

High Precision, SI-traceable, Mid-Infrared Molecular Spectroscopy

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Summary—We present SI-traceable mid-infrared high-resolution saturated absorption spectroscopy measurements conducted on methanol. Resolutions of few hundreds of kilohertz and record sensitivities of a few kilohertz (10^{-10}) on transition center frequencies are obtained in a multi-pass cell. Promising results have also been obtained in transmission of a 3-m long Fabry-Perot cavity yielding resolutions of a few tens of kilohertz which paves the way to the sub-kilohertz (10^{-12}) level of vibrational frequency accuracy.

Keywords—optical frequency comb; frequency stabilization; frequency transfer; quantum cascade laser; mid-infrared high-resolution molecular spectroscopy.

I. INTRODUCTION

There is a growing demand for high-precision molecular spectroscopy in the mid-infrared (MIR, 3-25 μm), the so-called molecular fingerprint region hosting intense and narrow rovibrational molecular transitions, with applications ranging from fundamental physics and metrology, to atmospheric monitoring and astrophysics. The development of quantum cascade lasers (QCLs) covering most of this spectral region, puts into reach of precision measurements many new molecular species and transitions. We have developed in the last years a set-up located at Laboratoire de Physique des Lasers (LPL) for the frequency control and tuning of a 10.3 μm QCL, using a near-infrared (NIR) optical frequency comb (OFC) locked to a SI-traceable ultra-stable NIR reference signal produced by LNE-SYRTE, the French metrology institute for time and frequency, and transferred to LPL via a fiber link.

Here we show the potential of such a system for high resolution vibrational spectroscopy, reporting MIR saturated absorption spectroscopy measurements on a room temperature gas phase of methanol, either in a multi-pass cell or a Fabry-Perot cavity, allowing us to reach kilohertz to potentially sub-kilohertz uncertainties on line positions. This represents several orders of magnitude of improvement over previous measurements. Our set-up allows us to also observe new spectroscopic features in methanol, such as weak lines previously unreported.

II. QCL STABILIZATION AND TUNABILITY

The experimental setup is shown in Fig. 1. Details can be found in references [1,2]. An ultra-stable reference signal at 1.54 μm is transferred from LNE-SYRTE to LPL via a 43-km long fiber link with active compensation of the propagation-induced phase noise, which guarantees a transfer without any stability degradation [3,4]. The reference signal is the phase of a 1.54 μm laser diode locked to an ultra-stable cavity resulting in a stability below 10^{-15} from 0.1 to 10 s. Its absolute frequency is measured against a combination of a hydrogen maser and a sapphire cryogenic oscillator, themselves locked to a cesium fountain primary standard at LNE-SYRTE. The reference frequency is thus SI-traceable and known with a total uncertainty at 1 s averaging time better than 4×10^{-14} that can potentially reach the 2×10^{-16} accuracy of the Cs fountain. At LPL, the sideband of a NIR optical local oscillator (OLO) generated in an electro-optic modulator (EOM) is phase-locked to the ultra-stable reference using a phase-lock loop (PLL1 in Fig. 1).

The repetition rate of a 1.54 μm OFC is stabilized by phase-locking one of its tooth onto the OLO carrier (via PLL2 in Fig. 1) after removal of the comb carrier-envelope offset frequency. Finally, a MIR QCL is phase-locked to the stabilized OFC via sum-frequency generation in a nonlinear crystal by mixing it with a dedicated 1.85 μm output of the OFC. This generates a new comb centered at 1.54 μm , which can be combined with the original stabilized comb to give a beat-note signal that is used to phase-lock the QCL (via PLL3 in Fig. 1). The stability of the frequency reference is copied to the QCL, which therefore exhibits a relative frequency stability below 10^{-15} from 0.1 to 10 s. Moreover, its absolute frequency is known with an uncertainty at the 10^{-14} level or better thanks to the traceability to the primary standards of LNE-SYRTE [1,2]. By scanning the NIR reference laser via the EOM, the setup allows us to scan the comb repetition rate and in turn the QCL frequency over a span of ~ 1 GHz, in order to perform spectroscopy.

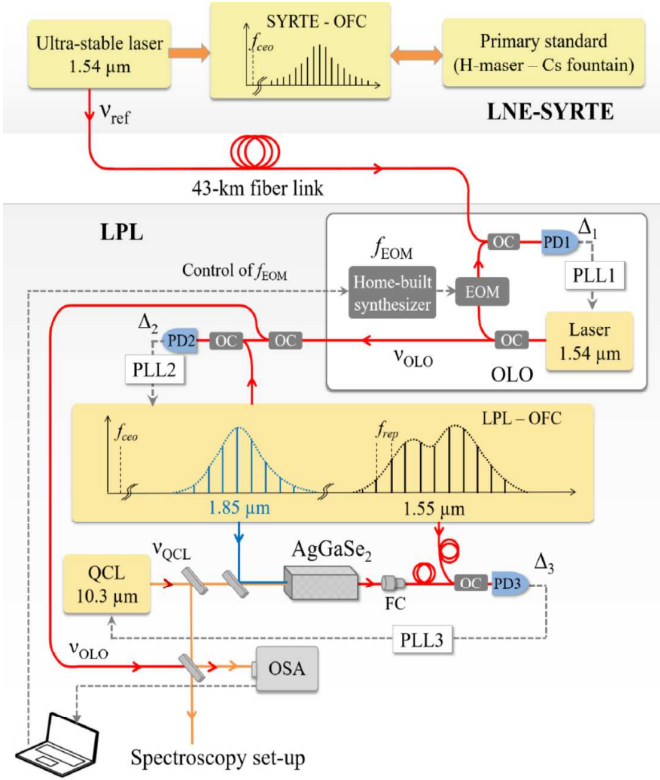


Fig. 1. Experimental setup. At LNE-SYRTE, an ultra-stable NIR frequency reference ν_{ref} is generated and its absolute frequency is measured against primary frequency standards (combination of a H-maser and a sapphire cryogenic oscillator locked to a Cs fountain) using an OFC (SYRTE-OFC). It is transferred to LPL through a 43-km long optical fiber link. At LPL, the repetition rate f_{rep} of a local OFC (LPL-OFC) is phase-locked to a tunable optical local oscillator (OLO, see text) itself stabilized to the ultra-stable reference. By phase-locking the QCL onto a high harmonic of f_{rep} via sum frequency generation in a AgGaSe₂ nonlinear crystal (see text), the stability, absolute frequency uncertainty of the NIR reference signal, as well as the local oscillator tunability, are transferred to the MIR domain. AOM: acousto-optic modulator, OFC: optical frequency comb, EOM: electro-optic modulator, PLL: phase-locked loop, PD: photodetector, OSA: optical spectrum analyser, OC: optical coupler, FC: fiber collimator.

III. HIGH-RESOLUTION SPECTROSCOPY

As illustrated in Fig. 2 and Fig. 3 (a), we have obtained frequency modulated saturated absorption spectra of methanol in a multi-pass cell (Aerodyne Research, AMAC-36 model, 20-cm long baseline, 36.4 m effective optical length) spanning up to ~ 1 GHz spectral windows. The 36.4 m absorption length of the multi-pass cell results in relatively high sensitivities, allowing us to work at relatively low pressures, typically between 0.1 and 10 Pa, resulting in linewidths in the range of a few hundreds of kilohertz and sensitivities on the line center of a few kilohertz [2] (see Fig. 2 and 3 (a)). At this level of precision, we have observed several lines of methanol unreported so far. Using the multi-pass cell has however some drawbacks: (i) a resolution limited to ~ 150 kHz by the beam size (0.8 mm waist) and the resulting transit-time broadening;

(ii) systematic resonance frequency shifts resulting from wave-front curvature, gas lens effects or the presence of interference fringes that cause line shape distortions. In the multi-pass cell, the uncertainty on the measured frequencies is then 1 to 10 kHz, limited by these systematic effects [2].

We are currently conducting measurements on methanol in a 3-m long Fabry-Perot cavity having a finesse of ~ 200 and an effective optical length of ~ 100 m, with which signals at lower pressures can be obtained, typically around 10^{-2} Pa. This allows us to work with 10 times wider beams and so to reach transit-time limited resolutions in the 10 kHz range. Moreover, most of the systematic effects inherent to the multi-pass cell are expected to be strongly reduced in the cavity thanks to the symmetrical geometry. We are aiming for tens of kilohertz resolutions and sub-100 Hz frequency uncertainties. Indeed, previous saturated absorption spectra of OsO₄ obtained at LPL in a 1.5-m long Fabry-Perot cavity allowed us to achieve a resolution of 25 kHz and an uncertainty of a few tens of hertz on the center frequency [1].

As illustrated in Fig. 3 b), first encouraging measurements in the 3-m long cavity. The overall uncertainty budget has yet to be established. Our preliminary investigations show that (i) statistical uncertainties on line centers at the few hundreds of hertz level, about an order of magnitude better compared to the multi-pass cell, are reachable and (ii) confirm the expected reduction of the contribution of systematic effects in the overall line position uncertainty. Nevertheless, as shown on Fig. 3 b), we observe a degradation of the signal-to-noise ratio compared to the multi-pass cell. An excess of QCL phase noise at high Fourier frequencies converted to amplitude noise in transmission of the cavity is most probably the source of this additional noise. The origin of this excess of noise is currently under investigation.

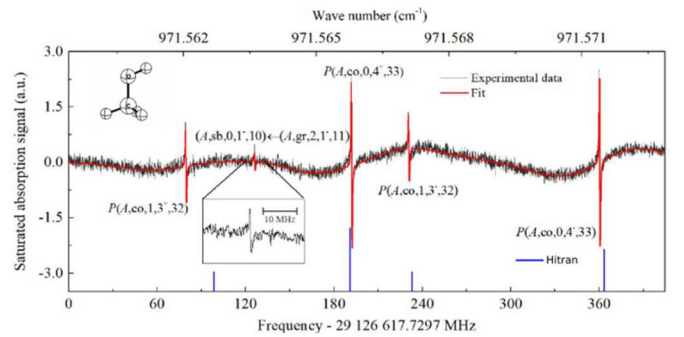


Fig. 2. Frequency modulated saturated absorption spectrum of methanol (CH₃OH), 1st harmonic detection. Wide scan showing continuous tunability of our frequency stabilized QCL over 400 MHz. Blue sticks indicate the line frequency positions reported in the HITRAN database. This wide scan is obtained in a multi-pass cell. Line positions are typically determined with uncertainties at the few kilohertz level [2].

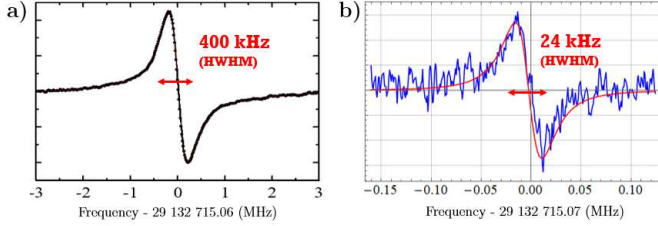


Fig. 3. Frequency modulated saturated absorption spectra of the rovibrational methanol line $P(E,co,0,2,33)$ of the CO-stretch vibrational mode, obtained in transmission of (a) the multi-pass cell and (b) the 3-m long Fabry-Perot cavity. (a) The multi-pass cell spectrum has a resolution of 400 kHz, which has allowed us to determine the line position with a global uncertainty of 7.4 kHz [2]. (b) The cavity measurement exhibits a resolution of 25 kHz. It is expected to lead to uncertainties on line positions of a few hundreds of hertz or better. Experimental conditions: pressure, 1 Pa (a) and $5 \cdot 10^{-2}$ Pa (b); modulation frequency, 20 kHz (a) and 2 kHz (b); frequency modulation excursion, 50 kHz (a) and 10 kHz (b); frequency step, ~ 15 kHz (a) and ~ 0.7 kHz (b); average of 1 pair (a) and 10 pairs (b) of up and down scans; total integration time per point, 200 ms (a) and 2 s (b); spectrum measurement time, 80.2 s (a) and 762 s (b).

IV. CONCLUSIONS

We report the stabilization of a 10 μm QCL to an ultra-stable reference signal operated at LNE-SYRTE and transferred to LPL via a fiber-link. We were able to conduct MIR spectroscopic measurements in a multi-pass cell around 10 μm with an unprecedented level of precision on methanol. We have also performed measurements in the multi-pass cell on a more complex molecule, trioxane ($\text{C}_3\text{H}_6\text{O}_3$), as well as on ammonia, two other species of atmospheric and astrophysical interest. Promising results in a Fabry-Perot cavity have been performed on methanol leading to a resolution improved by an order of magnitude compared to the multi-pass cell.

This work is an important step forward for our on-going efforts towards using complex molecules to perform spectroscopic tests of fundamental physics in the MIR, such as the measurement of the tiny parity-violating energy difference between enantiomers of a chiral molecule [5,6].

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