The combination of tunable and high spectral purity diode-pumped and diode lasers with periodically-poled nonlinear crystals is producing a revolution in near and mid-infrared spectroscopy of atoms and molecules. We shall report on frequency doubling from the infrared to the visible as well as on the difference frequency generation of infrared radiation. In spite of the low power generally available from frequency conversion in single pass configurations, narrow sub-Doppler recordings, suitable for frequency metrology, are observed. This opens new possibilities for precision spectroscopy of Helium and creates new links between atomic and molecular reference transitions. The newly available shot noise-limited radiation resonant with CO2 fundamental band provides higher sensitivity for the test of the symmetrization postulate.

1 Introduction

Development of new materials for efficient frequency conversion of laser sources is opening new perspectives in spectroscopy. These new sources are covering spectral regions previously out of reach for tunable and high spectral purity lasers. This allows to excite atomic and molecular transitions that can be particularly convenient for testing theories, creating new frequency standards and performing absolute frequency measurements, with outstanding sensitivity and accuracy. Nonlinear frequency conversion techniques extend the intrinsic tunability of semiconductor lasers or diode-pumped solid state sources, that are still unable to conveniently cover the visible-UV and the infrared region at wavelengths larger than about 2 μm. Diode-pumped nonlinear devices have also the advantage to transfer the generally low noise of these pump sources to the converted radiation. We have built two spectrometers that combine state-of-the-art photonic technologies and are based on periodically-poled crystals, one generating green radiation around 541 nm and the other infrared radiation at 4.3 μm.
2 Green generation and $I_2$ spectroscopy

An important motivation to generate tunable radiation around 541 nm is the creation of a stable frequency reference to lock diode lasers resonant with the $2^3S \to 2^3P$ transition of Helium at 1083 nm (2 x 541 nm). Recently, the most accurate measurement of the $2^3P_0 - 2^3P_1$ splitting of $^4He$ was reported using DBR (Distributed Bragg Reflector) diode laser sources at 1083 nm. This measurement could provide an accurate new estimation of the $\alpha$ fine structure constant or, alternatively, a stringent test of QED theory for two electron atoms. The same laser system can be used to perform accurate measurements of the hyperfine structure of $^3He$, as well as frequency measurements of the $2^3S \to 2^3P$ Helium transitions at 1083 nm. New values for the Lamb shift of the involved levels, isotope shift and $^3He$ nuclear radius could be inferred from these measurements, when combined with theoretical predictions. Since one of the major limiting factors for improving the accuracy of these measurements is the poor stability of existing frequency standards in this spectral region, like $Cs_3$ or He itself, we decided to double the frequency of our laser to have access to molecular iodine transitions in the green. In Fig. 1, a spectrum of the $^4He$ and $^3He$ at 1083 nm is shown together with a dense grid of $I_2$ absorptions at the doubled frequency.

In the 540 nm region concerned, $I_2$ transitions have very strong absorptions, with a saturation intensity as low as a few hundred $\mu W/mm^2$ for a typical saturated-absorption linewidth of about 1 MHz (FWHM), at temperatures close to 0 $^\circ$C. These features have allowed to get a frequency stability better than $10^{-13}$, locking a doubled Nd-YAG laser onto the nearby transitions around 532 nm. To generate the required power to saturate the $I_2$ transitions, we first pursued frequency doubling a fiber-amplified 1083 nm source, using type I birefringent phase-matching in a semi-monolithic MgLiNbO$_3$ crystal mounted in an enhancement cavity. The main drawback of this set-up was the additional loss of the cavity, which also added ample fluctuations in the green. To get rid of these problems, we explored the possibility to use a single-pass configuration for doubling. Comparing the saturation intensity of $I_2$ lines (given above) with the efficiency that can be obtained in LiNbO$_3$ with birefringent phase-matching, about $10^{-3} W^{-1}$, it turns out that a fundamental power of at least 1 W would be necessary to generate microwatts of green, that is a minimum requirement for having a signal/noise ratio sufficient for a good laser lock. Considering that commercially available diode lasers at 1083 nm deliver a maximum power of about 50 mW, with a linewidth of several MHz, it turns out that narrowing the laser at a few hundred kHz in an extended cavity configuration and using usual optics for beam-shaping and optical isolation of the laser, one may have no more than about 20 mW available for doubling. Present availability of periodically-poled nonlinear crystals allows to perform quasi-phase-matching instead of conventional birefringent phase-matching, with a net increase of the efficiency of about one order of magnitude, for frequency mixings ruled by the second-order susceptibility ($\chi_2$). We have therefore combined a commercial Ybd$^+$-doped fiber amplifier (IREPOLUS, Italy), which is able to boost 1083 nm radiation power up to about 1 W, with a Potassium-Titanyl-Phosphate (KTP) crystal specially designed at Tel-Aviv University (Israel) to quasi-phase-match 1083 nm radiation for doubling. With this set-up it has been possible to generate up to 5.5 mW of radiation tunable around 541 nm that allowed to observe saturated absorption dips of $I_2$. 

Figure 1. Fluorescence spectra of some $2^3S \to 2^3P$ transitions of $^3He$ and $^4He$ at 1083 nm in a metastable atomic beam, together with the possible $I_2$ reference frequency lines. The frequency of the $I_2$ lines have been translated from the visible to the IR dividing by two and they are labelled with the $I_2$ absorption alias number. Also, the levels of the helium transitions are indicated, and the frequency scale is relative to the $2^3S_1 \to 2^3P_2$ $^4He$ transition. The insert shows saturation dips for $^3He$. 
Table 1. Comparison of the frequency stability of a 1083 nm DBR semiconductor diode laser locked to different frequency references.

<table>
<thead>
<tr>
<th>Frequency reference</th>
<th>Molecular Cesium</th>
<th>Atomic Helium</th>
<th>Molecular Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line width (MHz)</td>
<td>75</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>S/N</td>
<td>600</td>
<td>1200</td>
<td>1800</td>
</tr>
<tr>
<td>Stability in 1 s</td>
<td>4.5 $10^{-10}$</td>
<td>3.0 $10^{-11}$</td>
<td>&lt; 2.0 $10^{-12}$</td>
</tr>
</tbody>
</table>

Figure 2. Absorption spectrum of the 5316 $I_2$ line at 541.62 nm. (a) Doppler broadened absorption ($T_2 = 8^\circ$C, $L_{cell} = 8$ cm). (b) Amplitude modulation sub-Doppler saturation spectrum ($I_{pump} = 2.5$ mW/mm$^2$, $I_{probe} = 0.1$ mW/mm$^2$). (c) First derivative frequency modulation sub-Doppler saturation spectrum ($f_m = 120$ kHz, $I_{pump} = 2.5$ mW/mm$^2$, $I_{probe} = 1.8$ mW/mm$^2$).

Combination of these three state-of-the-art components required a thorough characterization of each of them before assembling in this unique solid-state source. In particular, a careful measurement of amplitude noise and frequency broadening was necessary for the fiber amplifier that was used in a sub-Doppler resolution spectroscopic set-up; we also measured the doubling efficiency and the temperature and wavelength bandwidth for the KTP crystal$^8$. In Fig. 2, we show a Doppler–broadened spectrum of a $I_2$ absorption line (#5316)$^9$ and the fully resolved saturation sub-Doppler hyperfine components observed with amplitude modulation spectroscopy (Fig. 2 (b)) and first derivative low frequency modulation spectroscopy (Fig. 2 (c)). An isolated component of this spectrum can be used for frequency lock of the 1083 nm diode lasers. As a preliminary result, we have achieved a frequency stability at least one order of magnitude better than that of the previous frequency references at this wavelength (see table 1).

Fig. 3 shows how this set-up for iodine lock is going to be used as frequency standard for the accurate measurement of He frequencies. To use $I_2$ hyperfine transitions at 541 nm as accurate frequency references, a measurement with respect to other existing standards will be required. Convenient existing standards are $I_2$ transitions around 532 nm, that can be excited with a Nd-YAG laser at 1064 nm. Since the frequency gap between a 1083 nm and a 1064 nm source is about 4.89 THz, no existing photodiode could directly detect the beat. At present, several techniques could prove useful to fill this gap. For example, Metal–Insulator–Metal (MIM) diodes have long been used as very wide band mixers, encompassing a frequency range which goes from the microwaves to the visible$^{10}$. A fourth-order mixing on a MIM could be tried, using two CO$_2$ lasers separated by a frequency close to the 4.89 THz gap between Nd:YAG and 1083 nm diode lasers, also focused on the MIM. The CO$_2$ lasers can be locked, as is usually done, onto saturated fluorescence of CO$_2$ at 4.3 μm. A second interesting possibility for very wide bandwidth heterodyning is offered by the new scheme proposed very recently by Hänisch and coworkers$^{11}$. It is based on a mode-locked femtosecond pulsed laser that generates a comb of frequencies spanning a range that can be as wide as tens of THz. Similar bandwidths can now be obtained also with cw frequency combs, when combined with optical fibers$^{12}$. This approach could be used in the 1 μm region to cover the gap between Nd:YAG and 1.08 μm diode lasers.
3 Difference frequency generation at 4.3 μm and spectroscopy of CO₂

Another interesting possibility to create frequency links between the visible and the infrared region is offered by difference frequency generation. Considering that the transparency window of LiNbO₃ crystals spans from the visible to the 4.5-5 μm range, it is possible to have access to the fundamental vibration modes of many molecules, which have absorptions several orders of magnitude stronger than overtone transitions, already accessible to diode lasers. This increased line strength can allow to record lines with a very high signal/noise ratio having the additional advantage of a Doppler linewidth reduced by the longer wavelength (for example, the FWHM Doppler width for CO₂ transitions belonging to the fundamental band at 4.3 μm is only 130 MHz). High S/N ratio and narrow linewidth are both appealing features for a frequency reference. Also, the strong infrared absorptions and the low noise of spectrometers that incorporate diode lasers allow more sensitive detection of trace gases. In Table 2 is clearly shown that, using spectrometers having similar sensitivities, it is possible to gain more than five orders of magnitude for the minimum detectable concentration of CO₂, due to the much stronger transitions at 4.3 μm with respect to those at 1.58 μm.

In our set-up we generate radiation tunable around 4.3 μm using a cw Nd-YAG at 1064 nm, delivering a maximum output power of 800 mW, and a diode laser with an output power up to 150 mW, that is injection locked by another diode, mounted in an extended cavity configuration and tunable around 852 nm. With this source we have observed several Doppler limited CO₂ transitions, belonging to the most abundant ¹²C, to ¹³C and "hot bands" (0, 1, 0-0, 1, 1 band) lines for ¹²CO₂. Some of these lines have strong environmental implications, especially measurements of isotopic ratios at the level of 10⁻³⁻¹₀⁻⁻³, while hot band lines are important in view of the recently observed CO₂ laser lines belonging to the 9 and 10 μm hot bands.

As long as Doppler limited profiles are recorded, it is not particularly important to increase the conversion efficiency and the infrared generated power, nor to make a detailed study of the source noise or narrow the infrared

<table>
<thead>
<tr>
<th>CO₂</th>
<th>2ν₁ + 2ν₂ + ν₃</th>
<th>ν₁ + 2ν₂ + ν₃</th>
<th>ν₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR transition</td>
<td>P(8)¹⁵</td>
<td>R(24)¹⁵</td>
<td>R(16)¹³</td>
</tr>
<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>Spectrometer sensitivity (Hz¹/²)</td>
<td>7 10⁻⁸</td>
<td>7 10⁻⁷</td>
<td>2 10⁻⁷</td>
</tr>
<tr>
<td>CO₂ concentration (ppb in Hz¹/²)</td>
<td>1000</td>
<td>100</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Figure 4. Saturation spectroscopy spectrum of the $^{12}C^{16}O_2(0,0^0,0-0,0^0,1)$ R(14) absorption line at 4.3 $\mu$m. Solid trace: first derivative spectrum ($f_m = 1$ kHz, $I_{pump,probe} = 1$ mW/mm$^2$, $P_{CO_2} = 13$ Pa, $L_{cell} = 0.5$ mm). Dotted trace: laser scan; inset: first derivative of the Lamb-dip.

linewidth. All of these details become crucial when saturated-absorption Doppler-free spectroscopy is the goal. Considering that the saturation intensity $I_s$ is inversely proportional to the dipole moment squared $\mu^2$, transitions belonging to the fundamental bands are ideal candidates for performing sub-Doppler spectroscopy. In Fig. 4 we report a first derivative recording of the R(14) line of $^{12}C^{16}O_2$ at 2360.109 cm$^{-1}$, belonging to the fundamental vibro-rotational band. At the line center a saturated absorption signal can be seen. It demonstrates that, for the first time to our knowledge, sub-Doppler spectroscopy becomes accessible to very low power laser sources based on nonlinear mixing. This result was obtained with a power of about 10 $\mu$W and a noise close to the quantum limit. Coherent sources based on quasi-phase-matched difference frequency generation with high single-pass conversion efficiency can cover, at present, the infrared region up to about 4.5 $\mu$m, only limited by the LiNbO$_3$ transparency range. Therefore, frequency locking of lasers in the VIS-NIR, used as pump and signal sources, onto proper atomic and molecular references can be combined with the most recent frequency comb generation techniques, to allow the creation of a new set of accurate secondary frequency standards in the infrared. This direct link between the visible and the infrared could open new possibilities for spectroscopy-based measurements of fundamental physical constants and experimental tests of theories. In particular, the availability of frequency references wherever they are needed will provide full access to the most convenient atomic and molecular transitions. Moreover, the increased line-strength of infrared fundamental vibrational bands can push the sensitivity of theories testing to unprecedented levels. As an example, one can consider the most recent test of the symmetrization postulate$^2$. Using an overtone transition of CO$_2$ at 2 $\mu$m, the postulate was tested at the level of 2 parts in 10$^6$. Since the main limitation was represented by the transition line-strength, looking at data in table 2, it can be seen that the bound of possible violations could be improved of several orders of magnitude just using our DFG spectrometer tuned onto the 4.3 $\mu$m fundamental band of CO$_2$.

In conclusion, unprecedented coverage of the spectral region going from the infrared to the UV is now available, due to the impressive development of frequency conversion devices. New fascinating perspectives can be foreseen for high resolution spectroscopy.

Acknowledgments

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References


