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Ultra-sensitive mid-infrared cavity leak-out spectroscopy using a cw optical parametric oscillator

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ABSTRACT We report a portable, all-solid-state, mid-infrared spectrometer for trace-gas analysis. The light source is a continuous-wave optical parametric oscillator based on PPLN and pumped by a Nd:YAG laser at 1064 nm. The generated single-frequency idler output covers the wavelength region between 2.35 and 3.75 μm. With its narrow line width, this light source is suitable for precise trace-gas analysis with very high sensitivity. Using cavity leak-out spectroscopy we achieved a minimum detectable absorption coefficient of 1.2×10^{-9} /cm (integration time: 16 s), corresponding, for example, to a detection limit of 300 parts per trillion ethane. This sensitivity and the compact design make this trace-gas analyzer a promising tool for various in situ environmental and medical applications.

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1 Introduction

Monitoring trace amounts of volatile organic compounds such as hydrocarbons, aldehydes and alcohols helps us to investigate sources and sinks in atmospheric chemistry or to identify markers and elicitors of biochemical processes in biology and medicine. Various techniques of laser absorption spectroscopy detect these molecules by utilizing their infrared fingerprint spectra: multi-pass absorption spectroscopy [1], photoacoustic spectroscopy [2, 3], intracavity laser absorption spectroscopy [4], pulsed [5] and continuous-wave (cw) [6, 7] cavity ring-down spectroscopy (CRDS), etc. The sensitivity and selectivity in terms of concentration depend on both the characteristics of the apparatus used (noise-equivalent absorption coefficient, spectral coverage and resolution) and the molecular specifics such as structure and strength of the detectable transitions.

The mid-infrared region around $\lambda = 3$ μm is of particular interest because the fundamental vibrational transitions of the C–H bonds exhibit strong absorption that allows high sensitivity [8]. In this wavelength region cavity leak-out spectroscopy (CALOS), a continuous-wave variant of cavity ring-down spectroscopy, has achieved very high sensitivity (sub-ppb), selectivity and time resolution [9, 10]. These experiments were performed with a tunable sideband CO-overtone laser covering 14% of the spectral range between 2.6 and 4.1 μm. This laser system is stationary and requires liquid-nitrogen cooling [11]. Very recently, a portable difference-frequency-generation (DFG)-based CALO spectrometer for trace-gas detection allowed ppb-level measurement of ethane [12]. Another type of all-solid-state laser sources, the cw-OPOs [13], are currently undergoing important developments [14, 15] and new applications for them are being explored. In the field of trace-gas detection the mid-infrared cw-OPOs have already been applied to photoacoustic spectroscopy [16, 17]. The successful application of the cw-OPO for Doppler-free absorption spectroscopy [18] suggested the exploitation of its narrow line width for the very sensitive CALOS. The use of the cw-OPO for CALOS offers several advantages: as an all-solid-state laser system, it is transportable and independent of liquid-nitrogen or water cooling, in contrast to the gas laser. As an oscillator it converts the power of a single pump laser into mid-infrared power levels above 100 mW much more efficiently than difference-frequency generation, which needs two pump lasers for μW output power levels. Here we describe what is to our knowledge the first cavity leak-out trace-gas detector employing a cw-OPO. The experiments show that the spectral properties of the OPO meet the requirements for CALOS applications. In order to demonstrate the potential of such a combination for trace-gas detection, we present first results of time-resolved monitoring of dilute ethane concentrations.

2 Experiment

2.1 *Setup*

The CALOS optical setup consists of a continuous-wave pump-resonant singly-resonant optical parametric oscillator (OPO) (cw-PR-SRO), an acousto-optic modulator (AOM), a high-finesse leak-out cavity (LOC) and a fast photodetector. The OPO is installed on a moveable 120 cm × 75 cm bread board allowing a flexible use in different experiments. Moreover, a wavemeter, computer controls, data-acquisition electronics and a pressure- and flow-control system are part of the setup, which is sketched in Fig. 1. The PR-SRO is similar in design to a device used for photoacoustic experiments [16]. The detection system (LOC and

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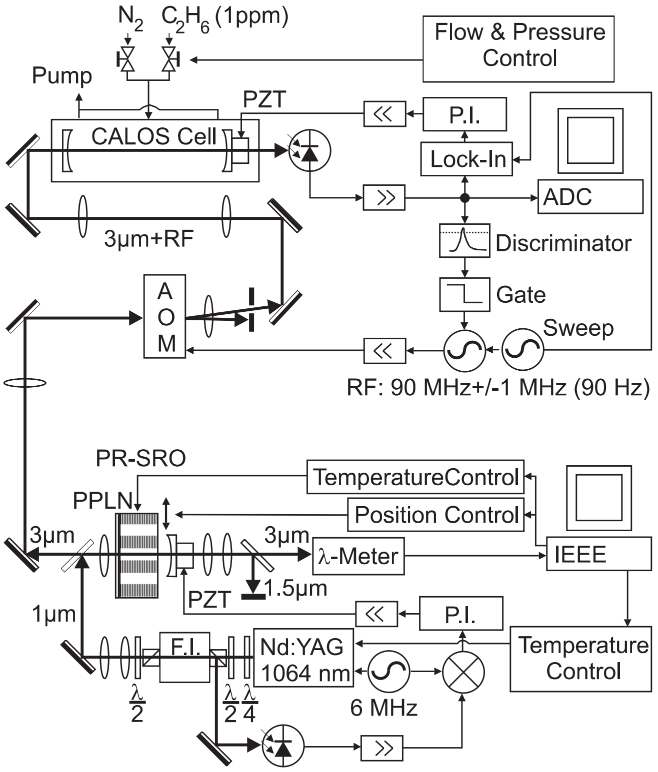

FIGURE 1 Scheme of the setup: combination of cw-OPO (*bottom*) with CALOS (*top*). PZT: piezoelectric transducer, P.I.: proportional integral amplifier, ADC: analog/digital converter, AOM: acousto-optic modulator, PR-SRO: pump-resonant, singly-resonant optical parametric oscillator, PPLN: periodically poled lithium niobate crystal, F.I.: Faraday isolator

detector) was developed as part of a sideband CO-overtone CALOS system [19]. The OPO utilizes a multi-grating periodically poled lithium niobate (PPLN) crystal (Crystal Technology, coating from Tafelmeyer) as a nonlinear medium. One crystal surface works as a cavity mirror and the other is antireflection-coated. The second cavity mirror is attached to a piezoelectric transducer to adjust the cavity length. A single-frequency diode-pumped Nd:YAG laser (Innolight, Germany) with 2.5 W output power at 1064 nm serves as the pump source. The incoming pump and the generated signal wave are both resonated in the same cavity, while equal amounts of the generated idler are emitted in both directions. The pump enhancement lowers the external oscillation threshold down to 270 mW and allows us to lock the OPO cavity to the pump laser. A quantum conversion efficiency of 30% yields a maximum idler output power of 2×100 mW. Frequency tuning of the idler wave is performed in three consecutive steps.

1. Coarse tuning between 2.35 and 3.75 µm is performed by selecting one of the 33 quasi-phase-matched gratings ($\Lambda = 28.98$–$30.9\,\mu$m) via a motor-driven translation stage.
2. Temperature tuning of the PPLN between 140 and 170 °C shifts the gain curve of the quasi-phase-matched parametric process, yielding complete spectral coverage.
3. Fine tuning can be performed by tuning the pump laser (9-GHz mode-hop-free, 40 GHz total), resulting in tuning of the idler wave (maximum of 200 MHz limited by mode hops in the PR-SRO cavity, see below).

A dichroic mirror separates the idler beam emitted through the concave cavity mirror from residual pump and signal radiation. This beam is fed into a wavemeter which measures the wavelength with 1-ppm accuracy. The idler beam in the backward direction is focused into a 40-mm-long germanium acousto-optic modulator. The deflected beam is mode-matched into the LOC by a telescope. The transmission through the cavity is monitored with a liquid-nitrogen-cooled InSb photodiode. The AOM also serves as an isolator for back-reflections from the LOC into the OPO. The CALOS cell is a stainless-steel tube which contains a 52.5-cm-long, high-finesse cavity formed by two 6-m radius of curvature mirrors, one of which is controlled by a piezoelectric actuator. The mirror reflectivity of 99.98% results in leak-out time constants up to 13 µs, corresponding to an effective optical path length of 3.9 km. A flow- and pressure-control system allows us to prepare different mixtures of certified trace gas with grade 5 nitrogen flowing through the cell at adjustable constant pressures.

Leak-out signals are obtained in the following way:

The AOM serves three purposes: interruption of the cavity excitation to detect the leak-out signal, controlled frequency tuning of the idler beam across the cavity resonance and reduction of the idler amplitude to match the characteristics of the existing leak-out detection system. A radio-frequency (rf) synthesizer generates a 90-MHz signal which is frequency-modulated with 1-MHz depth at a 90-Hz rate. This rf signal is added to the idler beam by the AOM, forming a deflected beam. The efficiency of the AOM was reduced such that only 2 mW were deflected in order not to saturate the detection system, which had been designed for the low-power emission of the CO overtone laser sideband spectrometer (typically 200 µW). Figure 2 shows the time-dependent detector signal when the idler beam is swept across the resonance of the LOC using the AOM. The beam excites the LOC every time the

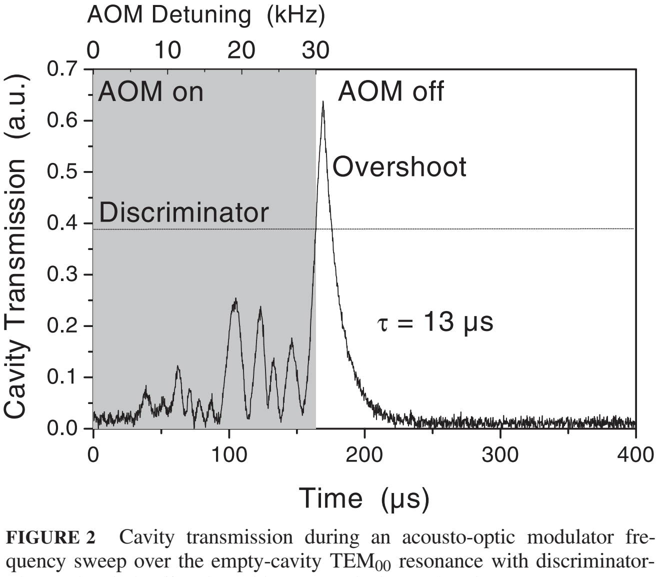

FIGURE 2 Cavity transmission during an acousto-optic modulator frequency sweep over the empty-cavity TEM$_{00}$ resonance with discriminator-triggered switch-off and resulting power leak-out signal

frequency matches a cavity mode. The fluctuations of the signal before the leak-out are due to cavity excitations by the jitter of the OPO. Once the detector signal reaches a preset voltage threshold during the sweep, a negative gate signal triggers the rf synthesizer to shut off the AOM. After a delay time caused by the electronics the input beam is switched off and the exponential leak-out of the standing optical wave is detected. The data is collected by a 12-bit analog/digital converter card. A slow-feedback loop acting on the piezoelectric transducer locks the TEM_{00} mode of the cavity to the mid-frequency of the sweeping idler beam. 50 leak-out events are averaged and only the exponentially shaped part of the transient is taken for the Levenberg–Marquardt fitting routine in order to eliminate errors resulting from the switch-off delay and overshoot.

To get approximate information [20] on the line width of the OPO idler beam, the LOC is used as a fixed-frequency interferometer. The idler beam is swept across the resonance using the AOM at 90 Hz and with a 1-MHz modulation depth. Integrated over 2 s, the envelope of the LOC transmission signal is a Gaussian curve with a FWHM of 56 kHz, indicating that the OPO line width is broader than the cavity line width (18 kHz) but still sufficiently narrow to significantly excite the cavity modes.

2.2 *Trace-gas monitoring*

The performance of the OPO-CALOS system was tested with stepwise-reduced concentrations of ethane between 75 ppb and zero in grade 5 nitrogen. The measurements were carried out at a total pressure of 100 hPa keeping a constant overall flow rate of 2.4 l/h. The absorption spectrum of ethane at 100 hPa had been measured before with a Fourier transform infrared (FTIR) spectrometer with 0.0025-cm^{-1} resolution [21]. The OPO was frequency-tuned to an idler emission vacuum wavenumber of 2990.096 cm^{-1}. As indicated in Fig. 3, this coincides with approximately the half-maximum of the ethane absorption feature formed by the lines of the ${}^{r}Q_1$ subbranch. (Why we did not tune to the maximum is discussed below.) The leak-out time constants τ were measured with a sampling time of 270 ms. The absolute absorption coefficients α are calculated using the relationship:

$$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) , \qquad (1)$$

where c is the vacuum speed of light and the empty-cell leak-out constant τ_0 was measured while only grade 5 nitrogen was flowing through the cell (see Fig. 4: signals at $t > 300$ s). The resulting time series of absorption coefficients is translated into concentrations using the absorption cross sections determined from an FTIR spectrum at the same wavenumber, pressure and temperature (Fig. 3) [21]. The measured concentrations follow the preset values within the gas-exchange time of the CALOS cell (see Fig. 4). The 1σ noise of τ_0 implies a noise-equivalent level of absorption of 4.8×10^{-9} /cm$\sqrt{\mathrm{Hz}}$. The $1/\sqrt{t}$ dependence of the standard deviation allows further averaging for up to 16 s to reach a noise equivalent of $\alpha = 1.2 \times 10^{-9}$ /cm. This corresponds to a concentration noise of 300 ppt ethane at this particular (nonoptimal) idler frequency. This sensitivity is comparable to the 500 ppt in 5 s achieved with the sideband CO overtone laser system and better than the 1 ppb minimum detection limit reported for the DFG laser system [10, 12]. Recently, Van Herpen et al. reported a detection limit for ethane of 10 ppt using a continuously tunable OPO with photoacoustic detection and scanning over a 0.4-cm^{-1}-wide absorption feature of ethane around 2996 cm^{-1} [17]. This very low detection limit did rely, however, on the assumption of a very stable background signal, which was two orders of magnitude larger than the photoacoustic signal generated by the gas at the detection limit.

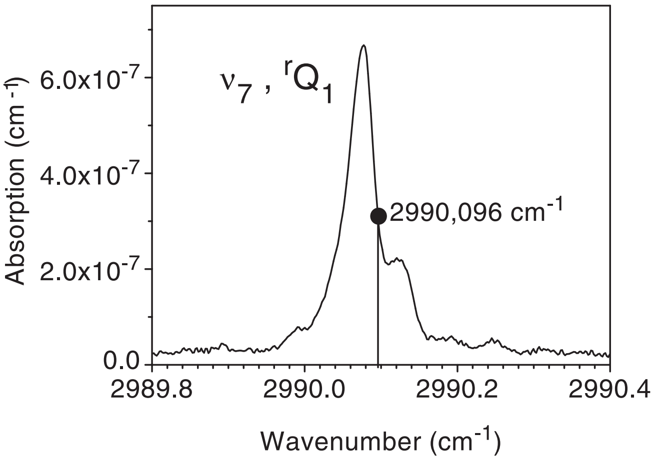

FIGURE 3 Room-temperature FTIR spectrum of ethane at a pressure of 100 hPa around 2990 cm^{-1} (${}^{r}Q_1$ subbranch of the ν_7-band) scaled from 500 ppm to 75 ppb. The *line* indicates the frequency position of the idler wave during the measurement shown in Fig. 4

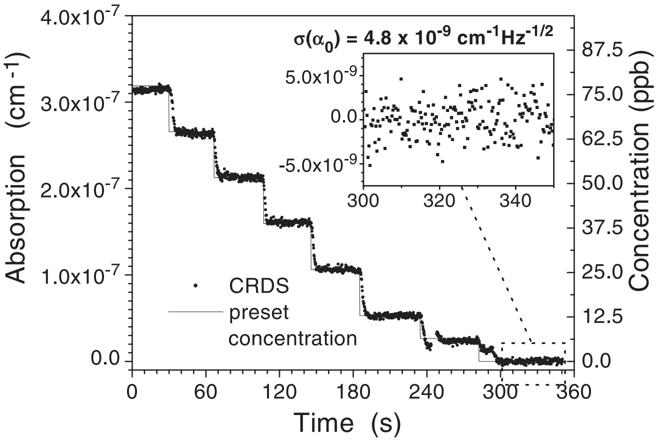

FIGURE 4 Time series of the measured absorption (*dots*) while a stepwise-diluted ethane concentration (*solid line*) flows through the CALOS cell (total flow: 2.4 l/h, pressure: 100 hPa); *left y-axis*: absorption; *right y-axis*: corresponding concentration (calculated from FTIR, see Fig. 3); 50 shots averaged to one data point; *inset*: data points during grade 5 nitrogen flow taken to calculate a noise-equivalent absorption of $\alpha = 4.8 \times 10^{-9}$ /cm$\sqrt{\mathrm{Hz}}$

3 Discussion

The results presented here justify the use of the cw-OPO as an all-solid-state laser source for CALOS, although more attention has to be paid to tunability and stability by a careful design of the OPO cavity compared to DFG systems, where one of the pump lasers provides for the frequency tunability. The OPO carries potential for even better performance by using its full frequency-tuning abilities and by adjusting the detector, electronics and data-acquisition schemes to a higher power level, which in our experiment was significantly reduced (2 mW) to avoid overload of any of the components. Frequency tuning of the idler wave to the maximum absorption would increase sensitivity by a factor of 2.5 (at the maximum of the ${}^{r}Q_0$ subbranch at 3000 cm^{-1}). In our case this was hindered by mode hops of the signal wave in the order of 50 GHz between local maxima of the gain curve. This restriction is most likely due to local perturbation in the intracavity surface of the PPLN crystal. Similar effects have been reported before for this type of short PR-SRO cavity. Possible solutions are the introduction of an intracavity etalon acting only on the signal wave in an elongated cavity [18] or the separation of the common (signal and pump wave) cavity into two independent cavities [22]. Such a dual-cavity setup will allow 9-GHz-wide smooth tuning by the pump laser and stable performance at any point of the spectral range.

In conclusion, we demonstrated for the first time that a cw-OPO is an attractive source for ultra-sensitive detection of trace gases using CALOS. The narrow line width and good frequency stability allowed an efficient excitation of the leak-out cavity. With these first experiments a sensitivity for ethane of 300 ppt was achieved. The high power has the potential to lead to sensitivities in the order of 10^{-10}/cm, i.e. below 100 ppt for ethane. The wide spectral emission range and portability of cw-OPOs offer the perspective to implement portable multi-gas-analysis systems suitable for field use.

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