New methods to frequency down-convert a broadband near infrared frequency comb into the mid-infrared by three-wave mixing are studied. Modulation of the second-order nonlinear coefficient based on the concepts of either nonlinear spectral holography or quasi-periodic modulation enables us to obtain different spectral shapes of the mid-infrared comb. It includes flat and broadband single-band or dual-band spectra, or a shape that exhibits two or even three sharp peaks at chosen frequencies. The methods we present can be used to tailor the frequency comb spectra to selected molecular absorption lines in the mid-infrared.

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1. INTRODUCTION

Optical frequency combs (OFCs) are coherent sources with a broad spectrum of discrete, narrow, and equally spaced lines, each having an absolute frequency that can be measured with extreme accuracy. Since their development, they have become essential tools for a variety of applications in the visible and near infrared (NIR) [1–3]: calibration of astronomical spectrographs [4], ultra-broadband coherent communications [5], visible/NIR spectroscopy and metrology [6,7]. Further applications require the extension of OFCs to other spectral regions, from the extreme ultraviolet to THz frequencies [8,9]. In particular, there is a strong interest in OFCs operating in the mid-infrared (MIR) spectral region (MIR combs), since therein lies the molecular “fingerprint” region, characterized by strong ro-vibrational transitions of simple molecules [10,11]. It is therefore expected that MIR combs keep pushing molecular spectroscopy to improvements in terms of precision, sensitivity, recording time, and spectral bandwidth [12]. They can facilitate new discoveries in various fields related to molecular science: transient chemical phenomena even at the ultrafast pump-probe scale [13], high-resolution molecular spectroscopy for trace gas detection or breath analysis [14], and others. Commercially available laser systems do not provide easy access to the MIR region; therefore, different strategies have been explored to obtain broadband coherent MIR sources: new laser gain media [15,16], micro-resonators [17], and nonlinear frequency conversion [18–20]. The latter is based on the use of several nonlinear crystal types, for example, orientation-patterned (OP) and periodically poled (PP). Employed in proper setups, these crystals enable down-conversion of NIR combs into the MIR by a difference-frequency generation (DFG) process and optical parametric oscillation (OPO) using a strong pump [21,22].

The standard DFG process assumes a PP crystal that is homogeneous and exhibits constant conversion efficiency along its entire length. The conversion efficiency curve is a single-peaked sinc-shaped function, limited by the phase-matching condition of the interacting waves. PP-DFG is well suited for converting narrowband single-frequency sources [23], since in this case, increasing the crystal length increases the conversion efficiency. But when narrowband single-frequency sources are replaced by broadband sources [19], the frequency conversion turns out to be severely limited by the phase matching and must be compensated by importantly decreasing the crystal length and adopting high power or pulsed pump sources [18]. For example, in a previous experiment [19], a 20-mm-long PP LiNbO3 crystal was employed for DFG, but it enabled efficient conversion of only a small portion of the entire NIR comb, with a phase matching full width at half maximum of 1.6 nm in the NIR (or equivalently 27 nm in the MIR). For spectroscopic applications in the MIR, it is often necessary to measure different absorption lines, for example those belonging to different isotopologues of a certain molecules, or to several different molecules. The lines can be separated...
by hundreds of nanometers in the MIR. In this case, the standard frequency conversion is not the optimal choice, owing to its narrow, single-peaked efficiency curve. A better option would be to have a converter with a broad and nearly flat efficiency, or a converter that will provide high conversion efficiency in the selected regions of interest, for example, absorption lines of selected molecules. The bandwidth limitation of the standard PP crystal can be overcome not only by decreasing the crystal length but also by using instead more sophisticated non-periodic poling of the nonlinear crystal, which allows widening the band of quasi-phase matching (QPM). One possible option relies on adiabatic frequency conversion [24,25], in which the phase mismatch varies slowly compared to the coupling length between the interacting waves. This method enables conversion of broadband pulses [26], exceeding one octave in span, with efficiency that approaches 100% [27], but it requires strong pump intensities, at the level of GW/cm², which are usually available only with very powerful pulsed pump sources.

A new method to shape the spectrum of signals generated in a nonlinear three-wave mixing process was proposed [28] and experimentally demonstrated [29]. It is based on encoding techniques that were originally developed in the computer-generated holograms [30], so that the required modulation pattern can be computed and imprinted directly on the quadratic nonlinear coefficient. Therefore, when a pump and a broadband signal wave illuminate the hologram, an idler wave with a desired complex spectrum is reconstructed. In this way, the proposed encoding scheme directly provides the required spectral shape of the nonlinear converter. As we will show below, shaping the conversion efficiency curve into any desired shape and, in particular, into a shape that is flat over a desired range is now possible using the technique of nonlinear spectral holograms [28,29].

Another alternative for spectral shaping is based on quasi-periodic modulation of the nonlinear coefficient [31]. This method enables us to obtain high (and narrowband) conversion efficiency at several chosen frequencies, and was previously used for applications such as multiple wavelength second harmonic generation [32], triply coincident second harmonic generation [33], cross-polarization wave generation [34] and simultaneous parametric down-conversion and signal-to-idler conversion [35]. Here we show how to apply quasi-periodic modulation for shaping the DFG efficiency curve so that it has two or three peaks, at arbitrary chosen frequencies.

Both design methods require binary modulation of the quadratic nonlinear coefficient, which can be easily implemented in ferroelectric crystals using the electric-field poling technique [36]. Spectral shaping through the nonlinear process represents a compact and robust method, offering wide tuning range and allowing the production of a broad or shaped radiation spectrum.

In this paper, we present design methods and experimental realizations of different types of spectrally shaped MIR combs.

These combs were generated by intracavity DFG involving a single-frequency pump beam (Ti:sapphire laser) tuned in the range 841–845 nm and a spectrally broad signal beam in the range 1032–1045 nm, provided by a metrological visible-NIR frequency comb. Such MIR frequency combs represent an important tool for the investigation of simple molecules such as carbon dioxide, with the isotopic species 12C16O2 and 13C16O2 and nitrous oxide, with the isotopic species 14N216O and 15N14N16O, which have strong transitions in the range 4–5 μm. In particular, we realized in the nonlinear crystal, made up of magnesium-oxide-doped congruent lithium niobate (MgO:CLN), six channels having different poling designs: our aim was to generate MIR combs with different spectral extensions and explore alternative methods in which the nonlinear crystals can provide spectral and temporal shaping for the converted comb.

2. SPECTRAL SHAPING IN A NONLINEAR PROCESS

In order to understand the spectral shaping properties in a nonlinear mixing process, let us consider DFG involving the complex amplitudes of a narrow pump (quasi-continuous wave) A1, a spectrally broad input pulse A2, and a generated wave A3. If the pump and input pulses can be approximated as undepleted, the generated wave can be described as the Fourier transform of the normalized, space-dependent nonlinear coefficient, d(z):

\[ A_3(\Delta k) = \kappa A_1 A_2 \int_{-\infty}^{\infty} d(z) e^{i\Delta k z} dz, \]

where the phase mismatch is \( \Delta k = k_1 - k_2 - k_3 \) and \( \kappa \) is the nonlinear coupling coefficient. In the case of a fixed nonlinear coefficient along a crystal of length \( L \), the space-dependent nonlinear coefficient is simply \( d(z/L) \); hence, the Fourier transform of the rectangle function would yield a sinc function for the generated intensity as a function of the wave-vector mismatch \( \Delta k \) [36], centered at \( \Delta k = 0 \). QPM interaction, in which the nonlinear coefficient is periodically modulated with a period \( \Lambda \), will only shift this narrowband sinc function to a new spatial frequency, \( 2\pi/\Lambda \).

We can now consider more sophisticated modulations of the nonlinear coefficient, beyond the periodic binary modulation that is commonly used in QPM interactions, in order to shape the conversion efficiency spectrum of the nonlinear process. Specifically, nonlinear spectral holography [28,29] can be used to shape the complex (i.e., both amplitude and phase) shape of the generated wave. This is a special variant of the binary Fourier hologram [30] that utilizes the Fourier transform relationship between the space-dependent nonlinear function and the spectrum of the generated wave (Eq. 1). Our goal is to design a nonlinear crystal with a desired spectral modulation function \( U(\Delta k) = U(\Delta k - \Delta k_0) \), around a central carrier wavenumber \( \Delta k_0 \) that is chosen to efficiently phase match the nonlinear process. The inverse Fourier transform of this (shifted) spectral function, that is, \( \text{IFT}\{U(\Delta k)\} = A(z) \exp[i\varphi(z)] \), is now used to modulate the nonlinear function in the following manner:

\[ d(z) = d_{ij} \text{sign}\{\cos[\Delta k_0 z + \varphi(z)] - \cos[\pi q(z)]\}, \]

where \( \text{sin}(\pi q(z)) = A(z) \). We note that although the nonlinear modulation is binary, that is, the nonlinear coefficient can only assume two values of \( +d_{ij}, -d_{ij} \), it is possible to fully control the complex spectral response by introducing phase shifts...
(using the term $q(x)$ and by varying the duty cycle (using the right term of Eq. (2), $\cos(\pi q(x))$).

Recently, nonlinear spectral holograms were used to shape the conversion efficiency spectrum in a sum-frequency generation process [29]. Here we use it for the first time in a DFG process for either a broad and nearly flat conversion efficiency spectrum or, alternatively, to have a converter that has high efficiency in two different spectral regions.

Another possibility for spectral shaping the nonlinear conversion is based on quasi-periodic modulation of the nonlinear coefficient [31], which enables us to simultaneously phase match several processes. This method is mainly suitable for obtaining high conversion efficiency at specific frequency, in contrast to spectral holograms that can be used to shape the entire conversion efficiency spectrum. In order to design the quasi-periodic structure, we applied De Bruijn’s [37] dual grid method (DGM). For simultaneously phase matching two (or three) different down-conversion processes, we first generated a quasi-periodic sequence of two (three) building blocks labeled A and B, (A, B, and C). By associating a different suitable physical length to each one of these building blocks, we obtain a 1D quasi-crystal that already supports desired wave vectors. A nonlinear quasi-periodic crystal is then obtained by modulating the nonlinear coefficient in the A and B (or A, B and C) blocks to be negative and positive, respectively.

### 3. Design of the Nonlinear Crystal

The crystal is designed for a DFG process with a NIR signal comb having a wavelength in the range 1032–1045 nm, and a tunable pump that was operated here in the range 841–845 nm, producing various wavelengths in the region 4256–4678 nm. In this range, several interesting molecules such as N$_2$O and CO$_2$ have strong absorption lines. As shown in Table 1, the crystal includes six different channels, each designed with a different spectral response. The channels are 1 mm wide and 20 mm long, and have a minimum domain width of 5 μm. For all the interactions considered here, we assumed that the three interacting waves are polarized along the crystal’s $z$ axis, and therefore, the nonlinear coefficient we employ is $d_{ij} = d_{33}$.

Let us now describe how the two design tools described above—nonlinear spectral holograms and quasi-periodic nonlinear crystals—can be used for shaping the spectral efficiency curve in a down-conversion process. We will demonstrate several efficiency curves—a broad and relatively flat curve, a broad dual-band curve, a curve that is efficient at two spectral regions, and a curve that is efficient at three different wavelengths. Nonlinear converters with these crystals can be used, for example, to simultaneously measure absorption lines of two different isotopes, such as $^{14}$N$_2$16O and $^{14}$N$^{15}$N16O or $^{13}$C16O$_2$ and $^{12}$C16O$_2$ lines.

A broad and relatively flat function can be provided through a filter whose amplitude response is given by

$$U_B(\tilde{\Delta}k) = \frac{1}{1 + (\frac{\tilde{\Delta}k}{\Delta_k})^a},$$

where here and in all the following designs, $\tilde{\Delta}k = \Delta k - \Delta k_0$ is the shifted phase mismatch, with respect to the phase mismatch for the central point. In channel 5 of the designed crystal, we chose a third-order filter, $n = 3$, which provides a trade-off between the minimum ripple in the band-pass region and the requirements for poling resolution of the nonlinear crystal. We designed a nonlinear spectral hologram [28,29], using the method described above (Eq. 2), with a central wavenumber of $\Delta k_B = 0.274$ rad/μm and a bandwidth of $\Delta k_B = 2.64 \times 10^{-4}$ rad/μm. For a pump wavelength of 845 nm, this crystal provides a fairly flat conversion of ~150 nm around 4.5 μm and a 3 dB bandwidth of ~250 nm. For comparison, a traditional PP crystal with the same length is approximately one order of magnitude narrower [10].

In case only two specific molecular absorption bands are of interest, we can design a nonlinear converter that is efficient at the two corresponding wavelengths. This is perhaps less flexible than the broadband converter, but it can provide higher efficiency at the chosen spectral region and avoid spectroscopic noise from unabsorbed wavelengths. We have tested several different options for achieving this goal. One realization that we utilized in channel 2 of the designed crystal relies on the Hermite–Gauss function. Previously, nonlinear spectral holograms based on the second-order Hermite–Gauss function were designed and realized [29]. Here, instead, we consider the third-order Hermite–Gauss function. The normalized amplitude of this function consists of four peaks—two relatively strong side peaks, having a peak value of 1, and two central and weaker peaks. By raising this function to the power of 20, the two side peaks maintain their maximal normalized value of 1 while becoming narrower, whereas the two central peaks become much weaker. Therefore, we obtain a frequency converter with two isolated peaks. Specifically, we start with the HG3 function:

$$U_{HG3}(\delta) = [8\delta^3 - 12\delta] \exp\left(-\frac{\delta^2}{2}\right),$$

where the central wavenumber was taken as $\Delta k_0 = 0.2478$ rad/μm, the Gaussian width is $\Delta k_r = 2.14 \times 10^{-4}$ rad/μm, and the normalized detuning is $\delta = 2\Delta k/\Delta k_r$. The HG3 function was raised to the power of 20, that is,$$

$$U(\delta) = [U_{HG3}(\delta)]^{20},$$

and this function was then used for the design of the spectral hologram. The spectral hologram is efficient at two different idler wavelengths, which are nearly 250 nm apart, around 4.4 and 4.65 μm.

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**Table 1. Schematic Representation of the Poling Design and Target Molecule for Each Channel of Nonlinear Crystal**

<table>
<thead>
<tr>
<th>Channel #</th>
<th>Molecule</th>
<th>Poling Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N$_2$O</td>
<td>Quasi-periodic design</td>
</tr>
<tr>
<td>2</td>
<td>N$_2$O</td>
<td>Narrow spectral hologram</td>
</tr>
<tr>
<td>3</td>
<td>N$_2$O</td>
<td>3-Wavelengths quasi-periodic design</td>
</tr>
<tr>
<td>4</td>
<td>CO$_2$</td>
<td>Quasi-periodic design</td>
</tr>
<tr>
<td>5</td>
<td>N$_2$O + CO$_2$</td>
<td>Broadband spectral hologram</td>
</tr>
<tr>
<td>6</td>
<td>CO$_2$</td>
<td>Wider spectral hologram</td>
</tr>
</tbody>
</table>

---


In order to further illustrate the flexibility of nonlinear spectral holography, we designed, in channel 6, a converter that supports two broad and separated spectral regions. This was done by convolving the two functions that we introduced earlier—the 20th power of the Hermite-Gaussian filter with a width of $\Delta k = 3.94 \cdot 10^{-5} \text{rad/\mu m}$ produces two distinct peaks, but then they can be broadened by convolving them with a third-order broadband filter, having a width of $\Delta k = 7.31 \cdot 10^{-5} \text{rad/\mu m}$. The function we used for designing the spectral hologram is

$$U(\tilde{\Delta} k) = [U_{\text{HG3}}(\Delta k)]^{20} \otimes U_B(\Delta k),$$

where the central wavenumber was taken as $k_0 = 0.274 \text{ rad/\mu m}$. The nonlinear converter provides two regions of relatively high efficiency in the range 4.3–4.5 \mu m.

The three nonlinear holograms are schematically shown in Fig. 1 in the real space and in the spectral domain.

In addition to these three designs that were based on spectral holography, we also studied the possibility of simultaneously phase matching either two or three different down-conversion processes by quasi-periodic modulation. The advantage of this method is that it enables us to achieve sharp peaks in the conversion efficiency spectrum at arbitrary wavelengths. In comparison to spectral holography, it is less suitable for shaping the spectral response (each peak has a sinc shape, as in the case of periodic poling) but if only very specific wavelengths are needed, then this method is adequate. In channels 1, 3, and 4 we designed three quasi-periodic converters using De Brujin’s [37] DGM. In two designs, implemented in channels 1 and 4, two processes (at two different idler wavelengths) were phase-matched. For the design, we started with the required phase-matching frequencies, for QPM the required wavelengths. We then calculated a quasi-periodic sequence, having two building blocks, labeled A and B, that will be efficient at these spatial frequencies. The modulation of the nonlinear coefficient was based on these two building blocks—all A blocks were poled to have a negative value of the nonlinear coefficient, whereas B blocks maintained a positive value for the nonlinear coefficient.

This is an alternative to the spectral hologram based on the 20th power of the HG3 function that we used in channel 2. In channel 1, the two peaks are approximately 250 nm apart, around 4.4 and 4.65 \mu m, while in channel 4 the two lines are much closer, only 44 nm apart, near 4.4 \mu m. Finally, in channel 3 we designed a converter that simultaneously phase-matches three processes, at wavelengths of 4417, 4629 and 4657 nm (for pump wavelength of 841 nm). In this case, we used three building blocks, labeled A, B, and C, where one of them had a negative nonlinear coefficient and the other two had a positive nonlinear coefficient. The required phase-matching frequencies and the size of the building blocks for the three quasi-periodic nonlinear crystals are shown in Table 2.

For all these designs we performed numerical simulations with the actual parameters of the crystal in order to confirm the expected performance. Specifically, we took into consideration the limited poling resolution (i.e., the minimum ferroelectric domain size was 5 \mu m) and the interaction length of 20 mm. The simulations were based on the split step Fourier method, assuming that all the interacting waves are plane waves. An illustration of the poling pattern and the calculated spectral efficiency curves for the three quasi-periodic designs are shown in Fig. 2.

### Table 2. Required Phase-Matching Frequencies and Size of the Building Blocks for Three Nonlinear Converters Based on Quasi-periodic Modulation

<table>
<thead>
<tr>
<th>Channel#</th>
<th>Phase-Matching Frequencies [rad/\mu m]</th>
<th>Building Blocks [\mu m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2760, 0.2723</td>
<td>11.5373, 11.3550</td>
</tr>
<tr>
<td>3</td>
<td>0.2766, 0.2761, 0.2723</td>
<td>7.6618, 7.6456, 7.5407</td>
</tr>
<tr>
<td>4</td>
<td>0.2733, 0.2726</td>
<td>11.5248, 11.4964</td>
</tr>
</tbody>
</table>

---

**4. CHARACTERIZATION OF THE NONLINEAR CRYSTAL**

Initially, the external dimensions of the MgO:CLN crystal were 25 \text{ mm} \times 9.8 \text{ mm} \times 1 \text{ mm}, but the input and output facets were cut and polished at a Brewster angle to prevent reflection losses. The final crystal length is about 23 mm, with a channel length of 20 mm.

The MgO:CLN crystal is inserted in an experimental setup for intracavity DFG, as shown in Fig. 3, similar to that described in [19]. It is based on an NIR-OFC with a repetition rate $f_r$ of about 1 GHz, generated by a mode-locked fs Ti:sapphire laser and spectrally broadened to more than one octave (500–1100 nm) by a photonic crystal fiber. The oscillator controlling $f_r$ is referenced to a Rb/GPS-disciplined 10-MHz quartz clock with a stability of $6 \times 10^{-13}$ at 1 s and an accuracy of $2 \times 10^{-12}$. Only the portion of the NIR comb spectrum above a 1-\mu m wavelength is exploited for the DFG process: it is selected by a dichroic mirror and amplified by an Yb:fiber amplifier, whose gain bandwidth limits...
the spectrum of the output radiation to the range 1032–1045 nm. Finally, it is injected into the ring cavity of a second continuous-wave (CW) Ti:sapphire laser by another dichroic mirror. There, it acts as signal beam in the nonlinear DFG process, where the pump beam is the intracavity Ti:sapphire radiation, to generate a MIR comb as idler. The MIR comb beam is then extracted from the cavity exploiting different refraction angles at the output angled facet of the nonlinear crystal. The crystal temperature is controlled by a Peltier cell.

In order to make the Ti:sapphire ring laser unidirectional and single frequency, it is optically injected by an external-cavity diode laser (ECDL). To keep the optical injection, the Ti:sapphire cavity length is stabilized against the ECDL frequency by an electronic control loop using the polarization-based Hänsch-Couillaud technique [38]; moreover, the ECDL frequency is locked to a tooth of the metrological NIR comb itself, so that the generated MIR combs are referred to a metrological absolute frequency reference, making them suitable for spectroscopic applications.

As a result, the generated MIR comb is characterized by a repetition rate equal to the \( f_r \) of the NIR comb used as signal source, and an offset frequency is given by the difference between the ECDL frequency and the frequency of the NIR comb tooth to which the ECDL is locked. Depending on the design of each channel, the pump wavelength has been tuned at one of two possible wavelengths (841, 845 nm) in order to obtain the desired MIR comb shape, whereas the signal was centered around 1040 nm, in coincidence with the most intense portion of the amplified NIR comb. For the spectroscopic characterization, the total power of the available signal beam has been set to around 1.2 W, whereas the amount of pump power circulating in the cavity reached values ranging from 1 to 15 W.

The overall power of the idler DFG radiation was measured with a liquid-N\(_2\)-cooled InSb photovoltaic detector. The maximum values achieved for each channel are reported in Table 3.

The per-tooth power of the generated MIR combs strongly depends on the conversion efficiency and the bandwidth of each channel, ranging from fractions to tens of nW. For the spectroscopic characterization of the MIR comb, the DFG radiation coming from the nonlinear crystal was dispersed by a reflective diffraction grating with 300 grooves/mm, mounted on a rotator stage and then focused on a Stirling-cooled InSb camera.

The image acquisition system was calibrated by using two light sources with known wavelengths as references: first, a quantum cascade laser emitting at 4.7 \( \mu \)m; and second, the light at 4.1 \( \mu \)m arising from a DFG process, in the nonlinear crystal itself, between the Ti:sapphire pump beam and a Nd:YAG laser (1064 nm) used as single-frequency signal beam instead of the NIR comb. Due to the broad spectral range of the converted combs, multiple MIR-camera images were analyzed and digitally combined to reconstruct the entire spectral intensity profile of the generated MIR radiation. As shown in Fig. 4, the measured MIR spectral line shapes match reasonably well the theoretical simulations (an offset is sometimes present).

Specifically, in channels 1, 2, and 4 we observe the two peaks in the idler spectrum near the designed wavelengths; channel 5 shows a broad spectrum and channel 6 shows the expected dual-band performance. It must be underlined that the described configuration gives a great advantage: the tunability of the pump source ensures the possibility of compensating for small spectral mismatch (as shown in Fig. 5). Channel 3 was designed to have three peaks, whereas in the experiment

<table>
<thead>
<tr>
<th>Channel #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power [( \mu )W]</td>
<td>1</td>
<td>8</td>
<td>4.5</td>
<td>34</td>
<td>2.5</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3. Average Output Power Measured for Each Channel of the MgO\(_{2}\)CLN Crystal

![Fig. 2. Left column: calculated spectral efficiency curves of the three quasi-periodic nonlinear converters. Dashed lines mark spatial frequencies at which high efficiency is required. Right column: illustration of nonlinear modulation patterns of three quasi-periodic gratings. Gratings are composed of either two or three building blocks, labeled A, B, and C. The white regions represent negative values of the nonlinear coefficient, whereas the black stripes represent positive values.](image1)

![Fig. 3. Schematic of experimental apparatus. BS, beam splitter; DG, diffraction grating; DM, dichroic mirror; FA, fiber amplifier; NLC, nonlinear crystal; P, gold mirror; PLL, ECDL/NIR comb locking loop; PM, plane mirror; SM, spherical mirror.](image2)
the two longer wavelength peaks could not be fully resolved, owing to the limited resolution of the spectroscopic setup. In all six cases, the measured power at longer wavelengths is smaller than predicted. In the simulations, we have accounted for the rapid increase of the idler absorption, from $\sim 0.1 \text{ cm}^{-1}$ at 4 $\mu$m to $\sim 1 \text{ cm}^{-1}$ at 5 $\mu$m [39]. Another possible contribution has been identified in the difference in group velocity at the signal (NIR comb pulses) and the idler (MIR comb pulses) wavelengths, which can lead to a reduction of the general DFG process efficiency; in addition, such an effect is also increased, up to a factor of 2, when the idler wavelength moves from 4.2 to 4.7 $\mu$m, which would be consistent with the intensity lowering observed in the longer-wavelengths region of the MIR spectra. We also observed ripples and dips in the spectral measurements of channel 5, which are caused by the spectral-dependent intensity variation of the NIR comb itself. The working temperature of the crystal was set by optimizing the Ti:sapphire power emission: the maximum has been identified for temperature values close to 15°C. As an exception, for channel 4, the round-trip losses in the cavity could be kept low for a broader range of temperature values of the nonlinear crystal; it allowed us to characterize different temperatures of the nonlinear crystal in the range 15–25°C. From these measurements, we concluded that the spectral changes are negligible within this temperature range, as expected from the thermal dispersion calculations [40]. The spectral line shape of the signal radiation (amplified NIR comb) could not be exactly determined: as a consequence, it was not possible to evaluate the signal power fraction selected by the phase matching effect, thus contributing to the DFG process, and thus to estimate the absolute conversion efficiency of the different channels.

5. CAVITY-ENHANCED SPECTROSCOPIC CHARACTERIZATION

For channel 4, we performed a deeper characterization. At first, we detected the MIR idler signal using a 1-GHz-bandwidth detector. As shown in Fig. 6, the FFT amplitude of the idler radiation over the whole bandwidth of the detector contains only one strong peak at 1.007 GHz, which corresponds to the repetition rate of the NIR-visible frequency comb. Such a peak, originated by the beatnote between adjacent modes of the MIR radiation, thus represents a strong clue of the “comb nature” of the converted light.

Moreover, in the inset of Fig. 6 the beatnote is zoomed over a span of 50 Hz: the beatnote is extremely narrow, limited only by the resolution bandwidth (RBW = 313.18 MHz) of the

**Fig. 4.** Bottom: experimental spectral line shape of the MIR combs (red line), resulting from the DFG process for each crystal channels, compared to the theoretical calculations (blue dotted line): (1) quasi-periodic dual-frequency converter; (2) narrow spectral hologram dual-frequency converter; (3) quasi-periodic triple-frequency converter; (4) quasi-periodic dual-frequency converter; (5) spectral hologram broadband converter; and (6) spectral hologram dual-band converter. Top: line intensities in the range of interest for the target molecular species: (a) $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$; and (b) $^{14}\text{N}_2^{16}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}$.

**Fig. 5.** Experimental spectral line shape of the MIR comb, resulting from the DFG process in crystal channel 4, with pump wavelength set at 841 nm (dotted line) and 845 nm (solid line).

**Fig. 6.** FFT amplitude of the idler radiation generated in channel 4. In the inset, the strong beatnote peak at 1.007 GHz is zoomed in a 50 Hz span; weaker sidebands are due to the locking system of the NIR comb repetition rate.
etition measured around 200 kHz. In a similar way, the time distance the x axis is related to the frequency detuning of the cavity, due to its length scan. Peaks are not equally time-spaced due to the sinusoidal shape of the cavity length modulation.

spectrum analyzer, suggesting that the frequency conversion process maintained the phase-relationship between the comb modes. Most important, we coupled the MIR comb into a high-finesse Fabry–Perot (FP) cavity, having a free spectral range (FSR) of about 166 MHz and finesse of 5000, so that the Vernier ratio between the cavity FSR and the repetition rate of the comb is 1/6. The cavity could also be filled with a gas, and its length can be modified with a piezoelectric (PZT) actuator, making it suitable for direct Vernier spectroscopy [41] of the gas under study. In fact, when the Vernier ratio is exactly 1/6, all MIR comb teeth are simultaneously resonant with the FP cavity and are transmitted. By slightly changing the Vernier ratio, we obtain a condition where only one DFG comb tooth is resonant and transmitted by the cavity. In this condition, scanning the cavity length by means of the PZT, many DFG comb teeth are transmitted once each by the cavity, yielding a high-resolution spectrum of the incoming MIR comb. This also enhances the absorption length and, subsequently, the sensitivity, by a factor of Finesse/π. In our case, 500 kHz detuning enables us to singularly disperse the comb teeth on a 1-FSR scan of the cavity. In Fig. 7, we report preliminary results, with an empty cavity, obtained with a cavity length scan much smaller than a FSR: it shows only a zoomed portion of the transmission peaks out of the cavity for one of the two narrow bands of the MIR idler generated in channel 4 (designed for detection of N2O molecules). After calibration, the x axis time scale could be related to the frequency detuning of the cavity. For our cavity, the width of a single peak was measured around 200 kHz. In a similar way, the time distance between two nearby peaks could be related to the comb repetition rate = 1.007 GHz (see Ref. [19]). The peak intensity fluctuations likely originated from the power distribution of the amplified NIR comb acting as signal source, which is not constant among neighbor peaks. Although this measurement is a preliminary result with low signal level (tens of μV), mainly due to technical reasons, we underline the good signal dynamic range of the resolved MIR comb spectrum, which looks encouraging for direct absorption spectroscopy.

6. CONCLUSIONS
In conclusion, we have experimentally demonstrated a technique that can be used to down-convert a broad input spectrum into a desired spectral shape in a nonlinear DFG process. Two design schemes were employed—nonlinear spectral holography and quasi-periodic modulation. We have realized different spectral shapes, including a broadband and flat shape, dual-broadband shape, and narrowband shapes with multiple peaks at chosen frequencies. The spectral analyses show a reasonable correlation between the experiments and the theoretical simulations.

More important, the tunability of our source ensures the possibility of compensating for the spectral mismatch, allowing the addressing of any specific molecular absorption within the working range. The characterization also shows that, as expected, both frequency conversion efficiency and bandwidth are essentially independent of the nonlinear crystal temperature.

This method can thus be applied to molecular spectroscopy, providing the spectral shaping of a MIR comb in a DFG process, and it also provides the possibility to finely tune the interacting pump and signal beams according to the desired spectral features. Although the available power is low, it can be enhanced by adopting strategies such as a pulsed pump source instead of a CW pump, or waveguides. Furthermore, the same concept can be used to up-convert the comb into the ultraviolet spectral region.

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REFERENCES