Continuous-wave optical parametric oscillators for mid-infrared spectroscopy

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ABSTRACT

The atmospheric window at 3 to 5 μm is one of the most important spectral regions for molecular spectroscopy. This region accommodates strong fundamental vibrational spectra of several interesting molecules, including species relevant for air quality monitoring, medical diagnostics, and fundamental research. These applications require excellent spectroscopic sensitivity and selectivity. For example, atmospheric research often needs precise quantification of trace gas fractions of down to the parts-per-trillion level (10^{-12}), with the capability of resolving individual spectral features of different molecular compounds. This sets stringent requirements for the light source of the spectrometer in terms of output power, noise, and linewidth. In addition, the wavelength tuning range of the light source needs to be large, preferably over the entire atmospheric window, in order to enable measurements of molecular fingerprints of several compounds. Continuous-wave optical parametric oscillators (CW-OPOs) are one of the few light sources that have the potential of combining all these favorable characteristics. This contribution summarizes our progress in the development of CW-OPOs, with an emphasis on precise frequency control methods for high-resolution molecular spectroscopy. Examples of new applications enabled by the advanced CW-OPO technologies will be presented. These examples include a demonstration of world-record detection sensitivity in trace gas analysis, as well as the first characterization of infrared spectrum of radioactive methane $^{14}CH_4$.

Keywords: Nonlinear optics, optical frequency conversion, infrared spectroscopy, molecular spectroscopy

1. INTRODUCTION

The definition of high-resolution molecular spectroscopy is somewhat ambiguous, but it can be understood as a method that is capable of resolving individual absorption lines of gas-phase samples. In practice, this requires a laser or laser-like coherent light source. The linewidths of rotational-vibrational absorption lines of gas-phase molecules are of the order of a few GHz in atmospheric conditions, and can be narrowed down to the 100 MHz level by lowering the sample pressure, such that the effect of collisional broadening is reduced to below that of Doppler broadening. The capability of resolving individual absorption lines is extremely important in many applications where small traces of target gases need to be measured from samples that contain a large number of interfering molecular compounds. The possibility of measuring narrow spectral features is often the only way to reduce the spectral interference, and thus to obtain good selectivity in spectroscopic analysis.

Trace gas analysis often requires the capability of detecting and quantifying parts-per-billion or even parts-per-trillion level concentrations of target gases in complex gas matrixes. Typical applications include air quality monitoring, medical diagnostics, and industrial process gas monitoring [1,2]. Similar techniques are used in fundamental research, for example to compile spectroscopic databases and to gain information of molecular structures. Fundamental molecular spectroscopy often requires much better spectral resolution than the applications in trace gas detection. As an example, this contribution includes a couple of examples of Doppler-free measurements with a resolution of about 1 MHz.

The focus of this paper is on techniques that are suitable for high-resolution spectroscopy in the mid-infrared region, which is the spectral range of strong rotational-vibrational transitions and which thus fundamentally offers the possibility of measuring small trace gas concentrations. At the same time, the availability of laser sources suitable for high-resolution spectroscopy is limited in the mid-infrared region, even though quantum cascade laser (QCL) and interband

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cascade laser (ICL) technologies have become commercially available. Yet, coherent light sources based on nonlinear optics offer certain advantages over the QCLs and ICLs, especially in laboratory applications. Most importantly, the singly resonant CW-OPOs (CW-SROs) discussed in this paper offer a unique combination of high output power (> 1 W), narrow linewidth (~ 1 MHz) and broad spectral coverage (several hundred nanometers) within the 3 to 5 µm region, which is one of the most important spectral bands for molecular spectroscopy [1]. This region can be conveniently covered with CW-SROs based on periodically poled lithium niobate (PPLN).

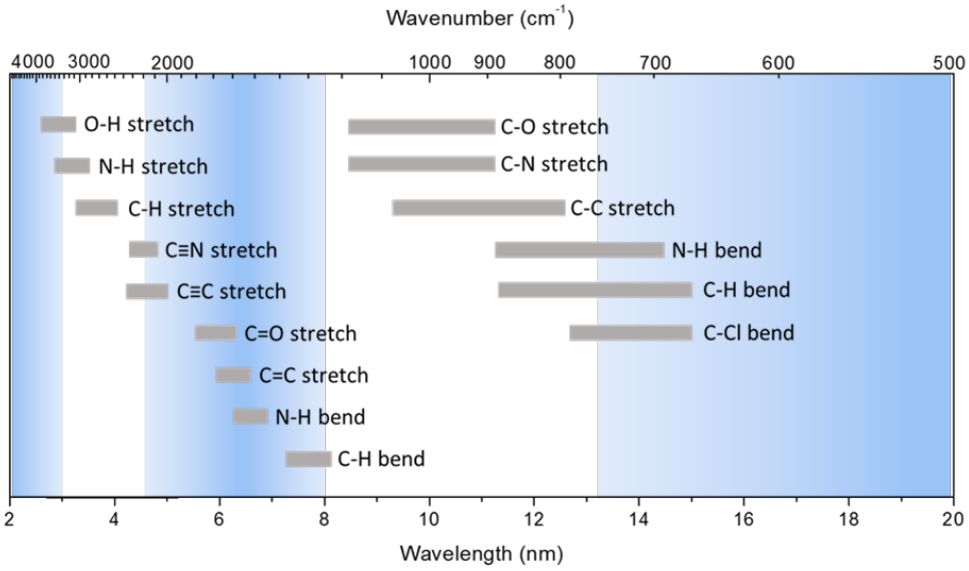

Figure 1. Spectral regions of some important fundamental vibrational transitions (group frequencies). The regions shown in blue indicate strong atmospheric attenuation, mainly due to absorption caused by water vapor. The water absorption is smaller (but not zero) within the so-called atmospheric windows, at approximately 3 – 5 µm and 8 – 13 µm. Another important interfering species is CO_2, which absorbs strongly *e.g.* at 4.5 µm and above 13 µm. The C-H stretching vibration region at *c.a.* 3 to 4 µm is particularly important for a number of applications.

Although the exact requirements set for the light source vary depending on the application, high-resolution molecular spectroscopy typically needs the following characteristics:

1. Wide spectral coverage in the spectral region of interest. For molecular spectroscopy, this typically means mid-infrared wavelengths that correspond to fundamental vibrational transitions. The fundamental transitions are generally one to two orders stronger than the respective overtone transitions in the near-infrared region. (On the other hand, near-infrared detectors and other optical components are usually of better quality than their mid-infrared counterparts. Depending on the spectroscopy technique, this may countervail the fundamental benefits offered by the mid-infrared transitions). For applications like trace gas analysis, operation within one of the atmospheric windows is preferred in order to minimize the spectral interference caused particularly by water vapor. The main spectral ranges of interest are summarized in Fig. 1.

2. Sufficient output power and beam quality. The required power level naturally depends on the application. For direct laser absorption experiments, less than 1 mW can be adequate, even if taking into account the modest detectivities of mid-infrared detectors. In general, > 10 mW is needed for ease of operation, especially if the light beam is to be coupled into a high finesse cavity or a wavelength meter. Certain techniques benefit from much larger powers. For instance, the photoacoustic spectroscopy and saturation spectroscopy discussed here may need watt-level CW powers.

3. Narrow linewidth and low noise. Trace gas analysis typically requires the capability of resolving Doppler-broadened absorption lines, which means that the light-source linewidth should be << 100 MHz. Applications in Doppler-free spectroscopy require a linewidth of *c.a.* 1 MHz or smaller, as will be exemplified below. Low power noise is naturally

beneficial in order to detect weak signals, although there are methods that are relatively insensitive to power fluctuations. Examples of such methods include balanced detection and cavity-ring-down spectroscopy.

4. Single-mode operation and long-term stability. One of the most important requirements in molecular spectroscopy is that the laser should operate in a single longitudinal mode reliably and without mode hops. In addition to mode hops, frequency jitter and drifts may compromise the quality of spectroscopic measurements, especially if the wavelength cannot be continuously monitored during the experiment. Again, the required level of stability depends on the intended applications, but even trace gas measurements typically require a long-term instability of less than a few hundred MHz. Active stabilization of the laser frequency at a level much better than this is often useful in fundamental research, such as in Doppler-free spectroscopy.

In practice, it is very challenging to achieve a mode-hop-free tuning range of much larger than a few tens of GHz. A typical practical requirement is approximately 1 cm^{-1} (30 GHz), which makes it possible to find the targeted absorption line and scan over it. In laboratory conditions, a wider spectrum can be recorded by stitching together several scans.

Requirements 1 and 2 of the above list are relatively straightforward to achieve. Already the first continuous-wave SROs demonstrated in the 1990's reached hundreds of nanometers of wavelength tuning range, several watts of output power, as well as excellent beam quality[3]. With the modern pump lasers, PPLN crystals and high-quality mirrors, such properties can be obtained quite easily. What remains a challenge is reliable and mode-hop-free long-term operation of the CW-SRO instrument. Although most of these issues can be adequately solved by careful engineering of the instrument and are well addressed even in some commercial instruments,[4] also scientific challenges exist. For example, the importance of group velocity mismatch and group velocity dispersion on CW-SRO stability has been identified only quite recently[5].

The purpose of this contribution is to introduce techniques that we have developed in order to improve the CW SRO frequency stability and control. The improved performance is demonstrated by examples, which show how CW-SROs can be used in high-resolution molecular spectroscopy from trace gas detection to fundamental spectroscopy.

2. SINGLY-RESONANT CW OPO

2.1 Experimental implementation

The basic construction of a CW-SRO is shown in Fig. 2. The most common implementation is essentially the same as in the first CW-SRO demonstrations[3]: A high-power pump laser beam at 1064 nm is focused into a nonlinear crystal, which is typically a 5 cm long PPLN crystal. The crystal is placed inside a bow-tie resonator, which is singly resonant for the near-infrared signal beam (wavelength ~ 1.5 µm), The mid-infrared idler beam (~ 3 µm) is entirely coupled out. The CW-SRO threshold power with a 1064 nm pump laser is typically of the order of 1 W. Up to several watts of single-frequency output light in the mid-infrared region can be achieved using an Yb-fiber-amplified pump laser that outputs 10 W or more.[6]

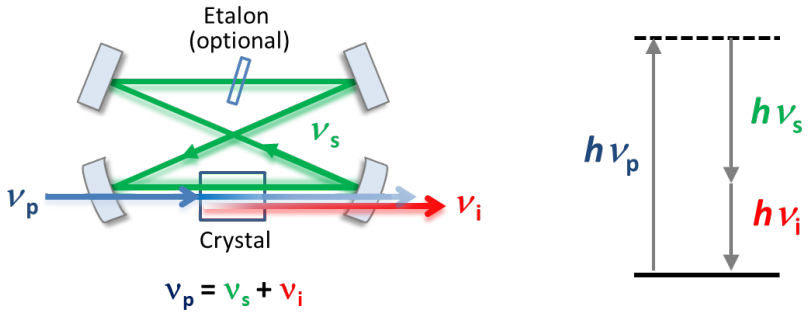

Figure 2. A typical CW-SRO instrument, which converts pump photons (frequency ν_p) to signal (ν_s) and idler (ν_i) photons. Periodically poled lithium niobate PPLN is the most common nonlinear crystal material for mid-infrared generation in the 3 to 5 µm spectral region.

Most CW-SROs have an intracavity etalon (Fig. 2) to reduce mode-hop probability, as well as to achieve more deterministic frequency tuning properties between the mode hops. We have shown that the mode-hop probability can be essentially suppressed even without an etalon, if only the PPLN temperature is carefully controlled.[7,8] We have also demonstrated that the use of a grating as frequency-selective cavity element can offer certain advantages compared to etalons.[9-11] These advantages are briefly summarized below.

2.2 Wavelength tuning strategies

The most common approach for CW-SRO wavelength tuning is the following: The desired wavelength is first coarsely set by mechanically translating the PPLN crystal, which has in parallel several discrete poling periods or, alternatively, a fan-out structure. The phase-matching condition can also be altered by varying the crystal temperature, which typically allows the target frequency to be found with a precision of about 30 GHz. The precision of coarse wavelength adjustment maybe improved by additionally adjusting the angle of an intracavity etalon.[12] Mode-hop-free scans around the set point are subsequently carried out by tuning the pump laser frequency. (As the CW-SRO cavity fixes the signal wavelength for a constant PPLN poling period and temperature, the pump frequency tuning is directly transferred to the idler frequency). The maximum mode-hop-free tuning scan range is typically 30 to 200 GHz, which is ultimately limited by the pump laser. Mode-hop-free scans of over 1 THz have been demonstrated using a widely tunable pump laser.[13]

One of the approaches that we have introduced, in order to improve the precision of coarse wavelength tuning, is to replace one of the SRO cavity mirrors by a diffraction grating.[9] In this case, a standing-wave cavity design is preferred and fast wavelength tuning can be done simply by rotating the grating. The wavelength tuning range attainable by grating rotation is typically a few hundred GHz, depending on the width of the parametric gain profile. A wider tuning range requires the change of the PPLN poling period or temperature. The grating-cavity design efficiently suppresses mode hops during wavelength scanning, as the grating has just one gain maximum in comparison with the multiple transmission maxima of an etalon. Even better frequency selectivity can be obtained by using a narrow-band volume holographic grating (VHG, Bragg grating).[10] We have proven this experimentally by realizing stable single-mode operation of a VHG-stabilized CW-SRO very near the signal-idler degeneracy, where the parametric gain curve is several THz wide.[14,15]

Although the abovementioned “standard” wavelength tuning procedure can be automated[4,12] and provides a coarse mid-infrared tuning range of hundreds of nanometers, it is inherently slow. In particular, at least a couple of minutes is needed for the CW-SRO to stabilized after a change in PPLN temperature.[7] Much faster tuning can be obtained if the PPLN settings can be kept constant, while only the pump laser is tuned. Owing to favorable dispersion characteristics of PPLN, this is conveniently obtained by using approximately 800 nm pump wavelength instead the more common 1064 nm.[16] We have demonstrated an exceptionally wide CW-SRO tuning from 2.5 to 4.4 µm by using Ti:sapphire-laser pumping.[17] This whole range can be covered with just two PPLN poling periods – and, as an example, tuning from 3.3 to 4.5 µm can be done entirely by scanning the pump laser wavelength, without touching the PPLN or CW-SRO cavity. We have used the same approach to implement a simple and inexpensive diode-laser pumped CW-SRO.[16] An example of fast scan of the mid-infrared idler wavelength over 200 nm is illustrated in Fig. 3.

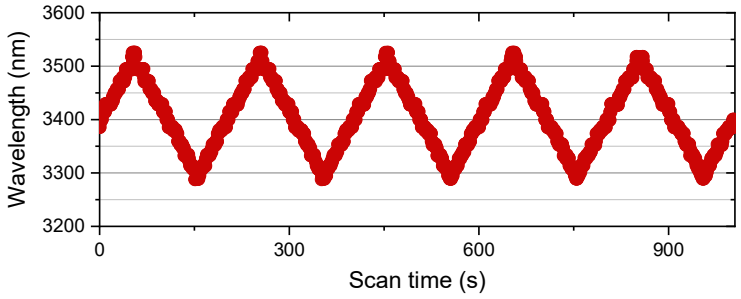

Figure 3. Example of over 200 nm coarse wavelength tuning that is obtained solely by tuning the pump laser, which is a 780 nm DFB diode laser amplified by a tapered semiconductor amplifier. The tuning speed demonstrated here is limited by the measurement speed of the wavelength meter that was used to track the wavelength. The tuning includes mode hops, between which approximately 30 GHz mode-hop-free tuning regions exist. The frequency scan rate within those regions exceeds 5 THz/s, which is achieved by tuning the pump laser current.

2.3 Frequency stabilization

The most important prerequisite for stable single-mode operation of the CW-SRO is careful stabilization of the nonlinear crystal.[7] The PPLN temperature stability should be better than 10 mK in order to avoid mode hops and to guarantee a side-mode suppression of better than 20 dB. If a high mid-infrared output power is needed and a high-power pump laser is available, it is often advantageous to deliberately increase the cavity losses for the signal wavelength.[18,19] Out coupling of a couple of % of the resonant signal power can significantly reduce photothermal effects as well as the onset of residual nonlinear processes or modulation instability.[5,18,20] When the idler wavelength of a 1064-nm pumped CW-SRO is tuned towards degeneracy and well below 3 µm, the parametric gain profile becomes very wide, generally leading to an increased probability of mode hops. In this case, the abovementioned grating-cavity design can be particularly beneficial. On the other hand, the fortuitous overlap of the corresponding signal wavelength (~1.8 µm) with a rather strong and dense water absorption spectrum can be utilized to stabilize the resonant signal wave.[21,22] Since the intracavity losses significantly increase at the frequencies of water absorption peaks, the SRO tends to find a stable operating point within the narrow spectral regions between the absorption peaks. (The cavity air always contains some water vapor unless evacuated or purged with nitrogen/dry air).

If the crystal temperature is properly stabilized, mode-hop-free operation of several hours can be obtained at a single operating point.[7] Further, if the CW-SRO cavity and pump laser wavelength are stable, the mid-infrared frequency may remain constant within a few tens of MHz, as demonstrated in Fig. 4. Such stability is enough to keep the mid-infrared frequency at a center of a Doppler-broadened absorption line. The CW-SRO frequency drifts can be suppressed also by active methods, for instance by locking to a wavelength meter. This approach typically guarantees a long-term stability of the mid-infrared frequency within approximately 100 MHz.

If a better stability or accurate knowledge of the absolute frequency is needed, the CW-SRO can be locked to a fully stabilized optical frequency comb, OFC.[23-26] True phase locking of a CW-SRO is technically quite challenging, because a pump laser with fast frequency modulation capability would be required. However, simple frequency locking or tracking can be realized by counting the beat frequency of the CW-SRO idler and the OFC.[23,27] This method does not influence the CW-SRO linewidth, but reduces the fractional long-term instability of the mid-infrared frequency to below 10^{-8}. This corresponds to a standard deviation of approximately 1 MHz and is exemplified in Fig. 4 (red). A somewhat faster locking can be realized *e.g.* by using a voltage-to-frequency controller to monitor the beat signal instead of a frequency counter.

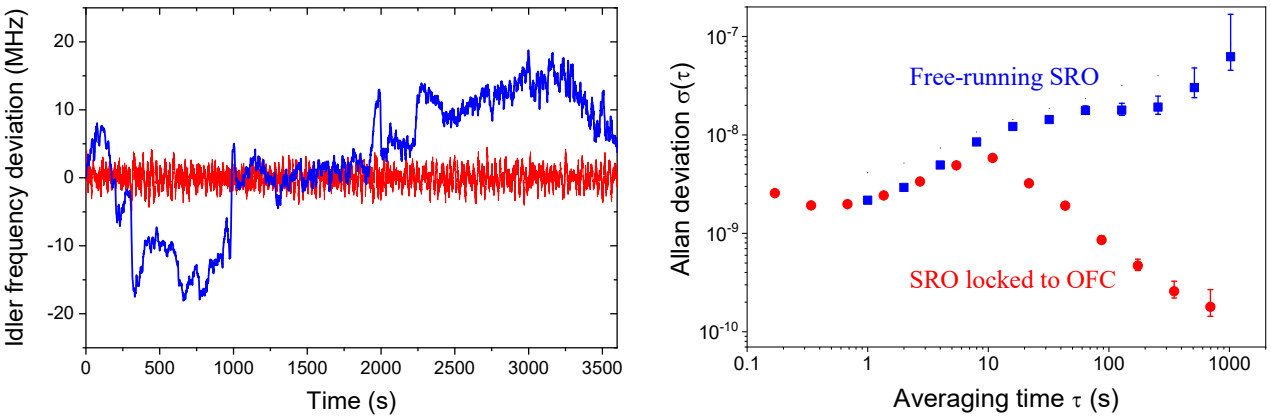

Figure 4. Left: Deviation of the mid-infrared idler frequency, as recorded over 1 h in stable laboratory conditions. The CW-SRO used in the measurements has a typical bow-tie resonator (Fig. 2) without etalon or any other frequency-selective optical component. The blue trace shows the frequency drift of a free-running CW-SRO. The red trace was recorded with the CW-SRO frequency locked to a fully stabilized OFC. Right: The respective Allan deviation plots, where the vertical axis is expressed as fractional frequency, *i.e.* relative to the mid-infrared frequency 90.9 THz. Note that the counter gate times were 0.15 s and 1 s for the OFC-locked and free-running measurements, respectively. (This explains the more noisy appearance of the red trace on the left).

2.4 Application examples

The stable CW-SRO described above have enabled various high-resolution spectroscopy experiments that would have been otherwise difficult or even impossible to perform. These light sources pair well with cantilever-enhanced photoacoustic spectroscopy (CEPAS), which is a highly sensitive spectroscopy method that does not require a photodetector and thus works equally well at all wavelengths.[28] We have used our CW-SRO instruments together with CEPAS detection to measure tiny concentrations of various trace gases. As an example, we have demonstrated a world-record detection limit of 650 parts-per-quadrillion (650×10^{-15} volume mixing ratio) for hydrogen fluoride, HF.[21] Another experiment made possible by the combination of high-power mid-infrared OPOs and CEPAS is spectroscopy of radioactive methane, $^{14}CH_4$. In the first reported measurements of $^{14}CH_4$ spectrum, we used a novel OFC-CEPAS method, which is based on a mid-infrared frequency comb that we generate by a singly-resonant femtosecond OPO.[29] We are currently performing a more detailed study of the $^{14}CH_4$ spectrum (ν_3 band at 3 μm) using a CW-SRO, which offers an improved signal-to-noise ratio and spectral resolution compared to the OFC-CEPAS measurements.

An important application of high-resolution spectroscopy is to measure center frequencies and other line parameters of molecular transitions. These parameters are collected in spectroscopic databases, which are essential for trace gas detection. The accuracy of databases is of uttermost importance for the reliability of trace gas measurements, for example in atmospheric monitoring. High accuracy in the line position measurements can be achieved by sub-Doppler spectroscopy, especially if the optical frequency can be referenced to a fully stabilized optical frequency comb. An example of the resolution enhancement provided by saturation spectroscopy is presented in Fig. 5, which shows measurements of a methane ($^{12}CH_4$) absorption line at 3221 nm. These measurements were performed with a VHG-stabilized CW-SRO, which has a 1-second linewidth of about 1 MHz.[11] The black trace of the left panel of Fig. 5 was recorded directly with the saturated-absorption setup. The measurement is interfered by a strong power modulation, which is caused by the CW-SRO pump laser. This interference can be suppressed by using a near-infrared balanced detection scheme, which allows a weak Lamb dip to be observed at the line center. The Lamb dip is better visible in the second panel of Fig. 5, which shows a zoom-in of the absorption line center.

Doppler-free resolution combined with a high detection sensitivity can be obtained by mid-infrared cavity-ring-down spectroscopy, which also allows reliable quantification of the sample absorbance.[24] In addition, we have developed a two-photon method, which combines two OFC-stabilized sources – a CW-SRO and a near-infrared diode laser – for Doppler-free molecular spectroscopy.[26,30] This new method gives access to vibrational energy states that are inaccessible directly by single-photon absorption. As an example, we have accurately determined energy levels of symmetric vibrational states of acetylene, C_2H_2.[26,30]

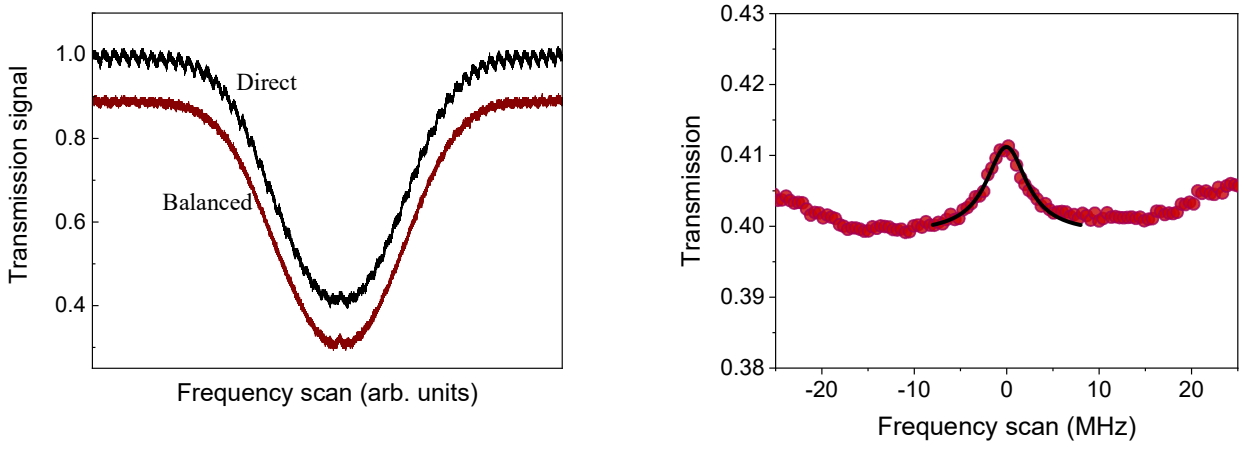

Figure 5. Left: A methane absorption line at 3221 nm measured with and without balanced detection. Right: A detail that shows the Lamb dip at the line center. The measurement was done using saturated absorption spectroscopy.

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