

Research Article

Effect of Measurement of Dew Point Temperature in Moist Air on the Absorption Line at 1392.53 nm of Water Vapor

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The HITRAN database (High-Resolution Transmission molecular absorption database) is an extremely helpful reference for selecting lines of molecular species. In the case of water vapor, a particular strong absorption line around $\lambda \approx 1392.5$ nm is suitable for the detection of molecules, not only because of its high strength but also because it is well separated from the neighboring transitions, thus avoiding any overlap. First, we present the optical system that uses a distributed feedback (DFB) laser diode, emitting around $\lambda \approx 1392.5$ nm with a power ≈ 3 mW and linewidth ≤ 10 MHz. For metrological needs, we are looking for a means to control the water vapor concentration in ambient air in near real time and especially when an optical chilled mirror hygrometer is used. The latter instrument is widely used due to its performance with regard to both accuracy and repeatability of measurements. Here, using the molecular absorption device the use of such an instrument is examined from the point of view of its impact on the measurement of relative humidity. This paper reports the measured frequency positions of the observed line at $\lambda = 1392.5337$ nm for different air pressures and compares them with the values given in the HITRAN database. In addition, we discuss the possibility of using water vapor detection by spectroscopy to observe the change of the shape and the position of the absorption line produced during measurements of the dew point temperature by the optical chilled mirror hygrometer.

1. Introduction

Water vapor concentration in air, often expressed as relative humidity, plays a key role in many fields including mass metrology. In this last scientific field, its value must be determined and controlled with great precision, during measurements of an unknown mass by comparison with a standard referenced in the International System of Units (SI) [1, 2].

The chilled mirror optical hygrometer is widely used in metrology and calibration laboratories as well as in industrial applications requiring high accuracy and good repeatability of relative humidity measurements [3, 4]. Indeed, the accuracy of measurements obtained with this type of instrument is generally better than those obtained with other devices based on different measurement principles (e.g., psychrometer, capacitive or resistive hygrometer). In this work, we consider a water vapor detection device based on the absorption spectroscopy technique [5, 6], to highlight and discuss the degree of invasiveness of the condensation hygrometer.

The sensitivity of the absorption measurement is fundamentally limited by the intensity of the absorption transition interrogated but also by the optical interaction path length. In the case of water vapor, a relatively intense isolated absorption line, centered around the wavelength of 1392.53 nm, is chosen to avoid any overlap with neighboring transitions.

Note that a related problem to that discussed in this paper has been considered by J. Weremczuk and al. [7] using another method of calculating the number of molecules condensed on the surface of the detector.

2. Theoretical Background and Absorption Signal

The water molecule has a very large number of absorption lines with relatively high intensities in the near infrared, notably in the band at 1378 nm (7255 cm^{-1}), as shown in Figure 1. The spectral widths of these lines range from a few megahertz to several gigahertz, depending on the pressure

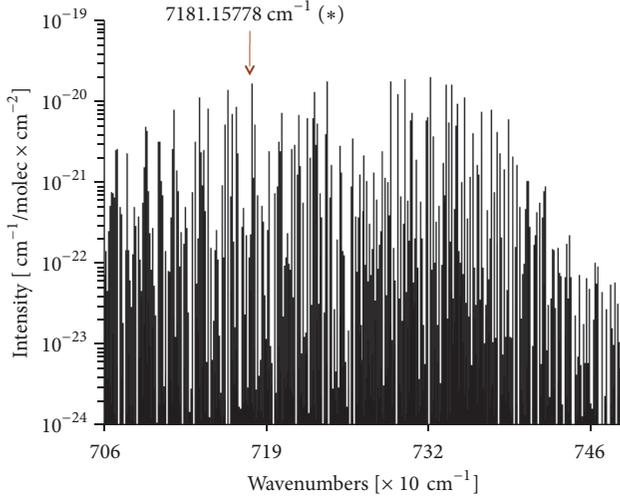


FIGURE 1: Overview of water vapor lines emission around 7181 cm^{-1} . (*): from HITRAN database.

and temperature conditions of the water vapor in the air and also those of the other species with which it is mixed.

In general, the wavelength emission of a single-mode DFB laser diode is tunable by variation of its operating temperature or the electric current that powers it, over several gigahertz in single-mode operation. Thus, to measure the wavelength at the center of the observed line, we chose to work at low air pressures, in order to fully scan the entire absorption profile.

In the case of our experiment, the available laser diode allowed mode-hop-free wavelength tunability, over more than 5 GHz, by variation of its electric current.

All the results, reported in this paper, were obtained for the absorption line at 1392.53 nm . Direct absorption spectroscopy is based on the Beer-Lambert law. Specifically, the intensity $I_0(\nu)$ of a monochromatic radiation, of frequency ν crossing a gas cell containing an absorbing species, at the frequency $\nu = c/\lambda$, undergoes a variation given by the following relation.

$$I_t(\nu, \ell) = I_0(\nu) \exp \{-S(T) g(\nu - \nu_0) \times P \times N \times \ell\} \quad (1)$$

$I_t(\lambda)$ is the intensity of the radiation after passing through the cell; $S(T)$ and $g(\nu - \nu_0)$ are, respectively, the intensity and the shape of the absorption line; P and N are the pressure and the mole fraction of the absorbing medium. ℓ is the length of the cell containing the absorbing species. Thus, the absorption line is obtained by tuning the laser wavelength so that it covers the entire width of the line. Details on this measurement procedure will be given in Section 3.

Figure 2 shows simultaneous recordings voltage obtained for the signals $I_t(\lambda)$ and $I_0(\lambda)$ for the line at 1392.53 nm .

$I_0(\lambda)$ corresponds to the intensity associated with the laser power at the entrance of the enclosure and $I_t(\lambda)$ to that observed after a course of the order of $\ell = 0.53 \text{ m}$ in the enclosure, for a wet pressure of 7 hPa .

Note that $I_0(\lambda)$ represents the laser power variation generated by the scanning of the current of the laser diode

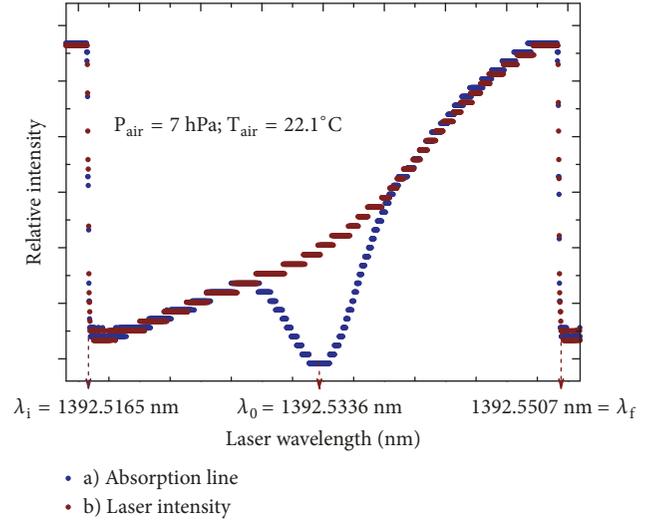


FIGURE 2: Transmitted intensities I_t and I_0 as a function of the laser wavelength around 1392.53 nm . (a) $I_t(\lambda)$ and (b) $I_0(\lambda)$.

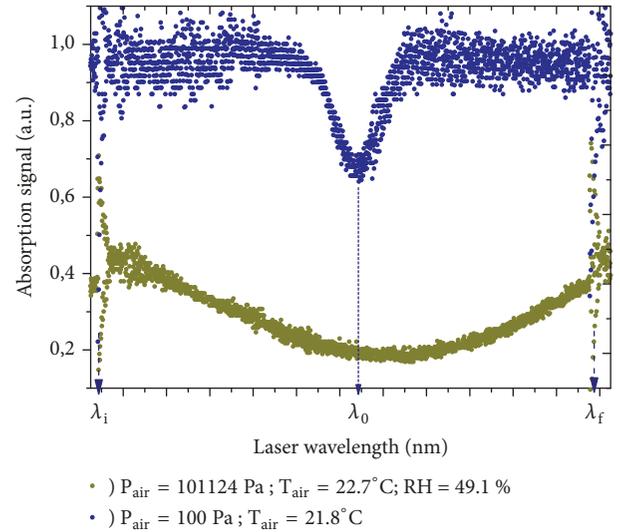


FIGURE 3: Absorption signal without laser background for the line at 1392.53 nm of H_2O .

by a voltage ramp, necessary to vary, without hop mode, the wavelength of the laser diode. Subsequently, we will present the results of the recordings of the absorption line corresponding to the ratio $I_t(\lambda)/I_0(\lambda)$, which gives the absorption line without the background laser power. In this representation, Figure 3 gives the recordings of the water vapor absorption lines observed for two moist air pressures.

The center of the absorption line is measured using a wavemeter (Burleigh, model 20DL) operating under primary vacuum, previously calibrated with a laboratory reference He-Ne laser at 633 nm . The resolution of the wavelength measurements, for fixed operating current I_{DL} and temperature T_{DL} of the laser diode, is of order of 10^{-4} nm .

In Table 1, the calculation results [8], as well as the updated value in HITRAN [9], are reported for the water

TABLE 1: Some wavelength values associated with the 1392.53 nm absorption line of water vapour at ambient temperature.

Reference	Wavelength (nm) Theory	Wavelength (nm) Experiment
[8]	1392,535	
This work		1392.5336 (0.0007)
[9, 10]		1392.5335 (0.0005)

vapor line positions from work of Toth [10]. The values indicated correspond to the wavelength in the vacuum, $\lambda_{\text{vac}} = 1/\sigma$, where σ is the wave number in cm^{-1} .

When the measurement uncertainty associated with the central wavelength of the absorption line at 1392.53 nm is included, the new measurement is in very good agreement with the value provided by the HITRAN database. Also, there might be effect of the moist air pressure that we considered on the position of the line center.

3. Experience and Measurement Procedure

A single-mode DFB laser diode for spectroscopy (SPECIDI-LAS D-Series from Laser Components) emitting around 1392.5 nm (power 3 mW, linewidth < 10 MHz) is used as the light source to detect water vapor, in air under a sealed enclosure, by the technique of absorption spectroscopy. The enclosure is equipped with a temperature sensor (a 100 ohm platinum resistance thermometer or Pt-100), a pressure gauge (Thermovac TM230), a resonant sensor barometer (Druck, model DPI 141), two hygrometric capacitive probes (Vaisala, model HMP 234), and chilled mirror hygrometer (GENERAL Eastern, model 1500). Each of these sensors is placed directly in the sealed enclosure. The temperature probe makes it possible to measure the temperature of the air with an uncertainty of the order of 10^{-2} K.

Figure 4(a) shows a schematic representation of the apparatus and Figure 4(b) a partial photograph of it. The pressure sensor (Druck model) allows one to measure the atmospheric pressure with an uncertainty of the order of 5 Pa. These sensors are previously calibrated from references in the laboratory. As for the dew point hygrometer, it is used here only to observe the effect on the water vapor absorption lineshape caused by the measurement method on which it is based. The laser beam is injected inside the measurement chamber through an optical fibre. It undergoes round trips between two flat mirrors, with appropriate coatings for an $R_{\text{max}} = 1392$ nm. The total pathlength ℓ of the laser beam can be adjusted between 0.53 m and 1.40 m.

The intensity of the laser beam $I_0(\lambda)$ is measured at the input of the enclosure (PD1 photodiode) and $I_t(\lambda)$ after a pathlength inside the enclosure (PD2 photodiode). Figure 2 shows the intensities, $I_0(\lambda)$ and $I_t(\lambda)$, observed as the wavelength of the laser is scanned between λ_i and λ_f by modulating the electric current through the laser diode over using a voltage ramp. The temperature of the laser diode is set and maintained constant to more than 0.02 K by means of a

proportional-integral-derivative (PID) type feedback control loop.

4. Experience and Results

4.1. Measurement of the Dew Point Temperature. As we have pointed out, once connected to a reference, the optical hygrometer makes it possible to obtain moisture measurements that are entirely satisfactory. However, to justify the fact that one needs to control the variations of humidity whenever it is used, we evaluated the order of magnitude of the perturbation of the air humidity caused by water vapor condensation on the mirror of the instrument, during the measurement of the dew point temperature. The moisture sensor of the hygrometer is installed inside the nonmagnetic stainless steel enclosure of volume 17 dm^3 . It consists of a 5 mm diameter mirror, of high optical quality, with temperature controlled for dew point measurements.

We have demonstrated the influence of the condensation hygrometer on the shape of the absorption line when it is switched on but also when it is stopped.

Figure 5(a) shows the effect of starting the hygrometer on the 1392.53 nm absorption line shape of water vapor in air at atmospheric pressure. The area between the two curves corresponds to the amount of water molecules trapped as condensate in the form of dew on the mirror of the hygrometer. To interpret this result, using a semiempirical approach, we have evaluated an order of magnitude of the amount of water vapor in the enclosure that condenses on the mirror of the hygrometer when it is set in operation.

This variation is also determined from measurements of relative humidity measured using a capacitive hygrometer and temperature sensor.

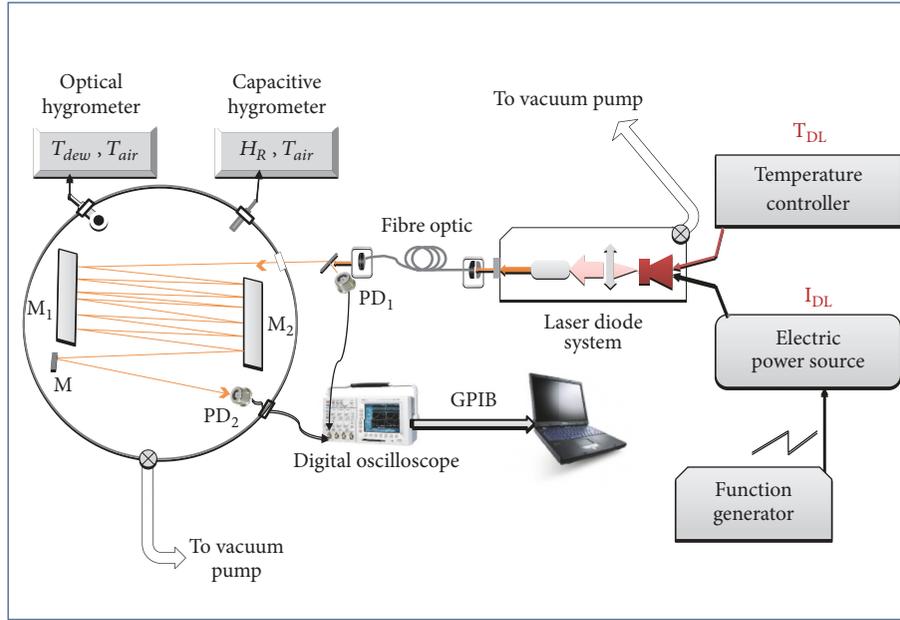
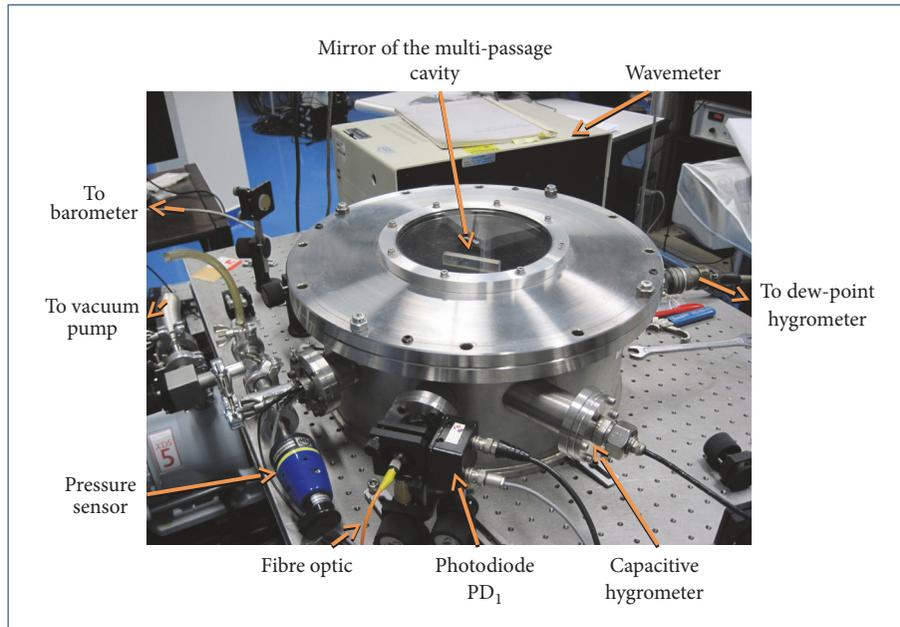
In the case of a moist air pressure of the order of 100 Pa, as shown in Figure 5(b), the effect of the hygrometer on the shape of the absorption line is obviously less marked because of the smaller amount of water vapor in the test chamber.

4.2. Dew Layer Stabilized on the Mirror of the Hygrometer. The variation of the number of water molecules in the enclosure, following the condensation of part of them on the mirror of the instrument, is evaluated on the basis of some approximations.

- (i) The thickness of the dew layer e_{dew} is estimated from the resolution of the normal eye $\mathfrak{R}_{\text{eye}}$, which is between 10^{-4} and 4×10^{-4} rad [11].
- (ii) Consequently, a stabilized dew deposit on the surface of the hygrometer mirror, which is observed at a distance d_{obs} of the order of 25 cm, will have an average thickness given by the following.

$$e_{\text{dew}} = \langle \mathfrak{R}_{\text{eye}} \rangle \times d_{\text{obs}} \approx 5 \mu\text{m} \quad (2)$$

- (iii) For a water molecule, we consider the accepted configuration with the OH bond length and angles shown in Figure 6.

(a) Experimental apparatus. PD₁, PD₂: photodiodes. M₁, M₂: flat multielectric mirrors

(b) Photograph of the experiment showing the measuring chamber with different sensors

FIGURE 4

To establish the bulk of a molecule of water in a given structure, we approximate it by a sphere of diameter equal to its greatest interatomic distance, i.e., $d_{\text{H}_2\text{O}} = 2 \times 0.958 \text{ \AA} \sin 52.25^\circ = 1.51 \text{ \AA}$, which makes its volume $V_{\text{H}_2\text{O}} \approx 1.80 \times 10^{-30} \text{ m}^3$.

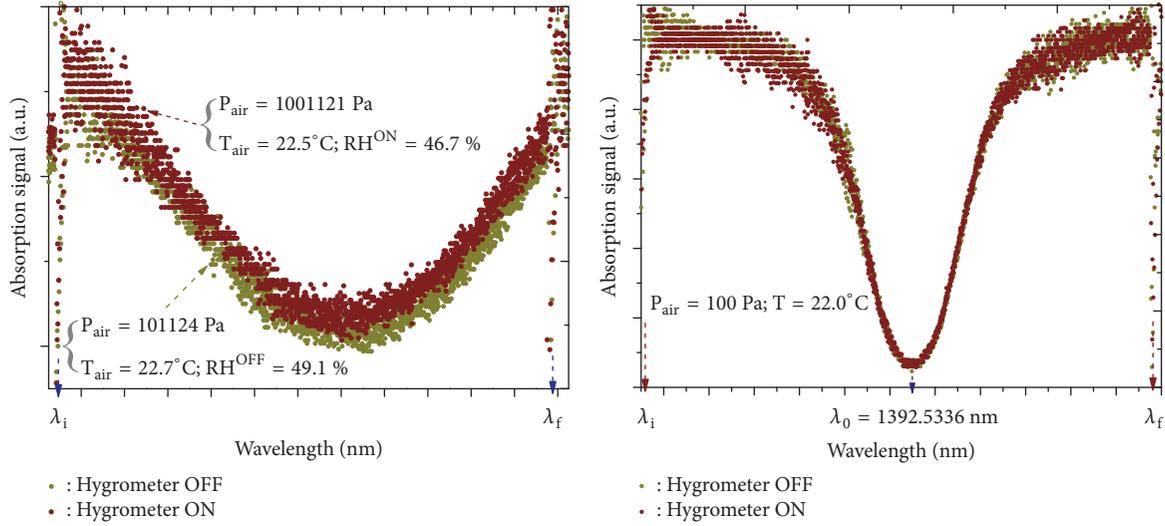
The volume of the dew layer which covers the surface of the mirror of diameter $\Phi = 5 \text{ mm}$ is estimated by the following relation.

$$V_{\text{dew}} = e_{\text{dew}} \times \pi \times \frac{\Phi^2}{4} \approx 1.0 \times 10^{-9} \text{ m}^3 \quad (3)$$

In the liquid state, the molecules lie close to each other because of the hydrogen bonds that form and break to give a disordered but very compact arrangement of molecules.

If this molecular arrangement is also found in the case of a dew layer, the number of molecules trapped is given by the following.

$$n_{\text{mol}} \approx \frac{1}{5} \times \left\{ \frac{V_{\text{dew}}}{V_{\text{H}_2\text{O}}} \right\} = 1.1 \times 10^{20} \text{ moléculas} \quad (4)$$



(a) Effect of dew point temperature measurement on the absorption line of water vapor at 1392.53 nm in air pressure at 1011.21 hPa

(b) Effect of dew point temperature measurement on the absorption line of water vapor at 1392.53 nm in air pressure at 100 hPa

FIGURE 5

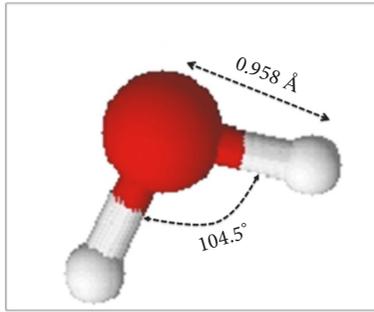


FIGURE 6: Geometry of water molecule.

The factor $1/5$ corresponds to the average filling fraction for the arrangement of the water molecules in the volume that dew layer forms on the mirror of the hygrometer. This ratio is deduced from a simple calculation considering that the dew layer has a density close to 1 g/cm^3 and a molar mass of 18.015 g . Translated in terms of mass, this number of water vapor molecules corresponds to a mass for the dew layer given by the following.

$$m_{dew} \approx \frac{1}{5} \left(\frac{V_{dew}}{V_{H_2O}} \right) \frac{M_a}{N_A} = 3,3 \times 10^{-3} \text{ g} \quad (5)$$

M_a and N_a are, respectively, the molar mass of the water vapor and the Avogadro's number.

4.3. Relative Humidity and Number of Water Molecules in Moist Air. The partial pressure of the water vapor in the humid air within the pressure vessel is given by the following.

$$P_{H_2O} = x_V \times P_{air} \quad (6)$$

x_V , is the molar fraction of water vapor in moist air: $x_V = x_{vw}(P_{air}, T_{air}) \times HR$.

Where $x_{vw}(P_{air}, T_{air})$ is the saturation vapor pressure, given by [12]:

$$x_{vw}(P_{air}, t_{air}) = \frac{e_w(T_{air}) f(T_{air}, P_{air})}{P_{air}} \quad (7)$$

Here $\ln[e_w(T_{air})] \cong (17.62 \times T_{air}) / (243.12 + T_{air}) + \ln(611.2)$ where T_{air} is in degrees Celsius.

For $T_{air} = 22.7^\circ\text{C}$, $e_w = 2752 \text{ Pa}$, the factor $f(T_{air}, P_{air})$, associated with water vapor in the air at this air temperature and pressure $P_{air} = 1011.27 \text{ hPa}$, is equal to $f \cong 1.0041$.

Therefore $x_{vw}(P_{air}, t_{air}) = 0.02733$; $x_V = 0.0134$.

The density of the water vapor is calculated from the relation: $\rho_V = (18,015 \times P_{air} \times x_V) / (Z \times R \times T_{air})$.

Then, $\rho_V \cong 9.9313 \text{ g} \times \text{m}^{-3}$.

Thus, the mass of the water vapor in the moist air, occupying the whole volume of the chamber (17 dm^3), before the hygrometer is switched on.

$$m_V = \rho_V \times 17 \times 10^{-3} = 0.169 \text{ g} \quad (8)$$

When the temperature of the hygrometer mirror reaches the temperature of the dew point, the change in the dew layer is stopped, and its temperature is then servo-locked at the temperature T_d of dew point. The mass of water vapor in air within the enclosure is then reduced to $m_V^{eff} = 0.166 \text{ g}$.

As a result, by using relation (5) and (8), the variation of the amount of water vapor decreases by $(m_V - m_V^{eff}) / m_V = 2,0\%$.

This means that under the conditions of the experiment, the use of a condensation hygrometer to measure the temperature of the dew point reduces the relative humidity by roughly 2%. Due to the level of measurement accuracy that is often sought, especially in mass metrology, such a perturbation of the moisture content cannot be ignored.

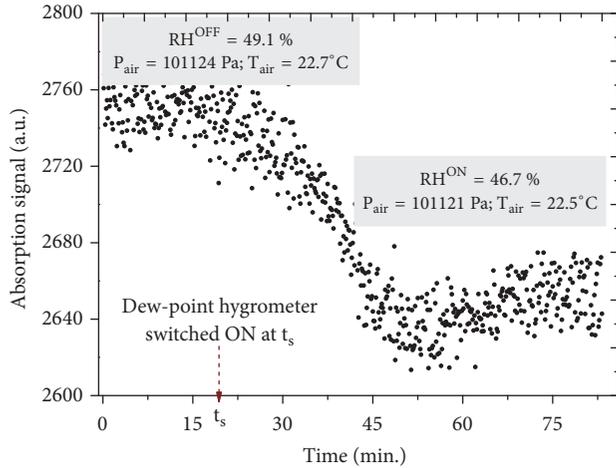


FIGURE 7: Absorption signal integrated over the entire absorption line of water vapor in humid air at atmospheric pressure showing the effect of starting the condensation hygrometer.

As shown in Figure 7, this effect on the absorption line at 1392.53 nm is quite apparent and measurable in relative value from the integrated signal over the entire extent of the absorption line. The relative humidity levels (HR^{OFF}) and (HR^{ON}), obtained with the capacitive humidity and temperature sensor, are 49.1% and 46.7%, respectively. Thus, the experimental difference, of the order of 2.4%, is quite comparable with the result of the calculation developed. This shows that the approach we have used to evaluate the perturbation of the moisture content of air during the operation of the condensation hygrometer is very realistic.

5. Discussion

In order to present, in another way, the effect of the measurement of the dew point temperature on the absorption line, we observe the variations over time of the absorption signal related to the total width of the line for different conditions of humidity and air pressure. The curve of Figure 7 shows the two phases of this absorption, observed under the same conditions as those of the recording of Figure 5. Presented in this way, the effect of starting the condensation hygrometer on the water vapor absorption signal is more apparent.

In the same way, the results obtained under conditions similar to those of Figure 5(b), which shows the evolution of the absorption signal over time, are displayed in Figure 8. In this experiment, the indications recorded with the capacitive temperature and humidity sensor, denoted in Figure 8 by HR^{OFF} and HR^{ON} , are not reliable. The only measurements are those of the moist air temperature, which is almost constant in both situations of the optical hygrometer and the total pressure of moist air.

6. Conclusion

The optical detection technique, based on selective absorption by atoms and molecules, still has applications in

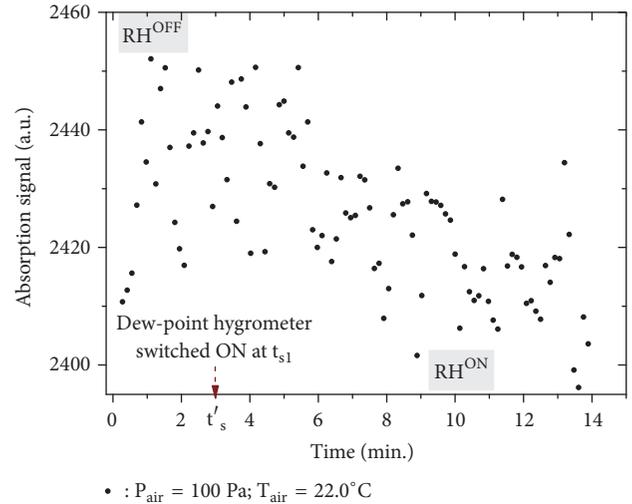


FIGURE 8: Absorption signal integrated over the absorption line of water vapor in 100 hPa air pressure.

various fields. Indeed, the development of new wavelength laser sources with tunable emission in new ranges can be immediately exploited by this technique for detection of trace amounts of pollutants in extreme conditions (high temperature, high pressure, irradiated area, etc.). In this work, we used a low-power single-mode DFB laser diode to probe water vapor in air contained in a closed chamber that can be put under an air pressure ranging from 1 atmosphere ($\approx 10^5$ Pa) down to about 10 Pa. Examination of the absorption line at 1392.53 nm, of water vapor in air, allowed a new measurement of the central wavelength to better than 10^{-3} nm. This value is in a good agreement with that reported in the HITRAN database. This result also allowed us to observe and evaluate the variation of the amount of water vapor in the moist air, induced by the condensation process on the mirror of an optical dew hygrometer in the case of a closed and low volume enclosure. The calculation developed gives an order of magnitude quite comparable with that observed in the case of humid air at atmospheric pressure. Finally, this result shows that it is necessary to put in place a suitable procedure, depending on the experimental conditions related to the volume of the enclosure and its state with respect to the outside, when using a dew point hygrometer as a means to obtain a reliable measurement of the relative humidity of an air sample.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there are no conflicts of interest.

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