Transportable, highly sensitive photoacoustic spectrometer based on a continuous-wave dual-cavity optical parametric oscillator

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Abstract: We present an all solid state, transportable photoacoustic spectrometer for highly sensitive mid-infrared trace gas detection. A complete spectral coverage between 3.1 and 3.9 µm is obtained using a PPLN-based continuous-wave optical parametric oscillator pumped by a Nd:YAG laser at 1064 nm. A low threshold is achieved by resonating the pump, and spectral agility by employing a dual-cavity setup. An etalon suppresses mode-hops. Active signal cavity stabilization yields a frequency stability better than ± 30 MHz over 45 minutes. Output idler power is 2 x 100 mW. The frequency tuning qualities of the OPO allow reliable scan over gas absorption structures. A detection limit of 110 ppt for ethane is achieved.

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1. Introduction

Mid-infrared laser spectroscopy is a powerful tool for monitoring trace amounts of volatile organic compounds in biology, environmental analysis and medicine. These molecules possess strong absorption fingerprint spectra in the 3 µm wavelength region. Molecules of interest are, e.g., ethane and ethylene, both as spectroscopic benchmark molecules and as markers for metabolic processes in living organisms. Ethane is produced by plants, animals and humans as a result of lipid peroxidation of cell membranes [1-3]. Ethylene is an indicator for plant stress [1,3]. In the 3 µm region photoacoustic spectroscopy (PAS) has been established as a method of high sensitivity, selectivity and time resolution [3]. In photoacoustics sensitivity scales with laser power. The CO overtone laser has proven its usefulness offering several watts of intracavity power at wavelengths between 2.8 and 4 µm [3]. Suiteability of this gas laser is limited by its size (about 2 meters in length), its dependence on liquid nitrogen cooling and the discrete tuning from line to line. A continuously tunable laser source is to be preferred, since it increases sensitivity and selectivity and allows an easier analysis of gas mixtures. To this end, cw difference frequency generation (DFG) and, with significantly higher power and hence the much better choice for PAS, optical parametric oscillators (OPO) have been employed [4-7]. Frequency agility is an important feature for practical trace gas detection. Herpen *et al*. used a 15 W cw pump laser at 1064 nm to achieve 2.2 W widely tunable cw 3 µm idler radiation with a singly-resonant OPO (SRO) [7]. Our goal was to set up a SRO using a pump source of moderate power. The approximately 5 W SRO threshold can be lowered significantly by pump resonance. In a common cavity pump-resonant SRO tunability is limited by mode hops, often preventing access to a desired frequency [8]. Here we present a dual-cavity design (pump and signal resonated in separate cavities) with an intracavity etalon, solving these frequency tuning problems [9]. A linear setup is realized, without using an intra-cavity beamsplitter. We demonstrate a tuning method that does not require a tunable pump laser. This new OPO is applied in a transportable photoacoustic spectrometer.

2. OPO setup

The continuous-wave, pump-resonant, singly-resonant optical parametric oscillator (cw-PR-SRO) is set up in a linear dual-cavity design (Fig. 1) and uses periodically poled lithium niobate (PPLN) as the nonlinear medium [10]. The crystal (19 mm x 50 mm x 0.5 mm, length x width x thickness) contains 19 gratings with poling periods between 28.64 µm and 30.16 µm for quasi-phasematching (QPM) and is mounted inside a temperature controlled (LFI-3751, Wavelength Electronics ®) self-designed oven ensuring a PPLN temperature stability of 8 mK (standard deviation) over 4 hours. The operating temperature is between 150 and 200 deg C to avoid photorefractive damage of the crystal [11]. The first crystal surface is HR coated for both pump (94.3 %) and signal (99.9 %) waves. The pump-cavity (length ~ 39 mm) is closed by a meniscus mirror (99.9 % pump reflection, AR < 2 % for signal and AR < 5 % for idler, r_{cav} = 30 mm, r_{vex} = 15 mm), while the signal cavity (length ~ 304 mm) is closed by a concave mirror (99.9 % reflectivity for signal, < 5 % for idler, r_{cav} = 450 mm). Both mirrors are attached to piezoelectric transducers (PZT) to adjust cavity lengths. The signal cavity has a free spectral range of 450 MHz. A galvanometer-mounted solid high-finesse

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etalon (YAG, 0.5 mm, ~ 50 % signal reflectivity coating) is inserted into the signal cavity to suppress spontaneous mode-hops. The pump beam waist (r_{waist} = 34 µm) is positioned at the front face of the PPLN crystal via a lens (f = 100 mm). The pump enhancement lowers the external pump threshold down to 380 mW (Fig. 2(a)). Using a 2.5 Watt Nd:YAG pump laser (1064 nm, Innolight Mephisto, linewidth ~ 1 kHz / 100 msec, frequency drift ~ 1 MHz / min) a maximum idler output power of 2 x 100 mW, leaving from both faces of the cavity, is achieved. The pump cavity is locked to the laser via the Pound-Drever-Hall (PDH) method [12]. The pump laser is phase modulated (6.48 MHz) via its piezo actuator. The beam reflected from the OPO cavity is separated in the Faraday isolator and coupled into a photo detector. An error signal is generated and fed to the servo that regulates the pump cavity PZT. With the signal cavity not actively controlled, its length slowly drifts, resulting in modehops every 5-10 minutes.

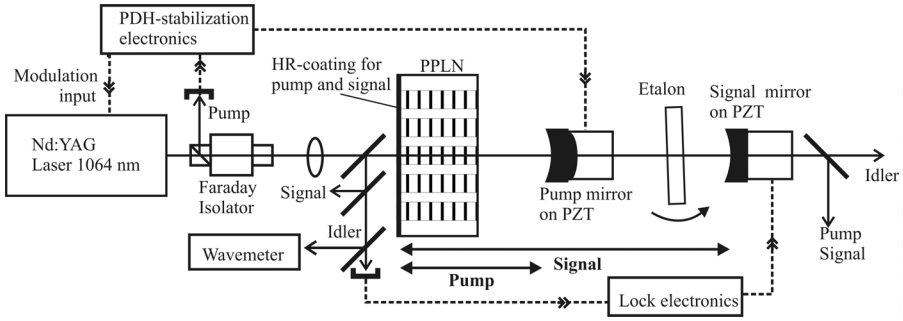

Fig. 1. Schematic of the linear dual-cavity cw-PR-SRO setup, including servos.

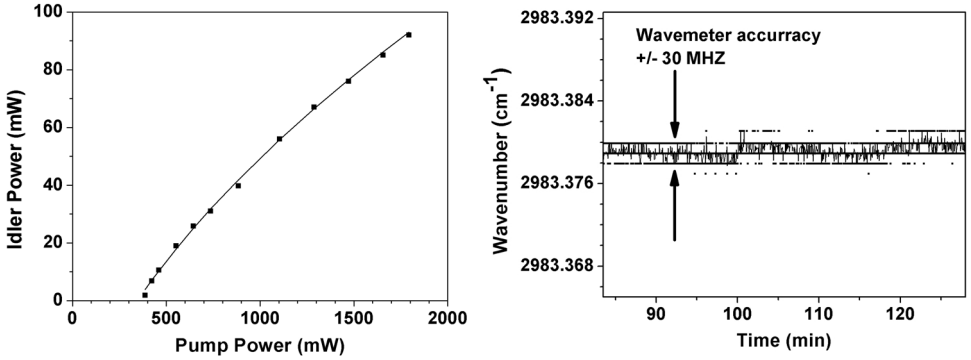

Fig. 2. (a) Single-side idler output power measured after a beamsplitter versus incident pump power (with fit according to theory [5]). (b) Frequency stability (digital wavemeter read-out and interpolation) with stabilized signal-cavity.

If long-term frequency stability is desired, the signal cavity can be locked (using a dither on the signal cavity PZT) to the point of maximum idler power. Mode-hop-free operation is then achieved over typically 45 minutes (Fig. 2(b)). During this time the idler frequency stability was better than the ± 30 MHz digital accuracy of our wavemeter (WA 1500, Burleigh). The power lock offers frequency stability without using e.g. an external reference gas absorption cell. Idler frequency tuning is done in five steps. Coarse tuning within the 3.1-3.9 µm operation range is performed by selecting one of the 19 QPM gratings via motor driven translation stage and temperature tuning of the PPLN crystal between 150-200 deg C. The corresponding signal tuning range is 1.46-1.62 µm. There are several options for frequency tuning combining etalon, signal cavity and pump frequency tuning. The tuning

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mode depends on the full widths of half maximum of the selected absorption structure to be scanned or used for trace gas detection. At atmospheric pressure typical widths are between 3 GHz (single pressure broadened lines) and 50 GHz (broad structures consisting of many overlapping lines). The lower limit is set by the width of Doppler-broadened lines at reduced pressure (typically 150 MHz). Mode hop tuning in steps of 450 MHz by turning the etalon via the galvanometer is sufficient for scanning molecular absorption structures at atmospheric pressure and is thus our preferred mode for PAS. Mode-hop tuning can be performed over 52 GHz without significant loss of idler output power (Fig. 3). If needed, fast continuous fine tuning over 450 MHz is reached by changing the signal cavity length via a piezoelectric transducer (Fig. 4(a)). Setting a new frequency within the 52 GHz etalon working range requires a few seconds and is limited by the refresh rate of the wavemeter and the iteration steps needed. We emphasize that a tunable pump laser is not necessary for the tuning mechanisms described up to this point.

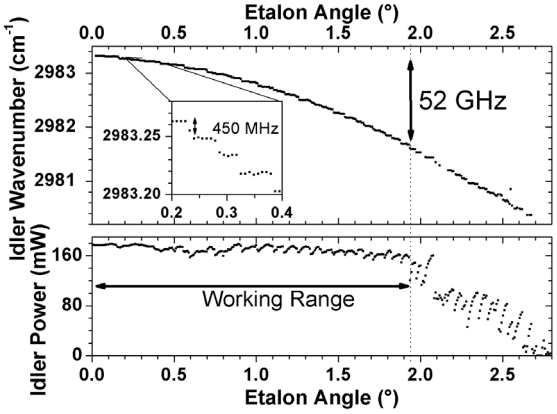

Fig. 3. Modehop tuning by turning the 0.5 mm etalon. Idler frequency (top) and idler power (bottom) as a function of etalon angle α.

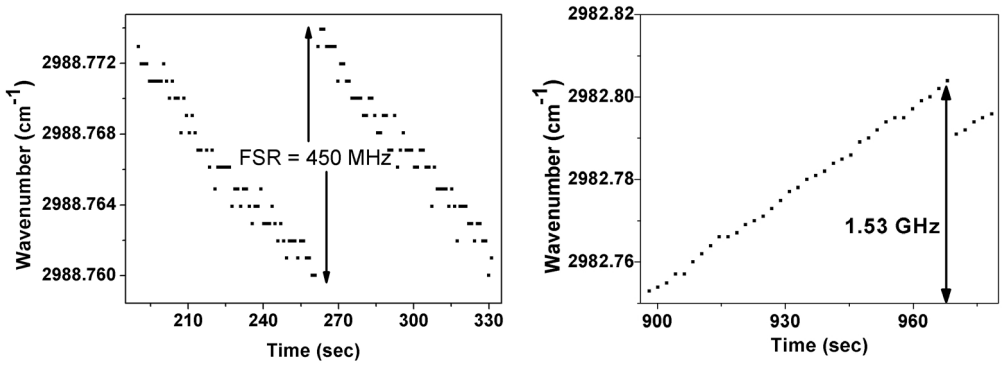

Fig. 4. (a) Fine tuning of idler frequency over one FSR of signal cavity by changing the signal cavity length. The discrete frequency values are due to the finite resolution of the wavemeter. Fine tuning (b) by tuning of the pump laser over 1.5 GHz.

Another tuning method utilizes the tuning range of the pump laser. Here the idler frequency is tuned by the same amount as the pump frequency while the signal frequency is fixed by the etalon in the signal cavity [7]. Although the gain curve shifts when the pump frequency is tuned, the magnitude of this shift (~ 35 GHz) and the width of the gain curve

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(several 100 GHz) are such that the spectral line shape of the etalon (FWHM ~ 37 GHz) is the dominant effect, thus preventing signal mode-hops [9]. Mode-hop-free idler tuning over the mode-hop-free tuning range of the laser (9 GHz) should be possible. Values up to 1.5 GHz have been achieved up to now (Fig. 4(b)). Small structures in the gain curve, possibly due to the optical coatings, may be limiting this range. An extension of the continuous tuning range should be possible by a combined tuning of etalon and signal cavity length.

An interesting feature of the dual-cavity setup is that by modulating the signal cavity length, we can implement a frequency modulation of the signal and idler waves at up to kHz rates and modulation depths greater than 200 MHz without influencing pump cavity stabilization. This feature can be used e.g. for generating an error signal for stabilizing signal and idler frequencies to an external cavity.

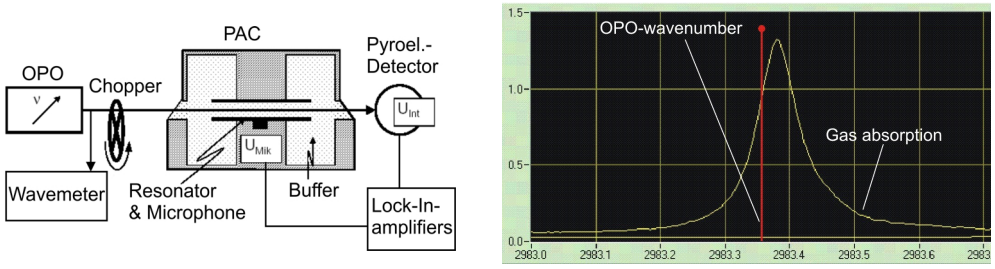

Fig. 5. (a) The OPO based photoacoustic spectrometer. (b) Screen shot of one feature of the LABVIEW (®) computer control program, comparing the current idler frequency with a gas absorption structure from a database.

3. Photoacoustic spectroscopy

The photoacoustic spectrometer (Fig. 5(a)) consists of the OPO, chopper, photoacoustic cell (PAC), pyroelectric detector and the wavemeter and is installed on a 120 cm x 75 cm bread-board. The amount of radiation absorbed by the molecules is measured by its conversion into heat. The 3 µm beam is modulated in amplitude at the resonance frequency of the photoacoustic cell, generating a standing acoustic wave. The signals from the microphone (Knowles EK3024) and the pyroelectric detector behind the cell are processed with two lock-in amplifiers (Stanford Research, SR 830). About 70 mW of idler power are available at the front-side of the PAC. For our measurements two different PAC were used. The small one (resonator length of 7 cm and diameter of 6 mm), which allows a fast gas exchange, has a Q-factor of 17.4. The large PAC (16 cm resonator length and diameter of 14 mm) has a Q-factor of 51.1. To avoid memory effects during gas exchange the inner surfaces of both cells are passivated against molecular adsorptions (Silcosteel ®, Restek).

The tunability of the OPO allows us to scan the strongest gas absorption structures in the 3 µm region. The collected data is processed by the spectrometer control computer program, that shows on-line the normalized photoacoustic signal as a function of time or laser frequency. The program also performs frequency setting, including PPLN temperature, grating period, etalon angle, signal-cavity length and pump frequency. Finding idler frequencies for trace-gas analysis is supported by a helpful screen showing the actual OPO frequency in combination with an uploaded gas absorption spectrum (Fig. 5(b)). Transportability of the spectrometer has been proven several times, when the spectrometer was moved between laboratories by man power and between cities by car. The spectrometer was fully operational within 1 to 3 hours after reaching destination. Within this period the electronic devices and the gas flow system are reconnected. Only minor effort is required for optical realignment.

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4. Measurements

At atmospheric pressure ethane and ethylene show absorption structures between 3 GHz and 30 GHz broad. These features can be covered sufficiently using the 450 MHz step etalon tuning. In Fig. 6(a) a scan of the $^{P}Q_1$ sub-branch of ethane is compared to an appropriately scaled Fourier transform infrared spectrum showing good agreement. Background signals due to window absorptions are present in the PAC. For the large PAC the noise level of this background (measured with hydrocarbon-free air) corresponds to a minimum absorption coefficient of 3.2 x 10^{-9} cm^{-1} at 10 seconds integration time, corresponding to a detection limit of 110 ppt for ethane. With the small PAC a minimum absorption coefficient of 7.1 x 10^{-9} cm^{-1} and a detection limit of 250 ppt are reached, limited by PAC-wall signals. A similar scan over the Q-branch of the ν_{11}–band of ethylene is shown in Fig. 6(b). If the absorption response of the PAC is calibrated with the ethane spectra, the measured ethylene absorption is found to be about 75 % of the data given by the HITRAN simulation [13]. Comparison of the traces shows, in addition, stronger structures in the photoacoustic scan. This may be due to incorrect HITRAN data for line positions and pressure broadening coefficients.

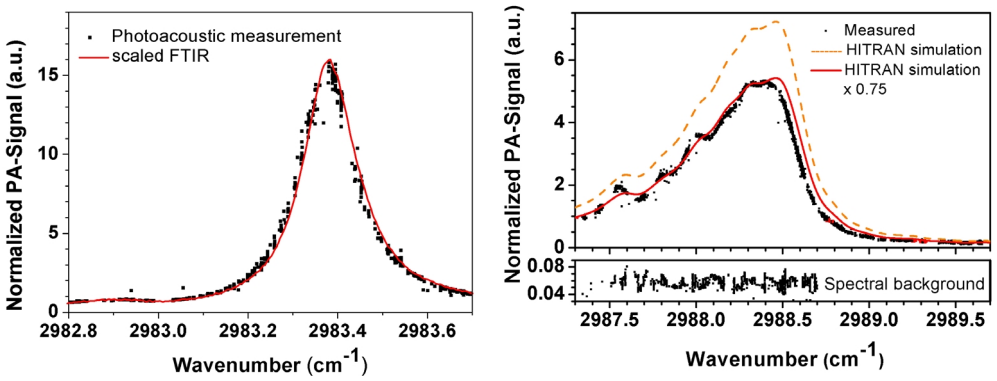

Fig. 6. (a) Scan over an ethane absorption peak (atmospheric pressure, ethane concentration 1ppm) using the small PAC. (b) 2 cm^{-1} wide scan over an ethylene absorption peak (atmospheric pressure, ethylene concentration 635 ppb) and the spectral background using the large PAC. Both scans performed with 450 MHz etalon mode hop tuning.

5. Summary

The dual-cavity PR-SRO combines low oscillation threshold with wide tunability. It allows to scan molecular absorption structures at atmospheric pressure and multi-gas analysis. With 70 mW available for photoacoustic spectroscopy we reach an ethane detection limit of 110 ppt. The OPO´s frequency stability allows time-resolved gas absorption measurements at any preset frequency. The system operates reliably and is easily transported. These results are important steps towards a fully automated, transportable all-solid-state spectrometer for long-term trace gas monitoring.

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