



# Optimal spectral region for real-time monitoring of sub-ppm levels of water in phosphine by cavity ring-down spectroscopy<sup>☆</sup>

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## Abstract

We have utilized cavity ring-down spectroscopy (CRDS) to characterize the pressure and carrier gas effects on the shape of a water absorption line. The half-width at half-maximum pressure-broadening coefficient for the water line at  $10687.36\text{ cm}^{-1}$  was measured to be  $58 \pm 6\text{ MHz kPa}^{-1}$  ( $0.20 \pm 0.02\text{ cm}^{-1}\text{ atm}^{-1}$ ) for water in phosphine ( $\text{PH}_3$ ). This value is twice as large as the pressure-broadening coefficient for the same absorption transition in the case of water in air. Strong interference from neighboring  $\text{PH}_3$  lines limits the sensitivity of the system in the region of this absorption line. We have also characterized the spectral neighborhood of several other water absorption transitions for the water– $\text{PH}_3$  system; these additional water– $\text{PH}_3$  CRDS spectra are presented. We have identified the spectral region around the water line at  $10667.76\text{ cm}^{-1}$  as optimal for CRDS measurements of the water– $\text{PH}_3$  system. Minimal interference from adjacent  $\text{PH}_3$  absorption transitions in this region enables high-sensitivity, real-time measurements of trace water in bulk  $\text{PH}_3$ . Utilizing this water line, our CRDS apparatus has an estimated detection limit of  $50\text{ nmol mol}^{-1}\text{ H}_2\text{O}$  in  $\text{PH}_3$ . © 2003 Elsevier B.V. All rights reserved.

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## 1. Introduction

Trace levels of water contamination in semiconductor source gases are currently difficult to measure quickly and accurately. The presence of  $\text{H}_2\text{O}$  and its constituents in source materials or

growth chambers is believed to cause decreased luminescent efficiency and to generally reduce device quality, particularly in Al-containing compounds. The inability to measure trace  $\text{H}_2\text{O}$  concentrations in specialty gases has led crystal growers to choose more expensive growth conditions that reduce sensitivity to water vapor. This situation motivates the development of new methods for measuring residual amounts of  $\text{H}_2\text{O}$  in bulk  $\text{PH}_3$  and other semiconductor gases.

We have developed a cavity ring-down spectroscopy (CRDS) apparatus for measuring trace  $\text{H}_2\text{O}$

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in bulk  $\text{PH}_3$  and other semiconductor source gases. To date, we have measured water concentrations in  $\text{PH}_3$  at the CRDS system at  $590 \pm 160 \text{ nmol mol}^{-1}$  (ppb),  $18.0 \pm 1.5 \text{ } \mu\text{mol mol}^{-1}$  (ppm), and  $730 \pm 60 \text{ } \mu\text{mol mol}^{-1}$  (ppm), for three different gas cylinders. We note that the first of these measurements probably included water vapor desorbing from the gas system walls, and the last was from a cylinder that was kept in use for 3 years beyond its recommended shelf life [1]. The CRDS system has also allowed us to identify gas purifiers with leaks and with high moisture outgassing. In previous work [1], we have used phosphine ( $\text{PH}_3$ ) characterized by CRDS measurements in the gas-source molecular beam epitaxial growth of AlInP to correlate the materials properties with moisture contamination. The O concentration in the AlInP measured by SIMS and photoresponse measured with current–voltage properties under illumination both were relatively insensitive to an increased level of water vapor contamination in the source  $\text{PH}_3$ , possibly because of the absence of reactive organometallic compounds in the growth chamber.

The CRDS system uses a near-infrared diode laser to probe absorption transitions of  $\text{H}_2\text{O}$  with high sensitivity. The  $\text{H}_2\text{O}$  concentration is derived from the measured area under an isolated water absorption line. By quantifying changes in  $\text{H}_2\text{O}$  line shape with pressure and composition of the bulk carrier gas, and by precisely measuring and stabilizing the background losses in the cavity, one can relate the peak height of the  $\text{H}_2\text{O}$  absorption line to the peak area. With this line shape information, the laser wavelength need not be scanned over the entire absorption line. Instead, by tuning the laser wavelength to the absorption line center, the peak absorbance can be continuously monitored to provide a sensitive measure of real-time changes in  $\text{H}_2\text{O}$  concentration.

The purpose of this work is to characterize the absorption spectrum of the  $\text{PH}_3$ – $\text{H}_2\text{O}$  system in the spectral region surrounding 940 nm to enable quantitative spectroscopic measurements of trace quantities of  $\text{H}_2\text{O}$  in bulk  $\text{PH}_3$ . Specifically, by characterizing the change in line shape for absorption by water in a  $\text{PH}_3$  matrix and by identifying the spectral region with minimal back-

ground losses from  $\text{PH}_3$  absorption, we may enable accurate real-time CRDS monitoring of trace water in bulk  $\text{PH}_3$ .

We have previously reported a detection limit of  $10 \text{ nmol mol}^{-1}$  (ppbv) of  $\text{H}_2\text{O}$  in  $\text{N}_2$  [1]. However, for the previously considered  $\text{H}_2\text{O}$  absorption line, the CRDS detection limit is 10–50 times higher for  $\text{H}_2\text{O}$  in  $\text{PH}_3$  due to the interference by weak absorption lines of the bulk  $\text{PH}_3$ . The  $\text{PH}_3$  absorption lines in this spectral region have not been previously mapped, so there is no known spectral window of lower  $\text{PH}_3$  absorption. To address this need, we measured the  $\text{PH}_3$  absorption spectrum in the neighborhood of several strong  $\text{H}_2\text{O}$  absorption peaks. These results enable us to identify an optimal  $\text{H}_2\text{O}$  line suitable for high-sensitivity measurements of trace  $\text{H}_2\text{O}$  in bulk  $\text{PH}_3$ .

## 2. Technique

CRDS [2,3] is a technique in which the absorption coefficient of a gas sample is obtained directly from measurements of the decay of radiant power circulating inside a high-finesse optical cavity. The resonating cavity is composed of two curved dielectric mirrors separated by a distance  $a$  and forming a stable optical resonator for laser light at frequency  $\nu$ . Following the abrupt termination of the laser excitation, the optical power leaking out of the ring-down cavity through the transmission of the back mirror is measured with a fast detector. The CRDS signal is an exponential decay characterized by the ring-down cavity decay time constant  $\tau$ . The decay time constant  $\tau(\nu)$  is inversely proportional to the sum of all single-pass losses within the cavity,  $L_{\text{tot}}(\nu)$ , and is given by

$$\tau(\nu) = \frac{a}{c L_{\text{tot}}(\nu)}, \quad (1)$$

where  $c$  is the speed of light in the medium within the cavity. In addition to background losses (including Rayleigh scattering as well as scattering and absorption by the mirrors), the loss may also include Beer–Lambert absorption of the circulating light by the material in the cavity. This

frequency-dependent change in  $L_{\text{tot}}(\nu)$  causes a corresponding change in the ring-down time constant. Because CRDS relies on measurement of a time constant rather than a change in amplitude, it is unaffected by intensity drift (due to variations in the light source, other optical elements, or ambient conditions) and can typically measure changes in loss-per-pass as small as  $0.05 \times 10^{-6}$  using commercially available low-loss mirrors. This sensitivity to small changes in loss enables the detection of small quantities of light-absorbing impurities in the cavity.

The base loss of the ring-down system can usually be treated as a slowly varying linear function over the measured spectral range, so that the measured CRDS spectra can be modeled as the sum of Voigt profiles [4] and a slightly sloped baseline. Consider the simplest case, where only a single absorption line of  $\text{H}_2\text{O}$ , with a line strength denoted by  $S_{\text{water}}$ , is present within the measured spectral range. Then the mole fraction of  $\text{H}_2\text{O}$ ,  $x_{\text{w}}$ , is given by

$$x_{\text{w}} = \frac{A_{\text{Voigt}}}{anS_{\text{water}}}, \quad (2)$$

where  $A_{\text{Voigt}}$  is the analytical area of the single Voigt profile given by a least-squares fit to the observed spectrum, and  $n$  is the total number density of the gas mixture. The Voigt profile is a convolution of the Gaussian and Lorentzian line shapes [5]. The Gaussian component is the Doppler width, which is a function of the absorbing species' frequency, molecular weight, and temperature. The Lorentzian component incorporates collisional broadening of the spectral line and is thus pressure-dependent. The pressure-broadening coefficient is given by the change in the Lorentzian half-width at half-maximum (HWHM) per unit change in pressure.

### 3. Experiment

The ring-down apparatus used here has been described in more detail elsewhere [1]. The system is composed of a symmetric ring-down cavity with mirrors of nominal reflectivity 0.999985 mounted in an evacuable volume. The internal surfaces

are electro-polished stainless steel tubing, and the internal volume of the system is approximately 0.2 l. A piezoelectric transducer precisely translates one cavity mirror, enabling active control of the optical length of the cavity. The probe laser is a tunable, continuous-wave, single-mode external cavity diode laser emitting in the spectral range 920–940 nm. The laser output passes through an acousto-optic modulator (AOM), and the first-order beam deflected by the AOM is used to pump the ring-down cavity. The passive decay of light from the ring-down cavity is initiated by switching the drive power to the AOM, yielding an effectively instantaneous ( $< 10$  ns) turn-off of the probe laser. Spectral scans are achieved by tuning the diode laser frequency through sequential longitudinal modes of the fundamental transverse mode of the length-stabilized cavity. At each mode, 25–30 decay signals are acquired; the ring-down decay times are averaged after fitting the decays individually over a period of more than  $10\tau$ .

Values from the most recent spectral line database [6,7] have been used for the transition line strengths. Uncertainties are not reported for individual lines but are reported overall as 2.5–5%; ongoing measurements of the  $\text{H}_2\text{O}$  line strengths utilizing primary thermodynamic-based standards of humidity generation [8] will lead to lower uncertainties in these line strengths. The transition frequencies (expressed as the wavenumber  $\tilde{\nu} = c\nu$ ), wavelengths and line strengths for the four  $\text{H}_2\text{O}$  absorption lines measured here are given in Table 1. The uncertainties in concentration reported here are standard uncertainties (i.e., one standard deviation) and represent uncertainties in the fit-derived Voigt area, temperature and pressure. Measurements were typically made on flowing gas samples between 5 and 15 kPa at 300 K.

### 4. Results

The absorption spectrum in the neighborhood of the water line centered at  $10687.36 \text{ cm}^{-1}$  was measured by CRDS at five different pressures ranging from 10 to 20 kPa (75–150 Torr) of bulk

Table 1

Transition wavenumbers, wavelengths and line strengths [6,7] for the water absorption lines used in the current CRDS measurements

Label	Transition wavelength (nm)	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	$S_{\text{water}}$ ( $\text{cm}^2 \text{MHz molecule}^{-1}$ )	$S_{\text{water}}$ ( $\text{cm molecule}^{-1}$ )
A	937.40350	10667.76	$1.96 \times 10^{-17}$	$6.55 \times 10^{-22}$
B	935.68451	10687.36	$2.05 \times 10^{-17}$	$6.83 \times 10^{-22}$
C	934.80509	10697.42	$1.75 \times 10^{-17}$	$5.84 \times 10^{-22}$
D	934.52070	10700.67	$1.56 \times 10^{-17}$	$5.19 \times 10^{-22}$

The line strengths are reported both in SI and spectroscopic units for a temperature of 296 K.

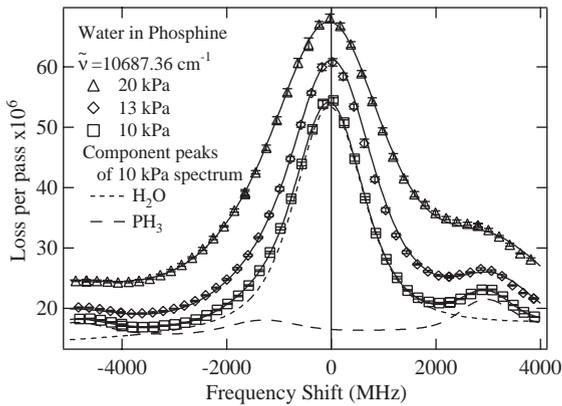


Fig. 1. CRDS spectra of water in  $\text{PH}_3$  at three pressures with an  $\text{H}_2\text{O}$  mole fraction of  $22 \mu\text{mol mol}^{-1}$ . Zero frequency shift corresponds to the center of the water absorption line at  $10687.36 \text{ cm}^{-1}$ . The additional features in the spectrum are due to absorption by the bulk  $\text{PH}_3$ . The spectra were taken for  $\text{PH}_3$  flowing at  $65 \pm 3$  standard  $\text{cm}^3 \text{min}^{-1}$ ; the  $\text{PH}_3$  was sampled directly from the  $\text{PH}_3$  cylinder without flowing through an in-line purifier. The solid lines represent a least-squares fit of the data to a sum of Voigt profiles and a linear baseline. The water concentration varies slightly for the three spectra, but all are within  $22 \pm 2 \mu\text{mol mol}^{-1}$ .

$\text{PH}_3$ . The peak widths increase with total pressure, as shown in the three representative spectra in Fig. 1. Lorentzian HWHM values were obtained by fitting these spectra with Voigt profiles for the water absorption peak and for the neighboring  $\text{PH}_3$  absorption peaks. From a linear fit to the Lorentzian HWHM values for the water absorption line, shown in Fig. 2, we obtain a value for the pressure-broadening coefficient of  $58 \pm 6 \text{ MHz kPa}^{-1}$  ( $0.20 \pm 0.02 \text{ cm}^{-1} \text{ atm}^{-1}$ ) for water in  $\text{PH}_3$ . This value is twice the broadening coefficient in air ( $28 \text{ MHz kPa}^{-1}$ ) [6,7].

The spectra shown in Fig. 1 were intentionally taken at relatively high water mole fraction in

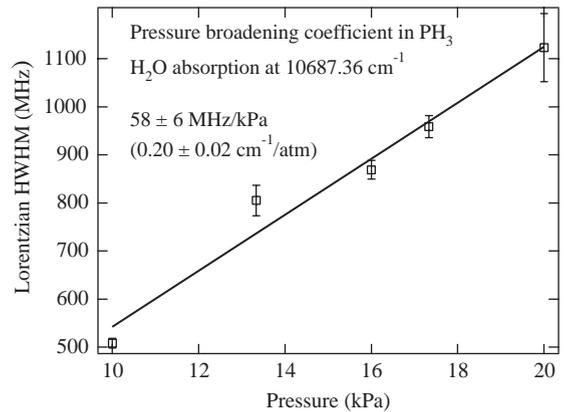


Fig. 2. Pressure-dependent variation in the Lorentzian HWHM of the water absorption line for water in  $\text{PH}_3$ . The Lorentzian HWHM was determined from the Voigt-profile fit of the water absorption peak, as shown in Fig. 1. The pressure-broadening coefficient ( $58 \pm 6 \text{ MHz kPa}^{-1}$ ) for the water– $\text{PH}_3$  system shown here is roughly twice the pressure-broadening coefficient ( $28 \text{ MHz kPa}^{-1}$ ) for water in air.

order to simplify the measurement of the pressure-broadening coefficient. The  $\text{H}_2\text{O}$  mole fraction in the three spectra shown in Fig. 1 varies slightly from spectrum to spectrum but is given by  $22 \pm 2 \mu\text{mol mol}^{-1}$  (often reported as 22 ppm) for all spectra shown. At  $\text{H}_2\text{O}$  mole fractions of less than  $1 \mu\text{mol mol}^{-1}$ , the nearby  $\text{PH}_3$  absorption lines (shown together as the dashed line in Fig. 1) complicate the interpretation of the CRDS spectra. The high background absorption due to  $\text{PH}_3$  limits the sensitivity of any optical absorption technique utilizing this water line at  $10687.36 \text{ cm}^{-1}$ .

Absorption spectra of  $\text{H}_2\text{O}$  in bulk  $\text{PH}_3$  for several relatively strong  $\text{H}_2\text{O}$  lines were surveyed. These spectra are displayed in Fig. 3, along with a spectrum at the  $10687.36 \text{ cm}^{-1}$  line for compar-

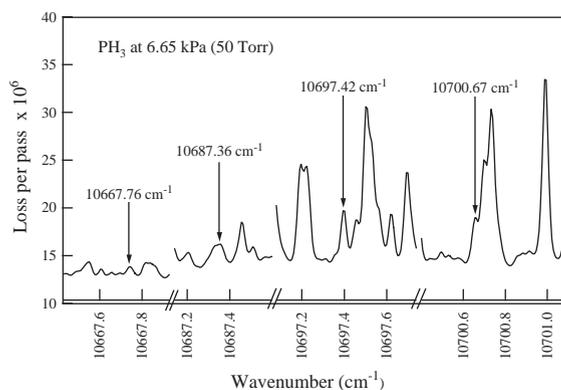


Fig. 3. CRDS spectra of water and  $\text{PH}_3$  absorption lines. Four of the most strongly absorbing water lines in the 930–940 nm spectral region were selected for this survey. In each spectrum, an arrow indicates the location of water absorption line. The overlap of  $\text{PH}_3$  absorption lines with the water absorption is particularly evident in the spectrum at  $10697.42\text{ cm}^{-1}$ . The absorption loss of the peak is approximately  $5 \times 10^{-6}$ , but no more than  $2 \times 10^{-6}$  is due to water absorption. This strong  $\text{PH}_3$  absorption in the spectral neighborhood of the water lines at  $10697.42$  and at  $10700.67\text{ cm}^{-1}$  complicates the determination of the water concentration. In contrast, the water line at  $10667.76\text{ cm}^{-1}$ , shown in a larger scale in Fig. 4, has only relatively weak  $\text{PH}_3$  absorption lines nearby.

ison. Inspection of Fig. 3 shows that the  $\text{H}_2\text{O}$  lines at  $10697.42$  and at  $10700.67\text{ cm}^{-1}$  are both adjacent to relatively strong  $\text{PH}_3$  absorptions. However, the spectrum in the vicinity of  $\text{H}_2\text{O}$  line at  $10667.76\text{ cm}^{-1}$  contains a much lower level of background absorption from the bulk  $\text{PH}_3$ . This spectrum is shown on a larger scale in Fig. 4. While there are several  $\text{PH}_3$  absorption lines near the  $\text{H}_2\text{O}$  absorption line, they are all relatively weak and interfere only minimally with the analysis of the  $\text{H}_2\text{O}$  absorption. The pressure-broadening coefficient for this water absorption line was found to be  $28 \pm 7\text{ MHz kPa}^{-1}$  ( $0.066\text{ cm}^{-1}\text{ atm}^{-1}$ ) in  $\text{PH}_3$ . (The air-broadened value for this line is  $29.1\text{ MHz kPa}^{-1}$ .) The  $\text{H}_2\text{O}$  absorption in Fig. 4 corresponds to an  $\text{H}_2\text{O}$  mole fraction of  $590 \pm 160\text{ nmol mol}^{-1}$ . By comparing the peak height with the experimental uncertainty in the measured loss, we estimate that the detection limit at this line is  $50\text{--}80\text{ nmol mol}^{-1}$  of  $\text{H}_2\text{O}$  in  $\text{PH}_3$ . This result is in contrast to previous measurements using the  $\text{H}_2\text{O}$  water absorption line at  $10687.36\text{ cm}^{-1}$  (shown in Fig. 1), in which it was

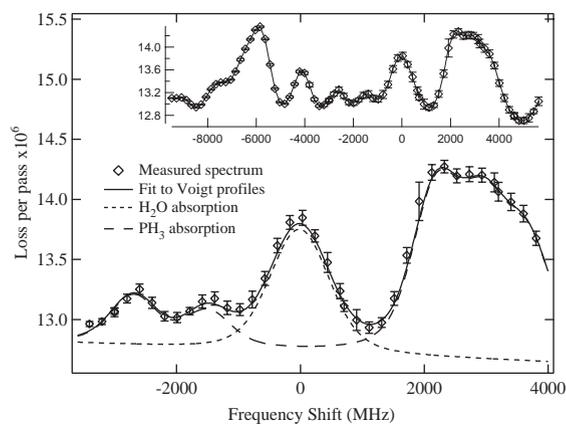


Fig. 4. CRDS spectrum of water and  $\text{PH}_3$  absorption near  $10667.76\text{ cm}^{-1}$ . The immediate neighborhood of the water peak is shown in the main graph; the inset displays a broader frequency range. The relatively weak interference from adjacent  $\text{PH}_3$  absorption lines makes CRDS measurements at this water line more sensitive than measurements at the other lines shown in Fig. 3. In this spectrum, a peak corresponding to  $590 \pm 160\text{ nmol mol}^{-1}$  of water is distinct. We estimate that as little as  $50\text{ nmol mol}^{-1}$  of water in  $\text{PH}_3$  will be observable. The spectrum was taken at  $6.65\text{ kPa}$  ( $50\text{ Torr}$ ) on  $\text{PH}_3$  flowing at  $84 \pm 2$  standard  $\text{cm}^3\text{ min}^{-1}$ ; the  $\text{PH}_3$  was sent through an in-line purifier before measurement.

difficult to distinguish  $\text{H}_2\text{O}$  mole fractions of less than  $800\text{ nmol mol}^{-1}$  water.

The background absorption due to bulk  $\text{PH}_3$  at  $6.65\text{ kPa}$  ( $50\text{ Torr}$ ) is shown as a dashed line in Fig. 4. With the knowledge of this background level, the concentration of water in  $\text{PH}_3$  may now be monitored in real-time by measuring the loss at the absorption line center. The background absorption will increase with pressure as the  $\text{PH}_3$  absorption lines broaden; this background level therefore must be measured for each pressure and checked often in high-accuracy work on measurements of low  $\text{H}_2\text{O}$  concentration.

## 5. Summary

For real-time monitoring of  $\text{H}_2\text{O}$  concentration with CRDS, knowledge of the baseline loss is required along with the expected height of the peak at different concentrations. The  $\text{H}_2\text{O}$  peak height will be affected by both the  $\text{H}_2\text{O}$  concentration and the total gas pressure. We have

measured a value of  $58 \pm 6 \text{ MHz kPa}^{-1}$  for the pressure-broadening coefficient (in  $\text{PH}_3$ ) of the  $\text{H}_2\text{O}$  absorption line located at  $10687.36 \text{ cm}^{-1}$ . This  $\text{H}_2\text{O}$  absorption line is the strongest  $\text{H}_2\text{O}$  absorption line in this wavelength region, which should enable the highest-sensitivity measurements of  $\text{H}_2\text{O}$ . However, the  $10687.36 \text{ cm}^{-1}$  line is immediately adjacent to several  $\text{PH}_3$  transitions that complicate the observed spectra. We have measured the combined  $\text{PH}_3/\text{H}_2\text{O}$  absorption spectrum in the neighborhood of several other strong  $\text{H}_2\text{O}$  absorption lines. Although  $\text{PH}_3$  absorption lines are present in all these spectra, a spectral region containing an  $\text{H}_2\text{O}$  absorption line with minimal  $\text{PH}_3$  interference has been identified. At this  $\text{H}_2\text{O}$  line at  $10667.76 \text{ cm}^{-1}$ , a peak corresponding to a  $\text{H}_2\text{O}$  mole fraction of  $590 \text{ nmol mol}^{-1}$  in bulk  $\text{PH}_3$  was clearly distinguishable from the  $\text{PH}_3$  background absorption. The detection limit at this line is estimated to be  $50 \text{ nmol mol}^{-1}$  of  $\text{H}_2\text{O}$  in  $\text{PH}_3$ , improving on previous measurements that were insensitive below approximately  $800 \text{ nmol mol}^{-1}$  of  $\text{H}_2\text{O}$  in  $\text{PH}_3$ .

Measurements using this  $\text{H}_2\text{O}$  absorption line should display high sensitivity for both static and time-dependent conditions.

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