Comb-assisted cavity ring-down spectroscopy for ultra-sensitive traceable measurements of water vapour in ultra-high purity gases

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Comb-assisted cavity ring-down spectroscopy for ultra-sensitive traceable measurements of water vapour in ultra-high purity gases

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Abstract. We report on the development of a comb-assisted cavity ring-down spectrometer for trace water mole fraction determinations in high purity gases. By tuning the laser light in coincidence with a H_2O absorption line at 1.3946 μm, we were able to determine sub-ppm relative concentrations of water vapour in N_2 with a sub-percent statistical uncertainty. The sensitivity of the spectrometer was carefully assessed, yielding a detection limit of about 2 nmol/mol.

1. Introduction

The measurement of the amount of water in air and other gaseous environments is of great need in several fields, including climate change research [1], materials science [2], and combustion studies [3]. Frequently, humidity measurements play an important role also for the aims of industrial process control. For instance, the fabrication of semiconductor devices requires complicated equipment in conjunction to high purity process gases, thus placing considerable demands on the performance of the gas handling systems. Specifications from the semiconductor industry are that the bulk gases (usually N_2, O_2, H_2, He and Ar) must have a residual water content that typically ranges from 5 μmol/mol to 5 nmol/mol [4]. In some particular cases, this request drops down to 1 nmol/mol. In fact, even at trace levels, water strongly influences electrical, chemical and mechanical properties of materials, impacting on the quality and performance of the semiconductor devices. Moreover, as water is a polar molecule, it is adsorbed on surfaces and then desorbed into any gas flow, thus making water vapour a problematic contaminant that cannot be effectively removed by purging with inert gases. Furthermore, high purity gases may still be contaminated when they pass through the gas distribution system, with severe consequences for the industrial processes themselves. For all the reasons mentioned above, significant efforts have been done by the scientific and industrial communities towards the improvement of measurement techniques, especially in terms of the achievable sensitivity. However, despite the enormous demand of capability of detecting very low water concentrations, available instruments are often limited by large uncertainties, low detection limits, and slow response time. In this respect, laser-based methods can be considered a valuable alternative to more conventional methods, such as capacitance-based sensors [5], ionization mass
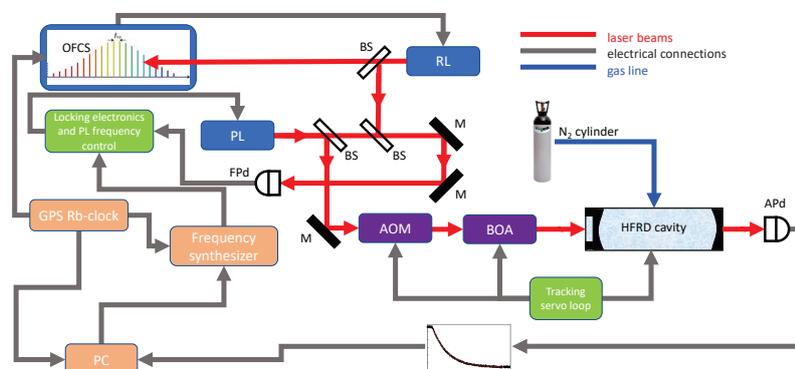
Figure 1. Schematic diagram of the CA-CRDS. OFCS stands for optical frequency comb synthesizer; RL, reference laser; PL, probe laser; BS, beam splitter; M, mirror; HFRD cavity, high-finesse ring-down cavity; FPd, fast photodiode; AOM, acoustic-optic modulator; BOA, booster optical amplifier; APd, avalanche photodetector; PC, personal computer.

spectroscopy [6], and dew-point chilled-mirror hygrometers [7]. In particular, cavity-enhanced absorption spectroscopy represents a very powerful method for ultra-sensitive gas detection and measurement with a high selectivity to a specific molecule, thus receiving an ever-increasing interest. Among the various techniques, cavity rind-down spectroscopy (CRDS) has proven to be a valuable tool for water detection in trace amounts, as shown in Refs. [8, 9, 10, 11], just to cite a few examples.

In recent years, CRDS is also benefiting from the use of near-infrared optical frequency combs synthesizer (OFCS). Because of their fine, discrete and stable spectral structure, OFCSs represent the ideal tool to be combined with CRDS to achieve high precision and accuracy, along with high sensitivity. In more detail, the use of CRDS in the detection of individual water lines with a comb-referenced probe laser enables for absolute determinations of the molecular number density, while preserving the highest levels of sensitivity.

Here, we report on the preliminary results of trace water measurements performed by means of a comb-assisted cavity ring-down spectrometer (CA-CRDS), working at the wavelength of 1.39 μm. With the spectrometer operating at 7170.277881 cm^{-1}, namely in coincidence with the H_2O $3_{2,2} \rightarrow 2_{2,1}$ transition of the $\nu_1 + \nu_3$ rovibrational band, we demonstrated the measurement of water vapour amount fractions down to 670 nmol/mol, with a statistical uncertainty of 4 nmol/mol. Furthermore, we show that, in its present configuration, the spectrometer can guarantee a detection limit as low as 1.9 nmol/mol.

2. Experimental setup
Fig. 1 shows a simplified sketch of the CA-CRDS. It represents an updated version of the setup reported in Ref. [11], already described in Ref. [12] to which we refer for a more thorough description.

Briefly, the optical layout consists of four modules: (*i*) an OFCS, traceable to a 10-MHz GPS-disciplined time base signal provided by a Rb-clock; (*ii*) a 10-kHz linewidth external-cavity diode laser (ECDL) that acts as a reference laser (RL), being locked to one of the comb teeth with an offset frequency, f_{BEAT}, of 20 MHz; (*iii*) a probe ECDL (PL), phase-locked to the RL, which is used for the interrogation of the gaseous samples; and (*iv*) a high-finesse ring-down (HFRD) optical cavity equipped with a tracking servo-loop circuit so that it can follow the PL while its frequency is scanned across a selected transition.

The HFRD cavity consists of two plano-concave high-reflectivity mirrors, spaced 43 cm apart
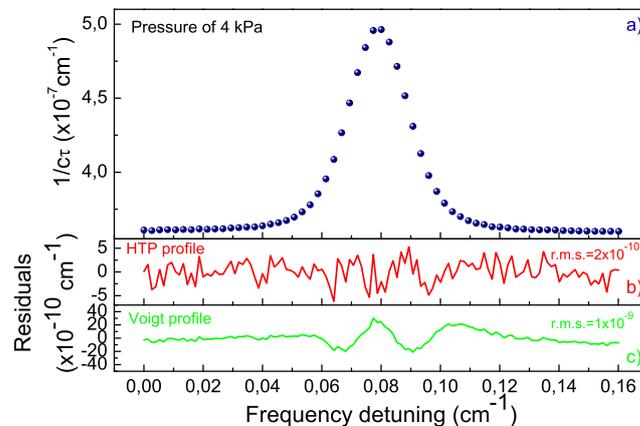
Figure 2. Panel (a): example of a CRDS spectrum of the water transition at a pressure of 4 kPa. Panel (b): example of residuals as a result of a fit to a HT profile. Panel (c): Same of panel (b) using a Voigt convolution.

by a Zerodur block, one of them being equipped with a piezo transducer for a fine tuning of the cavity length. The ring-down time under vacuum conditions was 96 μs (corresponding to a finesse of about 210000), while the cavity-mode width was 1.7 kHz. At the output of the cavity, an InGaAs avalanche detector (APd) monitored the light emerging from the resonator. The output signal of the APd was also used as input to a threshold detector, in order to monitor whether a resonance condition takes place while scanning the PL frequency. The threshold detector unit was part of the tracking servo-loop circuit that allows for high-resolution spectral acquisitions. The cavity was also equipped with a calibrated pt-100 thermometer and an absolute pressure gauge with a full scale of 13330 Pa, both having an accuracy of 0.05%.

A portion of the PL probe laser, after passing through an acousto-optic modulator (AOM), was amplified by a Booster Optical Amplifier (BOA) up to about 20 mW and then coupled to the HFRD cavity. The AOM, which produces a first-order diffracted beam with an up-shifted frequency f_{RF}=80 MHz, was also used as optical switch to initiate ring-down decays. An acquisition board with a 16-bit resolution was used to record the ring-down events.

The beat-note signal between the RL and the PL, as obtained by means of a 12-GHz bandwidth photodetector, was used for a tight lock of the two lasers. This latter was implemented with a variable offset (f_{OFF}, provided by a radio-frequency synthesizer) that could be controlled with the desired resolution in order to perform frequency scans of the PL around an arbitrary center frequency [13]. The frequency of the PL was given by $f_{PL} = N \times f_{REP} + f_{CEO} + f_{BEAT} + f_{RF} + f_{OFF}$, where N is the comb tooth order, $f_{REP} = 250$ MHz and $f_{CEO} = 20$ MHz are the OFCS repetition rate and carrier envelope offset frequency, respectively.

A LabView code was used to control the radio-frequency synthesizer, the data acquisition board, to collect ring-down events, and to record the gas pressure and temperature.

3. Results and discussion

Panel (a) of Fig. 2 reports the absorption spectrum of the $3_{2,2} \rightarrow 2_{2,1}$ H$_2$O line, belonging to the $\nu_1 + \nu_3$ band, recorded under a continuous flux of high-purity N$_2$ into the cavity, while keeping the pressure to the constant value of 4 kPa. The spectrum encompasses 120 spectral points over a range of 4.8 GHz and was obtained by uniformly stepping f_{OFF} at every 250 ms, thus reaching an overall acquisition time of 30 s. The loss per unit-length was calculated according to the well known CRDS equation $\frac{1}{c\tau(\nu)} = \alpha(\nu) + \frac{1}{c\tau_0}$, where τ (in s) is decay time, ν is the frequency of the PL (in cm^{-1}), c is the speed of light (in cm/s), $\alpha(\nu)$ (in cm^{-1}) is the absorption coefficient of the gas sample, and τ_0 is the ring-down time under vacuum conditions. It is worth noting that each of the spectral point of Fig. 2 comes from the average of five consecutive decay times.
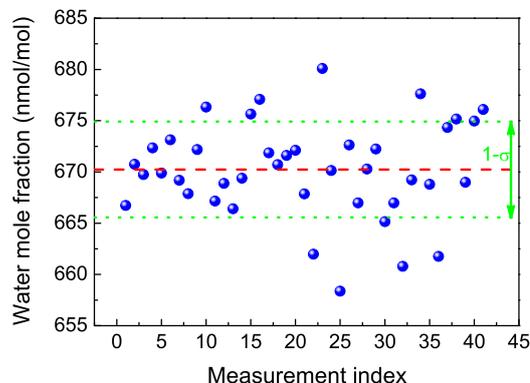
Figure 3. Example of short-term reproducibility in the X_W determination, as resulted from forty repeated measurements.

$\alpha(\nu)$ was modeled by means of the sum of a normalized Hartmann-Tran (HT) profile [14], $g_{HTP}(\nu - \nu_0)$, and a linear term on ν to take into account a possible slightly dependence of the mirrors' reflectivity on the laser wavelength. In details, $\alpha(\nu) = (P_0 + P_1\nu) + \alpha_{TOT} \times g_{HTP}(\nu - \nu_0)$, being α_{TOT} the integrated absorption coefficient which is proportional to the partial pressure of the residual water in the gaseous sample.

Panel (b) of Fig. 2 shows an example of fit residuals, whose root-mean-square (r.m.s.) value results to be 2×10^{-10} cm^{-1}, limited only by the experimental noise. For the fitting of an isolated line to a HT profile, eight parameters have to be considered [14]. In particular, they are the unperturbed line center frequency, ν_0, the Doppler width, Γ_D, the collisional width, Γ_L, the collisional shift, Δ, the velocity-changing collision frequency, β, the speed-dependent parameters for width, a_W, and shift, a_S, and the correlation parameter, η. As far as the analysis of the spectrum of Fig. 2 is concerned, Δ and a_S were fixed to zero since no asymmetries could be evidenced in the spectra, Γ_D was kept to the constant value corresponding to the measured temperature, β, η, and a_S were constrained to 1.54×10^{-8} cm^{-1}/Pa, 0, and 0.141, respectively, according to the finding of Ref. [15]. The remaining parameters (ν_0 and Γ_L) were considered as free, along with α_{TOT}, P_0 and P_1. It is worth noting that the r.m.s of the residuals was always comparable to the value reported above, regardless of the gas pressure.

We have also considered the possibility of using a simpler line shape model, namely a Voigt convolution. However, as shown in panel (c) of Fig. 2, the Voigt profile was incapable of fitting the recorded spectrum, yielding an overly broad profile, as evidenced by the clear "W" structure in the residuals. As already shown in Ref. [9], this occurrence justifies the use of a line shape model more sophisticated than the Voigt profile.

Once α_{TOT} is determined, the water mole fraction, X_W, could be easily determined according to the equation [16]:

$$X_W = \frac{\alpha_{TOT} k_B T}{pS} \tag{1}$$

k_B being the Boltzmann constant, S the line strength of the considered transition, T and p the measured temperature and gas pressure, respectively. For the aim of this work, we used for S the value provided by Lisak *et al.* [15], namely 2.0158×10^{-21} cm/molecule.

In order to test the capabilities of the CA-CRDS spectrometer, in terms of reproducibility, X_W was determined from the acquisition of several repeated absorption spectra. An example is shown in Fig. 3, where the results of 40 determinations are reported. All the measurements were performed with a gas flowing through the cell of about 2 l/min, with a constant pressure of 13 kPa. Such a flow was produced by using a pressure-forward controller and a diaphragm pump (not shown in Fig. 1). This was done to reduce sticking of water molecules on the cavity walls. The gas was sampled from a high-purity N$_2$ cylinder having a nominal purity of 99.9999% and a nominal value of the residual water content of 500 nmol/mol. We found a 1-σ reproducibility

of 4 nmol/mol, while the mean value was 670 nmol/mol. This result is not far to the expected one.

An important parameter that is useful to quantify is the minimum detectable water mole fraction, namely, the detection limit (DL). DL is proportional to the minimum absorption coefficient, α_{min}. In particular, the minimum detectable water mole fraction is $X_{Wmin} = \frac{\alpha_{min}k_BT}{pSg_{HTP}(0)}$ [17]. As for the experimental conditions of the X_W determinations of Fig. 3, assuming for α_{min} the mean value of the r.m.s. of the residuals of the repeated CRDS spectra, we could infer an X_{Wmin} of 1.9 nmol/mol.

4. Conclusions

We reported on the recent progress regarding the development of a comb-assisted cavity ring-down spectrometer, operating at 1.39 μm, for water mole fraction determinations. Based on the use of a pair of phase-locked extended cavity diode lasers, one of them being locked to a self-referenced optical frequency comb synthesizer, the apparatus allowed us the recording of high quality H_2O absorption spectra in high purity N_2 gas samples. We demonstrated the measurement of water vapour mole fractions of 670 nmol/mol with a statistical uncertainty of 4 nmol/mol. A detection limit as low as 1.9 nmol/mol have been also derived at a total gas pressure of 13 kPa. Such a detection limit corresponds to a H_2O molecular density of $5.9{\times}10^9$ molecules/cm^3, or to a partial pressure of $2.5{\times}10^{-5}$ Pa.

Further improvements in terms of sensitivity could be obtained in the near future moving the laser wavelength in correspondence of stronger water transitions. In particular, the $3_{0,3}{\rightarrow}2_{0,2}$ transition at 7183.01579 cm^{-1}, having a line intensity that is in the order of 10^{-20} cm/molecule, could allow to extend the detection limit to few hundred of pmol/mol.

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