Difference-frequency radiation around $4.3 \, \mu m$ for high sensitivity and sub-Doppler spectroscopy of $CO_2$

D. Mazzotti, G. Giusfredi, and P. De Natale  
*Istituto Nazionale di Ottica (INO), Largo Fermi, 6 I-50125 Firenze, Italy*  
mazzotti@generale.lens.unifi.it, giusfredi@fox.ino.it, denatale@fox.ino.it

J. Mitchell and L. Hollberg  
*National Institute for Standards and Technology (NIST), Boulder, Colorado 80303, USA*  
mitchj@ucsu.colorado.edu, hollberg@boulder.nist.gov

**Abstract:** We report on difference-frequency-generation (DFG) in periodically-poled lithium niobate (PPLN) around $4.3 \, \mu m$, using as pumping sources an injection-locked diode laser, tunable around 852 nm, and a diode-pumped Nd-YAG laser at 1064 nm. Peculiar features of the infrared generated radiation are a linewidth of about 100 kHz, amplitude fluctuations close to the quantum limit and a high conversion efficiency. Details of such a source configuration are given and potential applications to high sensitivity spectroscopy are discussed. With this set-up we were able to observe sub-Doppler lineshapes in the fundamental vibro-rotational band of $CO_2$. A characterization of these derivative profiles is reported.

**OCIS codes:** (190.2620) Frequency conversion; (300.6460) Spectroscopy, saturation; (300.6340) Spectroscopy, infrared; (300.6390) Spectroscopy, molecular.

**Introduction**

Periodically poled non-linear crystals and diode lasers represent a breakthrough in convenience for spectroscopic applications throughout the spectrum and particularly in the infrared. Indeed, they allow full spectral coverage of the mid-infrared region at wavelengths up to about 5 $\mu m$, encompassing the fundamental vibro-rotational bands of many molecules. Although Doppler-limited spectroscopy has already been demonstrated with difference-frequency-generation (DFG) in such crystals [1-6], present devices have not yet reached the performance of semiconductor or solid-state lasers for the highest resolution in high sensitivity spectroscopic applications. Desired improvements are narrower linewidth, quantum noise limited operation and a simultaneous increase of the IR output power.

**Source characterization**

We have developed a new experimental set-up that allows to produce an infrared beam (at $4.3 \, \mu m$) with a linewidth of about one hundred kilohertz, while preserving broad IR tunability, reducing the amplitude noise down to near the quantum limit and generating IR powers many times higher than the saturation limit of existing detectors. In this system the pump and signal sources are, respectively, a non-planar ring Nd-YAG CW laser at 1064 nm (InnoLight, maximum output power 800 mW) and a diode laser (slave laser, SDL 5422, maximum output power 150 mW). The latter is injection-locked by a low power diode (master laser, SDL 5401) mounted in an external-cavity Littrow-configuration (maximum power out of the cavity 23 mW). [7]
This master-slave configuration allows to use the broad tunability of external cavity diode lasers, as well as its narrow linewidth, while being able to take advantage of the full output power of the slave laser. Fig. 1 shows the measured fluctuations in the center frequency of the injected laser as compared to the same slave laser without any injection. As anticipated, for all time scales, there is a significant reduction in the injected laser’s frequency fluctuations.

![Fluctuations in the center frequency of the high-power diode laser under conditions of injection lock and not injection locked. Measurements were taken by using a side of a Fabry-Perot fringe as frequency discriminator.](image)

Most importantly, when the slave was injection locked, we measured the spectral distribution of the amplitude noise on the 4.3 μm beam and observed a noise reduction of up to 30 dB for Fourier frequencies between 1 and 4 kHz. We also investigated the composition of amplitude noise affecting the IR detector. Fig. 2 shows the spectral density of the noise from the InSb liquid-N₂ cooled detector.

The three traces shown were taken with the detector looking at: a mirror in front of it (which means the detector is looking at a background close to 77 K); a 25° C background; the same background except with the crystal oven heated at the operating temperature of 284 °C and occupying part of the field of view. From such measurements, we determined that about 60 % of the noise floor above quantum noise is due to background fluctuations and the remaining 40 % depends on internal detector noise. The former contribution can be reduced close to zero with use of appropriate optical cold filtering on the detector. The higher temperature trace corresponds to the case of the detector viewing the hot oven, which controls the periodically poled LiNbO₃ (17.5x10x0.5 mm) to the appropriate temperature to quasi-phase-match incoming radiation for 4.3 μm generation.
Fig. 2. Detector amplitude noise dependence on background temperature. Intrinsic detector noise coincides with the trace recorded at 77 K.

**CO₂ detection sensitivity**

After careful calibration of the detector responsivity with a reference black-body, we measured a maximum efficiency to the IR at 4.3 µm of 0.012 % W⁻¹ cm⁻¹, corresponding to a maximum IR power of 12 µW. This result enables to perform sub-Doppler spectroscopy on CO₂ transitions (saturation intensity $I_s$=1 mW/mm², for the strongest lines), taking advantage of the narrow IR linewidth. From amplitude noise measurements on the 4.3 µm beam and considering a signal of 2 µW (which saturates our InSb detector) we estimate a sensitivity of 0.01 ppb m Hz⁻¹/² (air-broadened lines) for this spectrometer. In table 1 we compare this value with those obtained with semiconductor lasers operating on the weaker CO₂ overtone bands near 1.6 and 2.0 µm wavelengths.

<table>
<thead>
<tr>
<th>CO₂ IR transition</th>
<th>2ν₁+2ν₂+ν₃ P(8)</th>
<th>ν₁+2ν₂+ν₃ R(24)</th>
<th>ν₃ R(16)</th>
</tr>
</thead>
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<tr>
<td>λ (µm)</td>
<td>1.577</td>
<td>2.002</td>
<td>4.235</td>
</tr>
<tr>
<td>S (cm/molecule)</td>
<td>1.2⋅10⁻²³</td>
<td>1.0⋅10⁻²¹</td>
<td>3.5⋅10⁻¹⁸</td>
</tr>
<tr>
<td>Sensitivity (Hz⁻¹/²)</td>
<td>7⋅10⁻⁸</td>
<td>7⋅10⁻⁷</td>
<td>4⋅10⁻⁷</td>
</tr>
<tr>
<td>Sensitivity (ppb m Hz⁻¹/²)</td>
<td>1000</td>
<td>100</td>
<td>0.01</td>
</tr>
<tr>
<td>Reference</td>
<td>[6]</td>
<td>[6]</td>
<td>This work and [8]</td>
</tr>
</tbody>
</table>

**Sub-Doppler spectroscopy**

Very recently, we were able to record saturated-absorption Lamb-dips, with our DFG source [9]. Fig. 3 shows a recording of the ν₃ R(14) CO₂ transition. We show the Doppler profile (trace a), and the corresponding Lamb-dip (trace b). The saturation Lamb-dip was not visible in the Doppler trace, recorded by
modulating the Nd-YAG amplitude using a chopper, but wavelength modulation of the Nd-YAG laser was required, giving a first derivative lineshape.

From data in Tab.1 it comes out that, if the very strong absorption of the ν3 R(14) and neighbouring lines lowers the saturation intensity, it also severely limits propagation in atmospheric air of peak-resonant IR radiation. Indeed, 1/e absorption is experienced in a distance as short as 5.8 cm by a beam propagating in air, considering a line strength of $3.5 \cdot 10^{-18}$ cm/molecule and a 0.3% (33 Pa) CO2 concentration in air. Therefore, atmospheric absorption is of main concern to perform spectroscopic experiments using radiation resonant with such lines. To overcome this problem, we enclosed our saturated-absorption set-up in a box and purged it with a slow flux of pure N2, thus reducing to about 30% the total absorption, mainly due to the 2 cm air-pathlength that separated the PPLN crystal from the box entrance.

To observe the saturated absorption lineshape, a proper combination of cell length, beam waist, modulation depth and gas pressure had to be chosen. Considering the very long natural lifetimes of the upper levels of these IR transitions, corresponding to a few tens of Hz, the observed linewidth is mainly determined by pressure and transit-time/wavefront-curvature broadening, IR linewidth contributing only about 100 kHz. We chose, for our set-up, a cell length of 0.5 mm, a beam-waist $w_0$ of 35 µm and a CO2 pressure of 10 Pa, therefore pressure broadening only contributed about 160 kHz (assuming a self-broadening coefficient of 15.7 kHz/Pa [10]) to the halfwidth at half maximum (HWHM), while the transit-time/wavefront-curvature broadening amounted to about 1.3 MHz. The expression for this contribution is [11]:

$$\gamma = \frac{\sqrt{2 \ln 2}}{2\pi} \frac{v}{w(z)} \sqrt{1 + \left[ \frac{\pi w(z) z}{\sqrt{R(z)}} \right]^2} = \frac{\sqrt{2 \ln 2}}{2\pi} \sqrt{\frac{k_B T}{m}} \frac{1}{w_0}$$  (1)
where $w(z)$ and $R(z)$ are, respectively, waist and radius of curvature at position $z$, $V$ is the radial mean velocity (rms) of the molecules, $m$ is the molecular mass and $T$ the absolute temperature. It is notable that the dependence on the position $z$, for a Gaussian beam, completely disappears.

The cell length was chosen equal to the Rayleigh range of the 4.3 $\mu$m beam, to have an homogeneous field along the cell. As a consequence, the cell was filled with a gas pressure around 10 Pa, to maximize the S/N ratio. Fig. 4 shows how the Lamb-dip signal varies, changing the CO$_2$ pressure in the cell.

![Plot](image.png)

**Fig. 4.** Dependence of the Lamb-dip amplitude as a function of the gas pressure. Saturated lineshapes were recorded using wavelength modulation technique. Signal was demodulated at the third harmonic frequency (obtaining a third derivative lineshape).

The waist size determines, through the transit-time/wavefront-curvature broadening, the observed linewidth $\gamma$ and, hence, the saturation intensity $I_S$, that quadratically depends on $\gamma$:

$$I_S = \frac{\varepsilon_0 c}{2} \left( \frac{\hbar \gamma}{\mu} \right)^2$$ (2)

Obviously, also the beam intensity $I$ increases quadratically with the beam waist so that the ratio $I/I_S$, determining the contrast, i.e. the ratio between Lamb-dip depth and the Gaussian profile amplitude, is about independent on the waist size, until the linewidth is due to transit-time broadening.

**Summary**

This novel diode-laser based DFG spectrometer, resonant with the strong $\nu_3$ absorption band, proved to be a useful tool for high sensitivity measurements of CO$_2$ concentrations. Sub-Doppler resolution was also demonstrated with a simple saturation set-up. Considering the broad tunability of this spectrometer
and the strong absorption bands of many other molecules, in this wavelength region, it may find application in atmospheric chemistry (global warming etc), biological systems, process monitoring and fundamental physics experiments.

**Acknowledgements**

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**References**

7. Mention of specific products is for technical clarity only and is not a recommendation.