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Broad-Range Detection of Water Vapor using Cavity Ring-down Spectrometer[†]

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Quantitative measurement of water vapor is essential in many fields including semiconductor industry, combustion diagnosis, meteorology, and atmospheric studies. We present an optical hygrometer based on cavity ring-down spectroscopy. The instrument is high-vacuum compatible, self-calibrated by using the free-spectral-range of the ring-down cavity made of low-thermal-expansion Invar. Using a single tunable diode laser working at 1.39 μm, detection of trace water vapor in vacuum and in high-purity helium gas, and also determination of humidity at ambient conditions, have been demonstrated. It indicates that the instrument can be used to detect the partial pressure of water vapor in a very broad range from 10^{-7} Pa to 10^3 Pa. Such an optical hygrometer can be potentially applied as a primary moisture standard to determine the vapor pressures of water (ice) at low temperatures.

Key words: Cavity ring-down, Water vapour, Ro-vibrational spectroscopy

I. INTRODUCTION

Detection of water vapor is of great needs in many fields including semiconductor industry, pure gas supply, petrochemistry, combustion analysis, meteorology, and environmental studies. However, due to the ubiquity of water, its strong interactions with metals, and lack of moisture-containing standard gases, it is still difficult to quantitatively determine trace water content in samples. Among miscellaneous methods used in different applications [1], condensation hygrometers, which measure the dew-point temperatures [2], may be most widely used in meteorology and atmospheric studies [3]. Dew-point hygrometers measure the absolute humidities, and they are often used to calibrate other humidity sensors [4]. Typical dynamic range of dew-point hygrometers is $-100°C$ to the room temperature, corresponding to a water vapor pressure of $10^{-4}-10^4$ Pa. Usually, the water vapor pressure (P_w) can be determined with a relative uncertainty of less than 1%, but the precision gets much worse at very low humidities ($P_w<0.1$ Pa, or dew-point below $-70°C$). In fact, the vapor pressures of water (ice) at such low temperatures have not yet been well determined [5].

Optical methods based on the spectroscopy of water molecules attract more and more interests in recent years [1]. In general, these methods measure the absorption spectrum at a transition of the water molecule. Under ideal gas conditions, the water content can be determined from the integrated absorption coefficient:

$$\int \alpha(\nu)d\nu = SN_w = \chi_w SN_0 \tag{1}$$

where $\alpha(\nu)$ is the observed absorption coefficient at frequency ν, S is the strength of the absorption line in cm/molecule, χ_w is the relative concentration of the water vapor, N_w and N_0 are the number densities of water molecules and the carrier gas, respectively. Therefore, provided an accurate line strength, which is only related to the intrinsic character of the water molecule and independent of any bulk quantities, absolute water content can be determined, regardless of the total pressure. Therefore, it can be potentially applied as a primary standard for moisture detection. In recent years, different types of optical hygrometers have been demonstrated. Fourier-transfer infrared (FTIR) spectroscopy is effective in multiple gases analysis [6], tunable diode laser absorption spectroscopy (TDLAS) is relatively simple and robust [7–9], and cavity ring-down spectroscopy (CRDS) has great enhancement in sensitivity [10–14]. The reported detection limit of water vapor varies from a few ppbv (part per billion by volume) to several hundred pptv (part per trillion by volume).

In principle, optical hygrometers can detect water concentrations with a wide range by using absorption

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lines with very different line intensities. Such a broad-range humidity detector will not only extend the sensitivity at lower water content, but also allow easy calibration by standard dew-point hygrometers. Moreover, such a spectrometer can also be used to precisely determine the line strength of water molecules (including the isotopologues) if the partial pressure of water vapor is given [15, 16]. In turn, the determined line strengths can be used to extend the cover range of hygrometers based on absorption spectroscopy.

In this work, we present a CRDS instrument for quantitative moisture detection. It is designed to compare with the primary trace-moisture standard under built in Chinese Meteorological Observation Centre. A low-cost distributed-feedback (DFB) diode laser at 1.39 μm is used to take the advantages of mature light sources and detectors. By detecting different transitions of the water molecule, it can cover a very broad detecting range from 10^{-7} Pa to 10^3 Pa. Ultra-high-vacuum compatible, can be directly connected with a vacuum system, and also used at ambient conditions, which allows wide applications in different circumstances.

II. EXPERIMENTAL SETUP

The configuration of the CRDS setup is presented in Fig.1. A DFB diode laser (NEL NLK1E5GAAA) with central wavelength of 1.39 μm is used as the light source. A beam of about 10 mW is coupled into a high-finesse ring-down (RD) cavity. The 100 cm long RD cavity is made of Invar to reduce the thermal expansion, and installed in a stainless steel chamber ended with ConFlat flanges. The chamber is temperature controlled by a feed-back loop, to keep the RD cavity at about 30 °C with a temperature drift below 0.003 K. The high-reflectivity (HR) mirrors (R=99.998%) can be aligned by a set of step-motors (Newport PicoMotor) using a controller outside the chamber. The laser frequency can be scanned in a step mode by controlling the injection current and the operation temperature. The light emitted from the RD cavity is detected by an avalanche photo-detector. Once the detected signal is larger than a preset threshold, a trigger signal will be produced and delivered to switch off the input laser beam by an acoustic-optical modulator (AOM). The trigger signal also trigs a digitizer installed in a personal computer to record the ring-down event.

The spectral scan is controlled by a program [17] to tune the laser frequency resonant to each longitudinal mode of the RD cavity, with a step frequency being equal to the free spectral range of the cavity (0.005 cm^{-1}). Therefore, the recorded spectrum is readily calibrated. The low-thermal-expansion character of the Invar cavity allows long-term operation without frequency jitters. On each frequency step, typically 20 ring-down events are recorded. A fitting procedure is applied to fit the recorded data using an exponential
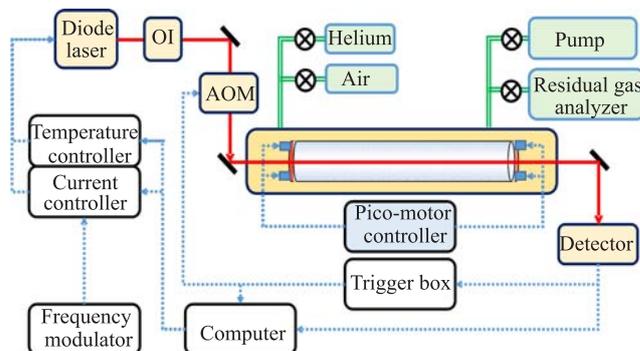

FIG. 1 Experimental setup for humidity measurement with a CRDS instrument. AOM: acoustic-optical modulator, OI: optical isolator.

function to obtain the decay time τ. The absorption coefficient of the gas sample, α, can be derived from the equation [18]:

$$\alpha(\nu) = \frac{1}{c\tau(\nu)} - \frac{1}{c\tau_0} \qquad (2)$$

where c is the speed of light, ν is the laser frequency, τ and τ_0 are the decay time of the cavity with and without sample, respectively.

The photo-detector has a bandwidth of a few MHz, which allows a minimum detectable decay time of a few microseconds without notable nonlinear response. The noise equivalent absorption coefficient is at the level of 10^{-10} cm^{-1}Hz$^{-1/2}$. Therefore, the spectrometer has a linear dynamic range of 1×10^{-10}–5×10^{-6} cm^{-1} in terms of the sample absorption coefficient. Assuming a Doppler-broadening line width of about 0.02 cm^{-1}, the detectable integrated absorption coefficient (see Eq.(1)) is in the range of 10^{-12}–10^{-7} cm^{-2}. In order to extend the detection range of the water concentration, we select different transitions to be used under different partial pressures of water vapor, and they are given in Table I. The line positions, intensities, and ro-vibrational assignments are taken from Ref.[19] and also available in the HITRAN database [20]. These lines are selected because they are well isolated to reduce the interference from other transitions of water or from other major atmospheric molecules. For experimental convenience, they can also be covered by a single laser diode. The integrated absorption coefficients of these lines at different water vapor pressures are shown in Fig.2.

Note that the typical uncertainty of the water line strengths available in most spectroscopy databases, for example, HITRAN [20], is about 2% and even worse for weak lines. However, the humidity can be measured with an accuracy better than 1% with a dew-point hygrometer at moderate humidities. By comparing the result from the CRDS instrument with that from other hygrometers, we can derive line strengths with better precision. In turn, the extended cover range of the CRDS instrument using different water lines can also be

TABLE I Transitions selected for water detection under different partial pressures of water vapor.

Position/cm^{-1}	Strength/(cm/molecule)	Molecule	Transition*	P_w range/Pa
7161.410	1.170×10^{-20}	$H_2^{16}O$	$3_{1,3}(101)\leftarrow4_{1,4}(000)$	$0-0.01$
7152.682	1.364×10^{-22}	$H_2^{16}O$	$4_{3,1}(200)\leftarrow5_{2,4}(000)$	$0.001-1$
7154.766	2.329×10^{-24}	$H_2^{17}O$	$2_{2,0}(101)\leftarrow3_{2,1}(000)$	$0.1-100$
7153.999	2.486×10^{-25}	$H_2^{17}O$	$5_{1,5}(101)\leftarrow5_{1,4}(000)$	$1-1000$

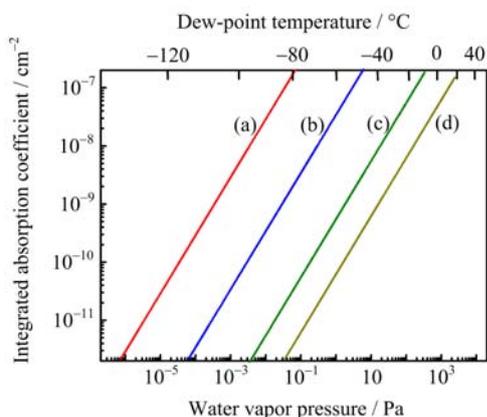* Ro-vibrational notations of upper and lower levels, as $J_{Ka,Kb}(v_1v_2v_3)$.

FIG. 2 Examples of different water lines selected for detecting water vapor concentration. (a) 7161.410 cm^{-1}, (b) 7152.682 cm^{-1}, (c) 7154.766 cm^{-1}, (d) 7153.999 cm^{-1}. Line parameters are given in Table I. The corresponding dew-points are derived according to the water vapor pressures given in Ref.[2].
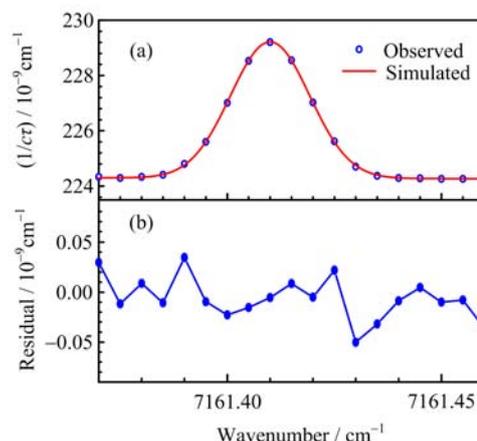

FIG. 3 The absorption spectra of trace water in a high-vacuum chamber. (a) The observed spectrum and the simulated one using a Gaussian profile. (b) The residuals between the observed and simulated spectra.
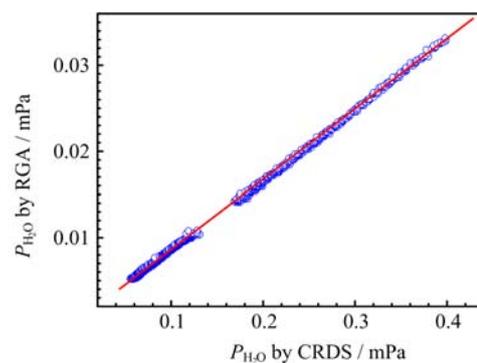

FIG. 4 Water vapor pressures determined by the CRDS instrument and recoded by a commercial residual gas analyzer (Stanford Research Systems RGA 200).

applied to transfer the precision in dew-point measurements to lower humidities while the uncertainty from traditional hygrometers gets larger.

III. RESULTS AND DISCUSSION

A strong $H_2^{16}O$ transition at 7161.41 cm^{-1}, with a line strength of 1.174×10^{-20} cm/molecule, is selected to detect very low water concentrations. Figure 3 shows a sample of the recorded spectrum of trace water in a vacuum chamber. It is an averaged spectrum of 86 scans recorded in about 1.5 h. A water vapor pressure of 5×10^{-5} Pa was derived from fitting the spectrum with a Gaussian function. The simulated spectrum and the fitting residuals are also presented in Fig.3. The noise level shown in Fig.3(b) is 2.5×10^{-11} cm^{-1}, which indicates a water detection limit of 2.5×10^{-7} Pa, or 25 pptv at a total pressure of 10 kPa.

Figure 4 shows the water vapor pressures determined by the CRDS instrument and those recorded by a residual gas analyzer based on a quadrupole mass spectrometer (Stanford Research Systems RGA 200). The data were recorded when the vacuum chamber was pumped by a turbo pump. The water vapor concentrations derived from the CRDS data have an excellent linear correlation with the RGA readings. However, there is a systematic factor of about 10 between the absolute results from CRDS and those from RGA. Actually, the comparison could be used to calibrate the absolute RGA readings.

An advantage of the spectrometer is that it can work under a wide range of pressures, from vacuum to normal pressures. As a demonstration, the water concentration in a pure helium gas (Nanjing Special Gas Ltd., stated
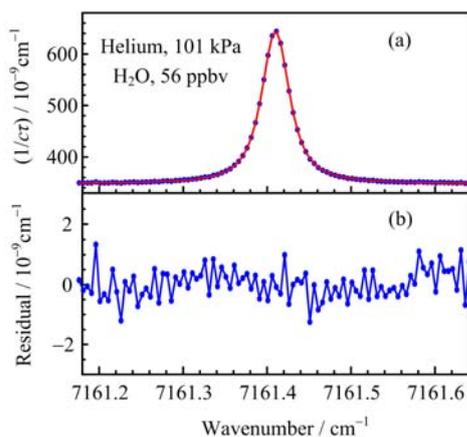

FIG. 5 The absorption spectra of trace water in helium gas. (a) The recorded spectrum and (b) the fitting residuals.
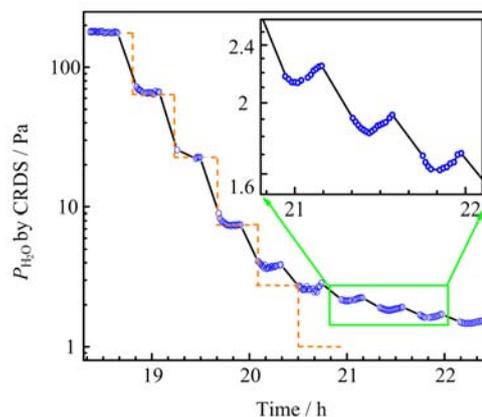

FIG. 6 Partial pressure of water vapor (open circles) measured during a diluting process. The dashed lines show the expected water concentration calculated from the diluting ratio. The increasing of residual water pressure, shown in the inset, is considered as a result of out-gassing from the chamber.

purity of 99.999%) was detected by measuring the water transition at 7161.41 cm^{-1}. Figure 5 shows the observed spectrum. The helium sample pressure in the CRDS chamber is 101 kPa and the partial pressure of water determined from the spectrum is 5.6 mPa, or a relative concentration of 56 ppbv.

In order to demonstrate the capability to measure higher water pressures, we filled the chamber with 40 kPa air, and every twenty minutes we diluted it to about 1/3 with pure dry argon gas. During the procedure, we recorded the spectrum of the water line at 7154.76 cm^{-1} (Table I) to determine the water concentration in the chamber. The results, together with the diagram of the diluting procedure, are shown in Fig.6. When the water vapor pressure got to be lower after several runs of diluting, the residual water concentration was larger than that expected from an ideal diluting. It is a result of out-gassing of water from the walls of the chamber, which is also clearly shown in the inset of Fig.6. Note that the whole chamber is bakeable, allowing detection of lower humidities which has been demonstrated in previous part.

IV. CONCLUSION

We built a cavity ring-down spectroscopy instrument as an optical hygrometer. It is high-vacuum compatible, bakeable, and can be applied either in vacuum condition or at high sample pressures. A few water lines at 1.39 μm, with different line strengths, are used to cover a broad range of water concentrations, from tens of pptv to a few percents. The spectrometer will be used to compare with the primary trace-moisture standard built in Chinese Meteorological Observation Centre. Its broad range coverage makes it very convenient to calibrate other hygrometers and pressure gauges.

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