reach.

Frequency tuning of such a stabilized MIR laser source, required for high-resolution spectroscopy, is achievable by scanning the near-infrared frequency referencing the comb. Tuning the frequency offset between the LNE-SYRTE optical reference and the LPL laser diode of frequency ν_{ref} (see equation (3)) would result in a tuning range of a few GHz.

This setup enables us to stabilize MIR laser sources in a much wider spectral range than is currently possible using the OsO_4 molecular standard. With the present setup the 9–11 μm range is accessible, limited by the nonlinear crystal and the central frequency of the auxiliary 1.85 μm comb output used in the SFG. Nevertheless, it can easily be extended to the whole 5–20 μm range with the proper comb spectrum and crystal optimization. Orientation-patterned GaAs would for instance ensure a wide tunability [35]. Our stabilization technique is thus particularly well suited to quantum cascade lasers that have achievable wavelengths covering the whole MIR region [36]. Moreover, the ongoing work on dissemination of optical reference through internet fibre networks over a continental scale [11] will eventually enable many laboratories to access an ultra-stable optical reference. Thus such ultra-stable and accurate MIR sources could benefit a very wide molecular spectroscopy community.

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