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# Quantitative Moisture Measurement with a Cavity Ring-down Spectrometer using Telecom Diode Lasers

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Moisture measurement is of great needs in semiconductor industry, combustion diagnosis, meteorology, and atmospheric studies. We present an optical hygrometer based on cavity ring-down spectroscopy (CRDS). By using different absorption lines of $H_2O$ in the 1.56 and 1.36 µm regions, we are able to determine the relative concentration (mole fraction) of water vapor from a few percent down to the $10^{-12}$ level. The quantitative accuracy is examined by comparing the CRDS hygrometer with a commercial chilled-mirror dew-point meter. The high sensitivity of the CRDS instrument allows a water detection limit of 8 pptv.

**Key words:** Cavity ring down spectroscopy, Moisture, Trace detection, Diode laser

## I. INTRODUCTION

Detection of moisture, or humidity in gases is of great needs in various fields. The concentration of water vapor should be below 1 ppmv (part per million by volume, mole fraction) in fabrication of semiconductor and photoelectric devices [1]. There is a great demand of the capability detecting lower moisture levels in reactive gases used in semiconductor industry. Detecting trace moisture in fuels is also needed as a result of the increasing use of fuel ethanol. As a main product in combustion, concentration of water vapor is also a key factor in the diagnosis of flame and combustion processes. Determination of the humidity in ambient air is also of great importance in meteorology and atmospheric studies.

Because of the ubiquity of water, its strong interactions with metals, and lacking of moisture-containing standard gases, it is difficult to quantitatively determine the water content in samples. Miscellaneous methods for moisture detection have been used in different applications. Dew-point hygrometers, which measure the water vapor condensation temperature [2], are widely used in meteorology and atmospheric studies [3]. Chilled-mirror hygrometers can detect a dew-point in the range from $-100$ °C or so to the room temperature, which is equivalent to a water vapor pressure of $10^{-4}-10^4$ Pa (Fig.1), with an accuracy of about 1%RH near the room temperature [4], but the precision gets much worse at very low water concentrations. An at-

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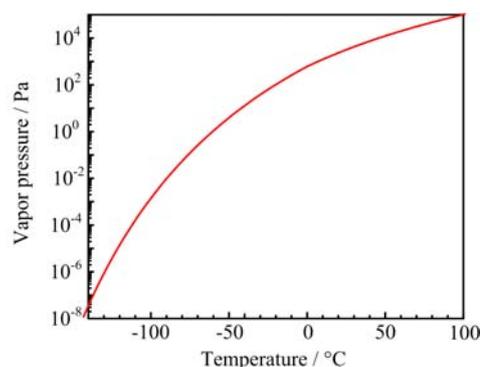*Author to whom correspondence should be addressed. E-mail: smhu@ustc.edu.cn

FIG. 1 Saturation vapor pressure of water calculated according to the formula given in Ref.[2].

mospheric pressure ionization mass spectroscopy could detect $H_2O$ in $O_2$ at the 1 ppbv (part per billion by volume) level [5]. A capacitance-based sensor for detecting trace moisture in gases and organic solvents has also been recently reported [6].

Optical methods based on the spectroscopy of water molecules attract more and more interests, especially in real-time trace moisture analysis [1]. Fourier-transfer infrared (FTIR) spectroscopy is effective in multiple gases analysis and has been applied to detect moisture in electronic specialty gases [7]. In the last two decades, laser-based spectroscopy techniques become more prominent. Tunable diode laser absorption spectroscopy (TDLAS) is relatively simple and robust, therefore has been widely applied [8–10]. Cavity ring-down spectroscopy (CRDS) using cw diode lasers provides great enhancement in sensitivity and receives increasing interests in recent years [11–15]. The reported detection limit of water vapor varies from a few ppbv

to several hundred pptv (part per trillion by volume).

In this work, we present a CRDS instrument for quantitative trace moisture detection utilizing telecom distributed feedback (DFB) lasers. The absorption lines of $H_2O$ near 1.56 and 1.36 μm are used to determine the water concentration in high and low humidity environments, respectively. Such an optical hygrometer can be used to measure water concentration from a few percent down to several pptv. The quantitative accuracy is verified by comparing to a commercial chilled-mirror hygrometer. The instrument can achieve a water detection limit of 8 pptv, which is, to the best of our knowledge, improved by over one order of magnitude compared with those reported optical hygrometers.

## II. EXPERIMENTAL SETUP

The configuration of the CRDS setup is similar to that presented in our previous work [16] and it is shown in Fig.2. A single-mode distributed feedback diode laser is used as the light source. The laser frequency is scanned in a step mode by controlling the injection current and the operation temperature. A beam of about 10 mW is coupled into a high-finesse ring-down (RD) cavity. The cavity mirrors have a reflectivity of 99.998%. 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 delivered to switch off the input laser beam using an acoustic-optical modulator (AOM) and the ring-down event will be recorded by a digitizer installed in a personal computer. On each step of the laser frequency, typically 20 ring-down events will be recorded. A fitting program is applied to fit the recorded data using an exponential function to obtain the decay time $\tau$. The absorption coefficient of the gas sample, $\alpha$, can be derived from the equation,

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

where $c$ is the speed of light, $\nu$ is the laser frequency, and $\tau$ and $\tau_0$ are the decay time of the cavity with and without sample, respectively.

An integration of detected $\alpha$ around a selected absorption line of water molecule should be proportional to the concentration of the molecules in the sample,

$$\int \alpha(\nu)\mathrm{d}\nu = SN \qquad (2)$$

where $S$ is the strength of the line of water in $cm^{-1}/(molecules \cdot cm^{-2})$, and $N$ is the number density of water molecules. Therefore, the percentage of the partial pressure of water in the gas sample can be determined according to the following equation,

$$\chi_{water} = \frac{P_{water}}{P_{total}} = \frac{\int \alpha(\nu)\mathrm{d}\nu}{SP_{total}} \frac{RT}{N_A} \qquad (3)$$
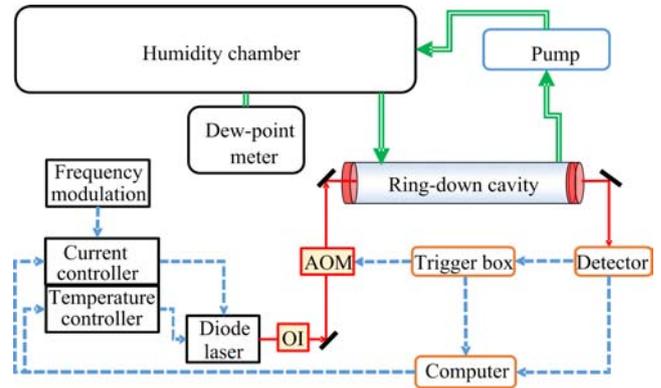
FIG. 2 Experimental setup for humidity measurement with CRDS compared with a chilled-mirror dew-point meter. AOM: acoustic-optical modulator, OI: optical isolator.

where $P_{total}$ is the total pressure of the sample, $N_A$ is the Avogadro constant, $R$ is the molar gas constant, and $T$ is the temperature of the gas sample.

## III. RESULTS

### A. Comparison with a dew-point meter, high humidity measurement

The quantitative accuracy of the CRDS hygrometer was verified by comparing with a chilled-mirror dew-point meter. The experimental setup is presented in Fig.2. A humidity chamber (Vötsch T/C 4-340, volume 335 L) is used to provide air samples with different concentrations of water vapor. The sensor of a chilled-mirror hygrometer (GE optica 1111H) is put in the chamber to continuously monitor the dew-point of the air sample. The ring-down cavity is connected to the humidity chamber using teflon tubes, and a dry pump is used to cycle the gas between the RD cavity and the humidity chamber. Note that both the temperature and pressure in the RD cavity are different from those in the humidity chamber, but the relative concentrations of water ($\chi_{water}$) should be the same. The total pressure in the humidity chamber is set to be 1 atm, while the pressure in the RD cavity is monitored by a capacitance manometer (MKS 627B) which has a relative accuracy of 0.15%.

The absorption line of $H_2^{16}O$ at 6392.2224 $cm^{-1}$, which has a line strength of $2.864 \times 10^{-25}$ $cm^{-1}/(molecule \cdot cm^{-2})$ given in the HITRAN database [17], was used for CRDS determination of the water concentration in the humidity chamber. The line is well isolated and its strength is suitable in the case of a relatively high water concentration. Both the CRDS measurements and the dew-point meter results have been collected at different temperatures and humidities, and are shown in Fig.3. Since the best performance of the humidity chamber can be achieved around the room temperature and at a
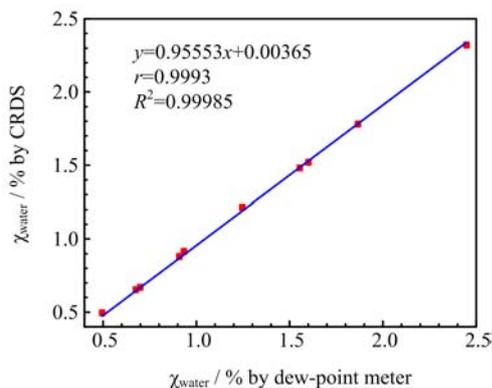
FIG. 3 Relative partial pressure of water vapor in the humidity chamber measured by CRDS and the dew-point meter.
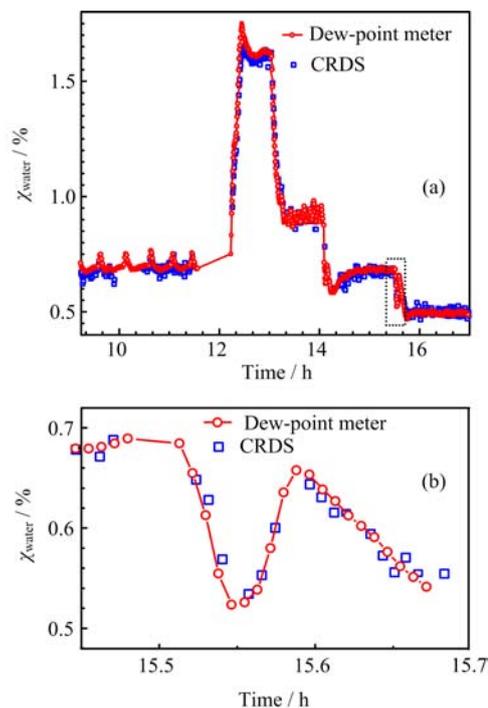


FIG. 4 (a) Five hours continuous measurement of the relative water concentration in a humidity chamber using a CRDS instrument and a dew-point meter. (b) Magnified picture of the data obtained around 15.6 h.

moderate humidity, the temperature was set $10-25$ °C and relative humidity was set between 30% and 70% RH.

It is clearly shown in Fig.3 that the CRDS determined relative concentration of water has an excellent linear correlation to that given by the dew-point meter. However, there is a systematic deviation of about 4.4% between them. Since the dew-point meter has a relative accuracy of 1% and the statistical uncertainty of the CRDS measurement is below 0.5%, the systematic deviation between the CRDS and dew-point meter results most likely comes from the uncertainty in the strength of the water line. As stated in the HITRAN database [17], the relative uncertainty of the line strength is 5%−10%. If we use a corrected line strength of $2.738\times 10^{-25}$ cm$^{-1}$/(molecule·cm$^{-2}$), instead of the value given in HITRAN, the relative deviation between the CRDS and dew-point meter results is only about 0.4%.

When we changed the condition of the humidity chamber, we recorded the CRDS spectrum once every one minute, and a program was applied to fit the spectrum to calculate the integrated absorption coefficient in real time. Both the CRDS results and dew-point meter data have been recorded and are shown in Fig.4. Apparently, they agree with each other throughout the whole process, and it is also illustrated in Fig.4(b). The relative deviation between both methods is at a level below 1%, which agrees with the relative accuracy of the dew-point meter and the control precision of the humidity chamber. One can also notice that there is a little delay between the CRDS results and the dew-point meter data. The reason is as the following: when the condition is changing in the humidity chamber, the dew-point meter responses immediately since the sensor is located in the chamber, while the change will not be detected by CRDS until the sample in the ring-down cavity has been refreshed. The delay time, about one minute in our case, is related to the pumping rate and the volume of the RD cavity (about 1 L).

## B. Low humidity, detection limit of water vapor

In the case of very low water concentration beyond the capability of the humidity chamber, a different but stronger water line is selected for CRDS measurement to maintain a sufficient sensitivity and precision. Figure 5 shows a CRDS detected water line at 7331.2435 cm$^{-1}$, which has a line strength of $1.238\times10^{-22}$ cm$^{-1}$/(molecule·cm$^{-2}$) given in the HITRAN database [17], about 450 times stronger than the line mentioned in Fig.3. The sample was pure nitrogen gas, continuously flowing through the RD cell. Using the line strength given in the HITRAN database, we can determine that the partial pressure of the water vapor in the cell was 0.395 Pa, corresponding to a water concentration of about 39.5 ppmv.

The detection limit is proportional to the minimum detectable absorption coefficient $\alpha_{\min}$:

$$\chi_{\min} = \frac{\alpha_{\min}}{SP_{\text{tot}}\phi_0}\frac{RT}{N_{\text{A}}} = \gamma\alpha_{\min} \tag{4}$$

where $\chi_{\min}$ is the minimum detectable concentration of the water vapor, $\gamma$ is the proportional coefficient, $S$ is the strength of the selected absorption line of $H_2O$, and $\phi_0$ is the height of the normalized line profile. In the case of a Gaussian profile,
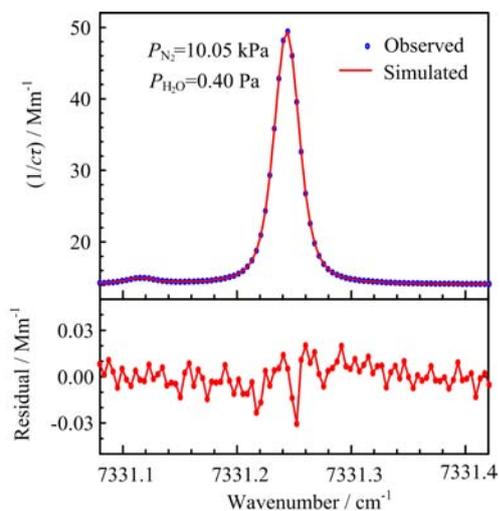
$$\phi_0 = \frac{\sqrt{4\ln 2/\pi}}{\Delta} \tag{5}$$

FIG. 5 An absorption line of water at 7331.24 cm$^{-1}$ detected by the CRDS instrument. Water vapor presents as impurity in a nitrogen gas sample. The determined partial pressure of water is 0.40 Pa. Upper panel: observed and the simulated spectra, lower panel: fitting residuals.

where $\Delta$ is the full width at halm maximum (FWHM). In the 1.36 $\mu$m region, a typical strong water line has a strength of $1 \times 10^{-20}$ cm$^{-1}$/(molecule·cm$^{-2}$), and if a total gas pressure of about 10 kPa is applied, the line profile can be well described by a Gaussian function with a FWHM of about 0.02 cm$^{-1}$. Therefore, we can get a $\gamma$ of about 0.8 cm. In this case, at a noise level of $\alpha_{min} = 1 \times 10^{-10}$ cm$^{-1}$ (as that shown in Fig.5), the corresponding water detection limit is 80 pptv. The sample pressure of 10 kPa is selected for optimized sensitivity and avoiding line overlapping. At a higher sample pressure, the pressure broadening could be dominant. If we cannot pump the RD cavity cell to the optimized pressure, for example, in an *in situ* measurement, a broader spectrum should be recorded. If the selected water line does not overlap with other lines, the integrated line absorption can still be used for quantitative analysis.

The detection limit of CRDS can be further improved by multiple spectrum averaging. Figure 6 shows an example of the averaged spectrum of $H_2O$ near 7335.7 cm$^{-1}$. After averaging over 100 spectra recorded in about 2 h, the noise level decreases by one order of magnitude, from $1 \times 10^{-10}$ cm$^{-1}$ to $1 \times 10^{-11}$ cm$^{-1}$. As a result, it corresponds to a water detection limit of 8 pptv.

## IV. CONCLUSION

We built a cavity ring-down spectroscopy instrument based on telecom DFB fiber lasers as an optical hygrometer. The concentration of water vapor is determined by measuring the absorption lines of $H_2O$. Strengths of water lines in the 1.3−1.6 $\mu$m region cover several orders of magnitudes, therefore we can
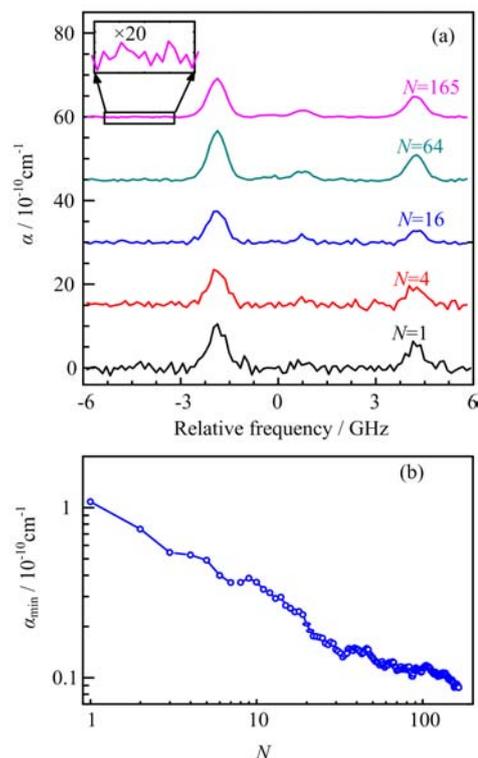


FIG. 6 (a) Averaged absorption spectrum of $H_2O$ near 7335.7 cm$^{-1}$. (b) Minimum detectable absorption coefficient ($\alpha_{min}$) from spectra with different averaging numbers ($N$).

select different water lines in the case of different humidities. A water line at 1.56 $\mu$m, which has a line strength of $2.7 \times 10^{-25}$ cm/molecule, is used to measure the relative concentration of water vapor (mole fraction) of about 1%. By comparing to a commercial chilled-mirror dew-point meter, we have demonstrated that the CRDS results agree with the dew-point meter with a statistical deviation of 0.4%. Stronger water lines in the 1.36 $\mu$m region are selected for measuring gases of lower humidity. A water line with a strength of $1.2 \times 10^{-22}$ cm/molecule is used to measure the mole fraction of water vapor at the ppmv level. The strongest water line in this region has a strength of $10^{-20}$ cm/molecule, which allows us to extend the detection limit of water vapor to about 8 pptv at a sample pressure of 10 kPa. Such a detection limit corresponds to a partial pressure of $H_2O$ of $8 \times 10^{-8}$ Pa, or a molecular density of $2 \times 10^7$ molecules/cm$^3$. The optical hygrometer, which has a sensitivity comparable to mass spectrometers, but being more portable and less expensive, can be very useful in miscellaneous applications and studies.

## V. ACKNOWLEDGMENTS

        

[1] H. H. Funke, B. L. Grissom, C. E. McGrew, and M. W. Raynor, Rev. Sci. Instrum. **74**, 3909 (2003).

[2] B. Handy, *The Proceedings of the Third International Symposium on Humidity and Moisture*, London, England: Teddington, 8 (1998)

[3] F. Hasebe, Y. Inai, M. Shiotani, M. Fujiwara, H. Voemel, N. Nishi, S. Y. Ogino, T. Shibata, S. Iwasaki, N. Komala, T. Peter, and S. J. Oltmans, Atmos. Chem. Phys. **13**, 4393 (2013).

[4] N. D. Milosevic, N. M. Stepanic, and M. M. Babic, Therm. Sci. **16**, 193 (2012).

[5] A. D. Scott, E. J. Hunter, and S. N. Ketkar, Anal. Chem. **70**, 1802 (1998).

[6] S. I. Ohira, K. Goto, K. Toda, and P. K. Dasgupta, Anal. Chem. **84**, 8891 (2012).

[7] H. H. Funke, M. W. Raynor, B. Yucelen, and V. H. Houlding, J. Electron. Mater. **30**, 1438 (2001).

[8] S. Q. Wu, J. Morishita, H. Masusaki, and T. Kimishima, Anal. Chem. **70**, 3315 (1998).

[9] C. S. Edwards, G. P. Barwood, P. Gill, B. Schirmer, H. Venzke, and A. Melling, Appl. Opt. **38**, 4699 (1999).

[10] B. Schirmer, H. Venzke, A. Melling, C. S. Edwards, G. P. Barwood, P. Gill, M. Stevens, R. Benyon, and P. Mackrodt, Meas. Sci. Technol. **11**, 382 (2000).

[11] S. Y. Lehman, K. A. Bertness, and J. T. Hodges, J. Cryst. Growth. **250**, 262 (2003).

[12] V. Vorsa, S. Dheandhanoo, S. N. Ketkar, and J. T. Hodges, Appl. Opt. **44**, 611 (2005).

[13] H. H. Funke, M. W. Raynor, K. A. Bertness, and Y. Chen, Appl. Spectrosc. **61**, 419 (2007).

[14] P. A. Y. Fiadzomor, D. M. Baker, A. M. Keen, R. B. Grant, and A. J. Orr-Ewing, Appl. Spectrosc. **62**, 1354 (2008).

[15] H. Abe and K. M. T. Yamada, Sens. Actuat. A **165**, 230 (2011).

[16] B. Chen, Y. R. Sun, Z. Y. Zhou, J. Chen, A. W. Liu, and S. M. Hu, Appl. Opt. **53**, 7716 (2014).

[17] L. S. Rothman, I. E. Gordon, Y. Babikov, A. Barbe, D. C. Benner, P. F. Bernath, M. Birk, L. Bizzocchi, V. Boudon, L. R. Brown, A. Campargue, K. Chance, E. A. Cohen, L. H. Coudert, V. M. Devi, B. J. Drouin, A. Fayt, J. M. Flaud, R. R. Gamache, J. J. Harrison, J. M. Hartmann, C. Hill, J. T. Hodges, D. Jacquemart, A. Jolly, J. Lamouroux, R. J. L. Roy, G. Li, D. A. Long, O. M. Lyulin, C. J. Mackie, S. T. Massie, S. Mikhailenko, H. S. P. Mller, O. V. Naumenko, A. V. Nikitin, J. Orphal, V. Perevalov, A. Perrin, E. R. Polovtseva, C. Richard, M. A. H. Smith, E. Starikova, K. Sung, S. Tashkun, J. Tennyson, G. C. Toon, V. G. Tyuterev, and G. Wagner, J. Quant. Spectrosc. Radiat. Transf. **130**, 4 (2013).