

# Oxygen Sensitivity of Krypton and Lyman- $\alpha$ Hygrometers

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## ABSTRACT

The oxygen sensitivity of krypton and Lyman- $\alpha$  hygrometers is studied. Using a dewpoint generator and a controlled nitrogen/oxygen flow the extinction coefficients of five hygrometers associated with the third-order Taylor expansion of the Lambert–Beer law around reference conditions for oxygen and for water vapor were measured. Latent heat flux corrections for cross-talk of the sensible heat flux are given as a function of the Bowen ratio. The spread observed in oxygen sensitivities calls for individual oxygen calibrations for each apparatus. It is found that the separation between the tubes is the crucial parameter with respect to the oxygen sensitivity. The oxygen-related nonlinearities in the Lambert–Beer law are stronger than those associated with water vapor. This leads to a strong reduction of the oxygen sensitivity at a more or less constant water vapor sensitivity when the separation between the tubes is doubled from 1.3 to 2.6 cm. This characteristic is supported by a sensitivity analysis of the theoretical response relations of both types of hygrometers, based on multiple emission and absorption lines. The findings of Tanner et al. are confirmed—the results of a previous study strongly overestimate the oxygen sensitivity of today's krypton hygrometers.

## 1. Introduction

Evaporation is a major contribution to the energy budget at the earth's surface. To estimate evaporation one often uses optical hygrometers like krypton and Lyman- $\alpha$  hygrometers. Unfortunately, both types react also to oxygen. In atmospheric conditions the oxygen concentration is inversely proportional to temperature, leading to a cross-talk between latent and sensible heat flux. To eliminate this, one must know the oxygen sensitivity of the hygrometer. Tanner et al. (1993) suggest that new experiments have shown that the oxygen-sensitivity coefficients published in the past (Tanner 1989) overestimate the oxygen sensitivity of the sensors that are currently in use by a factor of 2. This study is performed to quantify the oxygen sensitivities of two types of optical hygrometers, to provide a method to correct evaporation estimates in practice, to see if the ratio of the oxygen sensitivity to the water vapor sensitivity can be

optimized, and to find out if we can explain the scatter in oxygen sensitivities reported in the literature.

We will perform oxygen and water vapor calibrations of three different Campbell krypton hygrometers and two Mierij Lyman- $\alpha$  hygrometers and compare the resulting coefficient with those of Tanner (1989) and of Tanner et al. (1993). The experiment is set up as follows: the water vapor sensitivities of the hygrometers are calibrated using a dewpoint generator and ambient air. Oxygen sensitivities are calibrated at two different but constant humidities with a wetted nitrogen/oxygen mixture, of which the ratio is varied from 1:0 to 1:1 under more or less atmospheric conditions (pressure and temperature). We will estimate the extinction coefficients for oxygen and water vapor of the hygrometers associated with the third-order Taylor expansion of the Lambert–Beer law around reference conditions. The ratios of the first-order coefficients will be related to correction factors at reference conditions for latent heat flux estimates to correct for cross-talk of the sensible heat flux. Correction factors will be given as a function of the Bowen ratio. The higher-order coefficients express the nonlinearity in the Lambert–Beer law and they can be used to optimize the ratio of the oxygen sensitivity to the water vapor sensitivity via the separation between the tubes at reference conditions. The results for the krypton hygrometers will be compared with the results for the

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Lyman- $\alpha$  hygrometers and with the findings of Tanner et al. We will use analytic models for the response of the probes to assess if we can understand the characteristics that we observe in the experiment.

## 2. Theory

### a. Operational principles of an open path optical hygrometer

An open path optical hygrometer probes air for water vapor as follows: a light source emits a beam of ultraviolet light (for the krypton tube: 123.6 nm with a small secondary line at 116.5 nm, and for Lyman- $\alpha$ : 121.6 nm). A receiver measures which fraction of the emitted light is received at a distance of typically 1 cm. The frequency of the ultraviolet light is such that water vapor will absorb the light. The fraction of light absorbed per unit of length is proportional to the concentration of the vapor. The details are as follows. In Liou (1980, relation 1.34) we find the relations for the functional shape  $I(\nu)$  of an emission line around principal frequency  $\nu_i$  as a function of frequency  $\nu$ :

$$I(\nu) = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_i)^2 + \alpha^2}$$

$$\Rightarrow I(\lambda) = \frac{S}{\pi} \frac{a}{\left(1 - \frac{\lambda}{\lambda_i}\right)^2 + \left(\frac{a}{\lambda}\right)^2} \quad (1)$$

with

$$\lambda \equiv \frac{1}{\nu} \quad \text{and} \quad a \equiv \frac{\alpha}{\nu^2},$$

where  $S$  is the energy emitted by that line and  $\alpha$  is the half-width (frequency) at half-height. The pressure with which the tubes of the optical hygrometer are filled is not known and it may vary with temperature. The influence of variations in temperature  $T$  and pressure  $p$  around reference values  $p_0$  and  $T_0$  on the line's half-width  $\alpha$  is described by (Liou's relation 1.37):

$$\alpha = \alpha_0 \frac{p}{p_0} \sqrt{\frac{T_0}{T}} \Rightarrow a = a_0 \frac{p}{p_0} \sqrt{\frac{T_0}{T}}. \quad (2)$$

where  $\alpha_0$  (or  $a$ ) is the half-width at  $T_0$  and  $p_0$ . Since the tubes are closed the number of krypton particles is constant and we can substitute the equation of state into relation (2) to find:

$$\alpha = \alpha_0 \sqrt{\frac{T}{T_0}} \Rightarrow a = a_0 \sqrt{\frac{T}{T_0}}. \quad (3)$$

This implies that a variation in gas temperature of 10% gives a variation in spectral width of 5%.

We now construct a model  $I_{kr}(\lambda)$  for the emission spectrum of a krypton tube by adding two functions of type as given by relation (1): one at wavelength  $\lambda_1 =$

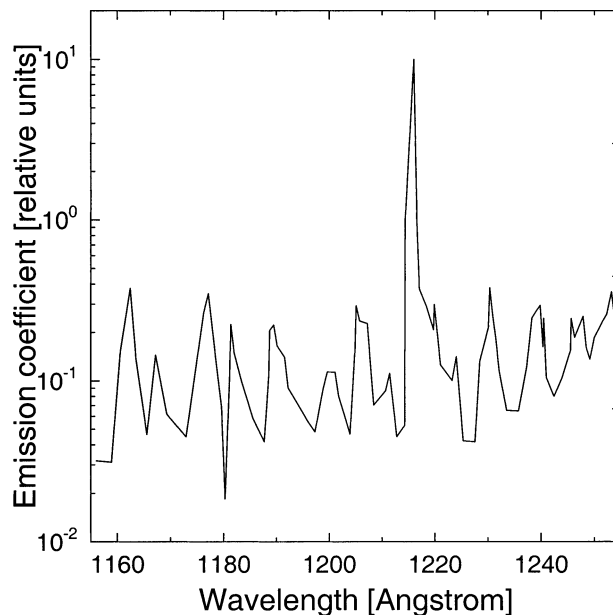


FIG. 1. Emission spectrum of Mierij Meteo Lyman- $\alpha$  following Buck (1981).

1164.87 Å with (relative) energy  $S_1 = 200$  (this is the secondary band) and one at wavelength  $\lambda_2 = 1235.84$  Å with (relative) energy  $S_2 = 650$  (the primary band). Wavelengths and relative strengths are taken from Weast and Astle (1980; Table E-265):

$$I_{kr}(\lambda) = \frac{200}{\pi} \frac{a}{\left(1 - \frac{\lambda}{1164.87}\right)^2 + \left(\frac{a}{\lambda}\right)^2} + \frac{650}{\lambda} \frac{a}{\left(1 - \frac{\lambda}{1235.84}\right)^2 + \left(\frac{a}{\lambda}\right)^2}. \quad (4)$$

The response of a Lyman- $\alpha$  hygrometer is found from this relation by replacing the two emission lines by a single line at 1216 Å. A more detailed Lyman- $\alpha$  model is found when one uses the nonideal emission spectrum measured by Buck (1981) (see Fig. 1). Spectral width  $a$  (in Å) is taken to have the same value for both spectral lines. The idea behind this is that the two bands stem from the same molecules and the origin of the spectral width is found in the dynamics of those molecules. The value for  $a$  can still be chosen, but will not exceed 3 Å (seen from Fig. 1 of the Campbell krypton user guide).

Absorption spectra  $\kappa_w(\lambda)$  for water vapor and  $\kappa_o(\lambda)$  for oxygen are copied from Watanabe et al. (1953); see Fig. 2. The values are given at STP conditions (25°C and 1 atm pressure).

Spectrum  $R(\lambda)$  of the light received by the krypton hygrometer's detector tube is now given by the product of the emitted krypton spectrum and an exponential function implementing the absorption spectrum of the

atmospheric gases ( $x$  is the separation of the tubes in cm):

$$R(\lambda, \rho_w, \rho_o, x) = I_{kr}(\lambda) \exp \left[ -x \left( \kappa_w(\lambda) \frac{\rho_w}{\rho_{w,STP}} + \kappa_o(\lambda) \frac{\rho_o}{\rho_{o,STP}} \right) \right]. \quad (5)$$

We now assume that the sensitivity of the krypton's detector does not vary with frequency. This may not be strictly correct since magnesium fluoride windows have been implemented to reduce the oxygen sensitivity. By this assumption the results of this study will therefore provide upper limits for the effects caused by oxygen interference. For any given set  $(\rho_w, \rho_o, x)$  we can now calculate the signal strength  $V$  of the hygrometer via integration:

$$V(\rho_w, \rho_o, x) \equiv \int_0^\infty R(\lambda, \rho_w, \rho_o, x) d\lambda. \quad (6)$$

This is a nonlinear relation between the sensors signal and the densities of water vapor and of oxygen. In practical applications, the general approach is to construct a Taylor series of the logarithm of (6) around reference conditions. Including nonlinear effects (included for reasons that will become clear later) the response  $V$  of a hygrometer (with tube separation  $x$ ) is related to the respective gas thicknesses  $F_i \equiv x\rho_i$  (where  $\rho_i$  refers to the densities of constituents water vapor and oxygen) via the Lambert–Beer law:

$$\begin{aligned} -\ln V(\rho_w, \rho_o, x) &= -\ln V(\rho_{w,ref}, \rho_{o,ref}, x_{ref}) + k_w \Delta F_w \\ &+ l_w (\Delta F_w)^2 + m_w (\Delta F_w)^3 \\ &+ k_o \Delta F_o + l_o (\Delta F_o)^2 + m_o (\Delta F_o)^3 \\ &+ \text{higher-order effects in } \Delta F_w \\ &\text{and } \Delta F_o, \end{aligned} \quad (7a)$$

$$\begin{aligned} \Delta F_w &\equiv x\rho_w - (x\rho_w)_{ref} \\ &\sim x_{ref}(\rho_w - \rho_{w,ref}) + (x - x_{ref})\rho_{w,ref}, \end{aligned} \quad (7b)$$

$$\begin{aligned} \Delta F_o &\equiv x\rho_o - (x\rho_o)_{ref} \\ &\sim x_{ref}(\rho_o - \rho_{o,ref}) + (x - x_{ref})\rho_{o,ref}, \end{aligned} \quad (7c)$$

where  $k$ ,  $l$ , and  $m$  indicate first-, second-, and third-order extinction coefficients, which are given by

$$\begin{aligned} k_i &= -\frac{1}{x_{ref}} \frac{\partial \ln V}{\partial \rho_i} \Bigg|_{ref} & l_i &= -\frac{1}{2x_{ref}^2} \frac{\partial^2 \ln V}{\partial \rho_i^2} \Bigg|_{ref} \\ m_i &= -\frac{1}{6x_{ref}^3} \frac{\partial^3 \ln V}{\partial \rho_i^3} \Bigg|_{ref}. \end{aligned} \quad (8)$$

Subscripts  $w$  and  $o$  refer to water vapor and oxygen, respectively. Gas thicknesses  $F_i$  express how many molecules of the respective kinds a bundle of light will meet per unit cross section of the bundle. Relation (7) is a

third-order Taylor expansion around atmospheric conditions and around a reference separation of the tubes. Tanner et al. (1993) adopt the following atmospheric reference conditions: pressure 101 325 Pa, temperature 305 K, and zero humidity; for  $x$  they give no reference value. We make a slight modification to these conditions: instead of zero humidity we will refer to 10 g H<sub>2</sub>O (m<sup>-3</sup>). The reason is that estimates for the extinction coefficient for water vapor at zero humidity are highly inaccurate, because they involve the derivative of a fit function at its boundary. Our extinction coefficients refer to these modified atmospheric conditions. We estimate reference oxygen concentration  $\rho_{o,ref}$  (based on 21% oxygen volume) to be 0.2685 kg m<sup>-3</sup>. The reference value for separation  $x$  is still a free choice. In this study we will give  $k_i$  for three separations: for the (arbitrary) separation during the experiment, for  $x = 1.3$  cm ( $\equiv k_{i,1.3}$ ) and for  $x = 2.6$  cm ( $\equiv k_{i,2.6}$ ). Nonlinear terms in (7) can originate from saturation or from multiple or broad emission lines. To find sensitivity  $s_i$  of the sensor to the gas concentrations, we differentiate theoretical response relation (7). For arbitrary conditions  $(\rho_w, \rho_o, x)$  this gives

$$\begin{aligned} s_i &\equiv \frac{\partial}{\partial \rho_i} - \ln V(\rho_w, \rho_o, x) \\ &= k_i x + 2l_i x [x_{ref}(\rho_i - \rho_{i,ref}) + (x - x_{ref})\rho_{i,ref}] \\ &+ 3m_i x [x_{ref}(\rho_i - \rho_{i,ref}) + (x - x_{ref})\rho_{i,ref}]^2. \end{aligned} \quad (9)$$

For reference conditions only the first-order effect remains, giving

$$s_i \Big|_{\rho_{w,ref}, \rho_{o,ref}, x_{ref}} = k_i x_{ref}. \quad (10)$$

When the hygrometer is used in conditions that deviate strongly from reference conditions, for example, when the hygrometer is mounted on an airplane and taken high up into the atmosphere or taken to Antarctica, then one should estimate sensitivities  $k_w$  and  $k_o$  from the derivatives of the calibrated Lambert–Beer law at appropriate, representative conditions for the experiment. To measure the influence of the nonlinearities on linear sensitivities  $k_i$ , we introduce the following ratios:

$$G_i \equiv \frac{2l_i \Delta F_{i,1.3-2.6} + 3m_i (\Delta F_{i,1.3-2.6})^2}{k_i} \quad (11)$$

with

$$\Delta F_{i,1.3-2.6} \equiv 1.3\rho_{i,ref}.$$

In this relation  $\Delta F_{i,1.3-2.6}$  is the jump in gas thickness caused by doubling the tube separation from 1.3 to 2.6 cm under reference concentration of the respective gas. The value of this jump is adopted since it is representative for an appreciable modification of the sensor in practice. Ratio  $G$  gives the fractional reduction (negative value) or enhancement (positive value) of the sensitivity when the tube separation is doubled from 1.3 to 2.6 cm under reference conditions.

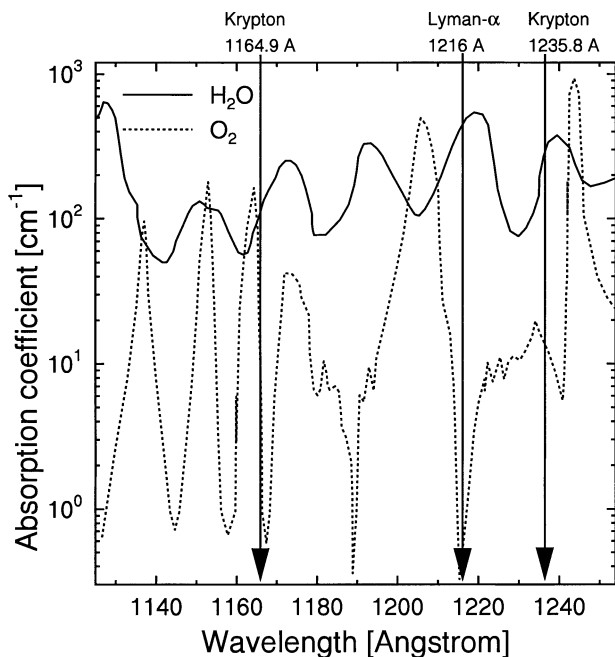


FIG. 2. Absorption spectra of water vapor and oxygen and emission lines of krypton and Lyman- $\alpha$ .

*b. Oxygen correction of evaporation estimates*

With sensitivities  $s_w$  and  $s_o$  we can calculate the oxygen correction for covariance estimates of any quantity  $y$  with humidity:

$$\overline{y' \rho'_v} \rightarrow c \overline{y' \rho'_v} \tag{12a}$$

$$c = 1 + \text{frac}_o m_o \frac{p}{RT^2} \frac{s_o}{s_w} \frac{\overline{y' T'}}{\overline{y' \rho'_v}}, \tag{12b}$$

where  $p$  is pressure (Pa),  $R$  is the universal gas constant ( $8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1}$ ),  $m_o$  is the mole-mass of oxygen, and  $\text{frac}_o$  is the fraction of oxygen molecules in the air (generally 21%; above forests or above burning terrain this constant may have a different value). To correct the humidity variance one has to use the square of this factor  $c$ . When the measurement is done at reference conditions, then (12b) reduces to

$$c = 1 + \text{frac}_o m_o \frac{p}{RT^2} \frac{k_o}{k_w} \frac{\overline{y' T'}}{\overline{y' \rho'_v}}. \tag{12c}$$

Application of (12c) to latent heat estimates  $L_v E$  gives relation (18) in the article by Tanner et al.:

$$L_v E \text{ (corrected)} = c(\beta) L_v E \text{ (raw)} \tag{13a}$$

$$c(\beta) = 1 + 0.23 \frac{k_o}{k_w} \frac{L_v \beta}{T}, \tag{13b}$$

where  $\beta$  is the Bowen ratio and  $L_v$  is the evaporation heat of water ( $2.45 \times 10^6 \text{ J kg}^{-1} \text{ K}^{-1}$ ). The factor of 0.23 is in  $\text{g K}^2 \text{ J}^{-1}$ .

**3. Setup**

To find extinction coefficients  $k_w$ ,  $l_w$ , and  $m_w$  for water vapor we have built a setup, which is shown in Fig. 3. Ambient air is fed to a Li-Cor dewpoint generator (type Li-610), which is set to a fixed input rate of  $1 \text{ L min}^{-1}$ ,

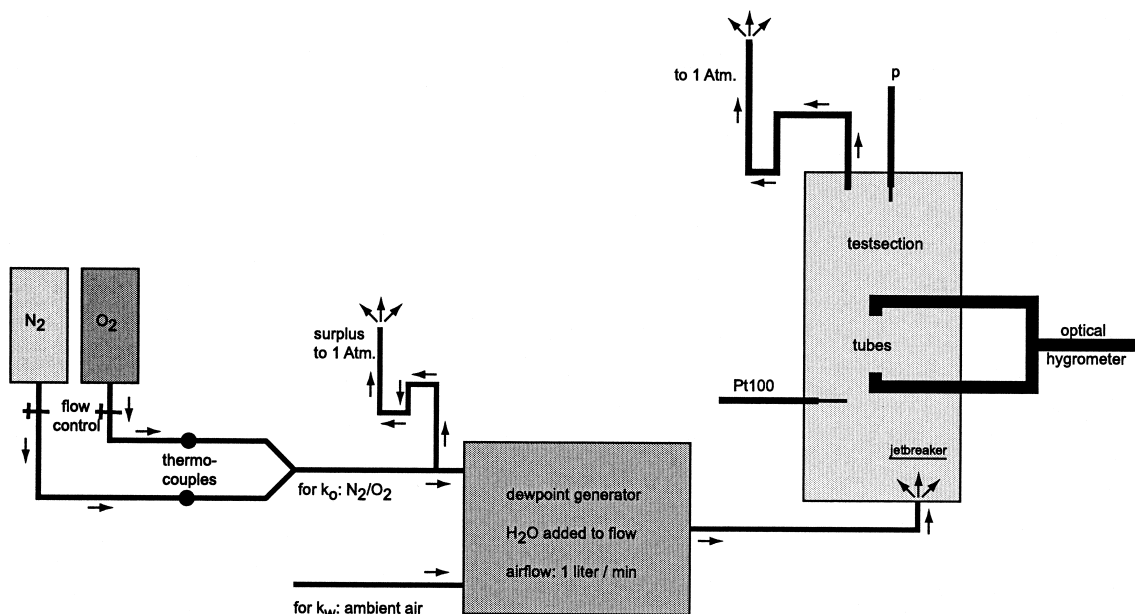


FIG. 3. Setup for the calibration of an optical hygrometer. Ambient air is used for the water vapor sensitivity and the  $\text{N}_2/\text{O}_2$  mixture is used for the oxygen sensitivity.

TABLE 1. Extinction coefficients for water vapor. Abbreviations Kr1, . . . , Ly2, etc. refer to the five different hygrometers specified in the first paragraph of section 3. Reference conditions are  $p = 101\,325$  Pa,  $T = 305$  K, and  $\rho_w = 10$  g m<sup>-3</sup>. Ratio  $G$ , estimated via relation (11), is the fractional increase of  $k_w$  (due to nonlinearity) when  $x$  is doubled from 13 to 26 mm. Values of  $G_w$  for krypton are insignificant. Coefficients  $k_{w13}$  and  $k_{w26}$  give extinction rates for  $x = 1.3$  cm and  $x = 2.6$  cm. Their values are only given when the corresponding gas thickness was within the calibration range.

	$k_w$ (m <sup>3</sup> g <sup>-1</sup> cm <sup>-1</sup> )	Separation (cm $\pm$ 0.1 mm)	$G_w$ (%)	$k_{w13}$ (m <sup>3</sup> g <sup>-1</sup> cm <sup>-1</sup> )	$k_{w26}$ (m <sup>3</sup> g <sup>-1</sup> cm <sup>-1</sup> )
Tanner (Kr)	0.15	—	—	—	—
Kr1	0.161 $\pm$ 1.5%	1.300	-7	0.161	—
Kr2	0.145 $\pm$ 1.6%	1.235	2	0.146	—
Kr3	0.131 $\pm$ 1.2%	2.605	-4	—	0.131
Kr3	0.147 $\pm$ 1.5%	1.300	-4	0.147	—
Ly1	0.101 $\pm$ 2.2%	2.115	-17	0.111	0.095
Ly2	0.086 $\pm$ 2.0%	2.520	-19	0.100	0.085

to set humidity with a tolerance of 0.15 g m<sup>-3</sup>. The wetted air is fed to the test section. The nozzle, through which the flow enters the test section, is fitted with a jet breaker to prevent the incoming flow from directly flowing to the section's outlet (which could lead to long residence times of gas residuals in the test section); furthermore, the nozzle has a series of little holes to enhance mixing of the constituents. The test section is an air-tight aluminium cylindrical construction around the hygrometer. Content of the test section is 200 cc. Temperature in the test section is monitored with a Pt100 element (calibrated against a reference thermometer) connected to an HP3497 D/A control unit and associated HP3456 digital voltmeter switched to low sensing current four-wire resistance measurement. The test section is set to atmospheric pressure via an open outlet tube (length 2 m, diameter 4 mm). The direction of the outflow is checked by feeding the flow through a glass of water. As long as there are bubbles, the setup is functioning correctly. The (small) pressure difference between the test section and the atmosphere is measured using a type Kal84 pressure transducer of Druck Nederland bv. Atmospheric pressure is read from a nearby (1 km) weather station (Haarweg) and reduced to sea level by correction for the height of the lab above the sea (6 m).

To find extinction coefficients  $k_o$ ,  $l_o$ , and  $m_o$  for oxygen, we feed the setup from Fig. 3 with a nitrogen flow (under atmospheric pressure) and monitor the hygrometer's response to a superimposed oxygen flow. Nitrogen (quality factor 5.0) is supplied by a 130-bar bottle and fixed to 1.5 L min<sup>-1</sup>. Oxygen (quality factor 2.5) is taken from a 100-bar bottle. A Teflon tube is used to connect the two bottles to Aalborg type GFC17 mass flow control units, which give the flow rate at specified reference conditions. After the passage of the two gasses through the flow controllers the respective temperatures are measured with fast manganese-constantan thermocouples. The two flows are merged. To set humidity, the resulting mixture is fed to the Li-Cor dewpoint generator, which (as before) is set to a fixed input rate of 1 L min<sup>-1</sup>. The surplus of N<sub>2</sub>/O<sub>2</sub> gas offered to the dewpoint generator (0.5 L min<sup>-1</sup> plus the oxygen flow level) leaves the setup through a long tube (2 m) to atmospheric pressure just before the dewpoint generator. To check that no ambient air is taken in at this

point the flow is fed through a glass of water. Bubbles indicate outflow. The wetted nitrogen/oxygen mixture is fed to the test section. The rest of the calibration procedure is the same as described for the water vapor calibration.

## 4. Water vapor calibrations

### a. Experiment

First we have calibrated the water sensitivities of the five hygrometers (from here to be called Kr1, Kr2, Kr3, Ly1, and Ly2). The Lyman- $\alpha$  hygrometers were both Mierij KOH-2 types. The three krypton hygrometers were three Campbell hygrometers type KH2O. Kr1 was fitted with an interface box with a different serial number; Kr2 and Kr3 had interface boxes with corresponding numbers. The responses of the hygrometers were recorded at dewpoint temperatures ranging from 2° to 18°C with step 1°C. This corresponds to absolute humidities ranging from 5 to 16 g m<sup>-3</sup> with a tolerance of 0.15 g m<sup>-3</sup>. The tube separations of the hygrometers, estimated with a tolerance of 0.1 mm, are listed in Table 1. Two-standard deviation tolerances are estimated for all quantities in every sample.

Dewpoint temperatures  $T_{\text{dew}}$  (°C) are converted into saturation pressures  $p_{\text{sat}}$  using Buck's (1981) relation:

$$p_{\text{sat}} = 613.65 \exp\left(\frac{17.502T_{\text{dew}}}{240.97 + T_{\text{dew}}}\right). \quad (14)$$

From this saturation pressure we find the partial pressure of water vapor at temperature  $T$  in the test section via the following relation:

$$p_v = p_{\text{sat}} \frac{p_0 + \Delta p}{p_0 + dp_{\text{licor}}}, \quad (15)$$

where  $p_0$  is the ambient pressure in the lab,  $\Delta p$  the overpressure in the test section, and  $dp_{\text{licor}}$  the overpressure in the dewpoint generator (which is derived from the water level in the fill-tube on the backside). The water vapor density in the test section is then found via

$$\rho_v = \frac{p_v}{R_v T}, \quad (16)$$



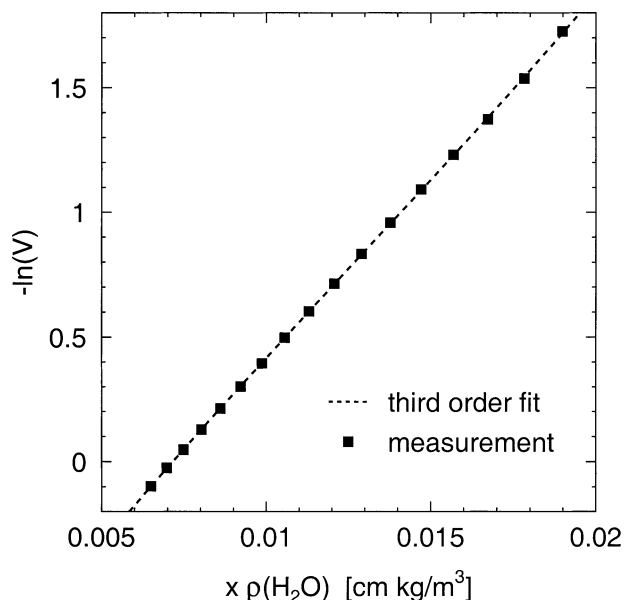


FIG. 4. Reponse of Kr2 to variations in gas thickness of water vapor (product of concentration and separation). Separation  $x$  is 1.235 cm. The continuous line is a third-order regression model.

where  $R_v$  is the specific gas constant of water vapor:  $461.5 \text{ J K}^{-1} \text{ kg}^{-1}$ .

#### b. Results

Third-order Chebyshev polynomials, orthogonalized on the range of the water vapor concentrations in each calibration, were used in an error-weighted least squares regression [taking into account both  $x$  and  $y$  errors, see van Dijk (1999), appendix A] to model the logarithmic hygrometer response as a function of gas thickness  $F_w \equiv x\rho_w$ . As an example we have plotted the water vapor calibration of Kr2 (at 12.35 mm) in Fig. 4. The resulting estimates for linear water vapor sensitivities  $k_w$ ,  $k_{w13}$ ,  $k_{w26}$  [via relation (8)] and for nonlinear interference ratio  $G_w$  [via relation (11)] are given in Table 1. All  $G_w$  for krypton are insignificant when compared with the measurement error. This explains why they disagree with the results in the last two columns. Estimates of  $k_{w13}$  and  $k_{w26}$  are found via the derivative of the response curve at the corresponding gas thickness, and values are only provided when these gas thicknesses are inside the calibration range. The tolerances for  $k_w$  in this table are estimated via (8) as the geometric mean of the stochastic relative tolerances from the regressions and the relative tolerances in the tube separations. We see that Tanner's value for  $k_w$  for his krypton tube is in the range of values in our study. From the values of  $G_w$  for krypton tubes we see that  $k_w$  changes by only a few percent when the separation between the tubes is doubled from 1.3 to 2.6 cm. This shows that for krypton tubes the values for  $k_w$  can be assumed to be independent from the tube separation (although accurate evaporation estimation of

course requires an individual calibration of the hygrometer). For Lyman- $\alpha$  hygrometers the influence of nonlinearities in the Lambert-Beer law on  $k_w$  amounts to nearly 20% when the separation is doubled from 1.3 to 2.6 cm, showing that one cannot adjust their separation without making a recalibration for  $k_w$ .

From Table 1 we see that the UV light from the krypton hygrometers reacts more strongly to water vapor than the UV light from the Lyman- $\alpha$  hygrometers. The scatter in values between individual hygrometers of either type shows that no universal calibration constant can be used and that each instrument will have to be calibrated individually.

The dependence of the extinction coefficient on the separation between the tubes can be connected with nonlinearities in the Lambert-Beer law, which are introduced by multiple emission and absorption lines with a finite width in the spectra. This is addressed in section 6.

## 5. Oxygen calibrations

### a. Experiment

To find the extinction coefficients for oxygen we produced a fixed nitrogen flow of  $1.5 \text{ L min}^{-1}$  and recorded the responses of the hygrometers at oxygen flow rates in the range between  $0.0 \text{ L min}^{-1}$  (pure nitrogen flow) and  $1.5 \text{ L min}^{-1}$  (half nitrogen, half oxygen). All hygrometers are calibrated at dewpoint temperature  $6^\circ\text{C}$  (absolute humidity  $6 \text{ g m}^{-3}$ ). In three cases (one krypton and two Lyman- $\alpha$  hygrometers) an additional oxygen calibration was carried out at  $16 \text{ g m}^{-3}$ . The extra dewpoint serves to see whether the simultaneity of the two extinction processes (oxygen and water vapor) leads to nonlinearity. Between 16 and 20 samples were taken for each calibration. Before each experiment the system is flushed for half an hour to let the water vapor concentration inside the test section reach equilibrium.

The oxygen flow rate is varied nonmonotonically (e.g., 0.1–1.5–0.2–1.3 etc.) to suppress systematic errors. Before the recordings of the samples the system is allowed to settle during some minutes. The responses of the hygrometer, pressure transducer, and thermometers showed convergence to a stable value within this delay. Two standard deviation tolerances are estimated for all quantities in every sample. Separations between transmitter and receiver tubes were estimated with a tolerance of 0.1 mm.

Combination of the ideal gas law with Dalton's law for the pressure of gas mixtures,

$$p = \frac{N}{V}RT \quad p_o = \frac{N_o}{V}RT = \rho_o R_o T$$

$$\frac{N_o}{V} = \frac{N}{V} \frac{\text{Rate}(\text{O}_2)}{\text{Rate}(\text{N}_2) + \text{Rate}(\text{O}_2)}, \quad (17)$$

gives the relation we used to estimate the oxygen density in the test section:

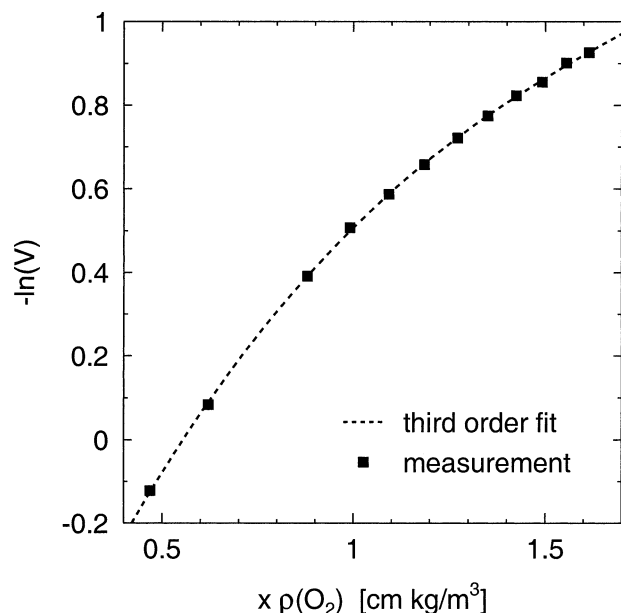


FIG. 5. Reponse of Kr2 to variations in gas thickness of oxygen (product of concentration and separation). Separation  $x$  is 2.41 cm. The continuous line is a third-order regression model.

$$\rho_o = \frac{\text{Rate}(\text{O}_2)}{\text{Rate}(\text{N}_2) + \text{Rate}(\text{O}_2)} \frac{(p_0 + \Delta p)}{R_o T}. \quad (18)$$

In this relation  $p_0$  is atmospheric pressure,  $\Delta p$  is the pressure difference between the test section, and atmospheric pressure,  $R_o$  is the specific gas constant for oxygen ( $259.83 \text{ J K}^{-1} \text{ kg}^{-1}$ ) and  $T$  temperature in the test section.  $\text{Rate}(\text{N}_2)$  and  $\text{Rate}(\text{O}_2)$  give the flow rates of the two gases taken from the flow controllers in liters per minute. In the first experiment, which was done with Kr1, we used a separation of 12.8 mm between light source and receiver. This resulted in clipping of the responses of the first two samples to the hygrometer's maximum output. To solve this problem we have performed all further oxygen calibrations at larger separations (values around 24 mm).

*b. Results*

We have optimized fit functions for all logarithmic responses as functions of oxygen thickness  $F_o \equiv x\rho_o$  using weighted least squares regression taking into account both  $x$  and  $y$  errors. Clipped samples were excluded from the fit. To facilitate the estimation of a tolerance level for the derivative of the model, which we will need to estimate the extinction coefficient, we have adopted Chebyshev polynomials orthogonal on the data range as base functions and constructed models of order 1 to order 4. All fit models were checked for outliers with the Chauvenet criterion (Chauvenet 1891, 558–566) which resulted in the elimination of not more than four samples. The degree of the final fit function is optimized by checking the residuals for systematic behavior. Third-order models were found to give the best representation of the measured samples. As an example we give the calibration of Kr2 in Fig. 5. The resulting values for linear oxygen extinction coefficients  $k_o$ ,  $k_{o13}$ ,  $k_{o26}$  and for nonlinear interference ratio  $G_o$  are shown in Table 2. Estimates of  $k_{o13}$  and  $k_{o26}$  are found via the derivative of the response curve at the corresponding gas thickness and values are only provided when these gas thicknesses are inside the calibration range.

From Table 2 we see that all our estimates for  $k_o$  for Campbell krypton hygrometers are smaller than the latest estimates by Tanner et al. For krypton hygrometers there is a dramatic difference between  $k_{o13}$  and  $k_{o26}$ : doubling the tube separation from 1.3 to 2.6 cm can reduce their oxygen sensitivity by a factor of nearly 3. For Lyman- $\alpha$  hygrometers the reduction is less strong, but still appreciable (20%). For both types of hygrometer the values for  $k_o$  are widespread, which implies that one cannot use a universal value for  $k_o$ : the oxygen sensitivities have to be individually calibrated for each hygrometer.

We see that the oxygen sensitivity does not vary with the dewpoint at which the calibration is made. This is consistent with our conclusion in the previous section, that the Lambert–Beer law can be assumed to be linear with respect to the water vapor thickness.

TABLE 2. Extinction coefficients for oxygen, estimated at 21% oxygen. Reference conditions are  $p = 101\,325 \text{ Pa}$ ,  $T = 305 \text{ K}$ , and  $\rho_w = 10 \text{ g m}^{-3}$ . Ratio  $G_o$ , estimated via relation (11), is the fractional increase of  $k_o$  when  $x$  is doubled from 1.3 to 2.6 cm. Coefficients  $k_{o13}$  and  $k_{o26}$  give extinction rates for  $x = 1.3 \text{ cm}$  and  $x = 2.6 \text{ cm}$ . Their values are only given when the corresponding gas thickness was within the calibration range.

	$T_{\text{dew}}$ (°C)	$k_o$ ( $10^{-3} \text{ m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )	Separation (cm $\pm$ 0.1 mm)	$G_o$ (%)	$k_{o13}$ ( $10^{-3} \text{ m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )	$k_{o26}$ ( $10^{-3} \text{ m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )
Tanner'85 (Kr)	—	8.5	—	—	—	—
Tanner'93 (Kr)	—	4.5	—	—	—	—
Kr1	6	$3.38 \pm 1.5\%$	1.280	-63	3.34	1.24
Kr1	16	$3.45 \pm 1.1\%$	1.280	-60	3.40	1.38
Kr2	6	$1.28 \pm 1.3\%$	2.410	-29	—	1.22
Kr3	6	$1.35 \pm 1.3\%$	2.425	-27	—	1.30
Ly1	6	$0.95 \pm 1.1\%$	2.115	-19	1.10	0.88
Ly1	16	$1.12 \pm 3\%$	2.115	-27	1.41	0.99
Ly2	6	$1.00 \pm 1.0\%$	2.520	-18	—	0.99
Ly2	16	$1.06 \pm 1.1\%$	2.520	-21	—	1.04

TABLE 3. Correction percentages  $100(c - 1)$  from relation (13b) for evaporation at different Bowen ratios for separations  $x = 1.3$  cm and  $x = 2.6$  cm. For the krypton tubes we used the value of  $k_w$  from the measurement for both separations. Tanner's values are listed for both separations, since the separation used in his study was unknown.

Bowen ratio	1.3-cm tube separation				2.6-cm tube separation			
	$\beta = 0.5$	$\beta = 1.0$	$\beta = 2.0$	$\beta = 5.0$	$\beta = 0.5$	$\beta = 1.0$	$\beta = 2.0$	$\beta = 5.0$
Tanner'89	5.2	10.5	20.9	52.3	5.2	10.5	20.9	52.3
Tanner'93	2.8	5.5	11.1	27.7	2.8	5.5	11.1	27.7
Kr1 dry	1.9	3.8	7.7	19.2	0.7	1.4	2.8	7.1
Kr1 wet	2.0	3.9	7.8	19.5	0.8	1.6	3.2	7.9
Kr2 dry	—	—	—	—	0.8	1.6	3.1	7.8
Kr3 dry	—	—	—	—	0.8	1.6	3.3	8.2
Ly1 dry	1.0	2.0	4.0	10.1	0.8	1.6	3.2	8.0
Ly1 wet	1.3	2.6	5.2	12.9	0.9	1.8	3.6	9.1
Ly2 dry	—	—	—	—	1.1	2.1	4.3	10.6
Ly2 wet	—	—	—	—	1.1	2.2	4.5	11.2

## 6. Oxygen-correction factors for latent heat fluxes

From coefficients  $k_w$  found in section 3 and  $k_o$  found in section 4 we calculate correction factors  $c(\beta)$  to correct latent heat fluxes (taken at reference conditions) for the hygrometer's oxygen sensitivity. Correction factors are estimated using relation (13b) for a range of Bowen ratios. In Table 3 our correction factors, presented as a percentage, are compared with those of Tanner et al. (1993). In section 3 we concluded that we can assume  $k_w$  to be independent from the separation between the tubes, but in section 4 we saw that  $k_o$  does vary significantly with the separation. For this reason the corrections are given for two separations: for  $x = 1.3$  cm and for  $x = 2.6$  cm. When a separation of 2.6 cm is set, then all our corrections for krypton hygrometers are smaller than those for the Lyman- $\alpha$  hygrometers and less than 10% even in arid conditions ( $\beta = 5$ ). To our opinion such a small correction factor may actually be called a *correction*. This is in contrast with the results of Tanner et al., who report corrections up to 28% for a krypton tube. In our opinion, such factors can no longer be seen as a correction, but they will have to be considered to be a zeroth-order component in the signal.

## 7. Sensitivity analysis

In this section we check if the theoretical model for the response of a hygrometer, that was presented in the first

section, can be used to explain why the oxygen sensitivity of these instruments decreases more strongly with increasing gas thickness than the water vapor sensitivity does.

We estimate extinction coefficients  $k_w$  and  $k_o$  numerically from relations (6) and (8). For the separation between the tubes, we adopt the two reference values that we used in the experiment:  $x = 1.3$  cm and  $x = 2.6$  cm. Differentiations are approximated with finite differences, where a variation in density of 1% is used. The extinction coefficients are estimated for wet air ( $10 \text{ g m}^{-3}$ ) under atmospheric conditions (1 atm pressure and 21% volume oxygen).

For compatibility with the experiments performed in this study, we have to be careful with the selection of gas densities: the experiments were isobaric (and approximately isothermic) and, consequently, the number of molecules in the test section was constant. Addition of water vapor thus implied reduction of the amount of oxygen. This characteristic of isobaric measurement influences the densities, which we have to select when we are estimating  $k_w$ . In our experiments we have calibrated in how much water vapor has a stronger absorption of krypton light than oxygen. The just described effect of gas exclusion has no influence on  $k_o$ , since in the corresponding experiment we fixed the water vapor density to a constant value (water vapor was added *after* the nitrogen/oxygen ratio was set).

TABLE 4. Extinction coefficients  $k_w$  and  $k_o$  and corrections  $100(c - 1)$  estimated from theoretical models for the response. For the krypton hygrometer we used a model with one emission line and a model with two emission lines. For the Lyman- $\alpha$  hygrometer we used a simple model with one emission line and a nonideal model with an emission spectrum following Buck (1981). Estimates are given for two tube separations: 1.3 and 2.6 cm.

Model	$\alpha$ (Å)	$k_{w13}$ ( $\text{m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )	$k_{w26}$ ( $\text{m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )	$k_{o13}$ ( $\text{m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )	$k_{o26}$ ( $\text{m}^3 \text{ g}^{-1} \text{ cm}^{-1}$ )	$c_{13} - 1$ (%), $\beta = 1$	$c_{26} - 1$ (%), $\beta = 1$
Kr 1 line	3.00	0.311	0.310	0.0174	0.0131	10.3	7.8
Kr 1 line	0.05	0.338	0.338	0.0119	0.0119	6.5	6.5
Kr 2 line	3.00	0.277	0.278	0.0206	0.0161	13.7	10.7
Kr 2 line	0.05	0.295	0.302	0.0249	0.0225	15.5	13.8
Ly 1 line	3.00	0.498	0.508	0.0177	0.0118	6.5	4.3
Ly 1 line	0.05	0.591	0.591	0.000 66	0.000 55	0.21	0.17
Ly Buck	3.00	0.456	0.463	0.0147	0.0099	5.9	3.9
Ly Buck	0.05	0.456	0.463	0.0147	0.0099	5.9	3.9



In practice, to suppress the less energetic emission line in the kr spectrum, which is more sensitive to oxygen than the more energetic one, the kr hygrometers were fitted with optical coatings. To include the effect of these coatings in our simulation we have made two runs for the krypton sensitivity: one with no suppression of the secondary line in the emission spectrum, and one where the secondary line is fully suppressed. For the Lyman- $\alpha$  hygrometer we made one run with a single emission line and a second run with Buck's emission spectrum from Fig. 1. With the above models we calculated extinction coefficients  $k_{w13}$ ,  $k_{w26}$ ,  $k_{o13}$ ,  $k_{o26}$  and the correction factors  $c$  [at Bowen ratio 1, see relation (13b)] for two different spectral widths of the krypton/Lyman emission lines:  $\alpha = 0.05 \text{ \AA}$  and  $\alpha = 3 \text{ \AA}$ . The results are shown in Table 4.

We see that all estimates for extinction coefficients are much larger than we found in the experiments. For all models, the influence on the extinction coefficient for water vapor by an increase in tube separation from 1.3 to 2.6 cm is 2% or less. This is in accordance with our experiment, where we found that with respect to water vapor the Lambert–Beer law can be assumed to be linear. Concerning the oxygen sensitivity we see that all models exhibit a reduction in oxygen sensitivity by 20%–30% when the separation is doubled from 1.3 to 2.6 cm. These values agree with the  $G_o$  values that we found in the experiment for all sensors but Kr1, which had a stronger reduction. The two-line model for the krypton hygrometer is more sensitive to oxygen than the one-line model, as could be expected from Fig. 2. The simple Lyman model with a thin emission line gives an underestimation of the influence of oxygen on evaporation estimates. From the analysis presented in this section, we conclude that we can explain the qualitative characteristics of the oxygen sensitivity of optical hygrometers from physical principles. The lack of quantitative correspondence between model and experiment may be connected with the resolution of the absorption spectra of oxygen and of water vapor or with optical coatings. Better estimates of the spectra and more information about the filters are required.

## 8. Conclusions

We conclude that we can confirm the findings of Tanner et al. (1993) that the oxygen sensitivity of krypton hygrometers, that was reported earlier by Tanner (1989), overestimates the oxygen sensitivity of recently manufactured Campbell KH2O krypton hygrometers. Tanner's recent value for the extinction coefficient by oxygen still overestimates the characteristics of our hy-

grometers by 25% and up to a factor of 3, depending on the choice of the individual hygrometers and on the separation of the tubes.

For krypton hygrometers we have shown that, with respect to variations in water vapor thickness, the Lambert–Beer law is sufficiently linear to allow for the use of  $k_w$  measured at one separation of the tubes in a setup where a different separation is used. For Lyman- $\alpha$  hygrometers the nonlinearity was small, but significant, such that accurate measurements can only be done when this type of hygrometer is calibrated at the same separation that will be used in the experiment.

We have seen that, both for krypton hygrometers and for Lyman- $\alpha$  hygrometers, the dependence of the Lambert–Beer law on variations in oxygen thickness is highly nonlinear, the nonlinearity being stronger for krypton hygrometers than for Lyman- $\alpha$ s. This characteristic can be used to optimize the oxygen sensitivity of hygrometers: by using a separation of 2.6 cm instead of 1.3 cm one reduces the oxygen correction term of evaporation estimates by a factor of 3 for krypton hygrometers and by 20% for Lyman- $\alpha$ s. When a separation of 2.6 cm is used, then the corrections for krypton hygrometers equal those for Lyman- $\alpha$  hygrometers. These corrections are still acceptable at high Bowen ratios, while the values taken from literature were not.

The spread in oxygen sensitivities of krypton hygrometers calls for individual oxygen calibrations of such hygrometers.

The decrease with tube separation of the oxygen correction term for evaporation estimates can be accounted for by a response model using multiple emission and absorption lines with finite width.

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