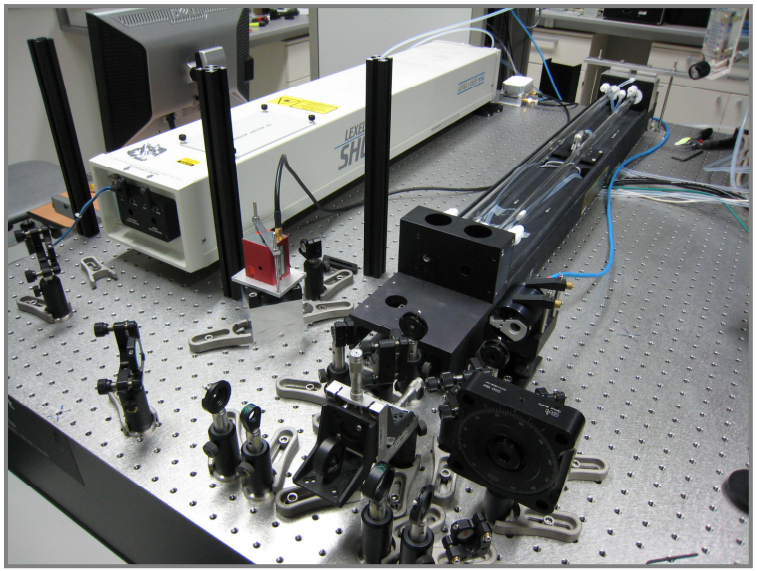
Laboratory laser-based measurements of ozone concentration in the Hartley Band and corresponding absorption cross section

M. Petersen, P. Moussay, J. Viallon and R.I. Wielgosz,
Bureau International des Poids et Mesures (BIPM)



Overview

- Introduction, ozone standard reference (Hg lamp, 254 nm) vs. Gas phase titration.
- Laser-based ozone concentration measurements at 248 nm.
- Future absolute determination of ozone absorption cross section at 244 nm, 248 nm and 257 nm.

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Ozone concentration standard reference

UV photometry

T Temperature in the cells

P Pressure in the cells

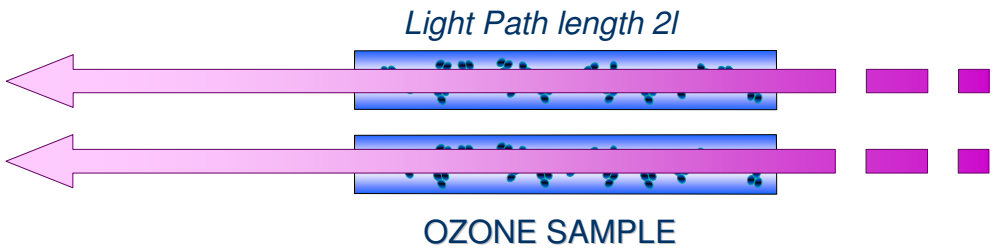
L_{opt} light path length

$$x = \frac{-1}{2\sigma L_{opt}} \frac{T}{P} \frac{R}{N_A} \ln(D)$$

N_A Avogadro constant
R Ideal gas constant
σ Absorption cross section

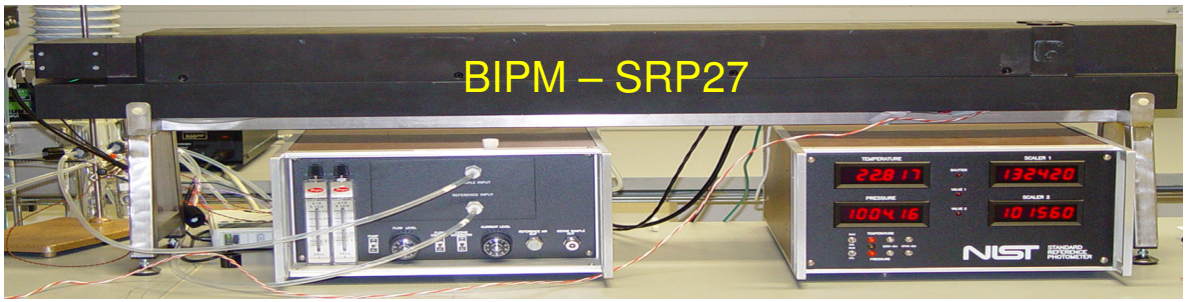
D Fraction between cells with and without ozone (transmittance).

➡ ***x* mole fraction of ozone in dry air (nmol/mol)**

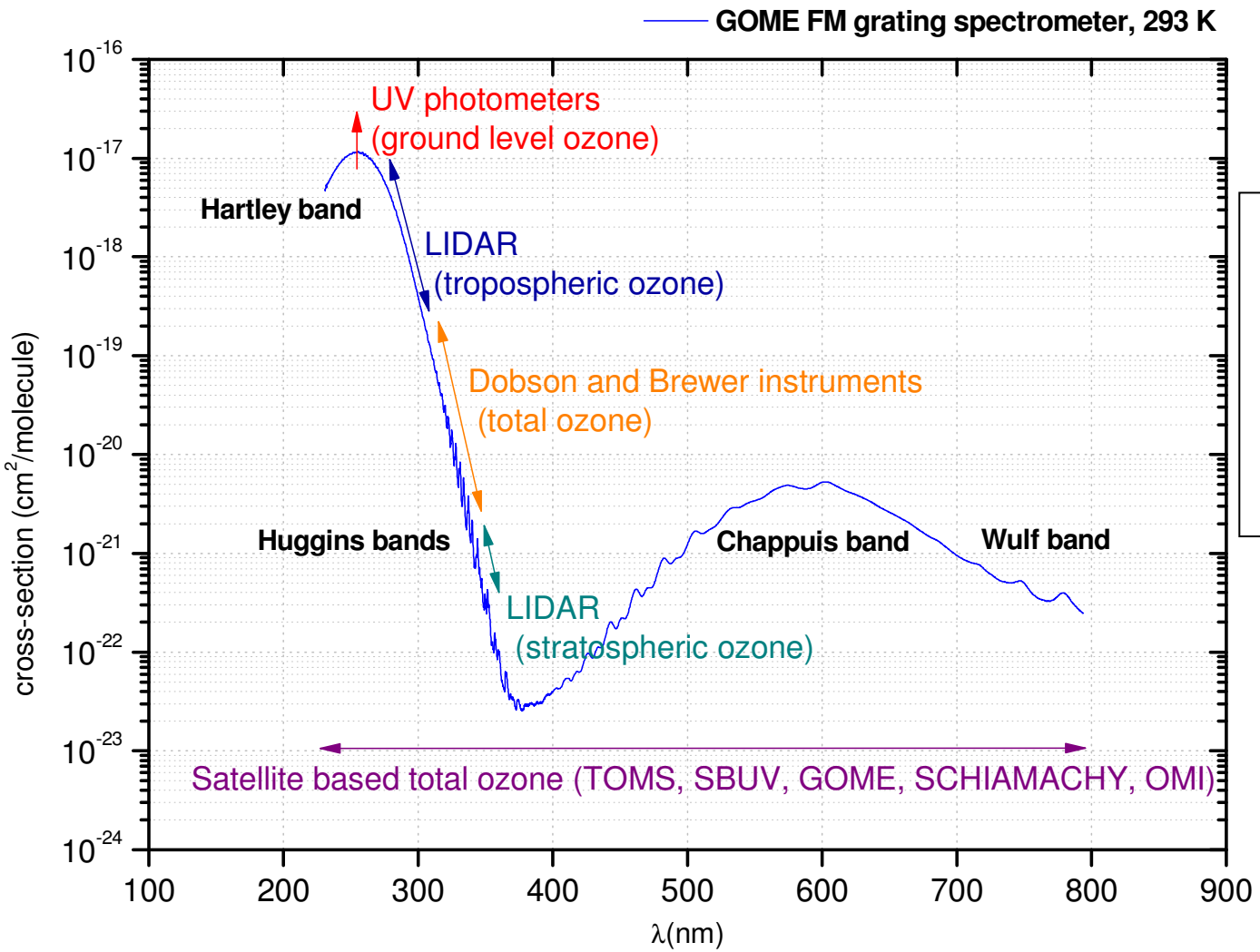


$$D = \frac{I(\text{cell1})}{I_0(\text{cell2})} \cdot \frac{I(\text{cell2})}{I_0(\text{cell1})} = T(\text{cell1}) \cdot T(\text{cell2})$$

Light source:
Mercury lamp
~ 253.6517 nm (in air)



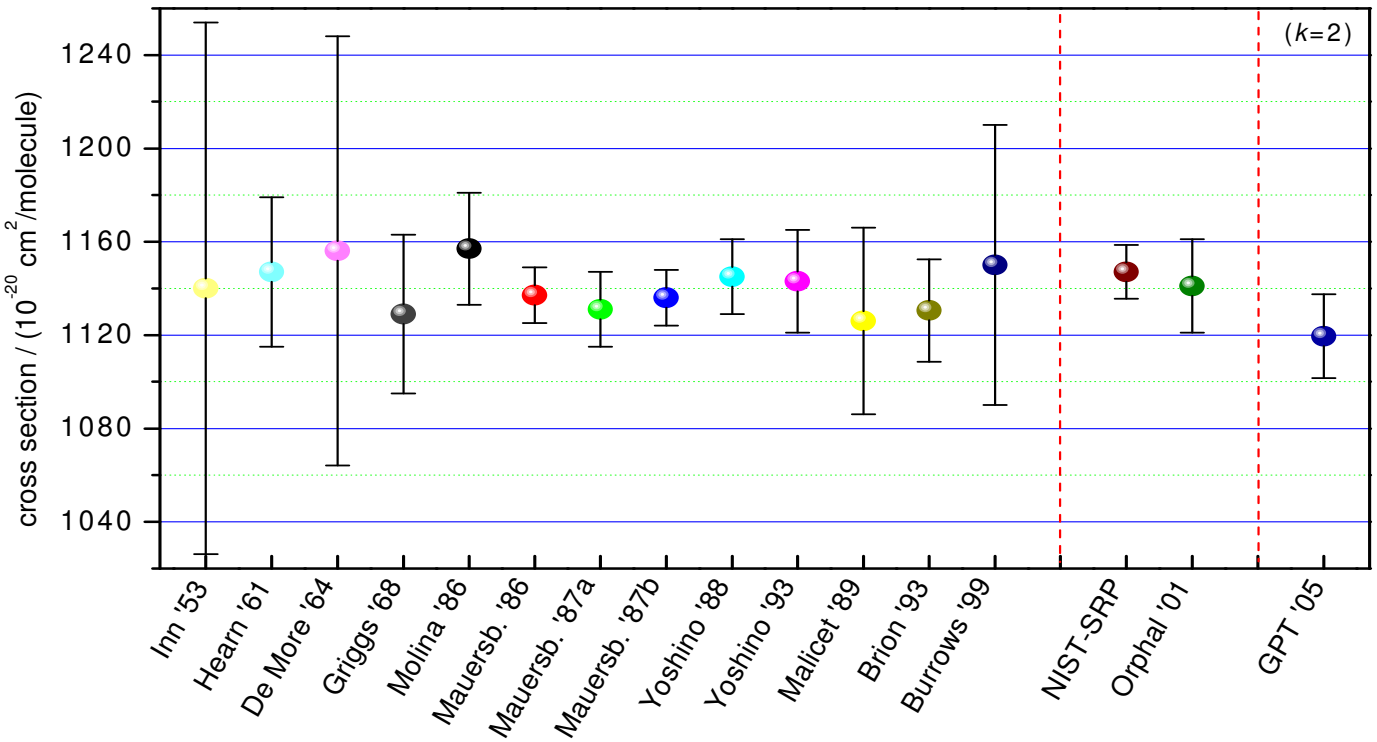
The Ozone absorption cross section



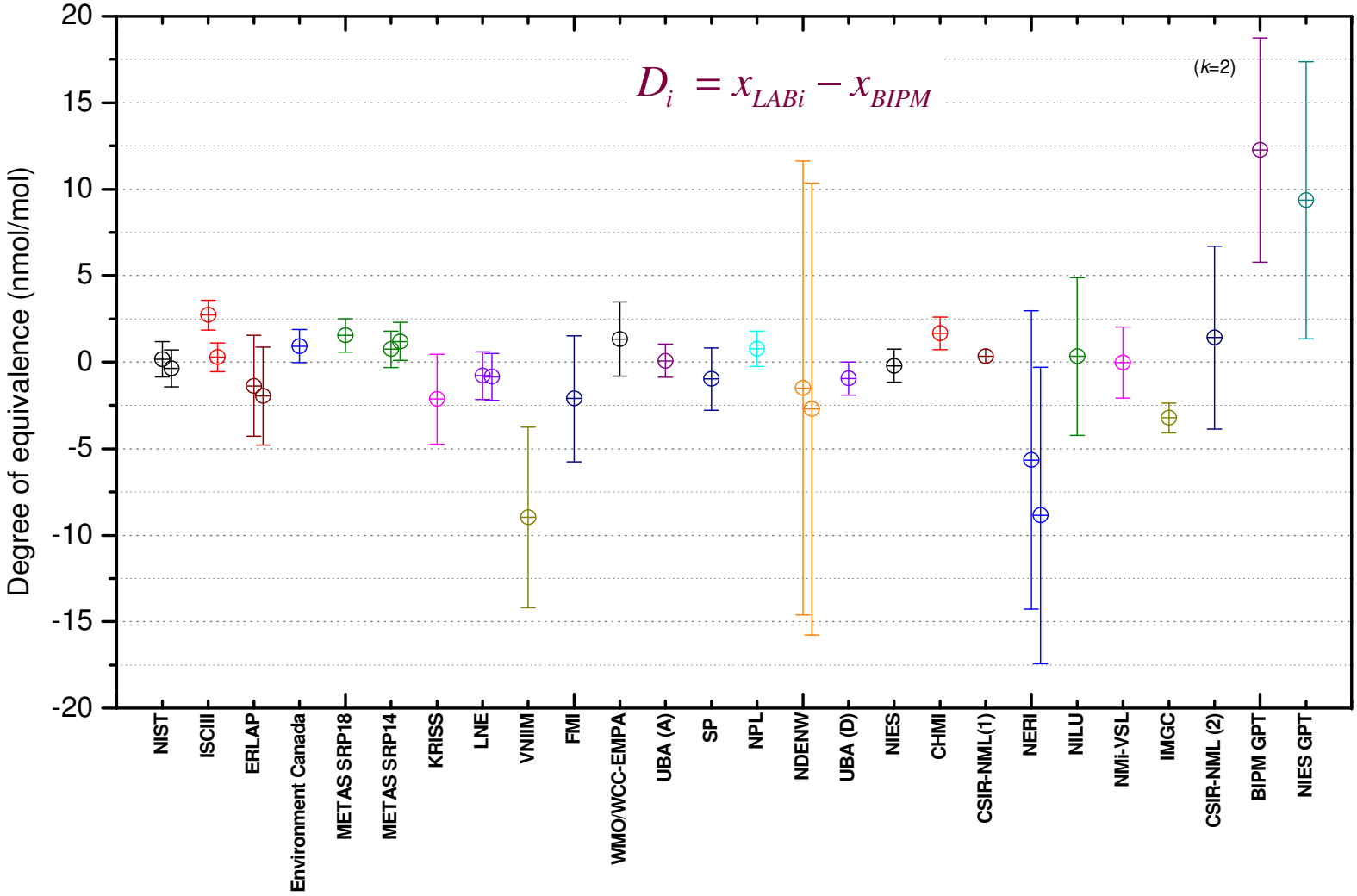
Most ozone absorption Cross section measurements (incl. Bass/Paur) are referenced to Hearns' measurement at 254 nm.

Ozone absorption cross section at 254 nm

The value of Hearn ’61 is used for the standard reference:
$1147 \cdot 10^{-20}$ cm^2/molecule



Pilot study CCQM-P28 Final results - D_i at 420 nmol/mol



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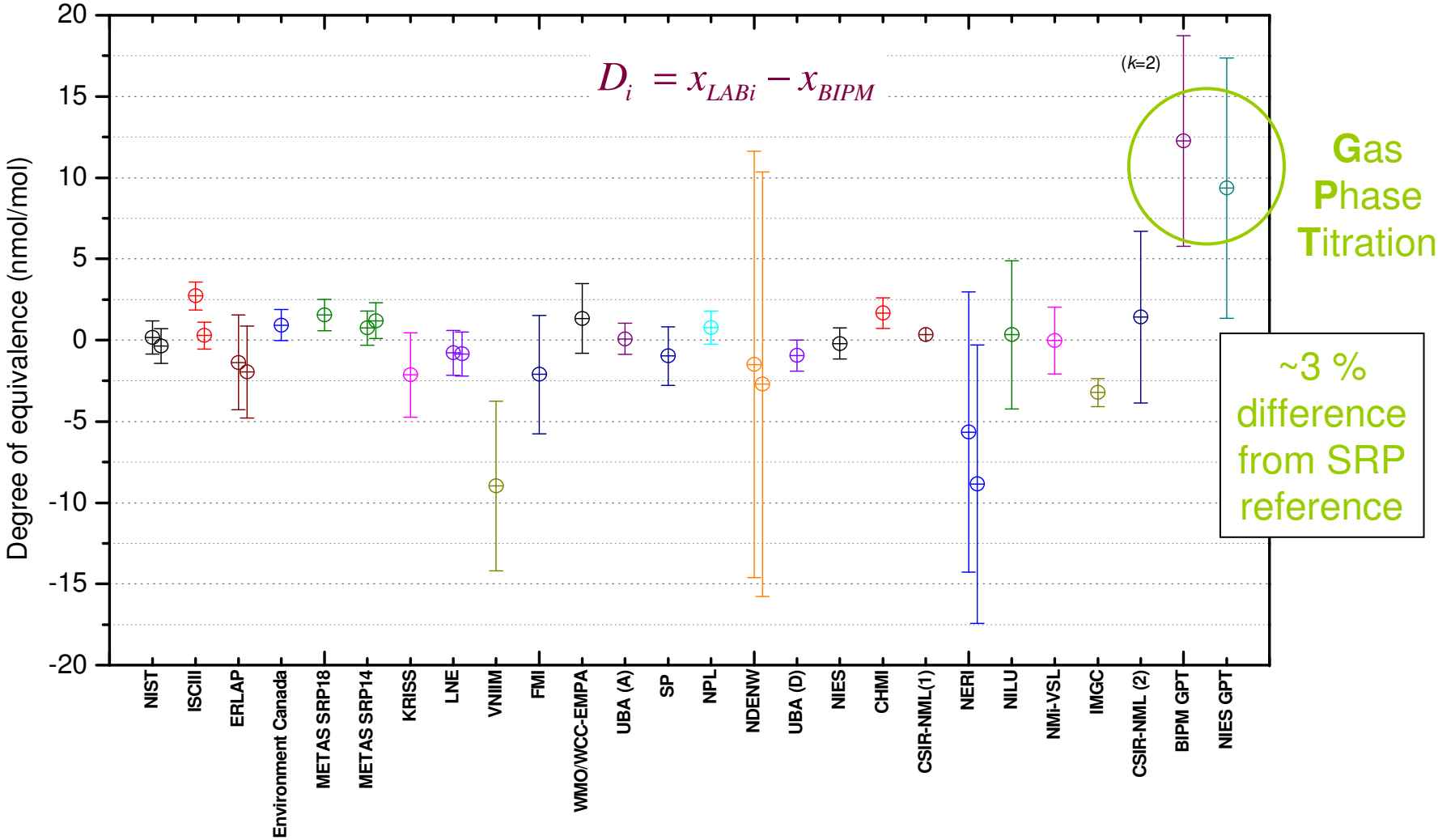
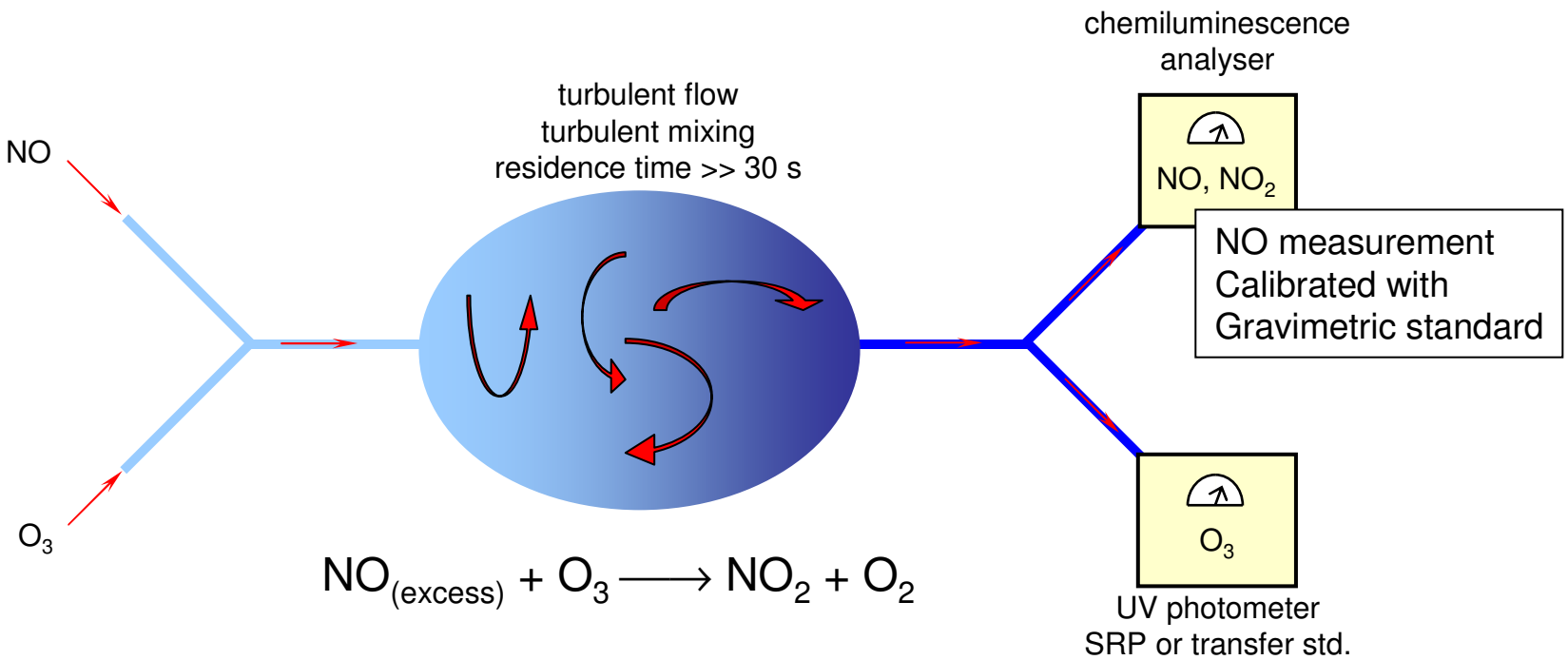


Gas Phase Titration



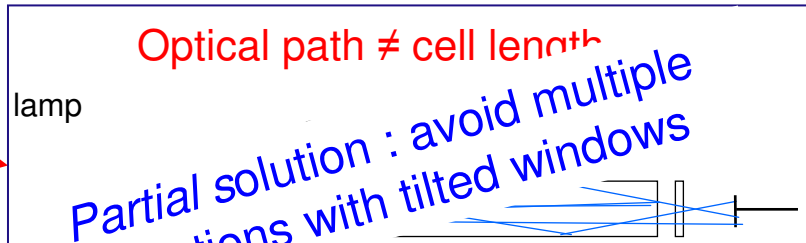
$$NO_{(excess)} + O_3 \longrightarrow NO_2 + O_2$$

Observed biases in the SRPs

Temperature not uniform

$$x = \frac{-1}{2\alpha L_{opt}} \frac{R}{N_A} \frac{T}{P} \ln(D)$$

Optical path ≠ cell length



Viallon, J., P. Moussay, J.E. Norris, F.R. Guenther, and R.I. Wielgosz, *A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer.* Metrologia, 2006. 43: 441-450.

- Introduction, ozone standard reference (Hg lamp, 254 nm) vs. Gas phase titration.

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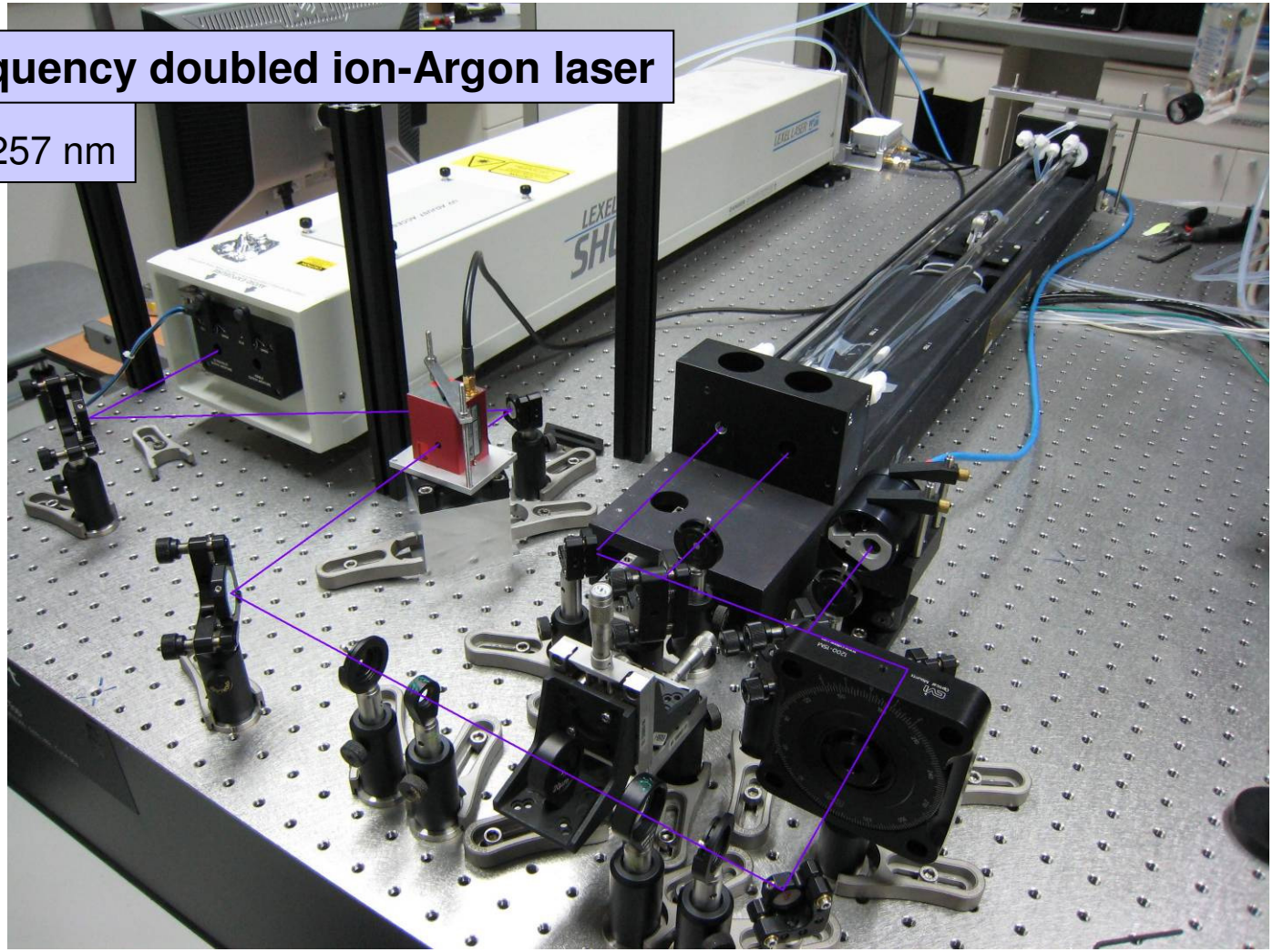
Laser-based Photometer

Frequency doubled ion-Argon laser

Wavelength
~ 244 nm, 248 nm, 257 nm



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Same principle as SRP's

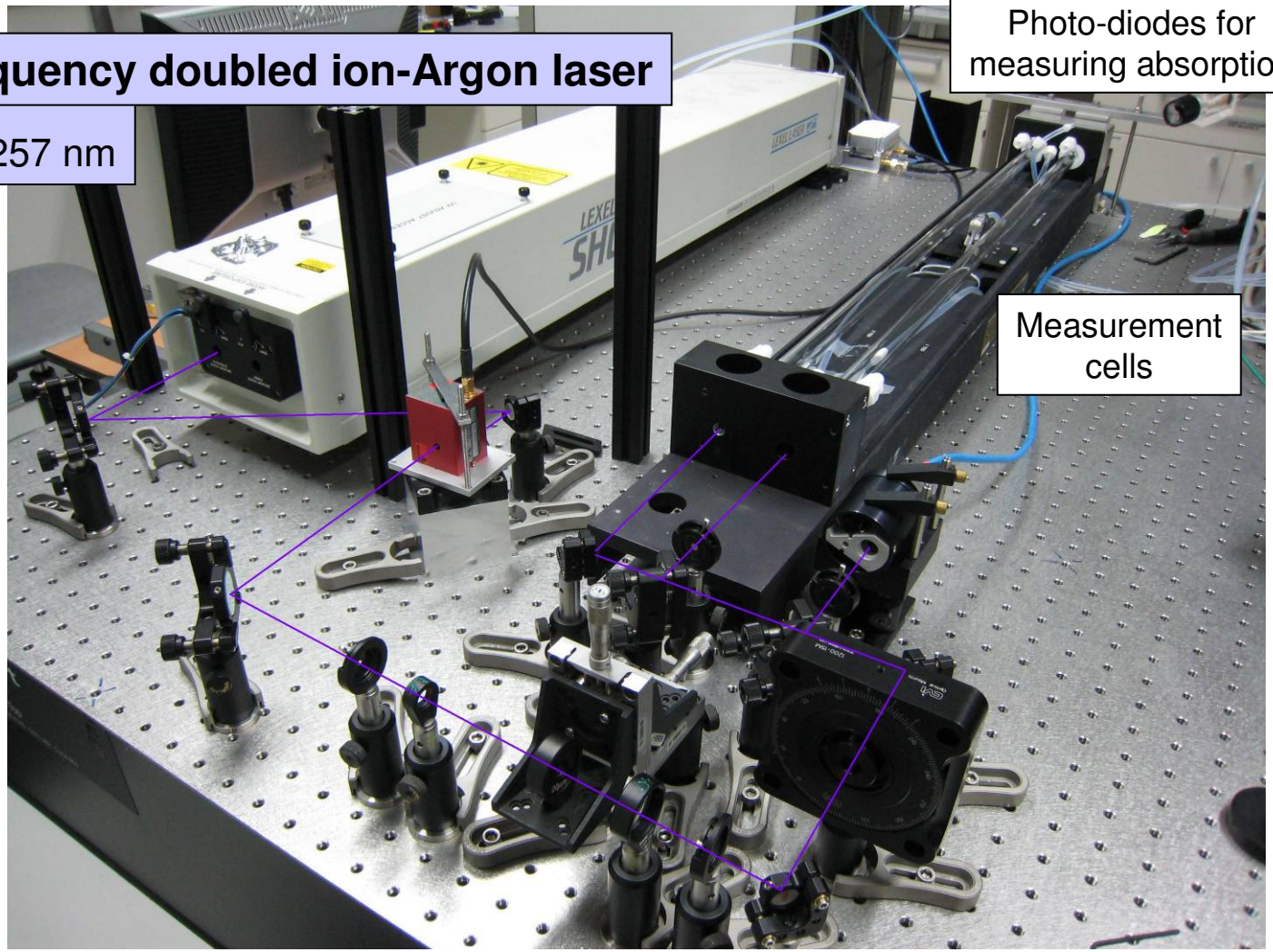

Photo-diodes for measuring absorption

Measurement cells

Laser-based Photometer

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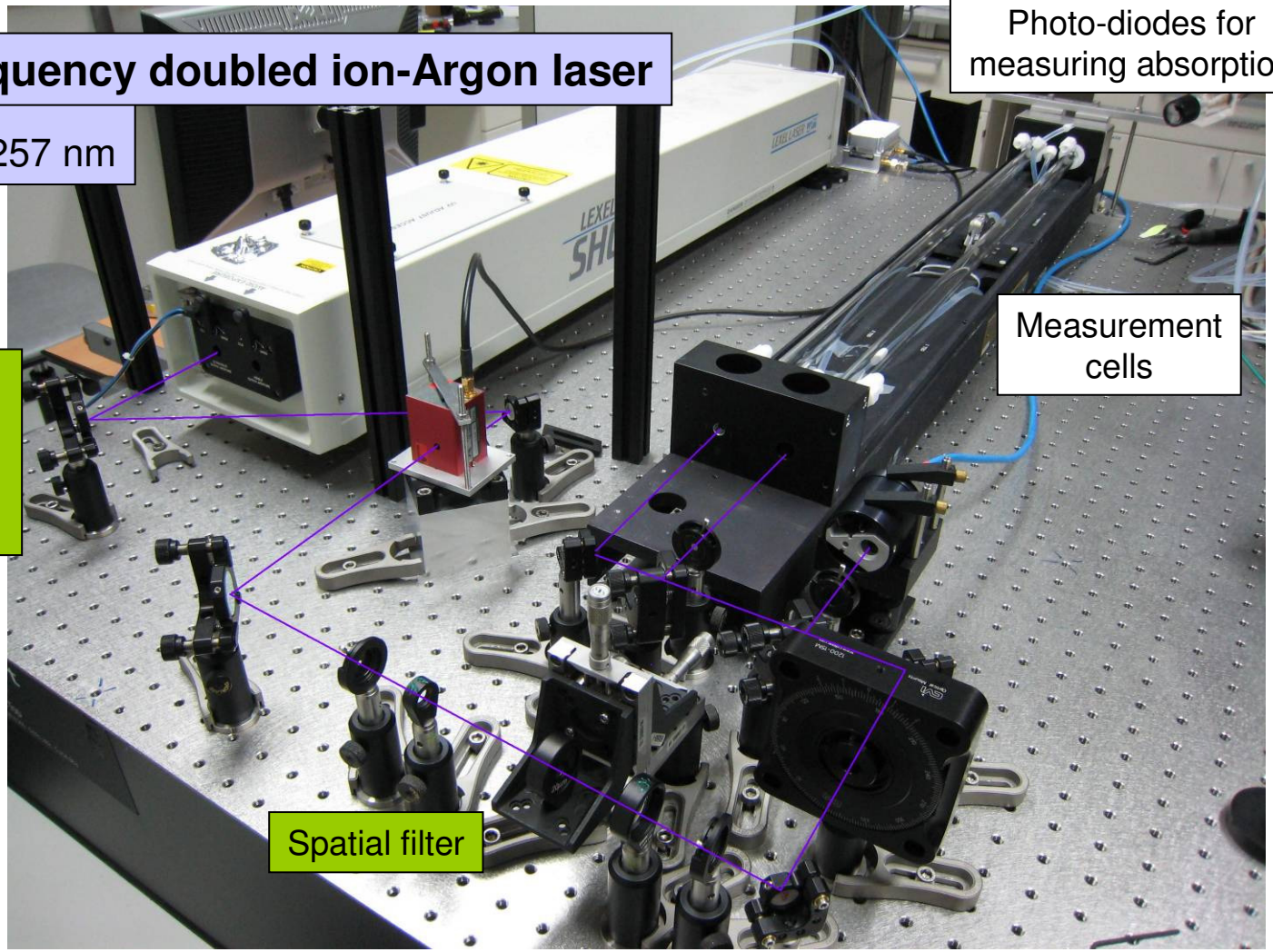
Same principle as SRP's

Due to non-gaussion beam shape a spatial filter is needed.



Laser-based Photometer

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Same principle as SRP's

Due to non-gaussion beam shape a spatial filter is needed.

measurement on single cell by power-stabilizing the light.

An acousto-optic modulator (AOM) is used to stabilize the laser-light.

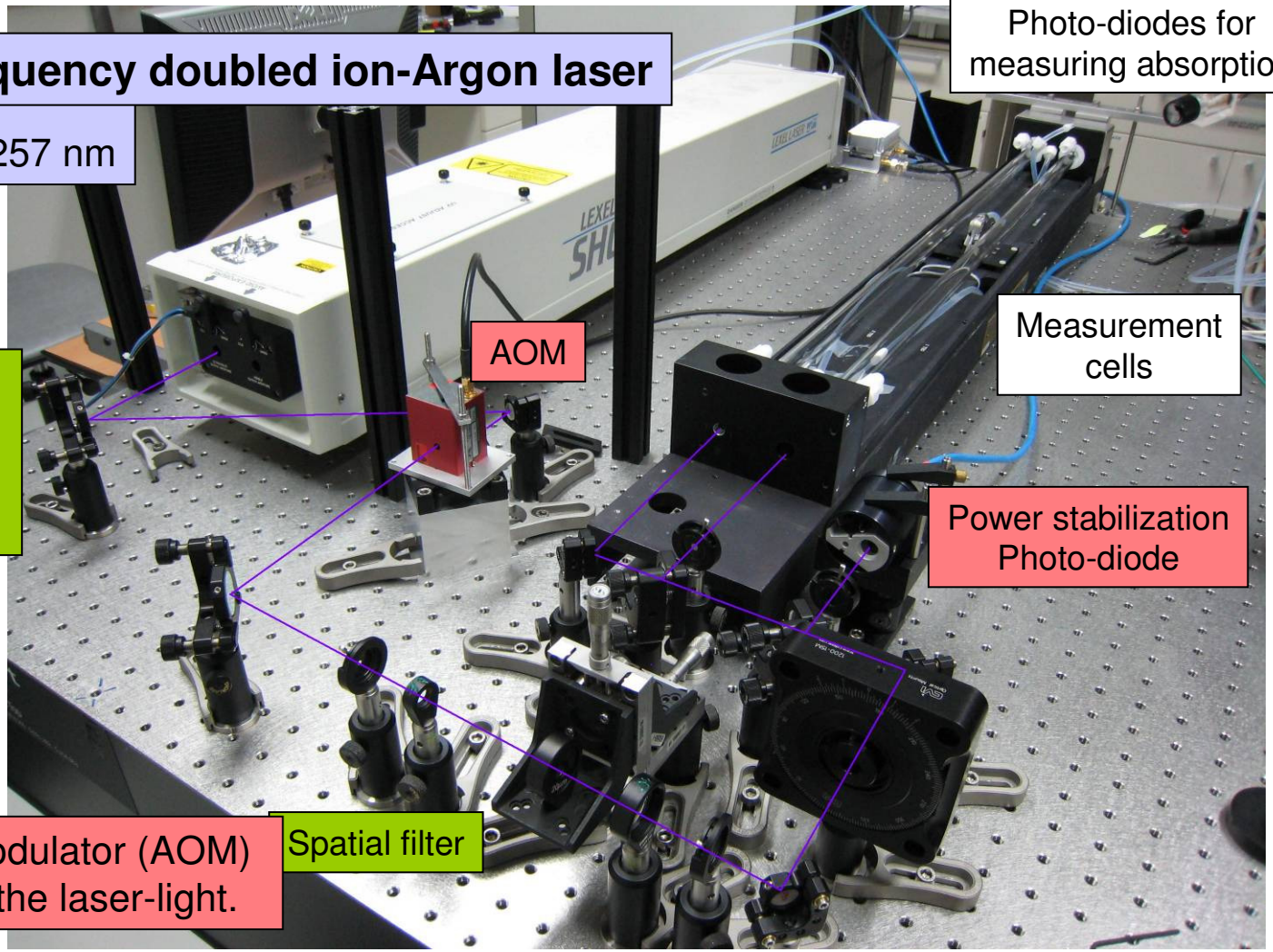


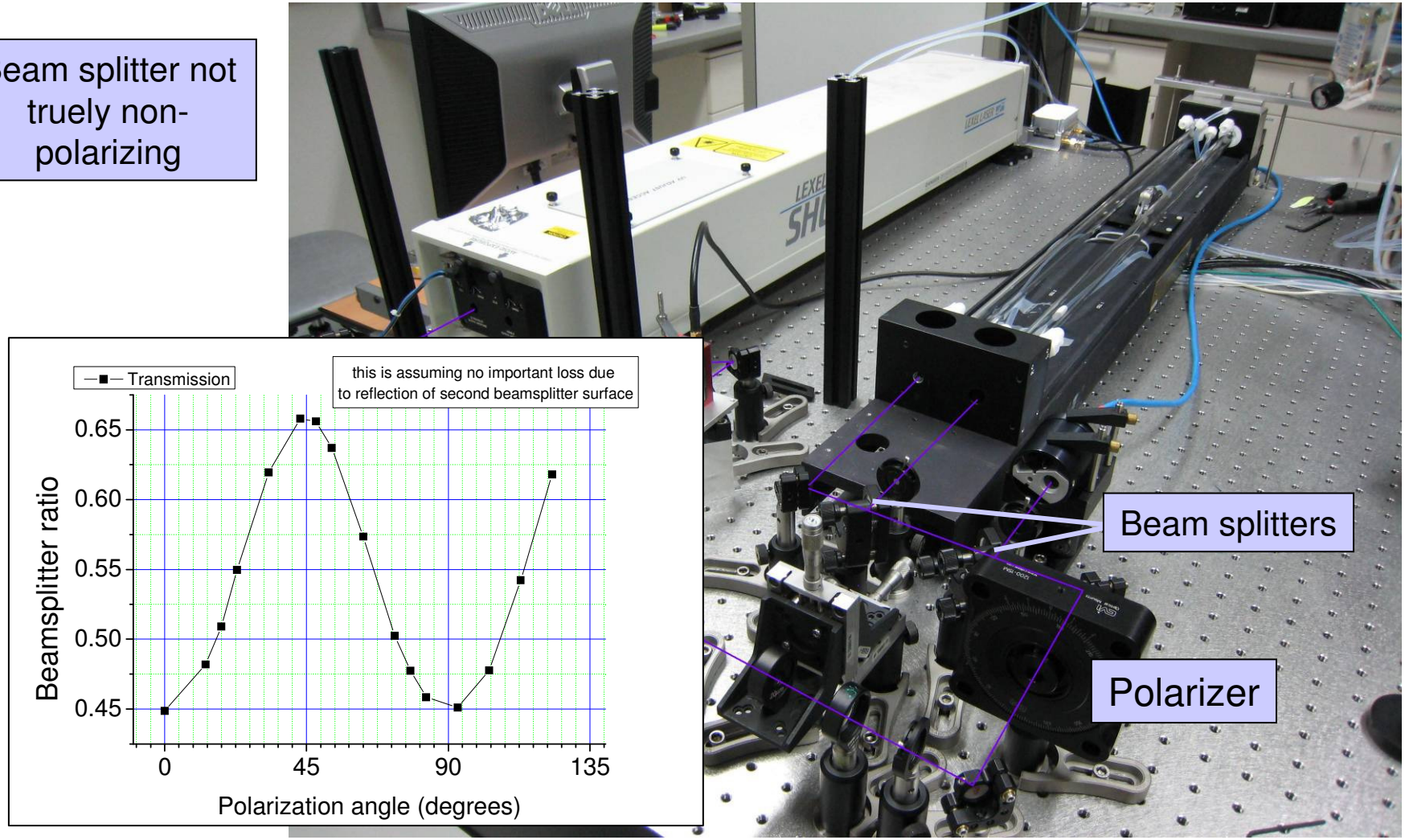
Photo-diodes for measuring absorption

Measurement cells

Power stabilization Photo-diode

Laser-based Photometer

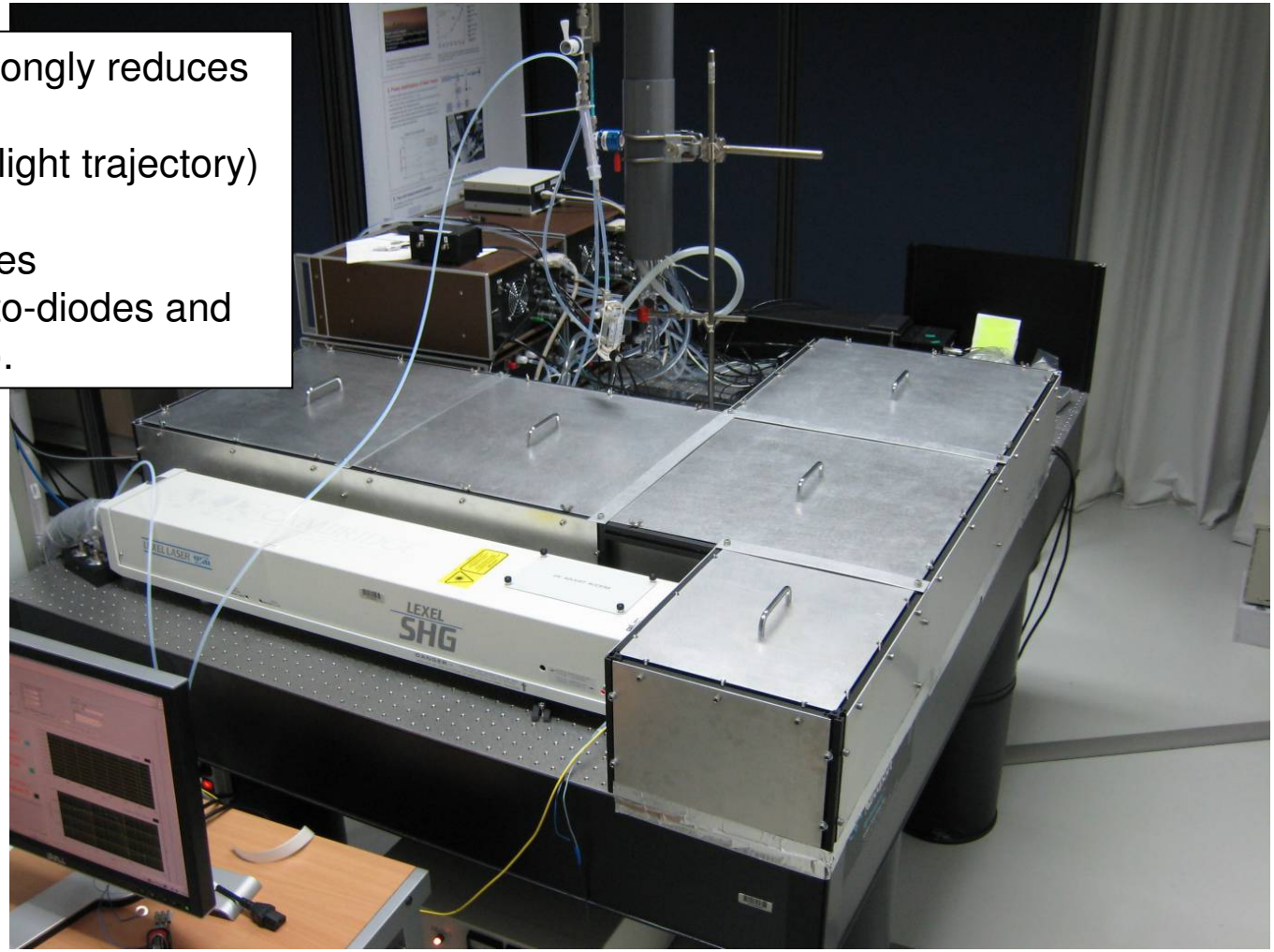
Beam splitter not truely non-polarizing



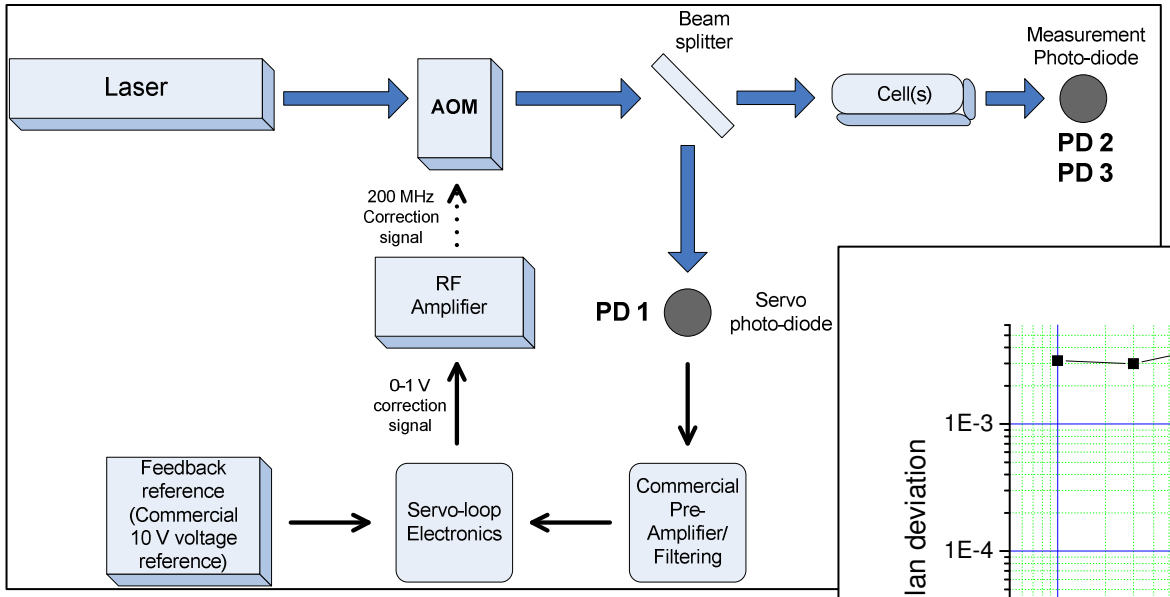
Better protection from the environment

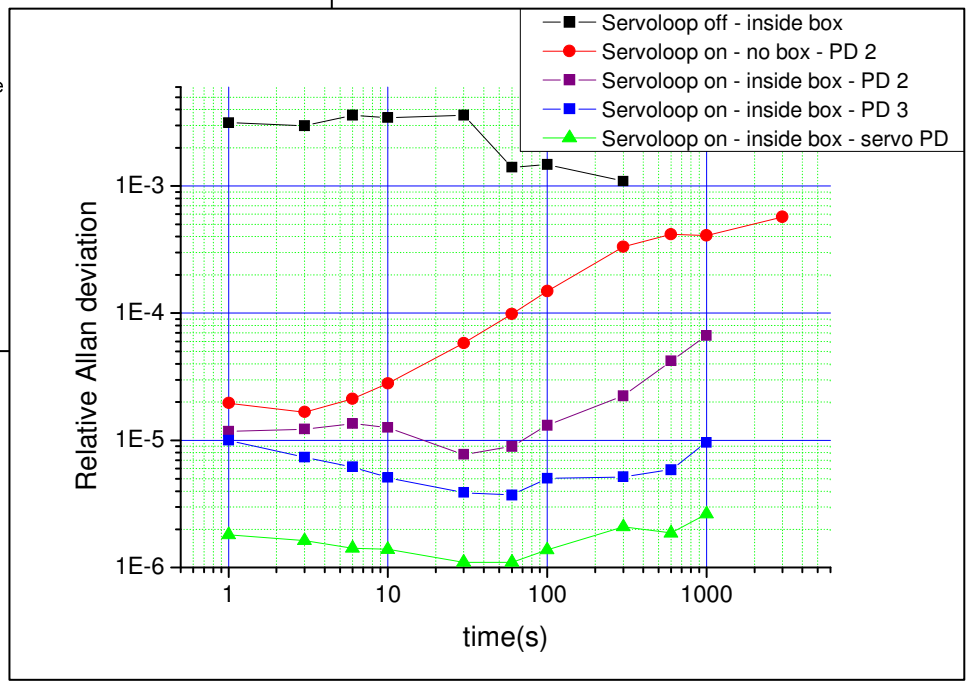
Box around setup strongly reduces

- turbulence (affects light trajectory)
- temperature-changes (affects optics, photo-diodes and measurement cells).



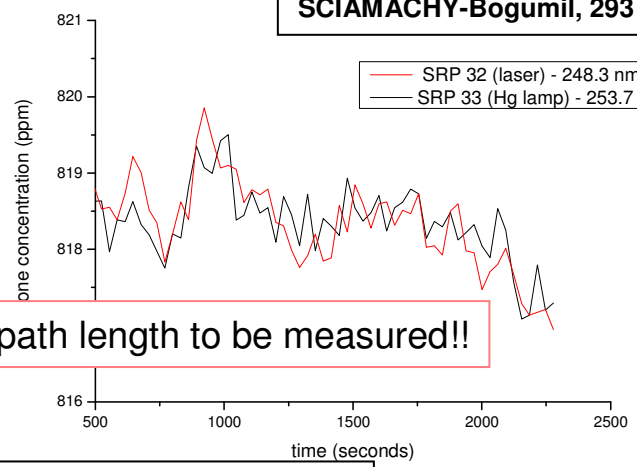
Power stabilization





Comparison between SRP 33 and the laser-based photometer (one-cell setup) at 248 nm

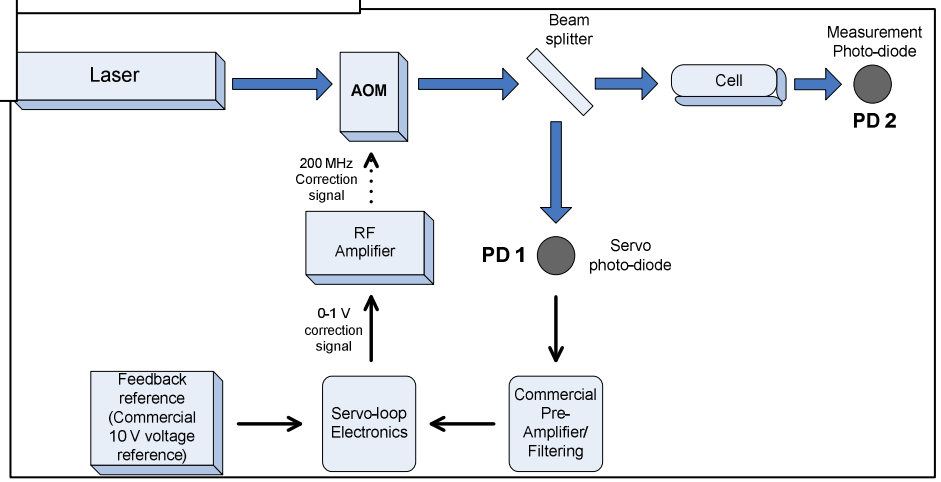
Cross section (rel. to Hearn value at 253.7 nm):
SCIAMACHY-Bogumil, 293 K, 2004



Optical path length to be measured!!

- Laser light (power) stabilized.
- Measurement cell is alternatively filled and emptied of ozone.
- Flush time of 10 s and a measurement time of 5 s.
- Ozone concentration is deduced from the ratio between light measured while there is ozone in the cell and the average light measured during the periods of before and after this period in which the cell is empty of ozone.

Daumont 92 leads to a 0.9 % difference between SRP (254 nm) and laser-based (248 nm) measurement of ozone conc.



Comparison between SRP 33 and the laser-based photometer

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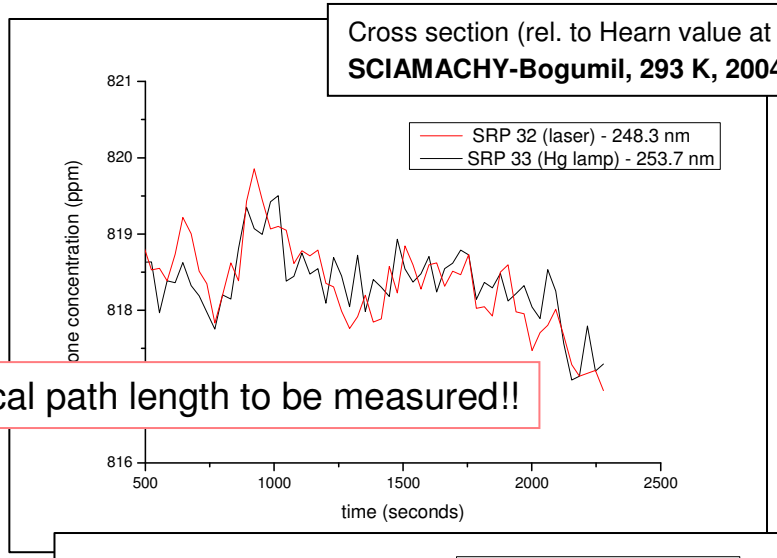
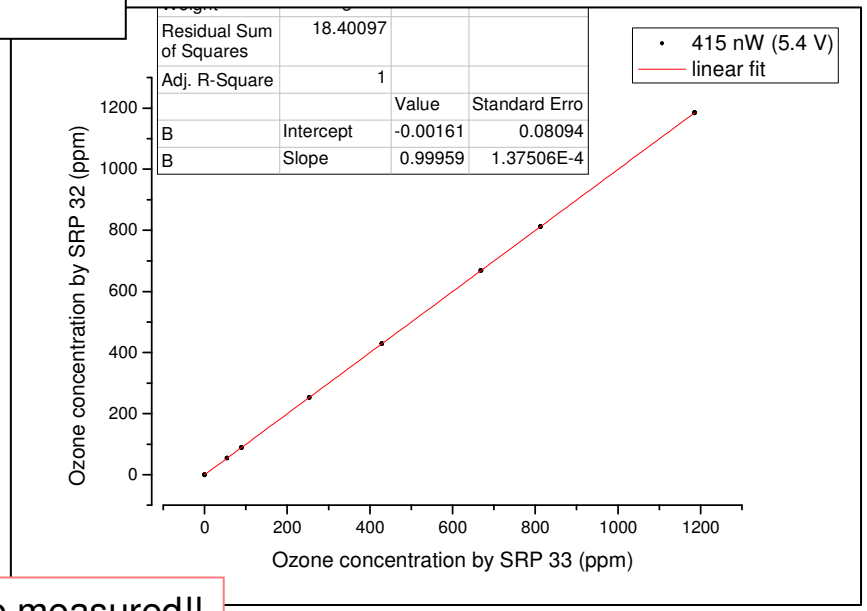
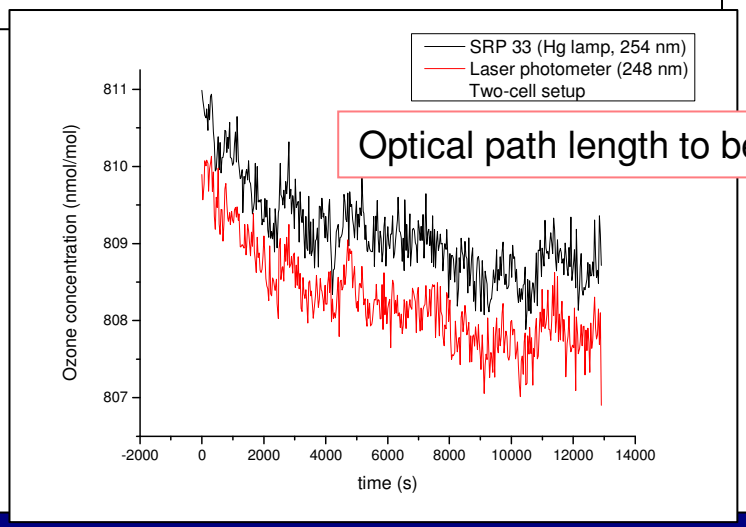


Optical path length to be measured!!





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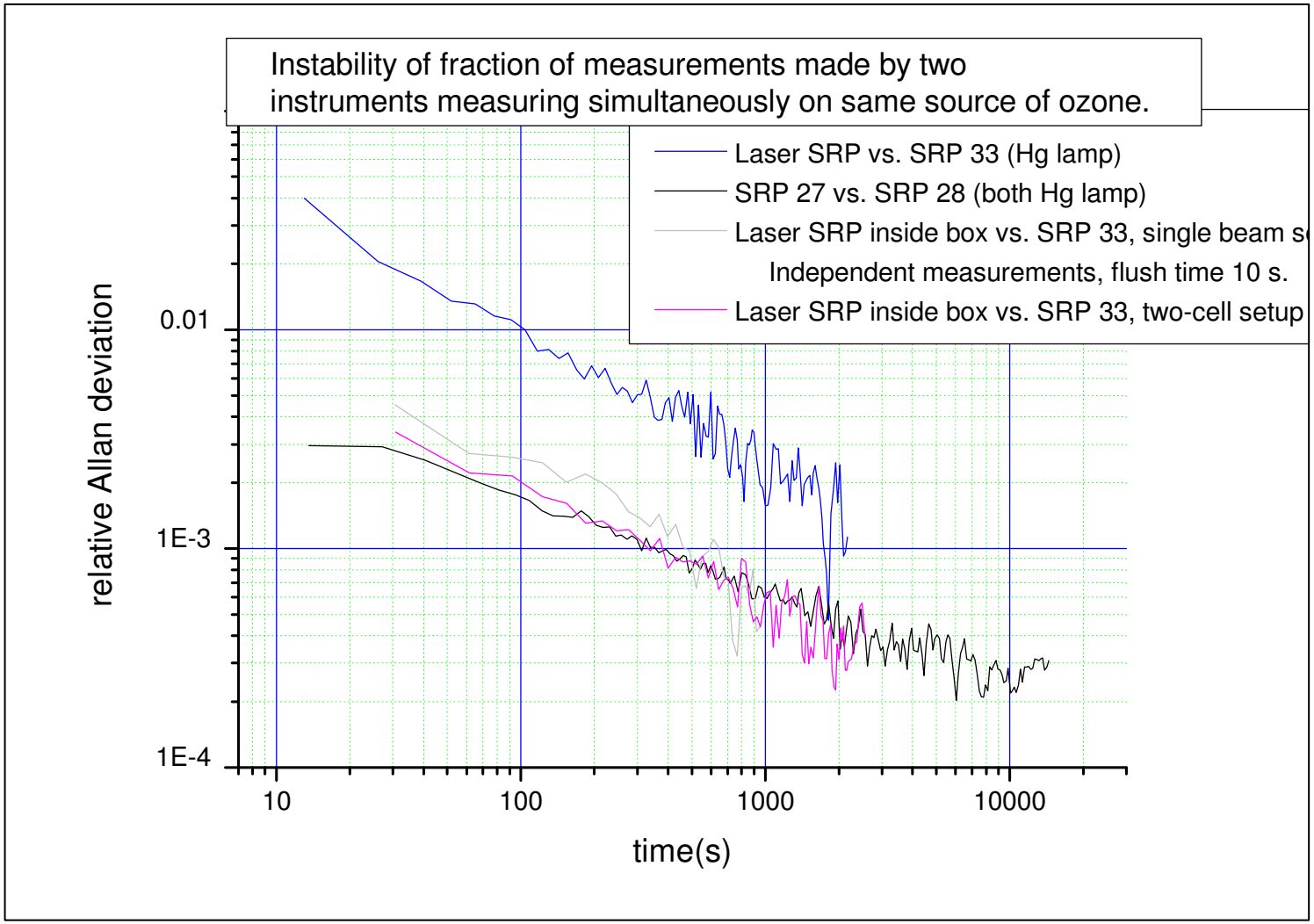
Comparison between SRP 33 and the laser-based photometer



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Plans for absolute measurements of the ozone absorption cross section at 244 nm, 248 nm and 257 nm

Mauersberger et al, 1986

- Fill a vacuum chamber with pure oxygen.
- Create ozone with ozone generator while continuously trap the ozone in a cryotrap at 77 K.
- Stop creating ozone and pump out remaining gas (mostly oxygen).
- Increase cryostat temperature to 80-90 K where the ozone has a vapour pressure of 0.1-1 mbar.
- Measure pressure. Measure oxygen/ozone ratio with mass spectrum analyzer.
- Rinse-and-repeat to eventually decrease oxygen concentration.

Daumont et al, 1992

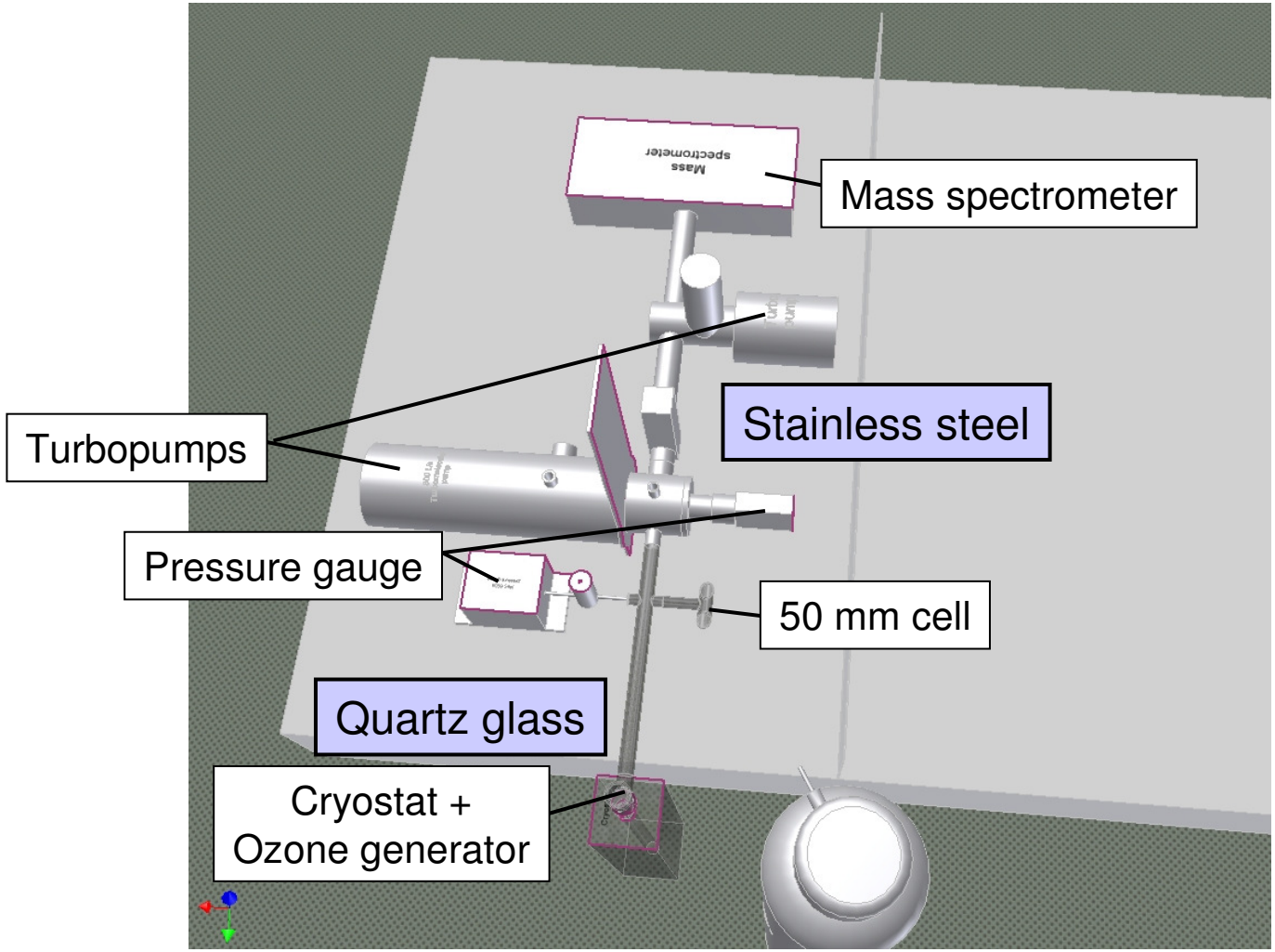
- Fill a vacuum chamber with pure oxygen at about 1 mbar. Close off vacuum chamber.
- Measure pressure.
- Create ozone with ozone generator while continuously trap the ozone in a cryotrap at 77 K.
- Stop creating ozone.
- Release all trapped ozone by (slowly) increasing cryotrap temperature.
- Measure pressure. Ozone partial pressure given by

$$p_{O_3} = 2\left((p_{O_2})_{init} - p_T\right)$$

- Simultaneously measuring of absorption of laser light in 5 cm long quartz cell and cell temperature.
- By using laser, optical path length can be determined more precisely.
- Determination of absorption cross section.

Target uncertainty: 0.5 %.

Planned setup for ozone cross section measurements



- Part quartz glass, part 316L stainless steel.
- High voltage ozone generator in quartz glass.
- 5 cm long measurement cell in quartz glass.
- Capacitive pressure gauge for precision measurement (0.1-1 mbar).
- Pirani/cold cathode pressure gauge for general pressure monitoring.

Main Points/Conclusion

- Further study of the difference between measurements of ozone concentration done by Hg-lamp and done by titration is needed.
- A laser-based photometer at 248 nm can reach same level of stability as the Hg-lamp based standard reference photometer.
- The BIPM is building a new experimental setup to measure the absolute value of the absorption cross section of ozone at 244 nm, 248 nm and 257 nm.

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