Trace Moisture Contamination in Ultra-High Purity Phosphine: Techniques for Measurement and Control

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Introduction

- Gas purity is critical to the production of III-V compound semiconductor devices
- Trace O from impurities such as H_2O, are incorporated into epitaxial layers during MOCVD processes
  - cause lattice defects and undesirable oxide formation
  - decrease luminescence of optoelectronic components
- Objectives:
  - Investigate methods for measurement of trace H_2O impurity in PH_3
  - Demonstrate moisture control through point-of-use purification

Measurement Techniques

- **Requirements of Trace Analysis Instrumentation**
  - Sensitivity and selectivity for H_2O in PH_3 at ppb levels
  - Rapid and accurate response
  - Rugged and capable of withstanding reactive gas
  - Long term stability
  - Ease of use and applicability to on-line monitoring
- **Techniques Investigated**
  - Chilled mirror hygrometry
  - Cavity ring-down spectroscopy
  - FTIR spectroscopy

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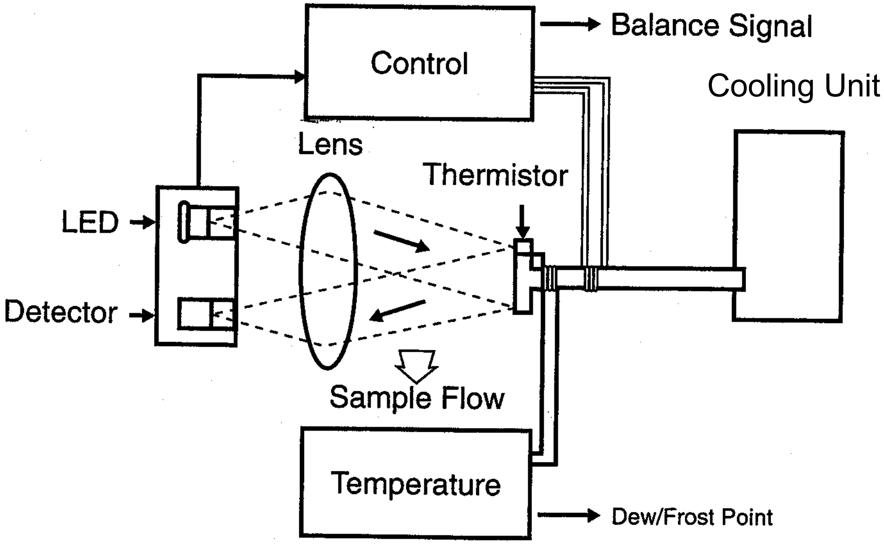
Chilled Mirror Hygrometry

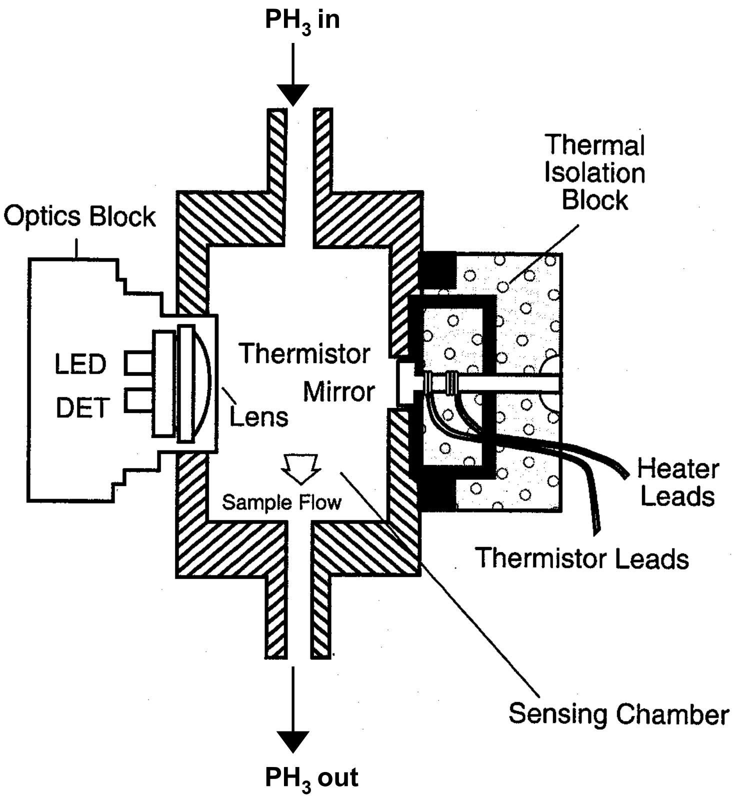
- Frost point is defined as the temperature to which a volume of gas must be cooled such that it becomes saturated with respect to ice.
- Exponential relationship between frost point and H_2O concentration is well documented in N_2
- Fundamental measure of H_2O concentration
- Capable of long-term accuracy and stability
- Calibration required in PH_3
- Condensation temperature of the PH_3 matrix gas limits the ultimate sensitivity of the technique

Chilled Mirror Hygrometer



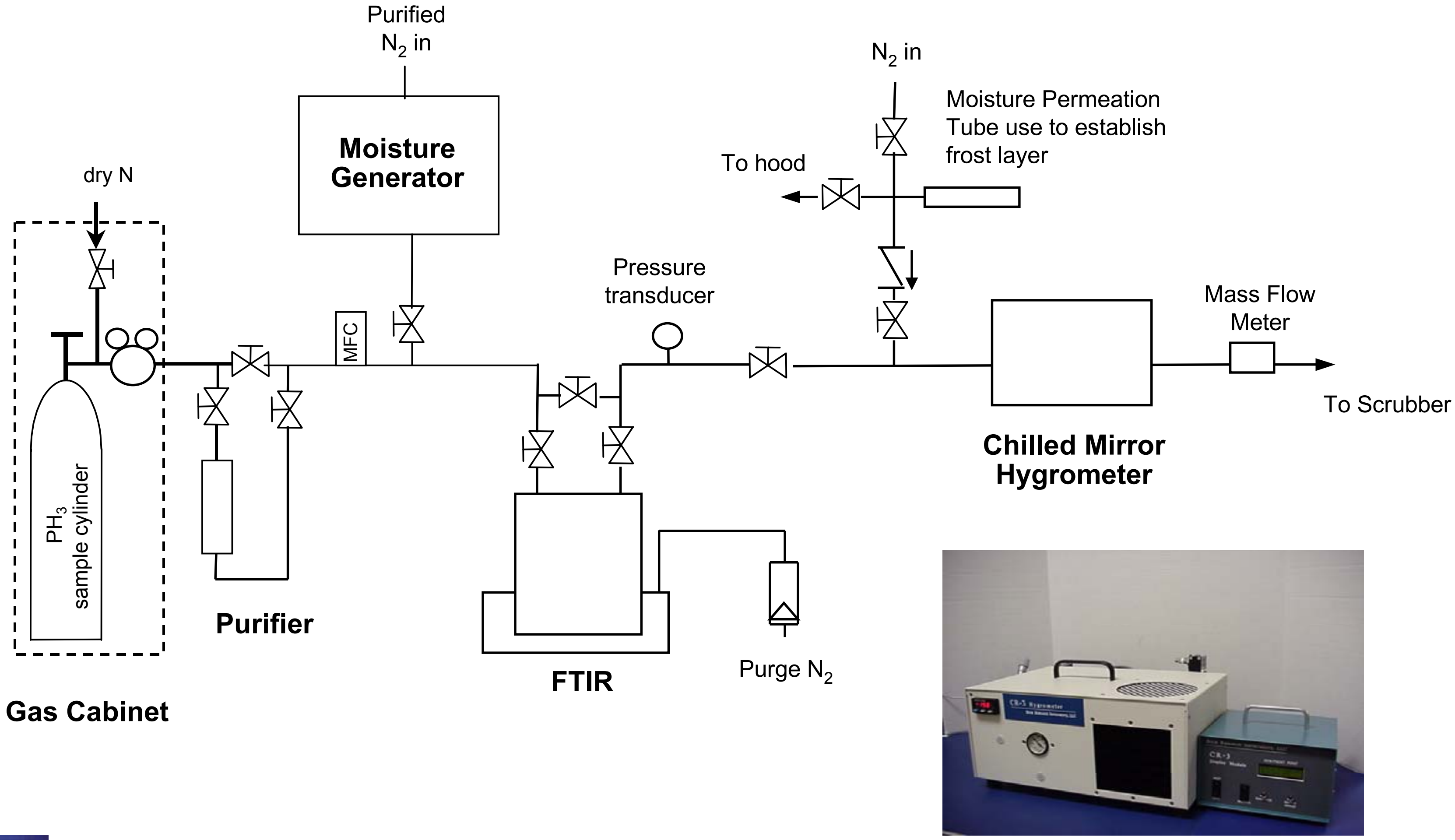
The mirror temperature is cooled until a frost layer is established. The mirror temperature is adjusted to maintain a constant condensation layer on the mirror. The layer is monitored optically and displayed as a balance voltage

Cryogenic Sensing Chamber and Mirror Assembly



Buck Research CR-3 Chilled Mirror Hygrometer

Setup for Evaluation of Chilled Mirror Hygrometer



Purified N_2 in

Moisture Generator

N_2 in

Moisture Permeation Tube use to establish frost layer

To hood

dry N

MFC

Pressure transducer

Mass Flow Meter

PH_3 sample cylinder

To Scrubber

Chilled Mirror Hygrometer

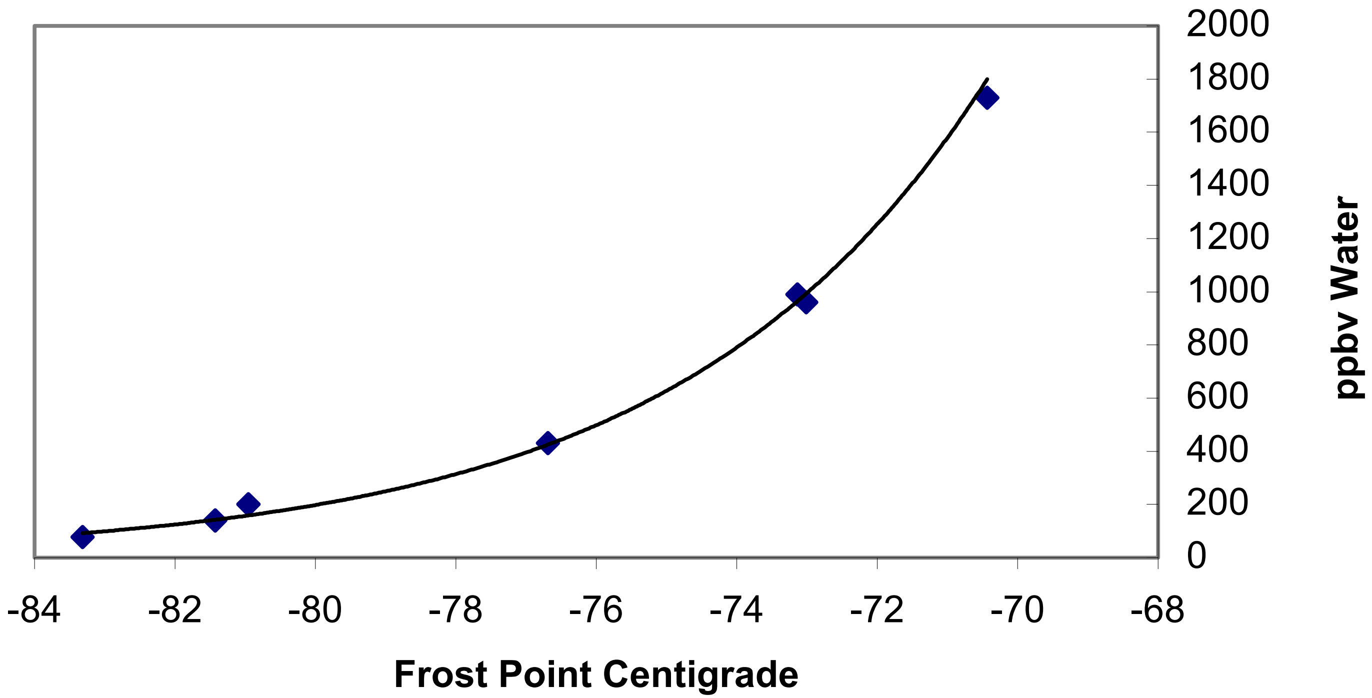
Purifier

FTIR

Purge N_2

Gas Cabinet

Calibration Curve for Moisture in Phosphine using the Chilled Mirror Hygrometer



- **Calibration points from 77 - 1730 ppbv moisture in PH_3 (1 slpm, 14.7 psia)**
- **Percentage of N_2 in PH_3 kept below 1% for all calibration points**
- **System equilibrated for ~4 hours at each moisture concentration**

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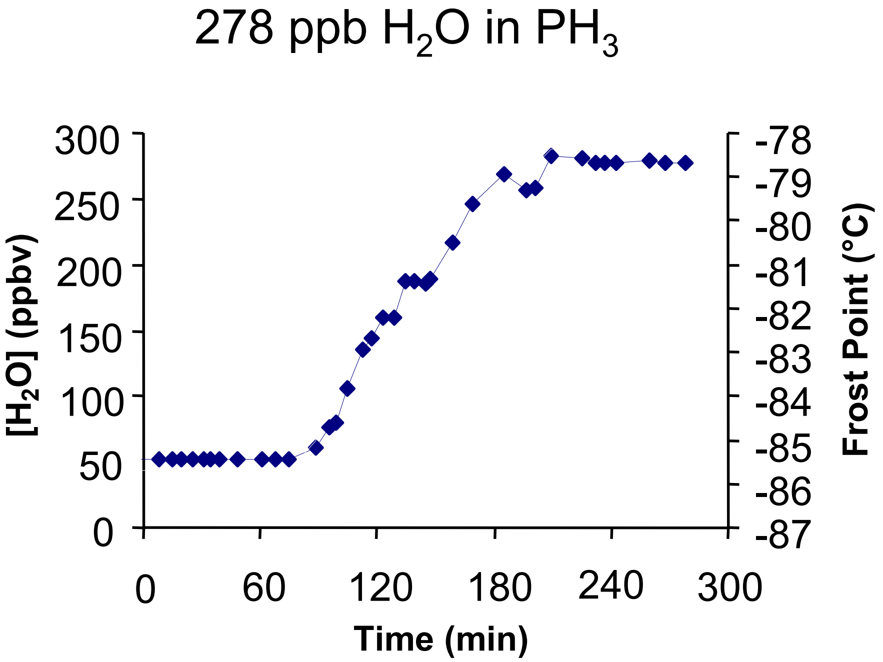
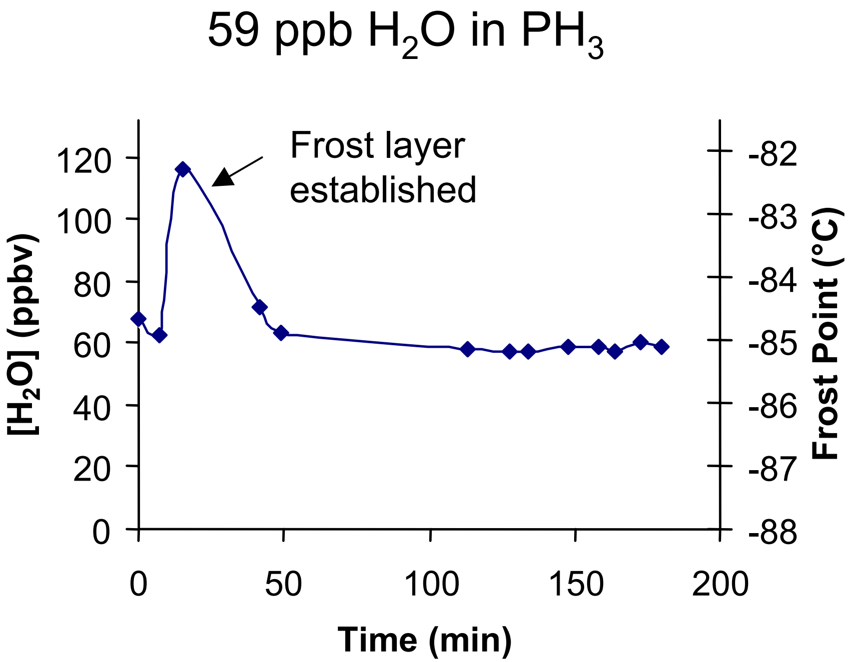
Moisture Detection in Phosphine Cylinder Sources Using Chilled Mirror Hygrometer





- PH_3 from cylinder source, (N5.7 purity) at 1 slpm
- Long equilibration time

- PH_3 from cylinder source, (Ultima 6N purity) at 1 slpm
- Once established, frost layer maintained during analysis

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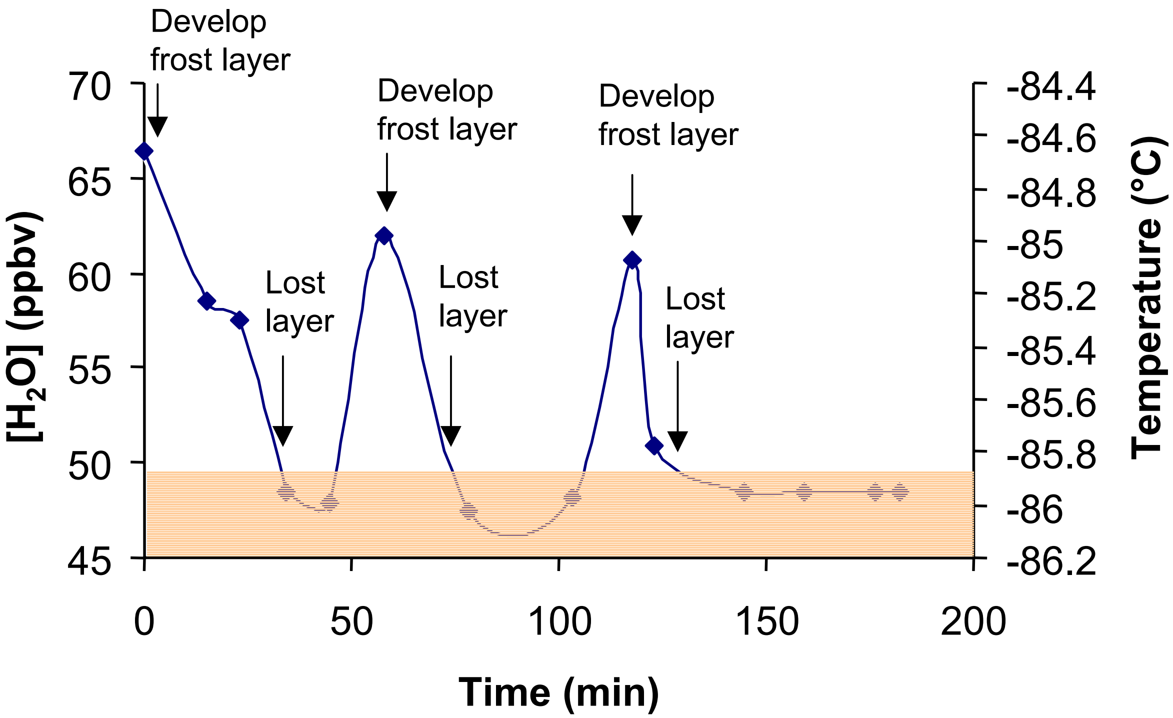
Detection Limit



- Mirror could not be cooled below minimum mirror set-point of -86°C due to potential condensation of liquid PH_3
- H_2O concentration in PH_3 less than detection limit

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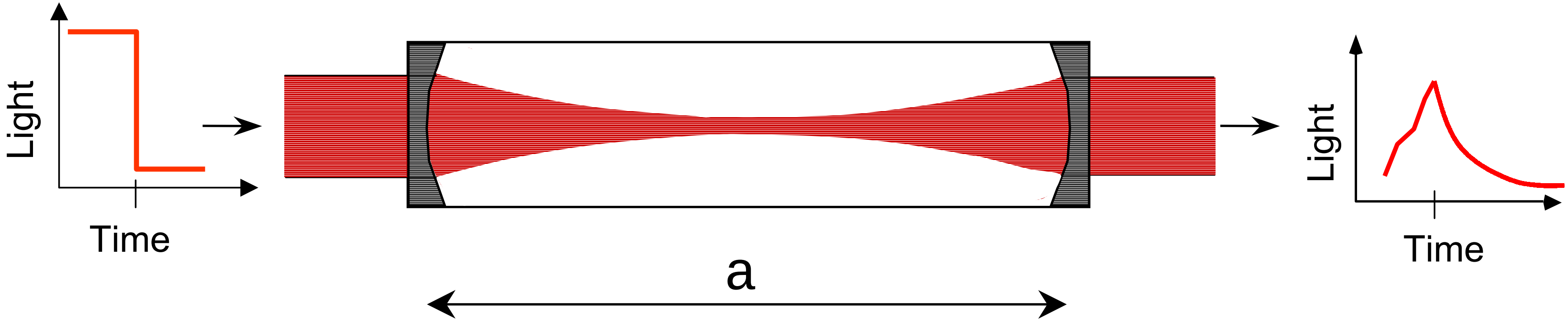
Observations with Chilled Mirror Hygrometer

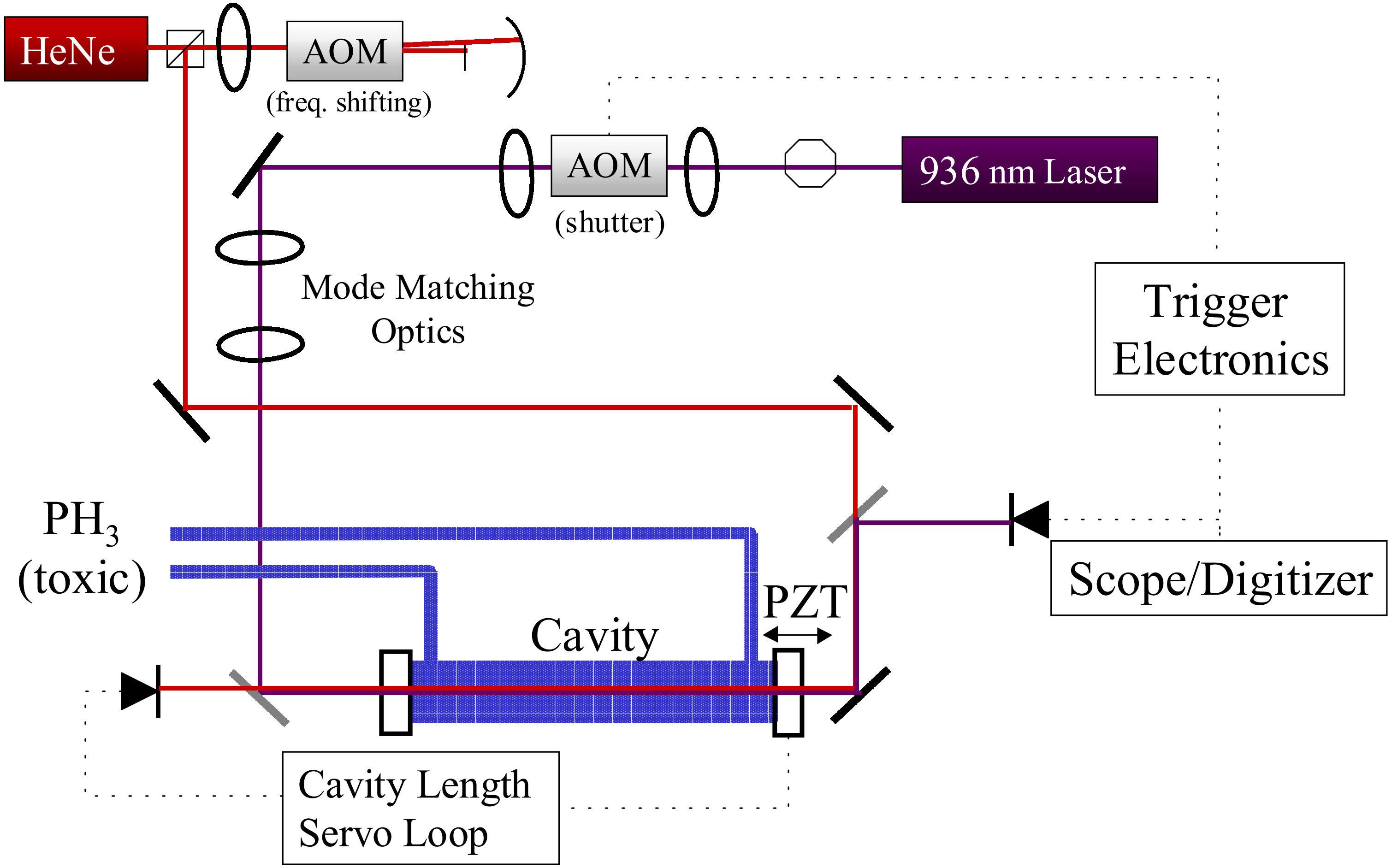
- Detection of H_2O in PH_3 possible down to ~55 ppb
- Reestablishing frost layer is time consuming and requires user intervention
- Mirror contamination occurs over time and results in noisy readings
- Regular cleaning
- Long equilibration time

Principle of Cavity Ring-Down Spectroscopy

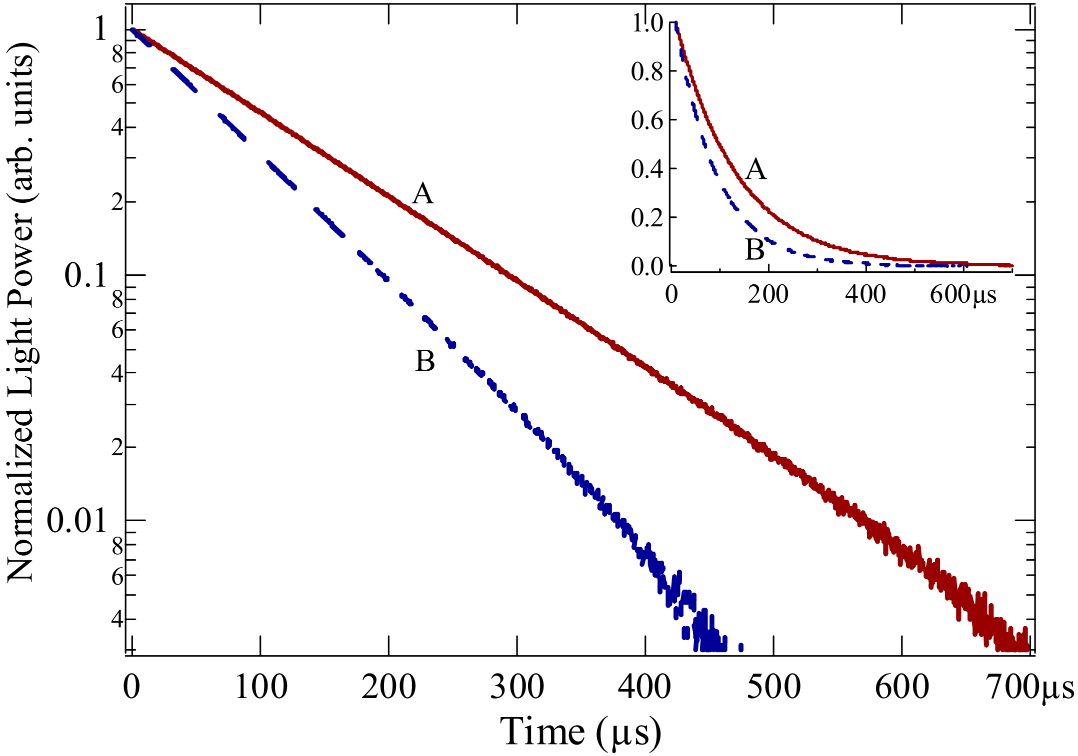


- Light is injected at a frequency, matched to an absorption frequency of the impurity being measured
- When the cavity and the input frequency are in resonance, the cavity fills with light
- The output light increases, triggering the shutter on the input light
- The light in the cavity recirculates and decays exponentially

Schematic of CRDS System at NIST



Ring-down Signals



$$\tau(\nu) = \frac{a}{c} \cdot \frac{1}{L_{tot}(\nu)}$$

t = ring-down time

a = cavity length

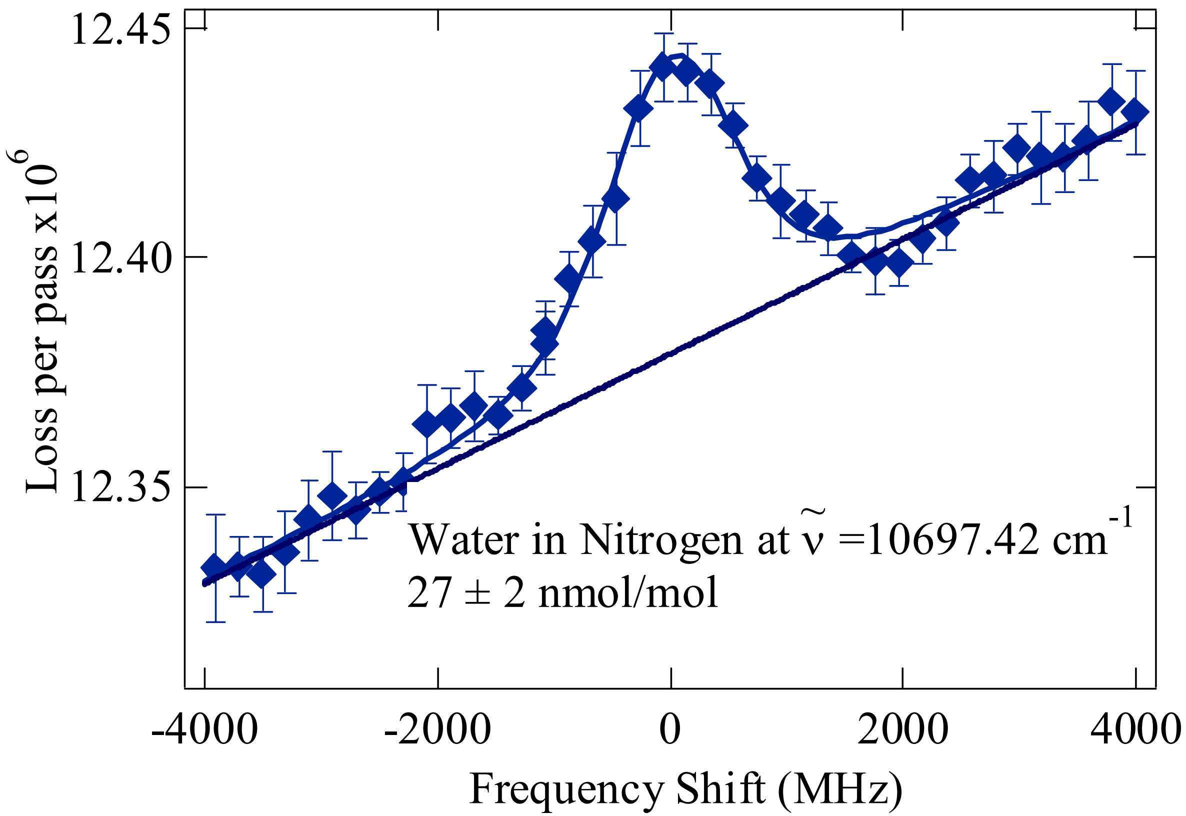
c = speed of light
(in cavity medium)

L_{tot} = total loss per pass

Ring-down time depends on

- base losses (frequency independent at this scale)
- absorption losses (frequency dependent)

CRDS Results: Dry cavity—nitrogen



$$\tau(\nu) = \frac{a}{c}\cdot\frac{1}{L_{tot}(\nu)}$$

Model absorption lines as Voigt profiles on a linear baseline.

Number density is then:

$$n = {}^{Area}\!/_{a\cdot S}$$

a = cavity length

S = absorption line strength

Water concentration is directly proportional to the peak area.

27 ± 2 nmol/mol water in nitrogen (27 ppb)

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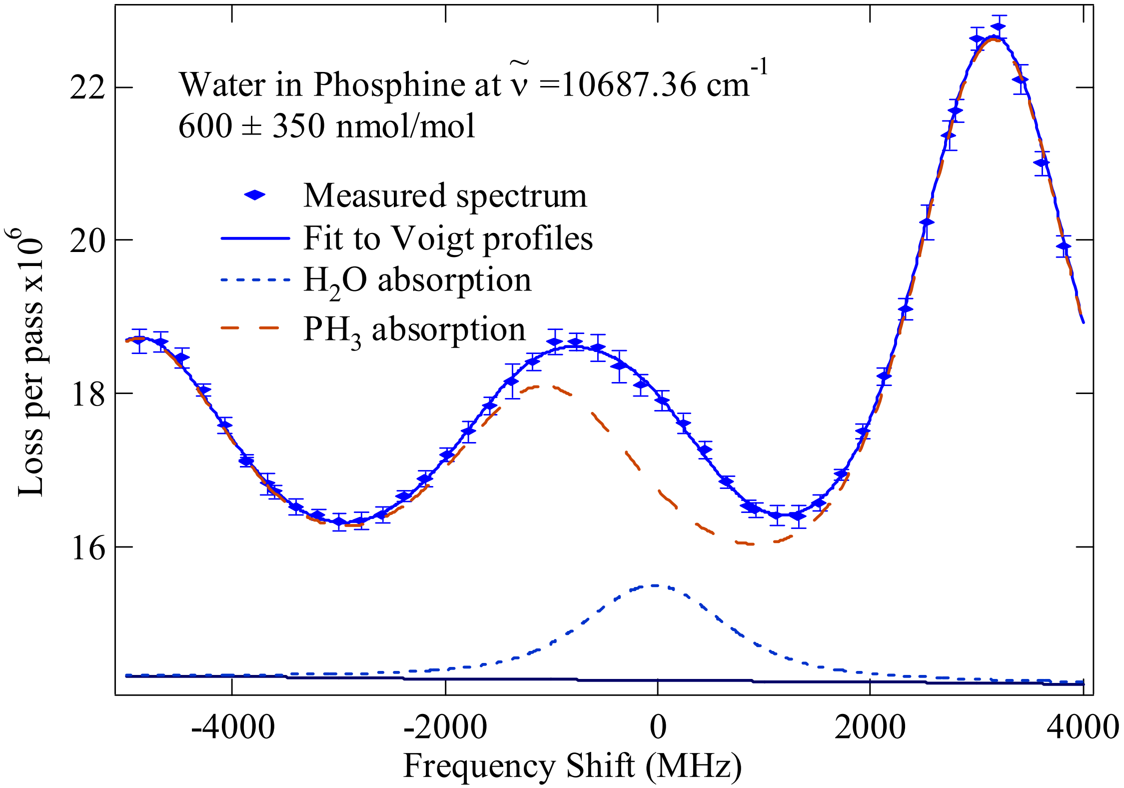
PH_3 Interference at 10687.36 cm^{-1}



- For low concentrations of H_2O, there is too much interference from unmapped PH_3 absorption to accurately deconvolve the absorption lines
- Detection limit in N_2 at this absorption line < 15 nmol/mol (15 ppb)

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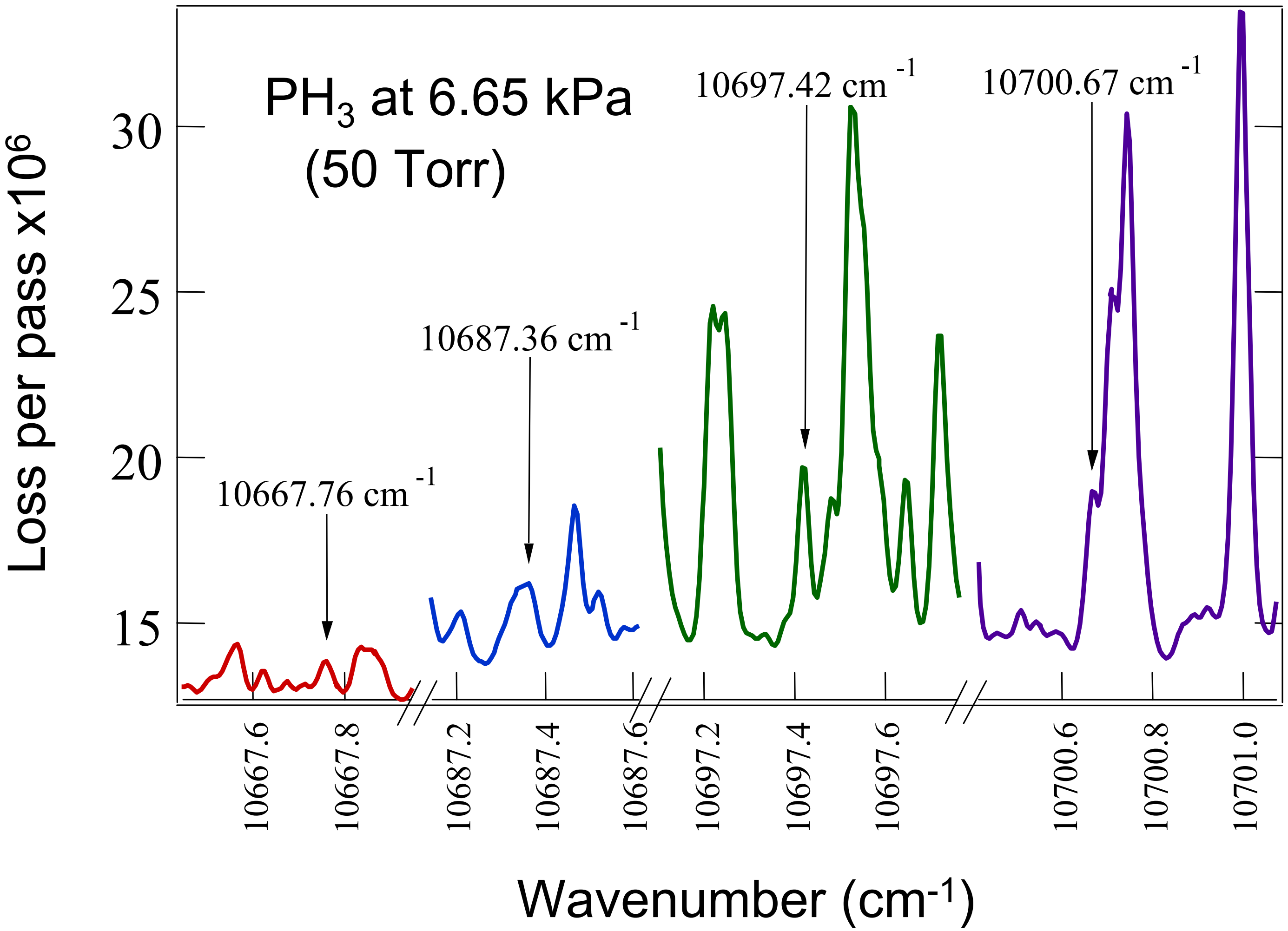
Survey of Strong H_2O lines near 935 nm



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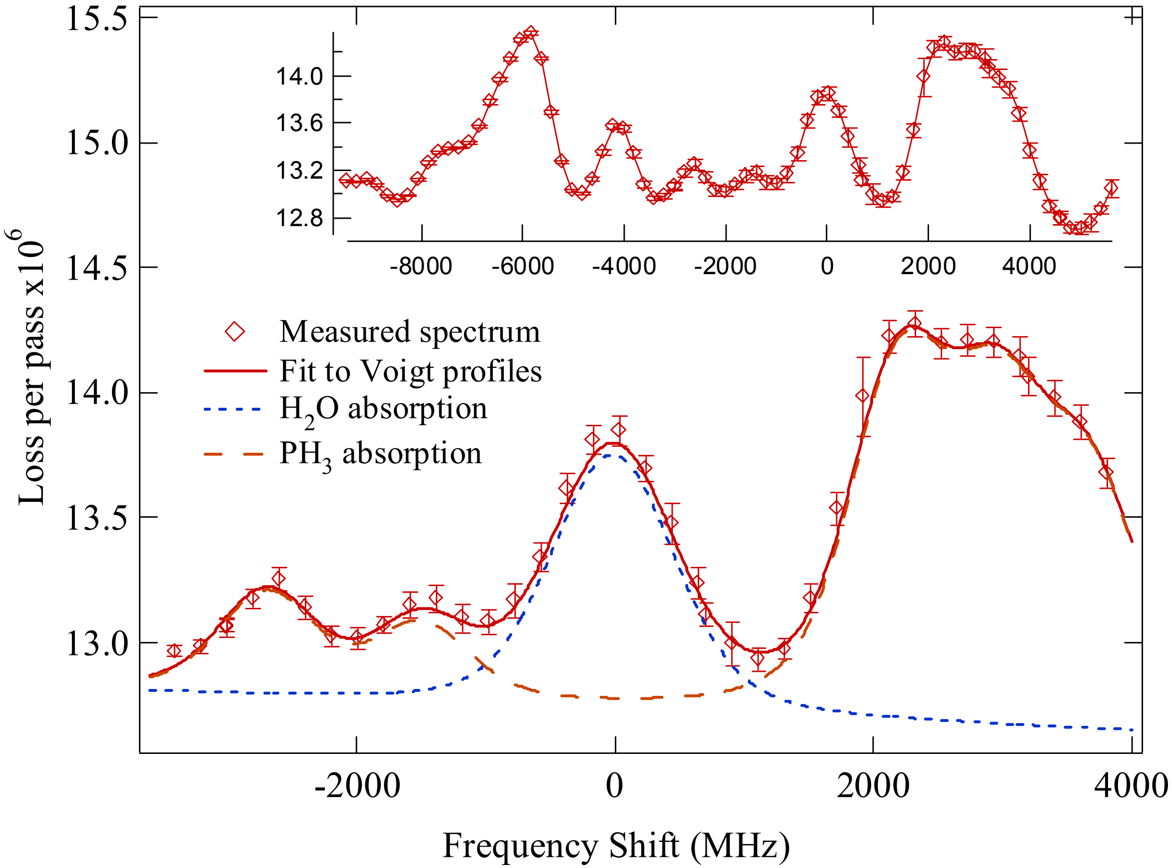
CRDS Spectrum: 6.65 kPa PH_3 at 10667.76 cm^{-1}

- H_2O mole fraction = 590 ± 160 nmol/mol
- Pressure-broadening coefficient = 28 ± 7 MHz/kPa
- Background also changes with pressure



Estimated detection limit = 50 nmol/mol (50 ppb)

CRDS Summary

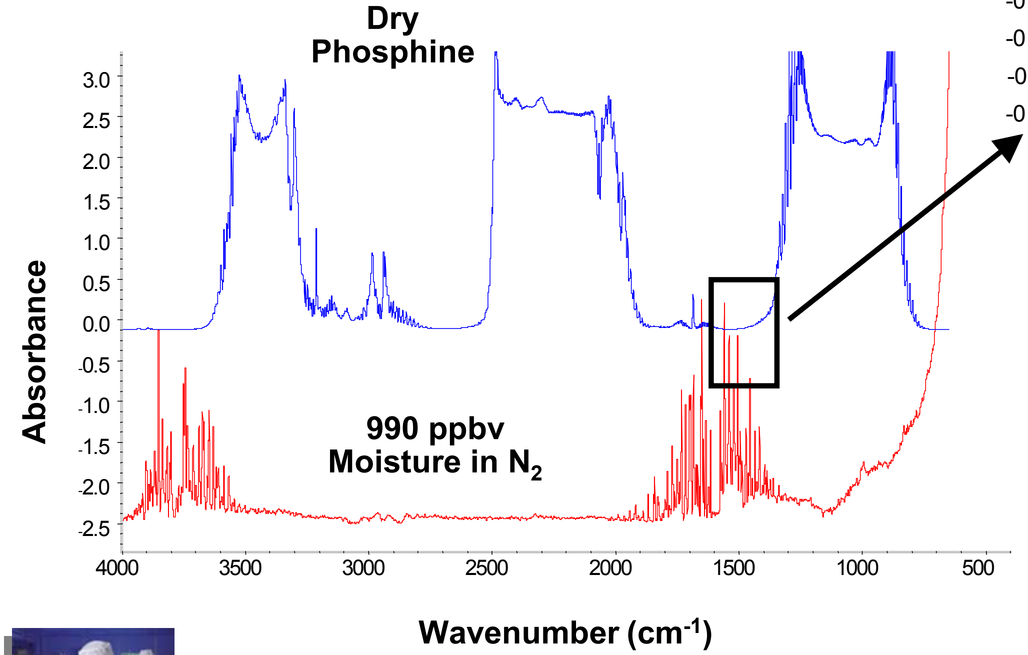
- Potential of CRDS for trace H_2O detection in PH_3 demonstrated by NIST researchers
- Challenge to find a moisture line in 935 nm region where PH_3 absorptions are minimal
- Estimate 50 ppb detection limit using line at 937.40350 nm (10667.76 cm^{-1})
- Future
  - Investigate other spectral ranges to lower detection limits

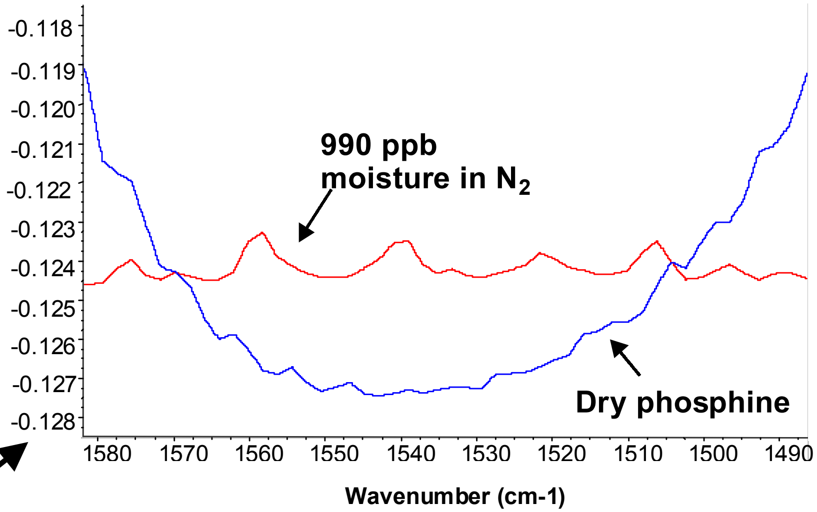
FTIR Spectroscopy

- Based on absorption of IR radiation by moisture impurity in a flowing gas stream within a gas cell
- Non-destructive technique
- Gas wetted parts can be selected for compatibility with phosphine
- Demonstrated sensitivity with long path-length cell
- Requires optimization of instrument design and measurement conditions

Infrared Spectrum of Dry PH_3 and Moisture in N_2

- H_2O detected in 1520 -1560 cm^{-1} region with minimal interference from PH_3 absorptions

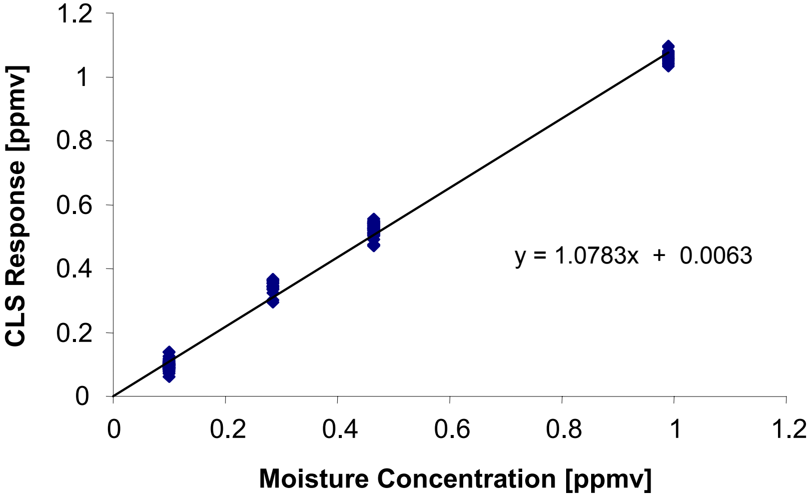




- Calibration spectra input into classical least squares software for quantitation
- 512 spectra, 4 cm^{-1} resolution to maximize signal to noise
- Quantpad analysis program

FTIR Response

- IR absorption of moisture follows Beer's law ($\log I/I_o = -abc$)
- Linear response for H_2O standards diluted in dry PH_3 matrix
- LOD_{REG}: 33 ppbv
- Dry N_2 bench purge required for long term stability
- Air must be excluded from sampling system to prevent PH_3 decomposition products affecting results



LOD_{REG} based on ordinary least squares method (SEMI C10-0698)

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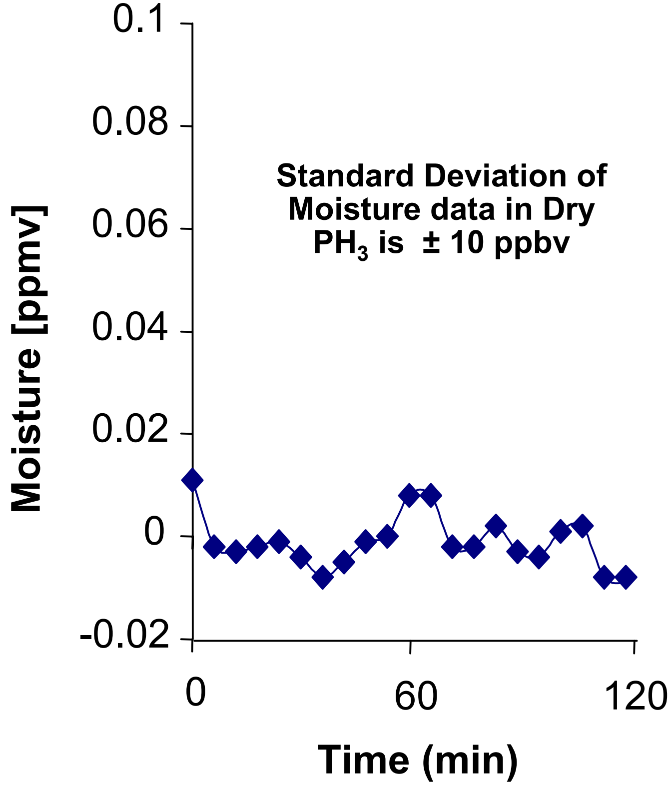
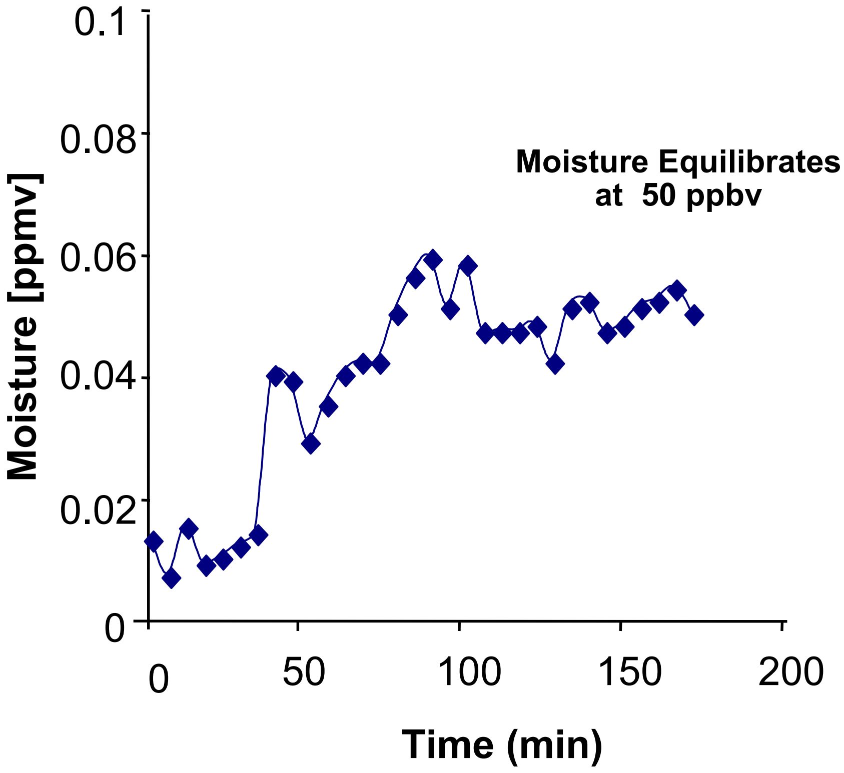
FTIR Detection of Moisture in PH_3

Dry PH_3



Standard Deviation of Moisture data in Dry PH_3 is ± 10 ppbv

PH_3 Ultima 6N Grade from Cylinder Source



Moisture Equilibrates at 50 ppbv

FTIR Observations

- FTIR currently method of choice for quantification of trace H_2O in PH_3
- Careful selection of H_2O bands required to optimize sensitivity
- Detection to ~30 ppb possible with low resolution instrument, an MCT detector and a 10 m pathlength cell
- Improved sensitivity (10-20 ppb) likely with dedicated FTIR analyzers optimized for on-line gas measurements

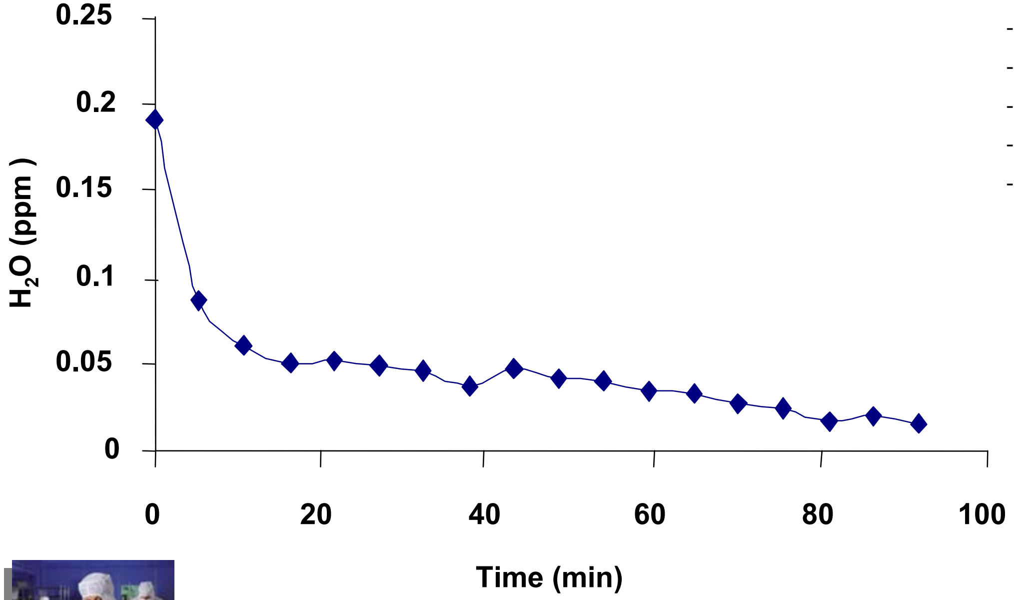
Moisture Control

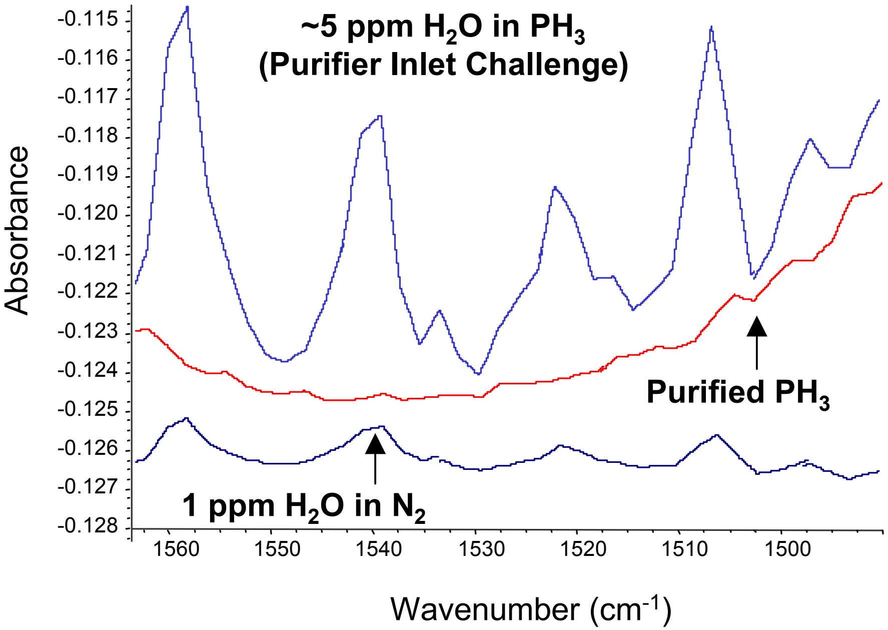
- Dry down of delivery systems exposed to atmosphere difficult due to adsorptive properties of moisture
- Gas phase moisture concentrations may vary over cylinder life, due to enrichment of water in the liquid phase
- Point-of-use purification provides a solution for consistent gas purity
- Efficiency of purifier materials evaluated using FTIR

Removal of H_2O in PH_3 by Point of Use Purifier

Removal of 5 ppm H_2O in PH_3 by Nanochem PHX Purifier at 0.4 slpm

<100 ppb H_2O reached in 10 min
H_2O level less than FTIR detection limit after 80 min





IR spectra showing features of 5 ppm inlet H_2O challenge and absence of features in purified PH_3

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Summary and Outlook

- Current techniques allow H_2O detection at tens of ppbs
- Performance of some III-V devices may be effected by H_2O at much lower levels than can be measured analytically
- Point-of-use purification important for consistent gas purity
- Next generation analyzers should provide single digit and sub-ppb level sensitivity
- Laser based systems have greatest potential of filling sensitivity requirement