Difference-frequency generation as a precise tool for high-resolution spectroscopy

S. Borri, P. Cancio, G. Giusfredi, D. Mazzotti, and P. De Natale*

Istituto Nazionale di Ottica Applicata (INOA),
Largo Fermi 6, 50125 Firenze, Italy

ABSTRACT

We illustrate some of the applications of coherent infrared spectrometers based on frequency conversion by difference frequency generation. We show that very high sensitivity molecular detection can be performed as well as sub-Doppler saturated spectroscopy. Moreover, we describe a setup that allows absolute frequency measurements in the infrared with metrological grade uncertainties.

Keywords: frequency conversion, mid-infrared, molecular spectroscopy, saturation spectroscopy, frequency metrology

1. INTRODUCTION

Second order frequency conversion processes represent a convenient way to generate tunable coherent radiation whenever appropriate laser sources are not available. However, for many years birefringent phase-matching has represented the only efficient way to generate radiation by nonlinear processes. An important step towards more powerful sources based on frequency synthesis has been the introduction of the concept of quasi-phase-matching. This innovation in the field of nonlinear optics has been accompanied by another crucial step, i.e. the development of powerful compact and low-noise diode-pumped laser sources emitting in the near-infrared region. Thanks to these two concurrent factors, both cw parametric down-conversion and frequency doubling are gaining importance as compact and tunable sources for high resolution spectroscopy in the visible and near-infrared. In terms of spectral coverage, a baricentric role has been played by laser sources emitting near-infrared radiation (roughly in the 780-1550 nm spectral range). Indeed, even infrared radiation at wavelengths up to 4.6 μm has been generated by use of difference frequency generation (DFG) and parametric down-conversion using near-infrared laser sources.

Only very recently, high-resolution sub-Doppler spectra have been recorded using these two nonlinear second-order processes. From the point of view of frequency control, difference frequency based sources are intrinsically more reliable than parametric amplifiers and oscillators. This is obviously due to the deterministic link between the difference frequency generated radiation and the two input laser frequencies. This deterministic link can be further exploited for frequency metrology in the infrared region. Indeed, the combination of DFG and femtosecond-based frequency comb generators is a natural way to extend the revolutionary metrological capabilities of this latter device to the infrared. This depends on the extremely wide spectral coverage of comb generators, that can often go from the visible-green to wavelengths longer than 1 μm, and on the use of pumping sources for DFG that emit within this spectral interval.

Another important issue that will be discussed in the next sections is the high-sensitivity detection that can be achieved using a DFG spectrometer. The key factors for achieving it are mainly two: the presence of the strongest fundamental ro-vibrational molecular bands in the spectral region covered by DFG and the possibility to use both low-noise and powerful cw diode-pumped lasers as "pump" and "signal" sources for DFG. These peculiar features have recently allowed not only to perform a test of fundamental principles of quantum mechanics with unprecedented sensitivity, but also to record Lamb-dip spectra in a dynamic range of linewidths as wide as more than 4 orders of magnitude. We will also discuss the intimate link between the high sensitivity and high resolution capabilities and the possibility to make accurate absolute frequency measurements.

* E-mail: denatale@inoa.it
2. EXPERIMENTAL SETUP

The DFG setup is shown in Fig. 1. The "idler" infrared radiation around 4.25 μm is generated by mixing "pump" radiation at 852 nm and "signal" radiation at 1064 nm via a $\chi^{(2)}$ nonlinear process. The pump radiation is provided by a master/slave diode laser system, with the master laser (50 mW output power), operating in the external-cavity Littrow configuration, which optically injects the more powerful slave laser (150 mW output power) at the same wavelength. The output port of an optical isolator is used to couple the master beam into the slave laser, playing with the relative linear polarizations.

Figure 1: Schematic of experimental setup. Legend: DL=diode laser, AP=anamorphic prisms, $\lambda/2$=half-wave plate, $\lambda/4$=quarter-wave plate, OI=optical isolator, CL=cylindrical lens, EOM=electro-optic modulator, DM=dichroic mirror, PPLN=periodically poled lithium niobate, BS=beam-splitter, PG=pressure gauge, RF=radio frequency, HV=high-voltage, PZT=piezo-electric transducer.
The main improvement of our present setup, with respect to that described in refs. 15-17, regards the optical power available for "signal" radiation. Previously, we have used a diode-pumped, monolithic Nd:YAG laser with a maximum output power of 800 mW at a wavelength of 1064 nm. Now, we boost this power up to 5 W by using a diode-pumped Yb-doped fiber amplifier seeded by a fraction of the Nd:YAG power.

Some optics provide the mode-matching of the slave diode laser beam to the fiber amplifier output beam: a pair of anamorphic prisms, a cylindrical lens, a telescope. A dichroic mirror overlaps the two s-polarized beams and a 100-mm-focal-length lens focuses the dichromatic pump/signal beam at normal incidence onto the nonlinear crystal. It is a z-cut, 40-mm-long periodically poled lithium niobate (PPLN) crystal, with a poling period of 23.0 μm and is thermally stabilized in a copper oven, within 1 mK, by use of a Peltier element, at the phase-matching temperature of 37 °C. Anti-reflection coatings on the input and output facets avoid Fresnel reflection losses. A 50-mm-focal-length CaF₂ lens provides a near-collimated idler beam after the nonlinear crystal. A half-wave plate provides the p-polarized beam that is transmitted through a Ge beamsplitter with one AR-coated face, placed at nearly Brewster angle (about 74°). This also acts as an optical filter for the pump and signal beams, mostly absorbing and partially reflecting them to the input fiber of a 7-digits wavemeter and to a confocal Fabry-Perot cavity for the pump radiation, with a free spectral range (FSR) of 75 MHz. The infrared beam passes through a quarter-wave plate (making the polarization circular) and is coupled to a FP cavity by a CaF₂ mode-matching lens with a focal length of 100 mm. The FP cavity has a confocal geometry with a mirror spacing of 115 mm, corresponding to a longitudinal FSR of 1.3 GHz. The two identical plane-concave CaF₂ dielectric mirrors are AR-coated on the plane face and HR-coated on the concave face for 4.25 μm. The measured finesse is F=550, corresponding to a full width at half maximum (FWHM) of the resonance peak Δν=2.4 MHz and to an effective absorption path length L_{eff}=40 m.

Frequency locking of the infrared radiation to the FP cavity is achieved by using a Pound-Drever-Hall (PDH) scheme. This technique, widely used in the visible and near-infrared regions, is difficult to implement in the infrared at such low power levels, also due to the lack of adequate detectors and photonic devices. In our setup, phase-modulation of the generated infrared beam is obtained by transferring, through the nonlinear process, the phase-modulation imposed to the signal beam at 1064 nm by an electro-optical modulator (EOM). Each of the two first-order sidebands at 1064 nm has about 2% of the power contained in the carrier. The frequency bandwidth of the liquid-N₂-cooled InSb photodiode, used to detect infrared radiation, is of 4 MHz and the detector diameter is 0.6 mm.

According to the detector frequency response, the EOM is driven at 3.6 MHz. The infrared radiation that is not coupled into the cavity (i.e. the part that is reflected) passes again through the quarter-wave plate (thus obtaining an s-polarized beam) to be then reflected to the detector by the Ge beamsplitter. A custom-built transimpedance preamplifier, carefully matched to the detector impedance, converts the photocurrent to a voltage signal. The error signal provided by the demodulating mixer is used to close the servo-loop onto the master diode laser. The "slow" part is processed by a proportional-integrating-derivative (PID) amplifier and is then fed to the piezo-electric transducer (PZT) that moves the feedback grating of the master diode laser. Instead, the "fast" part is sent directly to the master diode current driver.

For recording the transmission signal we scanned the cavity length (and therefore the frequency) by feeding a slow voltage ramp (16 s acquisition time) to three PZTs mounted onto one of the cavity mirrors.

As explained above, we decided to insert, in our setup, a fiber amplifier to boost the signal radiation to a power of 5 W. This was done mainly for two reasons. Since the infrared power generated by frequency difference in the PPLN crystal depends linearly on each of the pump and signal powers, we increase the idler power in a factor of 6-7. If, as measured in 15, the noise of the idler beam would stay close to the quantum limit at the frequencies of interest, this would immediately increase the overall spectrometer sensitivity as the square root of the power. The second advantage is the capability to record Lamb-dip spectra of transitions with a saturation intensity, I_s, higher than those previously accessible. This feature, as we will explain, is of particular interest for future applications of this DFG spectrometer to frequency metrology.
3. MEASUREMENTS

To compare the performance of the new setup with the previous one, we took recordings of sub-Doppler spectra for the same lines investigated in 17. As an example, Fig. 2 shows the direct-absorption spectrum of the (000-0001) R(78) line of $^{12}\text{C}^{16}\text{O}_2$ at 2391.099 cm$^{-1}$ as compared to a similar recording obtained with the setup without the fiber amplifier.

A Lamb dip can be seen in the center of both Doppler profiles, with a contrast that, in Fig. 2b, is as high as 13 %, close to the theoretical maximum of 13.3 %. Due to the higher optical intensity, it is better than the contrast measured in Fig. 2a for the R(76) line, with the previous setup. This comparison gives also an indirect confirmation that amplitude and frequency noise added by the fiber amplifier do not significantly affect the spectrometer sensitivity, whereas the higher available power extends Lamb-dip spectroscopy to bands and molecules having a higher $I_\text{f}$. For the recording in Fig. 2b, the beam waist at the cavity center, calculated assuming a purely Gaussian TEM$_{00}$ mode, is $w_0=280$ µm and the average
infrared intensity over the beam path inside the cavity is $I = 9 \text{ mW/mm}^2$, assuming an infrared power of 15 $\mu$W coupled to the cavity and a build-up factor of 200. For comparison, the beam waist at the cavity center for the spectrum in Fig. 2a was the same, but the average infrared beam intensity was $I = 5 \text{ mW/mm}^2$. The molecular line saturation intensity, calculated with a transition dipole moment $\mu = 7.5 \times 10^{-31} \text{ Cm}$, is $I_s = 11.2 \text{ mW/mm}^2$. The measured contrast of the Lamb dip in Fig. 2b is in good agreement with the value (12.5%) calculated from the ratio $I/I_s = 0.8$.

In Fig. 1 a frequency-comb generator has been included because we intend to phase-lock each laser, used as pump or signal for DFG, to a tooth of the frequency comb. In this way, the absolute frequency of the idler radiation is directly obtained by difference of the absolute frequencies of pump and signal. Therefore, in principle, one could imagine to perform absolute frequency measurements in the infrared region swept by the idler beam with an accuracy limited mainly by the comb generator and the phase-lock electronics. Of course, when measuring transition frequencies, the achievable accuracy in the center frequency determination depends directly on the signal/noise ratio of the recording and inversely on the transition linewidth.

Our cavity-enhanced spectroscopic setup can thus allow to maintain a sufficiently high signal/noise ratio even for relatively weaker transitions and to have access to sub-Doppler linewidths in a wide range of transition dipole moments. In our recordings, the main contribution to the linewidth (about 1.8 MHz HWHM) seems to be given by the infrared source, since time of flight broadening and pressure broadening only contribute, respectively, 190 and 310 kHz whereas the natural lifetime contributes 110 Hz. This suggests that the very significant reduction of the idler linewidth, expected by phase-locking pump and signal beams to the same frequency-comb, could increase the achievable accuracy of the line center determinations. If one assumes that the limiting accuracy for such frequency measurements would be proportional to the ratio between the signal/noise of the recording and the transition linewidth, one could also imagine to measure, once for ever, a wide number of ro-vibrational molecular transitions that could then be used as a "comb" of absolute frequency standards in the infrared for any other measurement in that range. The usefulness of such an approach obviously depends on the spectral coverage of saturable transitions and on their spectral density.

In Fig. 3 we report a plot of available ro-vibrational lines of a few simple molecules in the spectral range 3.1-5 $\mu$m (CO, N$_2$O, CO$_2$, CH$_4$, OCS), as taken from the HITRAN database.

In the upper part of Fig. 3 we plotted only lines with a strength $S > 10^{-22}$ cm (HITRAN units) whereas in the lower graph we put on the ordinates the squared dipole moment of each line. For clarity, we note that the dipole moment for lines belonging to the same ro-vibrational band does not appreciably change with the rotational quantum number and the different intensities are due to different energy level population and thus to different Boltzmann weights. In the lower graph, all lines above the dotted horizontal line can be saturated with a Lamb-dip contrast greater than the noise, assuming to use all the available power from the fiber amplifier (5 W) and to change properly the wavelength of the diode laser system.

**4. CONCLUSIONS**

We have shown that DFG-based spectrometers, at present, possess outstanding sensitivity for molecular detection together with a sub-Doppler resolution. Proper experimental setups, including phase-lock electronics to teeth of comb generators will probably give an insight into the ultimate limits of achievable resolution for this class of devices. This could eventually take to unprecedented accuracy for absolute frequency measurements in a wide infrared spectral range.

The most direct competitors of DFG spectrometers in the infrared region are quantum cascade lasers (QCLs). Such semiconductors lasers, first introduced by Capasso and co-workers, can be tailored to emit radiation in the desired wavelength interval. Although they have already shown to be powerful tools for high resolution spectroscopy in 4.5-10 $\mu$m range, their construction seems to be more difficult at emission wavelengths shorter than about 4 $\mu$m. The three main advantages of DFG spectrometers as compared to QCLs are the room temperature operation, the extremely narrow achievable linewidth and their direct link to metrological comb generators through the near-infrared pumping laser sources. Regarding this latter feature, DFG spectrometers can pave the way to a metrological use of QCLs. Indeed, as soon as an atlas of absolute frequencies of infrared ro-vibrational molecular bands measured with sub-Doppler resolution is compiled, QCLs will be directly referred to these peaks.
It will be interesting to see how simultaneous progress in cw laser power amplifiers and in the construction of more efficient and damage resistant nonlinear materials will be able to preserve a competitive advantage to DFG-based devices. A role could be played by multidimensional domain-ingeneered materials for quasi phase matched interactions, as well as by the development of semiconductor based nonlinear frequency converters. This latter technology represents the most important chance for frequency mixers towards necessary miniaturization and integration.

Figure 3: Infrared spectra of five common molecular gases at 296 K temperature.
ACKNOWLEDGEMENTS

The authors wish to thank the Gruppo Nazionale per la Vulcanologia and Istituto Nazionale di Geofisica e Vulcanologia (GNV-INGV) for supporting this work (project O2 of Programma Quadro Triennale 2000-2002).

REFERENCES