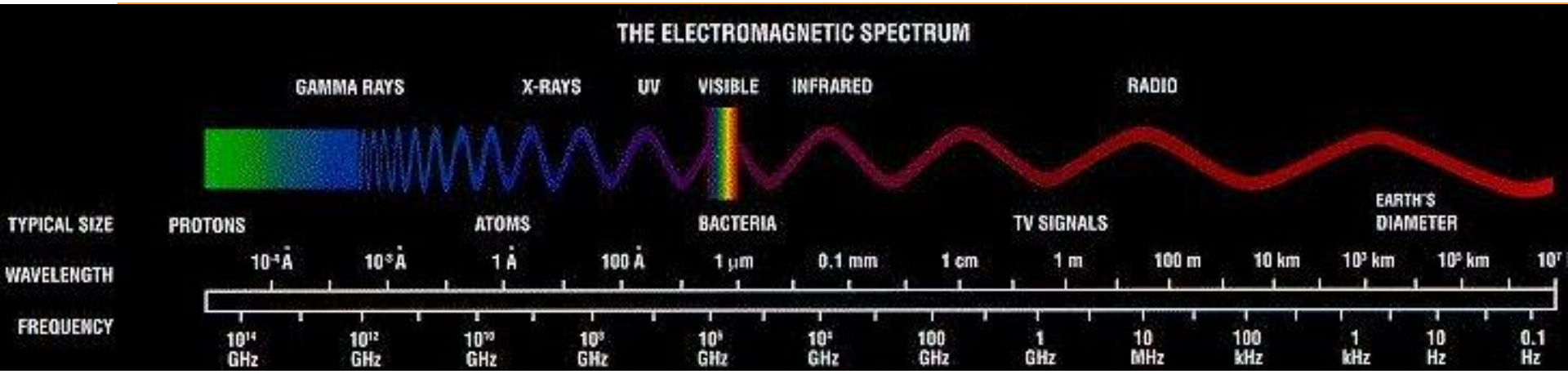
ICOS | INTEGRATED CARBON OBSERVATION SYSTEM

Continuous GHG Analyzer PICARRO

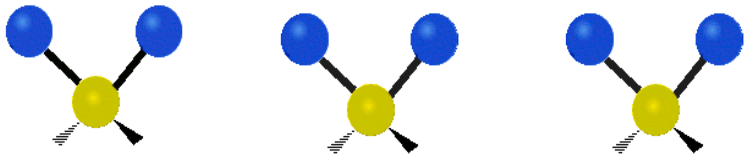
Olivier LAURENT

LABORATOIRE DES SCIENCES DU CLIMAT & DE L'ENVIRONNEMENT
cea cnrs UNIVERSITÉ DE VERSAILLES ST-QUENTIN-EN-YVELINES Institut Pierre Simon Laplace

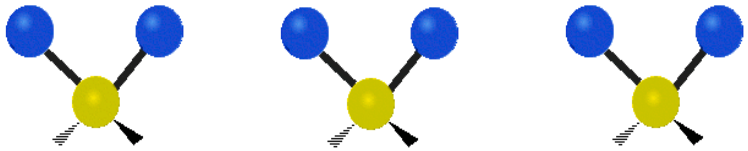
Infrared Spectroscopy



In Infrared (0.7 µm to 1000 µm) light absorption is related to the molecular vibration.

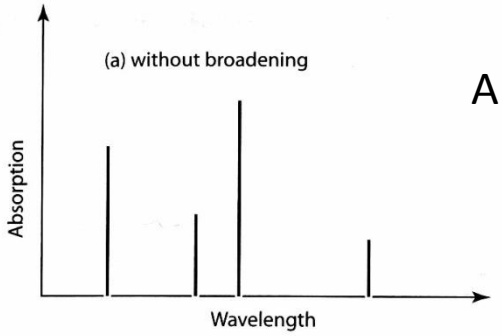


Symmetric Stretch Asymmetric Stretch Twisting

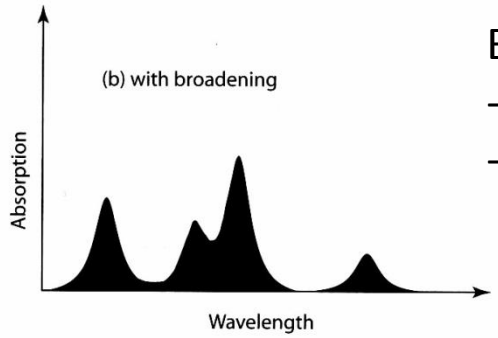


Wagging Scissoring Rocking

Types of Vibrational Modes



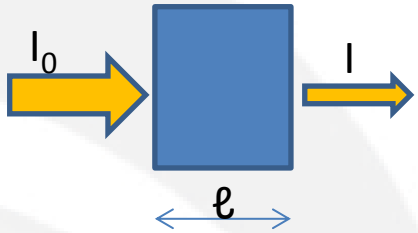
Absorption lines



Broadening:
-Doppler
-Collision (pressure)

Lambert-Beer Law

IR spectroscopy is based on the Lambert-Beer law (light absorption)



$$I = I_0 \cdot e^{-\sigma \ell N}$$

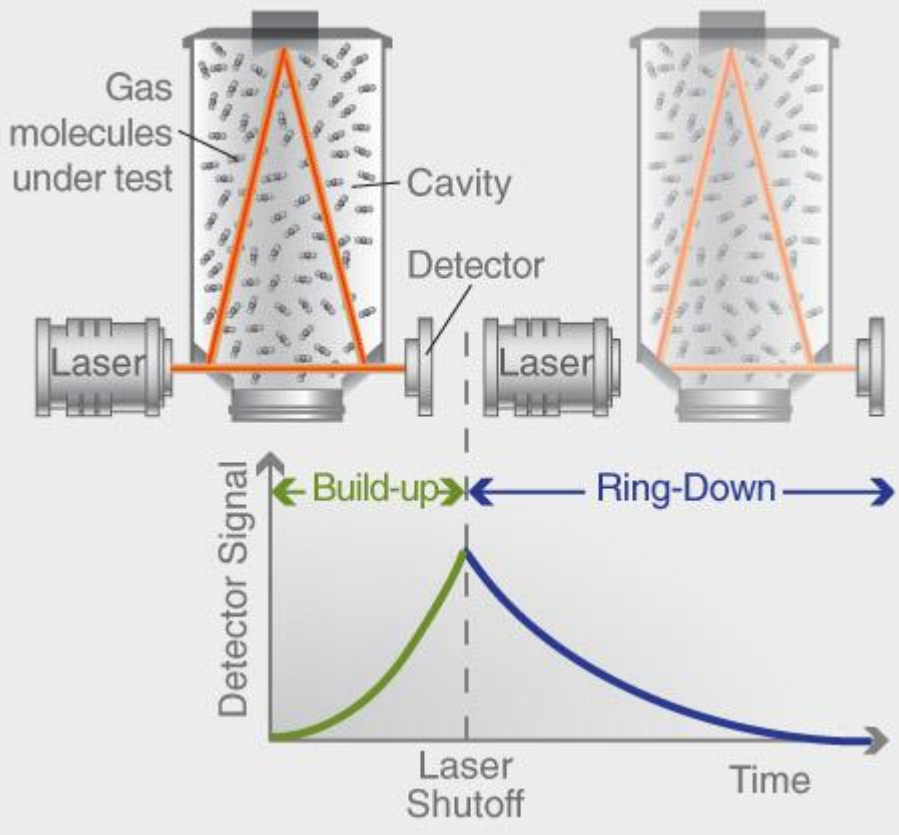
I_0 : Intensity of the incident light
I : Intensity of the transmitted light
σ : cross section of light absorption by a single molecule. Related to attenuation coef. ε
ℓ : optical path length
N : density (number per unit volume) of absorbing molecules

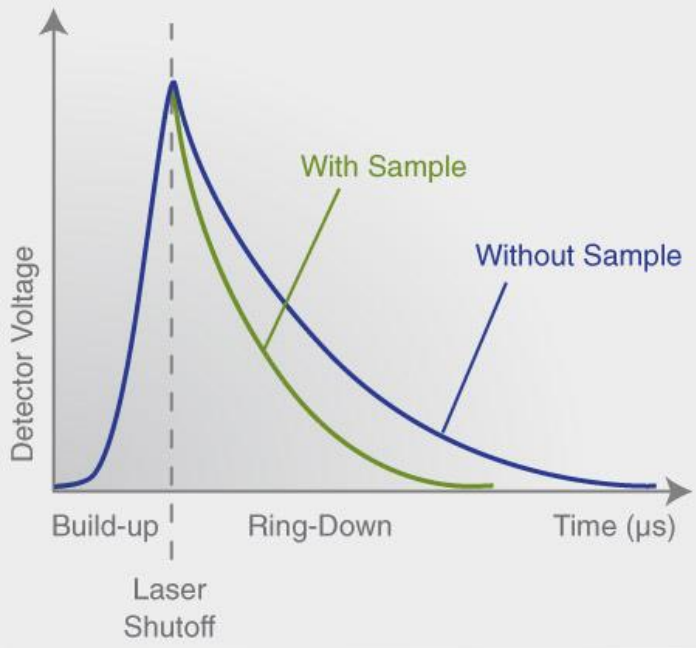
$$\varepsilon_i = \frac{N_A}{\ln 10}\sigma_i,$$

Absorbance :

$$A_\lambda = -\ln \frac{I}{I_0} = \sigma_\lambda \ell N$$

CRDS Technology

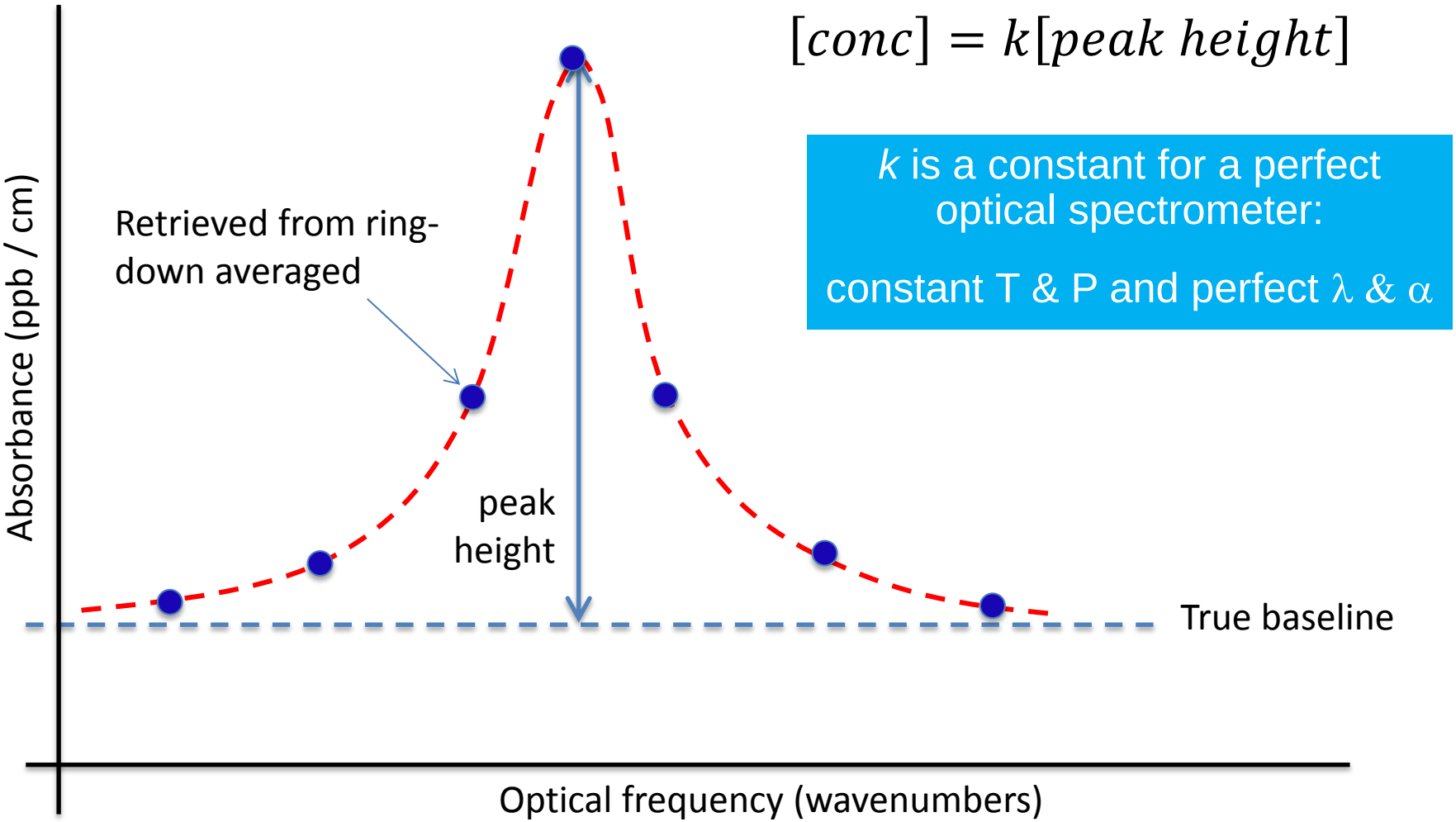


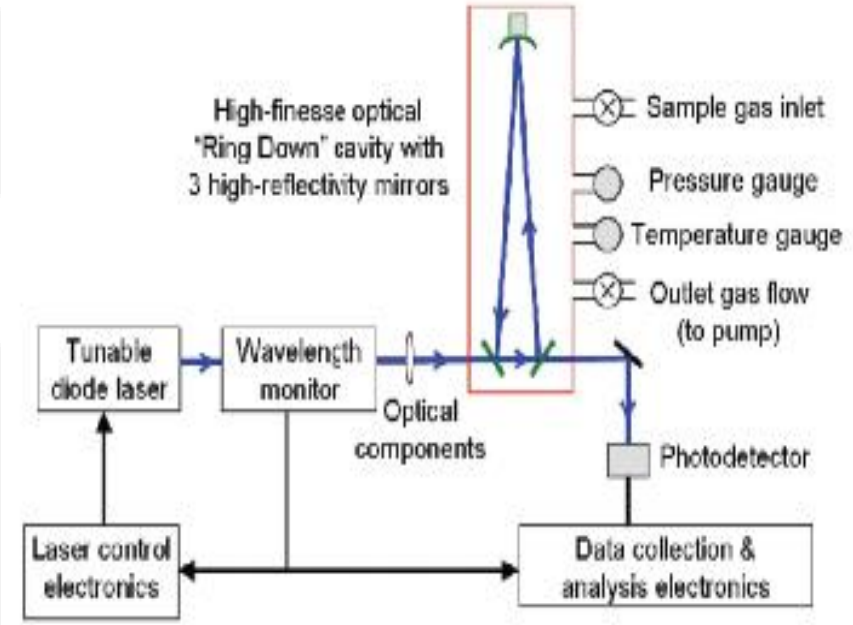


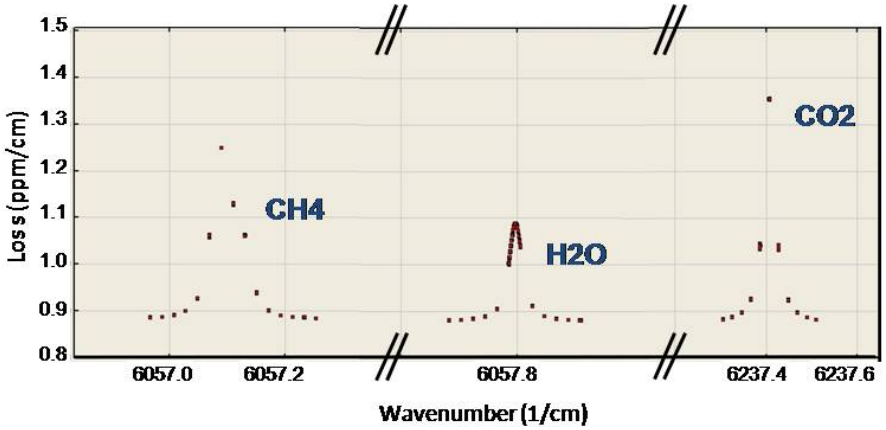
- Cavity ring down offers a long optical path in a small optical cavity
- CRDS is a **time decay** measurement, not directly the absorption
- During the build-up, the distance between the mirrors is adjusted to reach the resonance thanks to a mirror mounted on a piezo

For a given wavelength, Ring-downs are repeated and averaged to determined the corresponding absorbance

Measured (discrete) spectrum



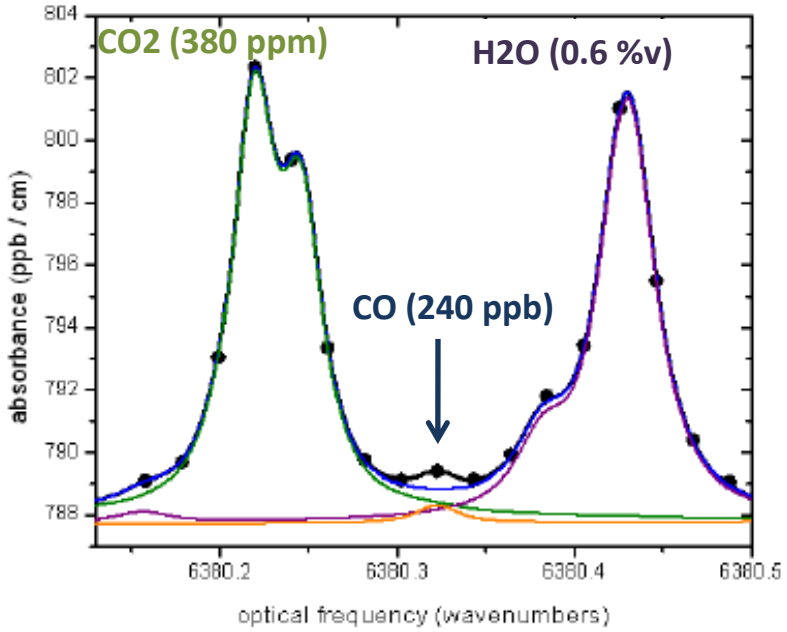




- G2301 (CO2/CH4/H20) use 2 tunable NIR Laser (Telecom CW diode): one at 1651 nm for $^{12}CH_4$ and H_2O and another one at 1602 nm for $^{12}CO_2$
- G2401 (CO2/CH4/CO/H2O) use a third tunable laser.
- Spectrum from a discret wavelength scann : for each measurement point of the spectrum a ring down decay is measured.

CO measurement in NIR : a Challenge

In Picarro instruments, CO is measured @ 1.57 µm



Chen et al, 2012

→ important spectral interferences from CO2 and H2O

→ direct interferences on CO baseline determination.

→ NB: CO concentrations derived from the CO peak heights

Correction implemented by Picarro (cf. White Paper, 2010): $COactual = COreported + \Delta CO$

Where $\Delta CO = A + B.H2O + C.(H2O)^2 + D.CO2 + E.(CO2).H2O$

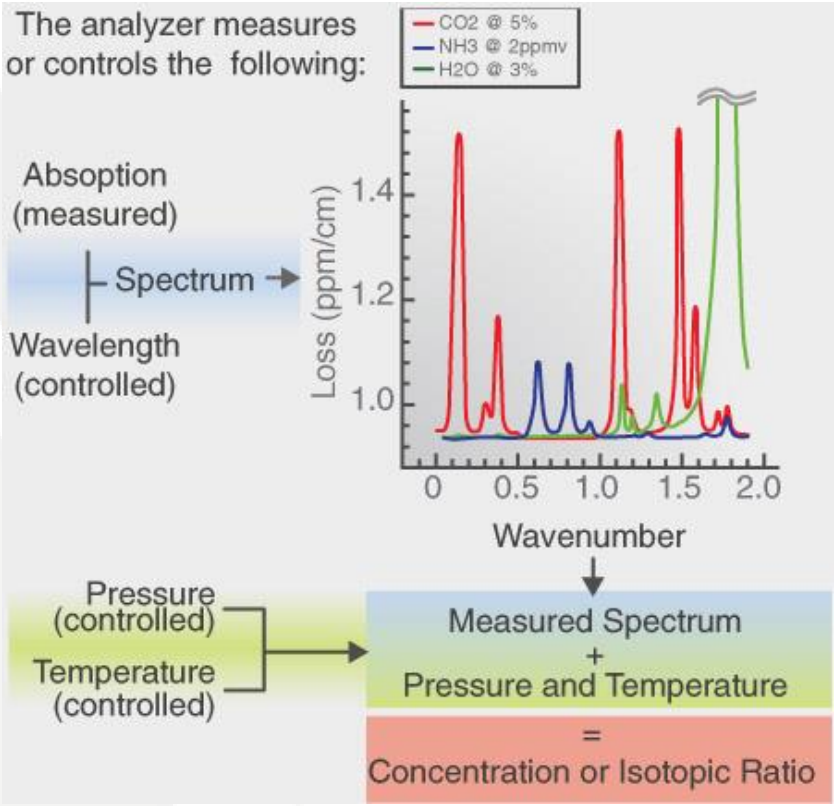
A: offset of CO reading reported in the absence of CO2 and H2O.

B: error that accounts for the direct interference of the H2O spectroscopic line.

C: error that accounts for the nonlinear contribution to the direct spectroscopic interference of H2O line (cf. error induced by self- broadening of the water line)

D: error that accounts for the direct spectroscopic interference of the CO2 line.

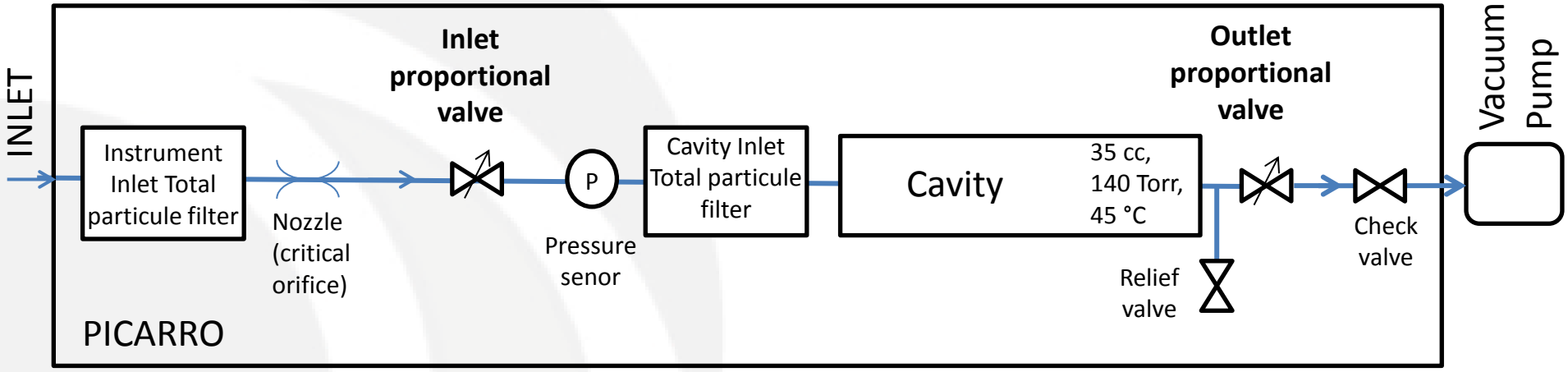
E: error induced by the error in the fit of the CO2 peaks due to cross-broadening of the CO2 line by H2O



- Concentration is derivated from time decay (related to light absorption) and the Cavity Pressure/Temperature
- The temperature and the pressure of Picarro's cavity is regulated.

- **<u>Important</u>**: the temperature and the pressure measurement is not taken into account for concentration (mole fraction) determination. The Picarro rely on its cavity temperature and pressure regulation.

Picarro Plumbing Design



The cavity pressure is regulated thanks to 2 proportional valves:

- Inlet Valve : fixed position (= 50 000)
- Outlet Valve : varying from 0 (Closed) to 65000 (fully open)

➢ The 2 proportional valves are Normaly Closed (Closed When no current applied)

The internal Instrument Total particule filter can be changed by user
Never disconnect the cavity inlet total particule filter (inside the HotBox)

The flow rate is fixed by the Nozzle (around 250 cc/min) if the pressure drop is suficient

Startup procedure

Starting the analyzer:

- Connect the Picarro inlet to the air distribution system. Make sure the air is well filtered (< 7 micron). Make sure the air sample analyzed is **NOT DRY** (ambient air)
- Connect the vaccum pump to the Picarro Rear Panel (Vacuum port)
- Switch ON the pump
- Switch ON the analyzer.
- No calibration should be performed during the 2 first hours (stabilization time).

Note: as the internal proportional valves are normaly closed, do not leave the pump running during a too long time without starting the analyzer (decrease the pump diaphragm lifetime).

The analyzer warm-up, which consists in regulating the Cavity temperature and pressure, can take up to 30 minutes depending to the instrument temperature. During this period, no measurement is performed.

Picarro installation requirements and Good Practice

- Never disconnect the Pump while the instrument is running.
- Synchronize the Picarro clock with a NTP Server (Internet or GPS)
- Always use a filter (<7 micron) on the instrument inlet even if there is an internal filter on the inlet (potential leak when changed; not easy to access).
- Do not over tighten the swagelok fitting on the Picarro inlet ()
- Perform a Calibration after having switched the instrument OFF-ON (wait at least 2 hours before starting the calibration).
- Tank pressure regulator should be set at 0.2 – 0.4 bar (depending the pressure drop of your setup).
- Save a « Print screen » of the Laser current value (Diagnostic\Ringdown\IL vs Time)
- Clone the Instrument HDD (Disque image) if Picarro update your system (Picarro will have a HDD image of the factory system)

Instrument proper functioning assessment

In order to check the instrument is working properly:

- Connect a Target tank (or select it on the distribution system) at the instrument inlet.
- After 10 minutes of stabilization, check the Raw data Standard Deviation (Display Statistics on the Picarro) on a few minute period. The values should be below the following limits:

  - CO2 < 40 ppb
  - CH4 < 0.5 ppb
  - CO < 10 ppb
  - H20 = around 0,000%v (even negative value reported)

If a leak is suspected, perform :

- a Picarro leak test (cf. ICOS procedure)
- A leak test by blowing (with a pipe) or using a dry air « aerosol » on the inlet fittings and inside the instrument.

Data file system

A specie is measured every 1-2 second.
The species are measured successively
All the species are measured within a 5 second cycle.

The G2000 serie offer 2 kinds of data file:

The data files include (columns):

- Time stamp
- Concentration values on the species measured
- Internal parameters (pressure, temperature, …)

Only a subset of the all the columns are required by ICOS

- **Synchronized**: a time stamp (line in data file) every 5 second with the concentration value of all the species measured during the last 54 second cycle. NOT USED IN ICOS

- **Not synchronized**: a time stamp (line in data file) at each measurement (1-2 seconds). The concentration value of the species not measured are duplicated from their last value. A parameter (a column in the data file) called « specie » identify the specie measured at each time stamp. USED IN ICOS

Shutdown procedure

3 kinds of Shutdown are available:

- **« Software only »** : only the Picarro Software is stopped.
  - Effect: only the Picarro Software is stopped
    the temperature and pressure regulation of the cavity is stopped
  - Purpose : Software intervention.
- **« in current state »:**
  - Effect: the Picarro will switch OFF (Hardware and software).
    the outlet and inlet valves will close with cavity pressure at 140 Torr.
  - Purpose : Hardware intervention **Without moving** the instrument
  - Risk : water condensation risk limited (cavity pressure at 140 Torr)
    risk of cavity contamination with vibration, movement…
- **« for shiping »:**
  - Effect: the Picarro will switch OFF (Hardware and software).
    the outlet and inlet valves will close with cavity pressure at the atmospheric pressure. MUST be filled with dry air if risk of water condensation (ex: shiping, storage, room temperature change)
  - Purpose :
    - ✓ Shiping, storage (if filled with dry air during the shutdown procedure)
    - ✓ Hardware intervention **requiring moving** the instrument
  - Risk : No water condensation risk limited if filled with dry air
    No risk of cavity contamination with vibration, movement…

TroubleShootings

Symptoms	Cause/Action
Outletvalve is oscillating from 0 to 65000	• Check the leak on the tubbing between Picarro and its pump. • Perform the Pump maintenance (diaphragm pump) or change the pump • Outletvalve failure (-> Picarro)
Cavity Temperature oscillating more than +/- 0.1 °C.	• Check the Fan of the instrument ventilating system are running • Clean the fan dust filter • Check the HotBox fans are running. If not replace them (every 3-5 years) (cf. HB fan replacement ICOS procedure)
The concentration of a species is reported to a 0 value (oftenly H2O)	• The WaveLength Monitor lost its configuration. Load Factory calibration (cf. the ICOS procedure)
Error messages in the Log display related to USB, port xxxxx. (data may not have been saved)	• Disconnect USB device (HDD) • Reboot the instrument
Data acquisition rate (data file) are lower than usual and irregular	• Check the laser current and adjust if necessary (cf . ICOS procedure)
« pressure too high » or « pressure too low »	• Check the pressure at the analyzer inlet. In case too loo, a filter (internal) is probably Clogged