Absolute frequency measurement of molecular transitions by a direct link to a comb generated around 3-μm

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Abstract: A 3-μm continuous-wave difference-frequency source is directly referenced to a mid-infrared optical frequency comb synthesizer by measuring their beat-note signal by a fast HgCdTe detector. Absolute frequency metrology of molecular vibration spectra is demonstrated by locking the 3-μm coherent radiation to the nearest comb tooth and tuning the comb mode spacing across the Doppler-broadened absorption profile of a CH_4 ro-vibrational transition.

OCIS codes: (120.0120) Instrumentation, measurement and metrology; (190.0190) Nonlinear optics; (300.6390) Molecular spectroscopy.

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1. Introduction

Nowadays, precision molecular spectroscopy is finding increasing applications in various fields such atmospheric physics, environmental monitoring and cosmological studies. The recent advent of optical frequency synthesizers (OFSs), based on mode-locked femto-second (fs) lasers, has opened new perspectives for absolute metrology on molecular spectra [1-4]. On the other hand, the mid-infrared (MIR) spectral region, endowed with the strongest ro-vibrational transitions, is the most favourable window for high-sensitivity and high-resolution spectroscopic investigations.

In a typical OFS-based metrological experiment, the emission frequency of a suitable continuous-wave (cw) laser is measured against the comb teeth providing an absolute frequency scale across the atomic or molecular resonance. So far, due to the limited availability of both cw lasers and OFSs operating in the MIR, only indirect schemes, based on parametric up (down) conversion, have been implemented in this spectral region [5-7].

A more direct approach is to create an OFS directly in the MIR window comprising the coherent source emission wavelength. For instance, a composite frequency comb ranging from the violet to the MIR (0.4-2.4 µm) has been obtained from a phase-controlled fs Ti:Sa laser and a synchronously pumped optical parametric oscillator [8]. A 270-nm-span frequency comb at 3.4 µm has also been produced by difference frequency generation (DFG) between two spectral peaks emitted by a custom-tailored mode-locked Ti:Sa laser [9]. In a previous work, our group has demonstrated generation of an OFS covering the range 2.9-3.5 µm in 200-nm-wide spans, based on a DFG process between a cw laser and a near-IR (NIR) comb [10]. Direct referencing of a cw tunable laser to such a MIR comb for spectroscopic use would be strategic for extending OFS-based frequency metrology to this spectral region.

In this respect, the relevance of the 3-µm window for molecular spectroscopy has triggered an intensive research activity for the realization of new quantum cascade (QC) lasers. This has recently culminated in the first demonstration of InAs/AlSb lasers emitting from 2.95 and 3.35 µm [11,12]. Nevertheless, pulse-mode operation still prevents such devices from being referenced to MIR combs.

In this work, we report the first direct frequency-comb referencing of a 3-µm DFG source. The idea of the experiment is sketched in Fig. 1. A cw 1-µm laser is simultaneously mixed with a 1.5-µm laser and the 1.5-µm portion of an Er-fiber-based OFS covering the 1-2 µm octave. In this way, two DFG processes take place simultaneously in the PPLN crystal, giving rise, respectively, to a coherent probe radiation and a comb, both at a 3-µm wavelength. Afterwards, the idler radiation is split in two parts: one beam, collected by a fast HgCdTe (MCT) detector, provides the beat-note signal used to lock the cw source to its closest comb

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tooth; the second beam is made to propagate through a gas sample cell. In this way, as the mode spacing of the MIR comb is swept, the 3-µm probe radiation is accordingly scanned across the molecular resonance of interest providing an absolute frequency scale.

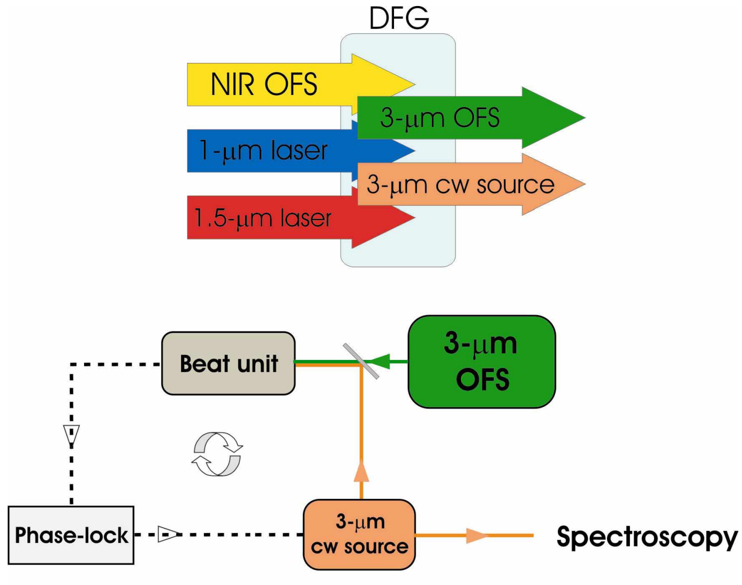

Fig. 1. Layout of the experiment: two simultaneous DFG processes in a PPLN crystal are exploited to produce an OFS and a coherent source at 3 µm. Then, the detected beat-note signal is used to phase-lock the probe radiation directly to the MIR comb, while a second beam is allowed to record molecular spectra with an absolute frequency scale.

2. Experimental setup and results

The experimental set-up is shown in Fig. 2. The DFG pump radiation is provided by a tunable external cavity diode laser (ECDL), emitting around 1 µm, which seeds an Yb-doped fiber amplifier delivering up to 0.7 W. The signal beams originate, respectively, from a tunable ECDL emitting around 1.5 µm and a NIR OFS (FC1500, MenloSystems) covering the 1-2 µm octave [10]. Its repetition rate (mode spacing) f_r=100 MHz and carrier-envelope offset frequency f_0 are stabilized against a 10-MHz BVA quartz which is locked, in turn, to a Rb-clock linked to the Cs primary standard via a global positioning system (GPS). The FC1500 beam used for the DFG process is taken before the spectral broadening unit and spans roughly 200 nm around 1.5 µm. After combining in a fiber splitter, the two signal beams simultaneously seed an Er-doped fiber amplifier (EDFA). The output consists of an amplified replica of the cw ECDL beam (1 W) and a co-propagating amplified frequency comb (0.7 W overall power) spanning the 1540-1580 nm (50000 teeth) interval, with an intensity distribution resulting from the convolution between the incoming comb spectrum and the amplifier gain curve [10]. Then, the pump beam is mixed to the signal radiation in the PPLN crystal giving rise to two DFG processes: a cw source (≈ 0.5 mW) and an OFS (≈ 100 pW per tooth) at 3-µm arise from the interaction of the common 1-µm pump beam respectively with the laser and the comb at 1.5 µm. Finally, the beat-note signal between the 3-µm cw source and its closest tooth is recorded by a 100-MHz-bandwidth, liquid-nitrogen-cooled MCT detector (V104-0.1-J1-1, Kolmar Technologies). At the same time, the reflection from a CaF_2 window (tens of µW) is used for gas-cell spectroscopy; since the power ratio between the 3-µm probe radiation and the MIR OFS is about 100, the co-propagating idler comb radiation negligibly contributes to the absorption signal.

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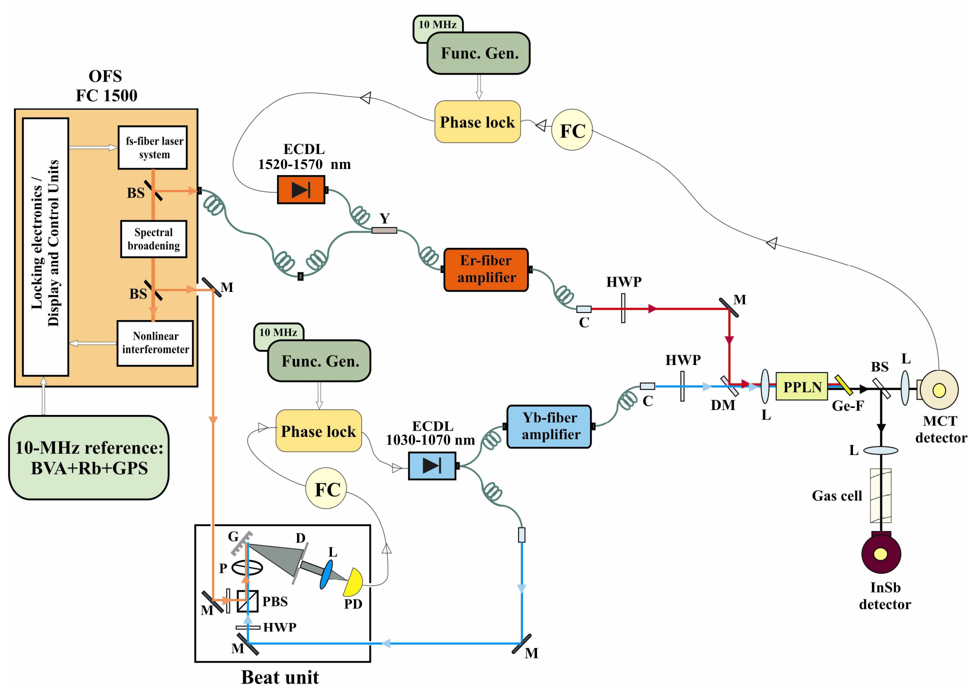

Fig. 2. Experimental set-up. First, the DFG pump source at 1-µm is phase-locked to the FC1500 comb. Then, the signal beams are obtained by simultaneous amplification of a cw 1.5-µm laser and the 1.5-µm portion of the NIR OFS. The DFG processes, taking place in the nonlinear crystal, give rise to a comb and a cw source at 3-µm. The IR beat note is used to phase lock the 1.5-µm laser, and therefore the 3-µm probe radiation, to the MIR OFS, while reflection by a CaF_2 window is used for gas-cell spectroscopy. The following legend holds: ECDL=external cavity diode laser, G=diffraction grating, M=mirror, HWP=half wave plate, PBS=polarizing beam splitter, P=linear polarizer, D=iris diaphragm, L=lens, PD=InGaAs photo-detector, DM=dichroic mirror, Ge-F=germanium filter, FC=frequency counter, BS=beam splitter, C=fiber collimator, Y=fiber splitter.

For the MIR comb to have the same metrological performance as the NIR one, the 1-µm laser linewidth must be reduced below the FC1500 tooth width (about 50 kHz). For this purpose, a secondary beam coming from the 1-µm laser is beaten with its nearest tooth N_1 in the FC1500 spectrally-broadened output. The detected note, at frequency f^1_{beat}, is sent to an analog+digital electronic servo that has a local oscillator (LO) input provided by a low-frequency synthesizer with the time-base locked to the 10-MHz BVA signal. The servo feeds corrections back to the laser by driving a three-paths electronic loop: one path acts on the external-cavity piezo transducer (PZT), while slow and fast current corrections, externally added to each other, act on a FET modulation input on the diode cathode. This results in a wide capture range as well as in a high-speed, low-noise performance [13]. A typical closed-loop beat note is shown in Fig. 3, where the servo bumps at 500 kHz, due to the slow current loop, are clearly visible. Also, the measured beat-note width is well below that of the FC1500 tooth (50 kHz), meaning that the linewidth of the 1-µm laser is narrowed down to the NIR comb tooth (see inset). As a consequence, the DFG comb teeth are as wide as those of the originary OFS.

As shown in Fig. 3, the signal-to-noise ratio (SNR) slightly exceeds 30 dB. However, a higher SNR would be desirable, but an intrinsic limitation is due to the fact that the laser

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wavelength falls at the lower-edge of the FC1500 spectrum. In these conditions, locking electronics cannot not work at its optimum performance; as a consequence, a small relative deviation of f_{beat}^1 mean value from its LO frequency in the order of $5 \cdot 10^{-4}$, is observed. Statistics of the counter readings over several minutes reveals a gaussian distribution with relative Allan deviation of $7\ 10^{-13}$ (for τ=1 s).

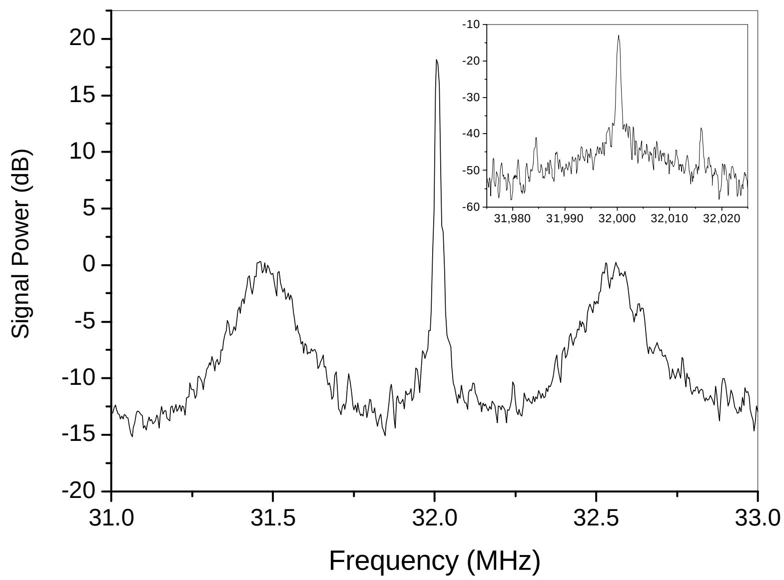

Fig. 3. Closed-loop beat-note signal at f_{beat}^1 between the 1-µm laser and the NIR OFS. The servo bumps at 500 kHz due to the slow current loop are clearly visible. The resolution and video bandwidth are respectively RB=3 kHz and VB=30 Hz. The inset shows the same signal for a frequency span of 50 kHz, (RB=300 Hz, VB=30 Hz), indicating that the 1-µm laser linewidth is narrowed down to the NIR comb tooth (about 50 kHz). In this way, the metrological performance of the FC1500 system is transferred to the 3-µm comb.

Now, since the NIR comb spectrum is given by $f_{NIR}^{comb} = f_0 + n \cdot f_r$, the absolute frequency of the 1-µm laser is given by $f_1 = f_0 + N_1 f_r + f_{beat}^1$, with f_{beat}^1 locked to its LO frequency. Then, the 3-µm comb is described by

$$f_{DFG}^{comb} \equiv f_1 - f_{NIR}^{comb} = (N_1 - n) f_r + f_{beat}^1 \equiv m \cdot f_r + f_{beat}^1 \qquad (1)$$

where m is an integer number labelling the MIR teeth. So, when the 3-µm coherent source is locked to the closest tooth M (with the offset f_{beat} close to the LO frequency), its absolute frequency is given by

$$f_{DFG}^{cw} = M f_r + f_{beat}^1 + f_{beat}, \qquad (2)$$

where the integer M is determined once and for all, while f_r, f_{beat}^1 and f_{beat} at a given time are provided by the frequency counters. The number M could be extracted in principle by measuring the frequency f_{DFG}^{cw} by a MIR wavemeter with an accuracy better than half the comb mode spacing [14]. In our case, due to the lack of such a precise wavemeter, f_{beat} is measured for two different values of f_r before locking the 3-µm source to the comb; then, mode number is calculated as $M = -\Delta f_{beat} / \Delta f_r$. Anyway, due to the relatively large

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frequency fluctuations of the MIR probe radiation (several hundreds of kHz over a few minutes) and to the maximum allowed change in the repetition rate (a few kHz), the error on *M* is about 400. In fact, this procedure allows to tune the MIR cw source in the spectral window of interest. Then, resorting to HITRAN Database (accuracy much better than 50 MHz in this region) is necessary for an exact determination of *M*.

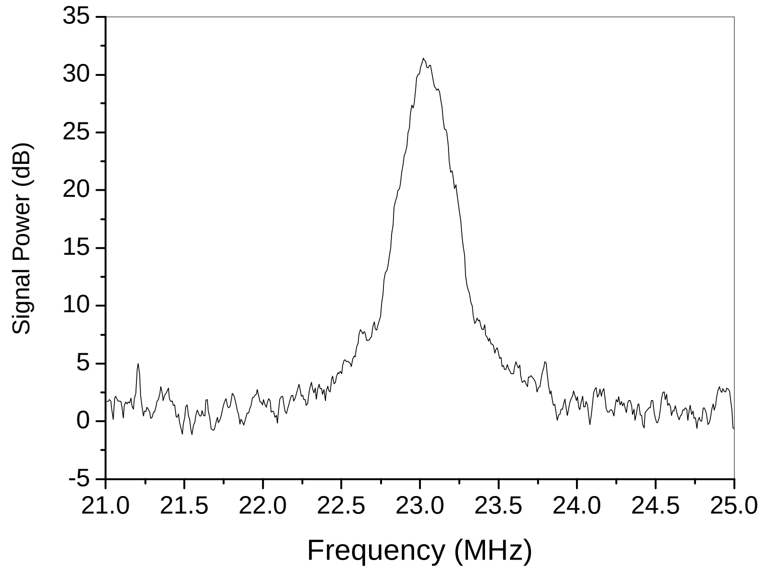

Fig. 4. Closed-loop beat-note signal as observed by the MCT detector directly at 3 μm (RB=1 kHz, VB=10 Hz). Such signal is simultaneously sent to a frequency counter for measurement of f_{beat}.

The closed-loop beat-note signal detected at 3 μm is shown in Fig. 4. Although the SNR is close to 30 dB, additional instabilities in the long-term operation are present, that can be mainly ascribed to amplitude fluctuations introduced by the Yb and Er fiber amplifiers. This manifests itself as a slow frequency drift in the closed-loop beat note frequency. In particular, the analog part of our PLL doesn't work in full operation, as it can successfully act only on the laser piezo (within 1-kHz bandwidth) and the current-driver modulation input (up to 20 kHz) of the 1.5-μm DFG signal laser. Indeed, a larger note width is observed (see fig. 4). Consequently, as shown in Fig. 5, a long-term instability (in addition to white noise) affects MIR radiation frequency, preventing the overall frequency measurement precision to benefit from long term averaging.

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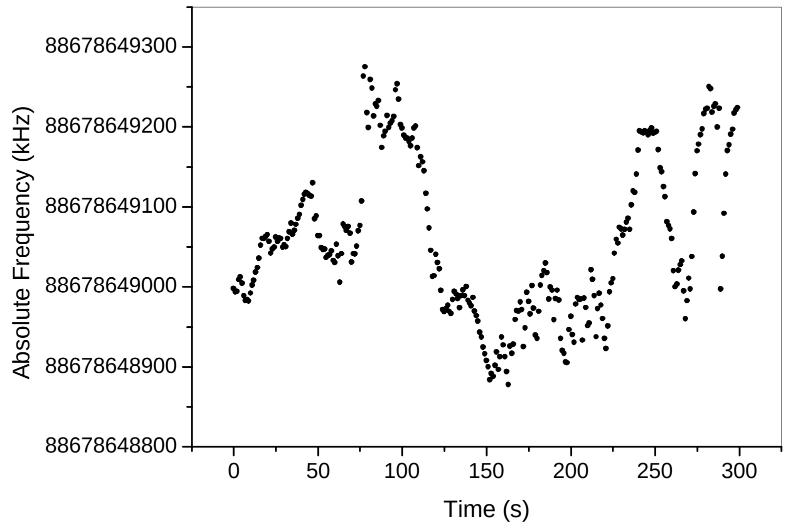

Fig. 5. Absolute measurement of the 3-µm cw source frequency performed using Eq. (2). The integer number M is determined according to the procedure described in the text, while f_r, f^1_{beat} and f_{beat} at a given time are provided by the frequency counters.

In spite of that, a 30-dB SNR does not affect the performance of our counters (included in the Menlo Systems comb control). Indeed we have simulated the above conditions, by a controlled noise source and a stable oscillator, and verified that the counters are able to count with accuracy and reproducibility at Hz-level down to 25 dB. This ensures that absolute frequency determinations are reliable.

With this in mind, absorption lineshapes of molecular resonances can be recorded over an absolute frequency scale by the 3-µm probe radiation. From Eq. (2) it is clear that as f_r is swept by discrete steps, the absolute frequency (*x*-scale) is determined by counting the frequencies f_r, f^1_{beat}, f_{beat} while the DFG power (*y*-scale) transmitted through the cell is simultaneously recorded. Since the maximum allowed continuous change for the comb mode spacing (i.e. avoiding unlocking and re-locking of f_r) is about 450 Hz, corresponding to $\Delta f^{cw}_{DFG} = M\Delta f_r \approx$400 MHz, a larger scan is accomplished by locking the 3-µm source to more consecutive teeth and scanning the repetition rate around each tooth. The result of this procedure is shown in Fig. 6, where, as an example, the (0000-0010) P(6) CH_4 transition is recorded in pure gas for a pressure of 50 mTorr. A Doppler profile is also fitted to the experimental points to extract the line-center frequency. The result is $\nu_c = 88679120 \pm 2\,\text{MHz}$, which is consistent with the value provided by the HITRAN database ($\nu_{HITRAN} = 88679125 \pm 3$ MHz) [15].

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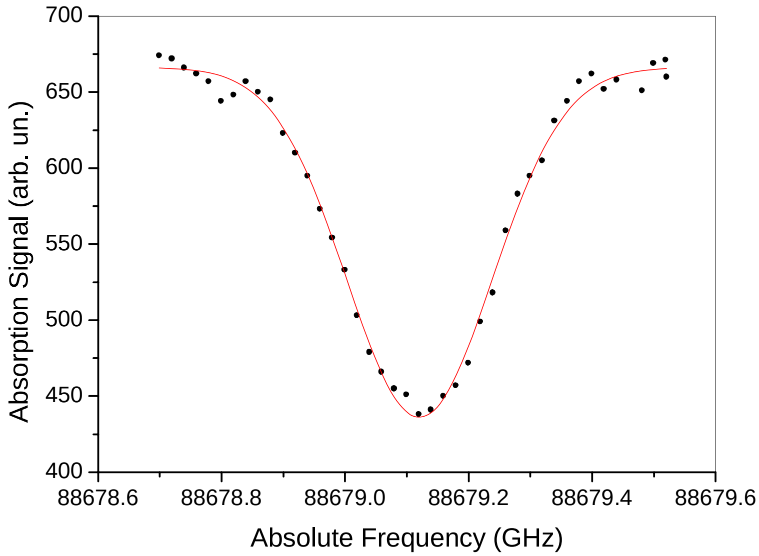

Fig. 6. Recording of the (0000-0010) P(6) CH_4 transition in pure gas at 50 mTorr. After phase-locking the 3-µm probe radiation to the MIR comb, its absolute frequency (*x* axis) is tuned across the molecular resonance by changing the comb mode spacing by discrete steps. This acquisition procedure takes less than one minute. Fitting a Doppler curve to the experimental points provides the line-center absolute frequency with a relative uncertainty of $2 \cdot 10^{-8}$ (88679120 ± 2 MHz).

3. Conclusions

In conclusion, for the first time, a cw tunable 3-µm source has been referenced directly to a MIR OFS. The beat-note signal provided by a fast MCT detector has also been used to lock the 3-µm radiation to its closest comb tooth. Currently, the frequency stability of the 3-µm laser is not yet competitive with other comb-referenced sources, reported in literature [2,9]. The basic limitation comes from by the PLL performance, which prevents from averaging over long periods to fully exploit the stability of the GPS system.

Recording of molecular spectra with an absolute frequency scale has been also carried out. In particular, the center frequency of Doppler-broadened CH_4 lines has been measured with an uncertainty of 2 MHz. The proof-of-principle character of our experiment envisages future application of QC lasers in the field of absolute frequency metrology in the 3-µm spectral region. Indeed, as already mentioned, work is in progress in several labs for the realization of more and more reliable QC lasers, eventually leading to precision-spectroscopy sources down to shorter emission wavelengths [11,16]. Furthermore, our approach may be straightforwardly applied to coherent radiation sources in different MIR windows if well-established IR frequency combs, either based on a DFG process or on supercontinuum generation through specialty optical fibers, become available [17,18]. By eliminating the need for tailored up-conversion processes, this would greatly simplify the accomplishment of comb-based metrological experiments for the ever-increasing community of spectroscopy end-users.

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