Harmonization of GOME, SCIAMACHY, GOME-2 ozone cross-sections

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Retrieval issues related to cross-sections

- **SCIAMACHY** total O_3 retrieval (using SCIAMACHY FM reference spectra) were **5%** higher than **GOME** (with GOME FM reference spectra) in the range **325-335** nm
- **GOME2** total O_3 retrieval (using GOME2 FM) is **9%** higher than calculated with resolution adjusted **GOME** FM
- **Harmonisation** of O_3 and NO_2 FM cross-sections from GOME and SCIAMACHY for a consistent retrieval
- Two approaches:
  - **reanalysis** of laboratory data from the CATGAS campaigns
  - new laboratory **measurements**:

sufficient accuracy to detect a 1% pro decade trend

Measurement quality demands*

- ✓ Wavelength coverage: of **240–1000 nm at 0.01 nm** spectral resolution or better;
- ✓ Absolute intensities accuracy: at least **2%** through the Hartley–Huggins and Chappuis bands;
- ✓ Vacuum wavelength accuracy: better than **0.001 nm**;
- ✓ Temperature range: **200–300 K** (covered in 10-15 K steps).

***J.Orphal, K.Chance .**Ultraviolet and visible absorption cross-sections for HITRAN*

Journal of Quantitative Spectroscopy & Radiative Transfer 82 (2003) 491–504

Experiments: Strategy

- Inherited experience from the previous researchers of IUP:
  - CATGAS GOME2 experimental set-up (**C**alibration **A**pparatus for **T**race **G**as **A**bsorption **S**pectroscopy) ;
  - experimental conditions used in CATGAS GOME campaign;
  - FTS (**F**ourier **T**ransform **S**pectrometer).
- Potential error sources analysis
- Modification of set-up and conditions set

Experimental Set-Up: Overview

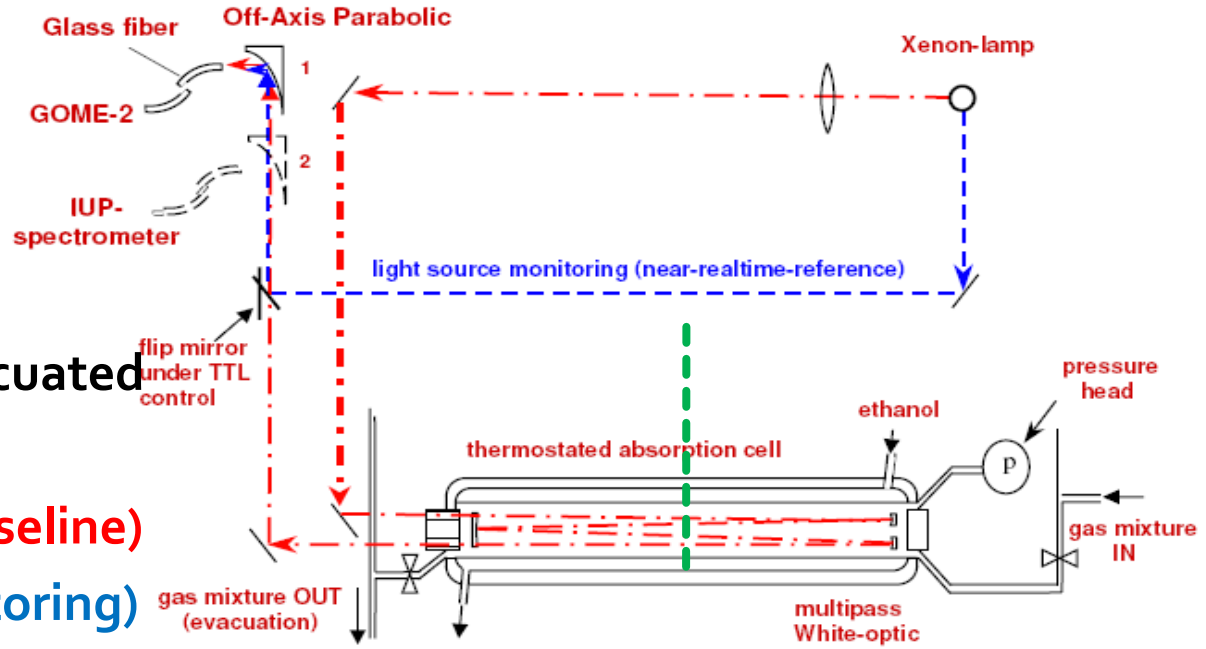
$$I(\lambda) = I_0(\lambda) \cdot \exp[-OD]$$

I – transmitted intensity, I_0 – initial intensity (baseline), *OD* - optical density

Xe Lamp: UV/VIS source

Detector: LN2 cooled chip

Cell: 120 cm long,
5 cm Dia
thermostated, evacuated



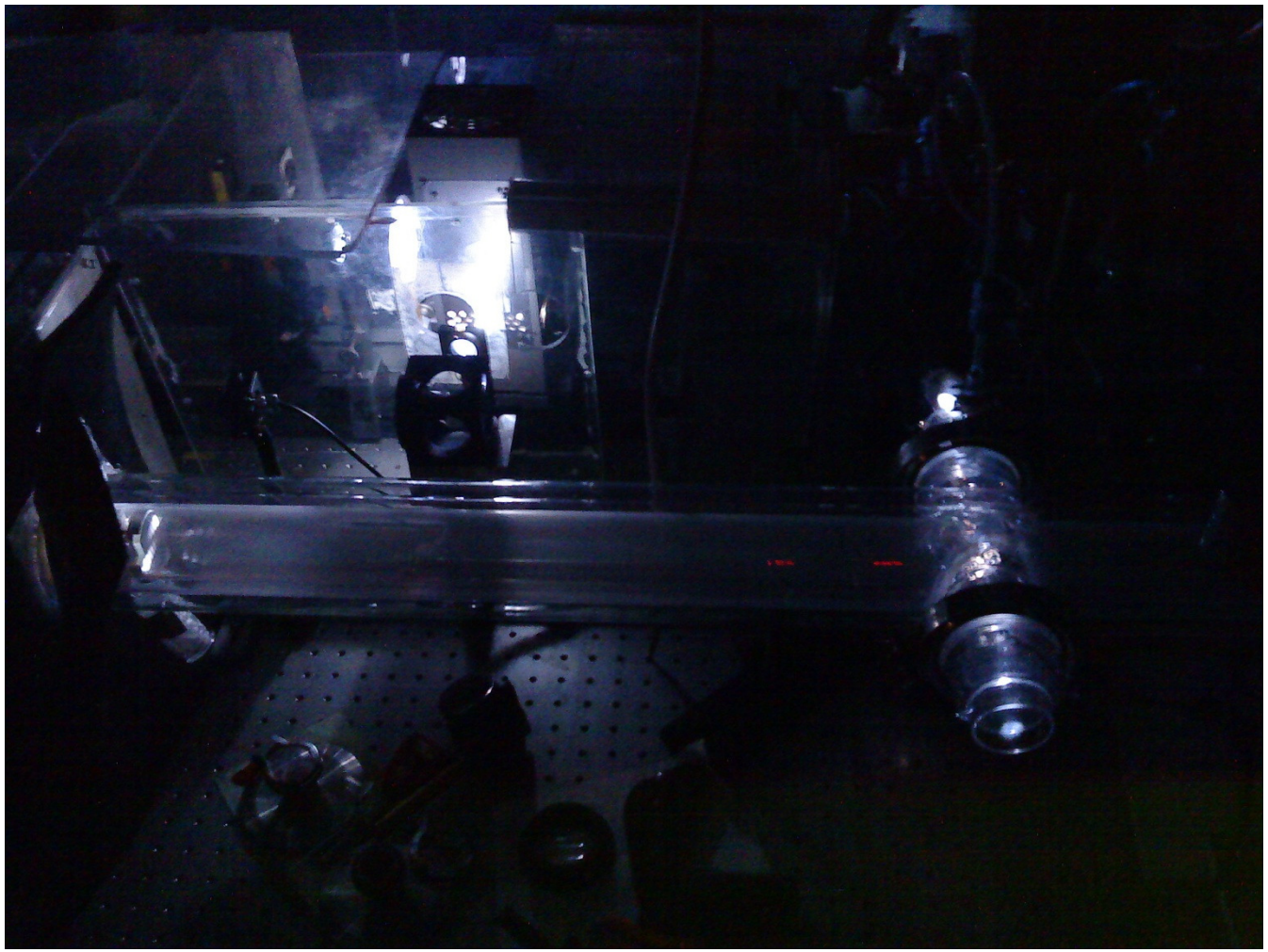
Red – „Cell" (absorption/baseline)

Blue – „Direct" (lamp monitoring)

Cross- path

HgCd lamp - wavelength calibration (not shown)

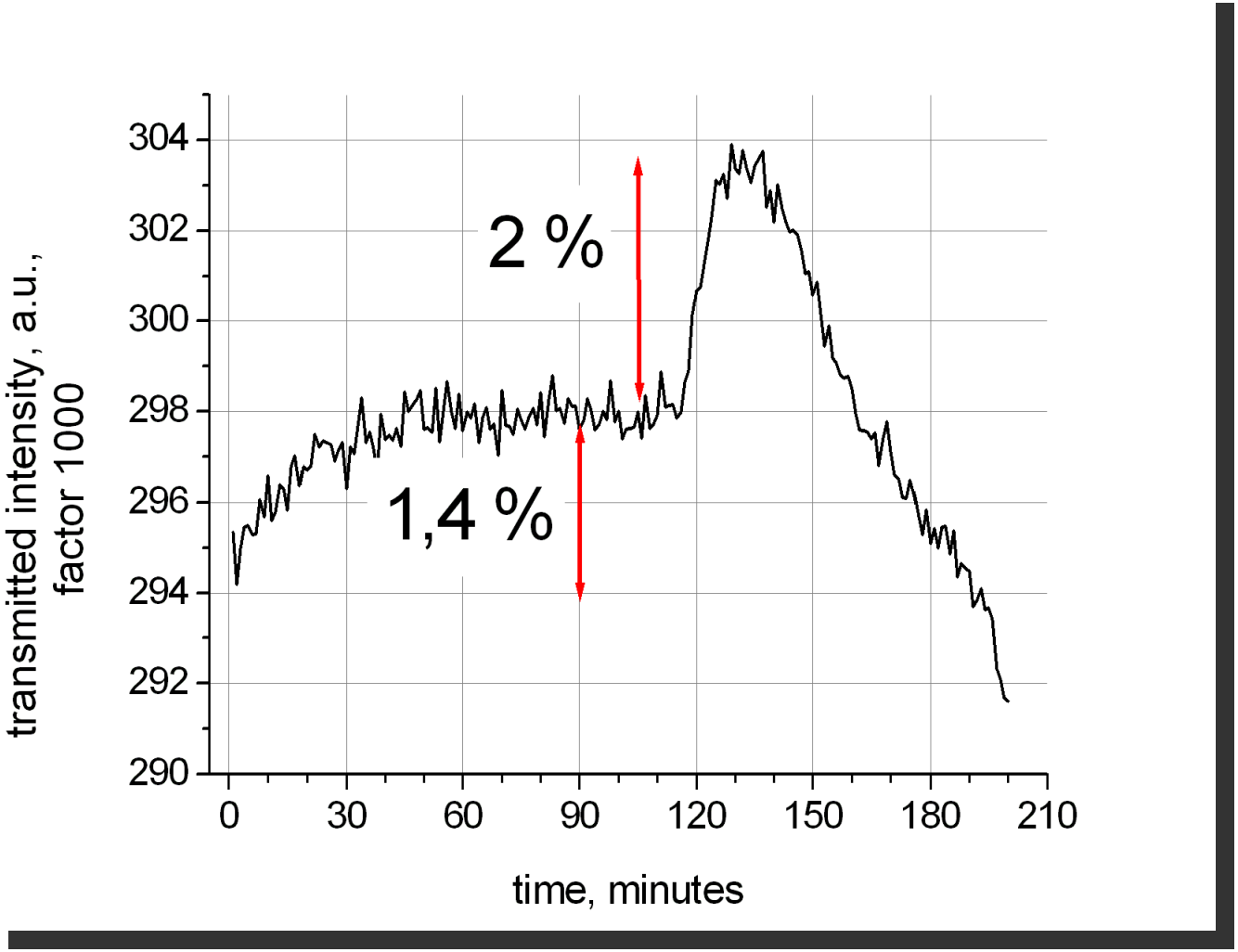
Experimental Set-Up: Overview



Grating spectrometer versus Fourier Transform Spectrometer

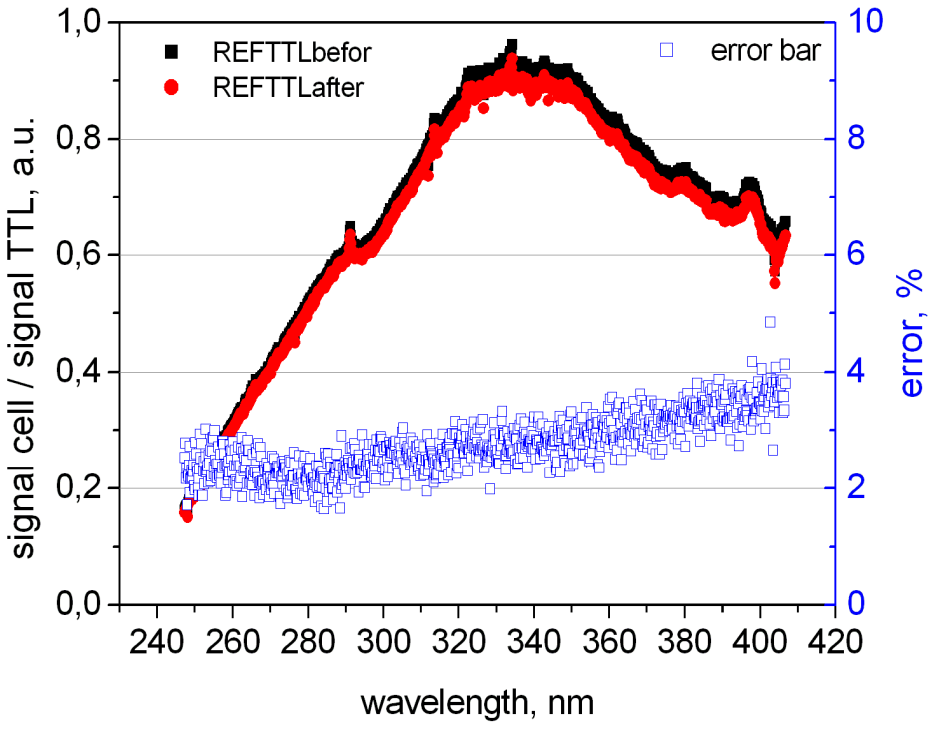
Parameter	Grating spectrometer	Fourier Transform Spectrometer
Spectral window, nm	250 - 400	?
Resolution, nm	0.18	< 0.02
Measurement time	Exposure, "short" (1 sec)	Scanning time, "long" (10 minutes)
Wavelength calibration	Hg-Cd lamp lines, fair	He-Ne laser, perfect

Error source I:
light source intensity drift (no O3, 335 nm)



Error source I:
baseline drift (no O3)

- ✓ Light source intensity drift:
  - ✓ Up to 4%
  - ✓ depends wavelength
- ✓ Correction with lamp monitoring signal does not help.
- ✓ Solutions:
  - ✓ Quick absorption measurements
  - ✓ Sufficiently long baseline measureme before and after + interpolation.

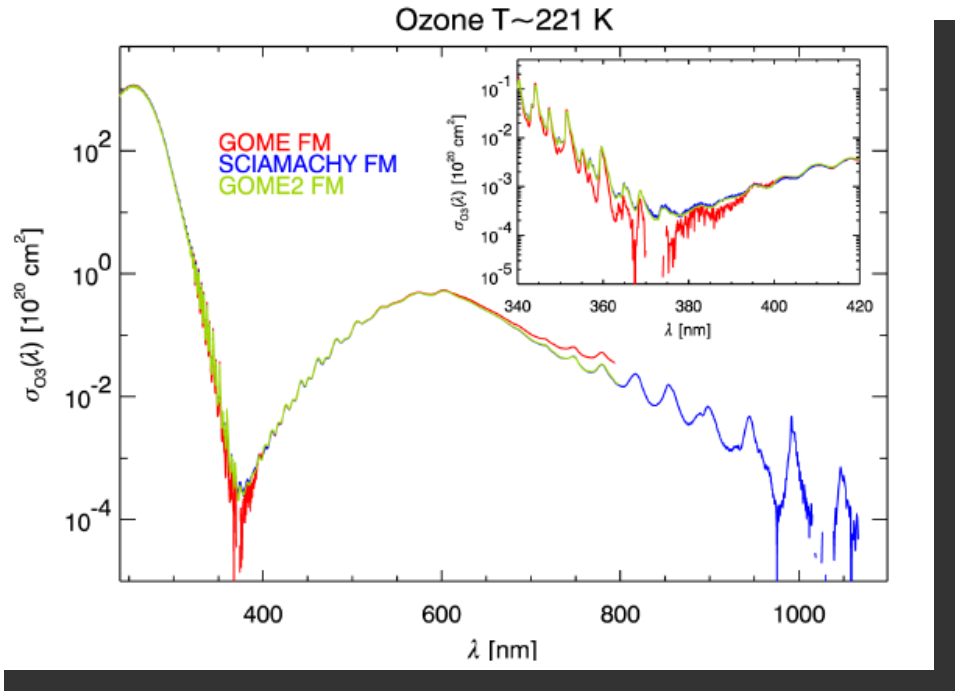


Cell1 / Direct1 ≠ Cell2 / Direct2

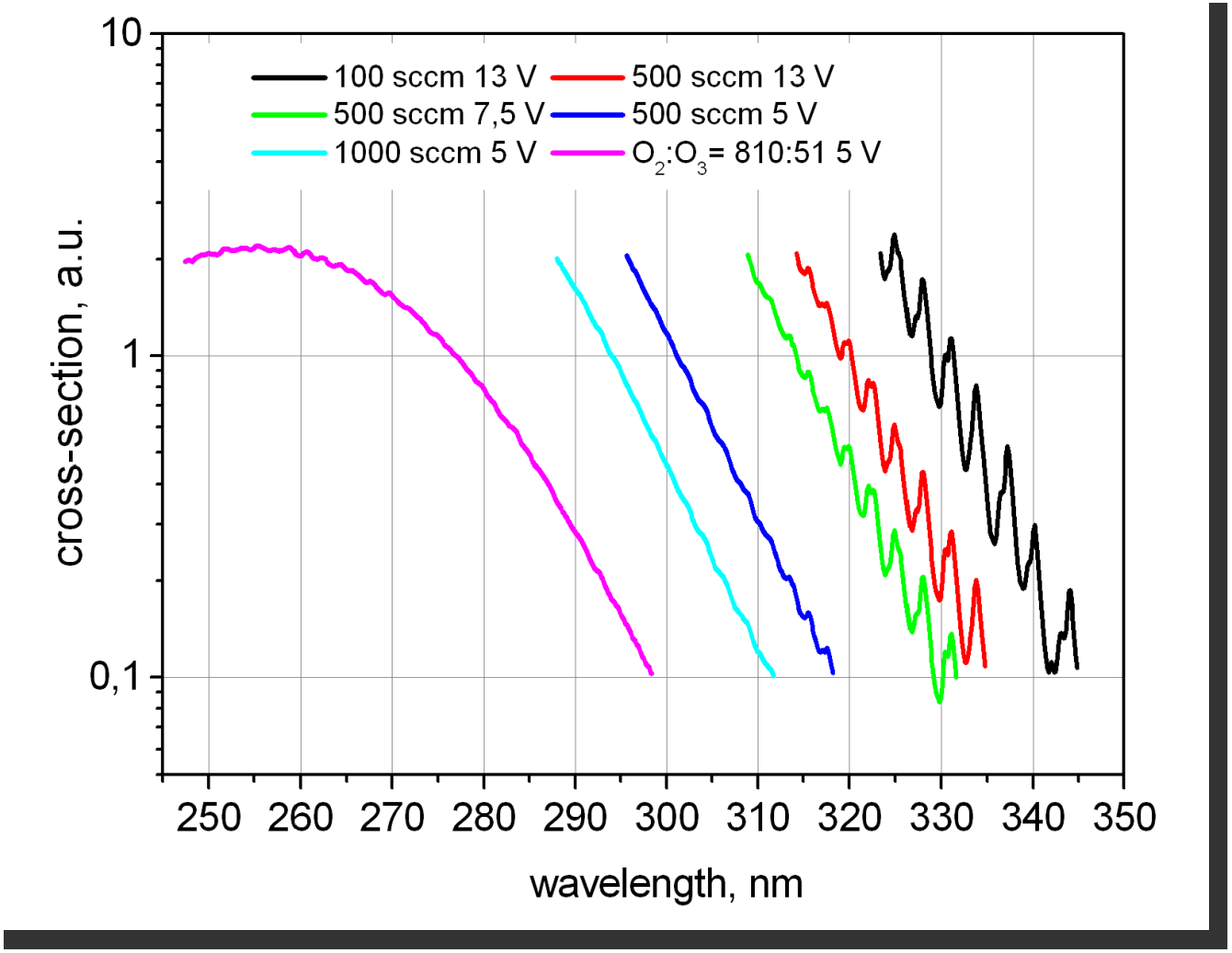
Error source II: O_3 cross-section span

- ✓ Cross-section σ changes by 7 orders;
- ✓ Equipment linearity: 0.1 < *OD* < 1;
- ✓ Product *NxL* changes by 7 orders;
- ✓ Set of conditions:
  - *L(length)*:
    - ✓ Multipass (number of passes up to 28);
    - ✓ Short cross-path
  - *N (O_3 density)*:
    - ✓ Flow rate though the ozone generator;
    - ✓ Ozone generator power;
    - ✓ O_2/O_3 dilution.
- ✓ Gluing spectra together:
  - ✓ Scaling;
  - ✓ Addition/multiplication of errors;
  - ✓ Numerical and experimental challenge.

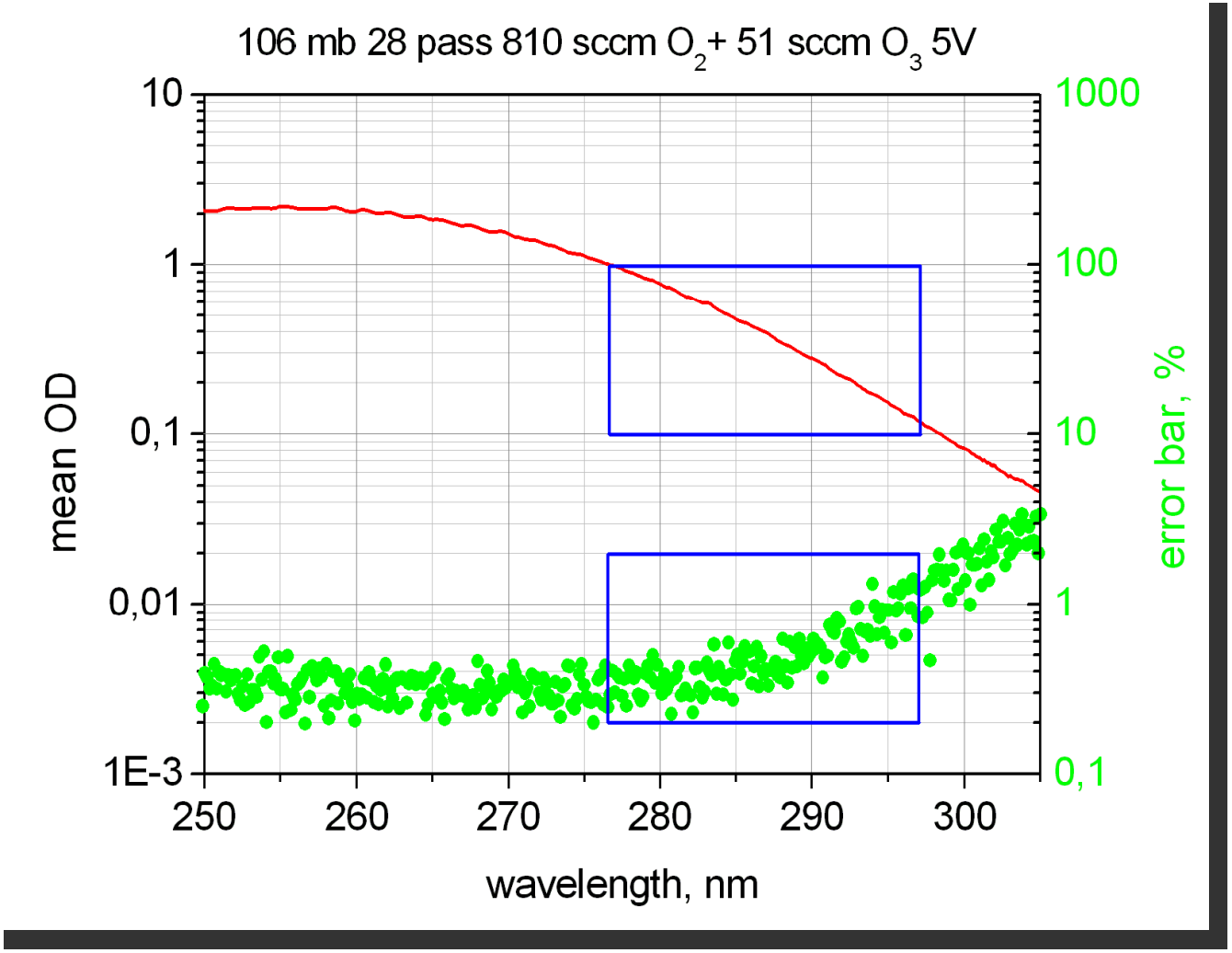
$$OD(\lambda) = N \cdot L \cdot \sigma(\lambda)$$



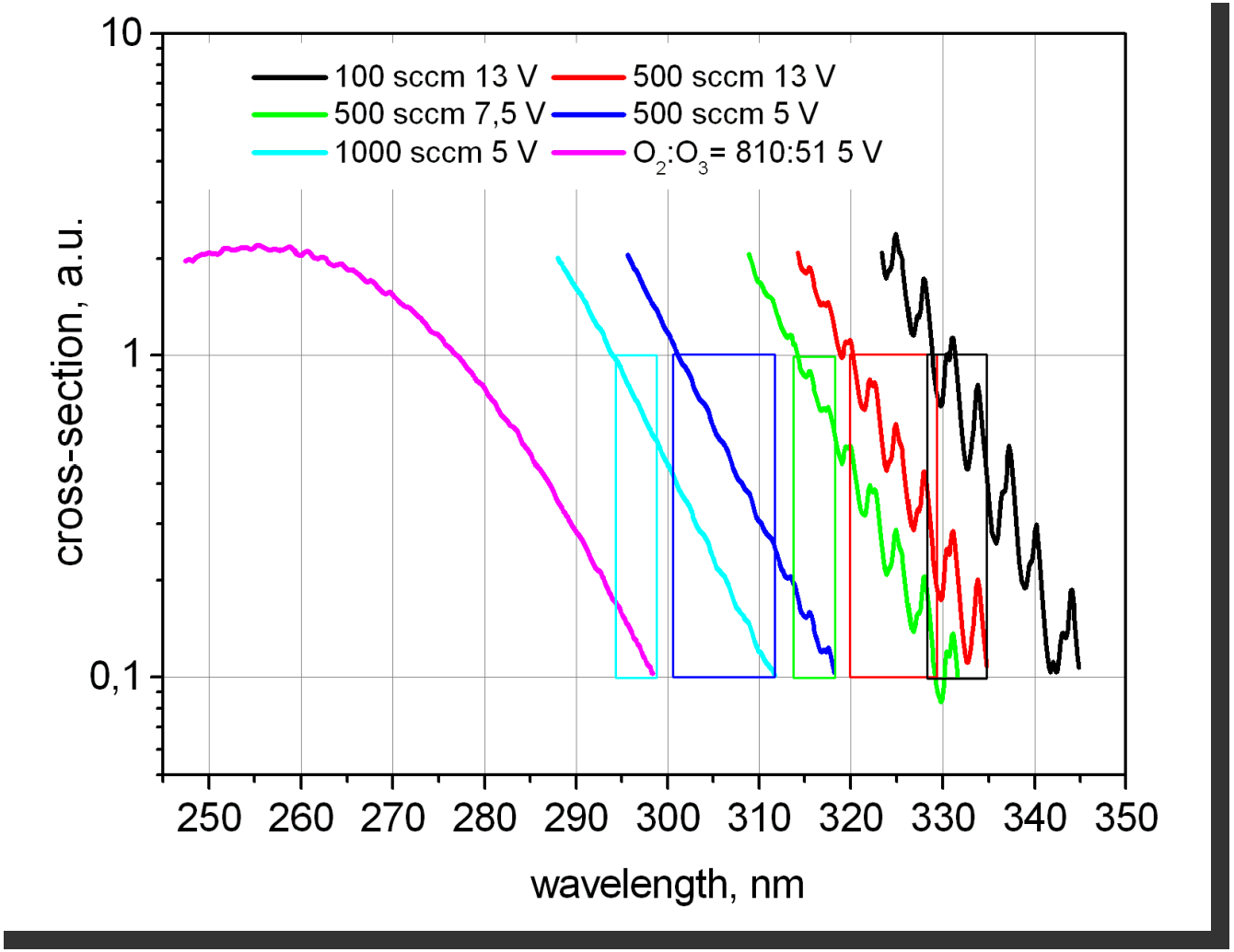
Scaling:
Partial Spectra at 293 K, 100 mbar



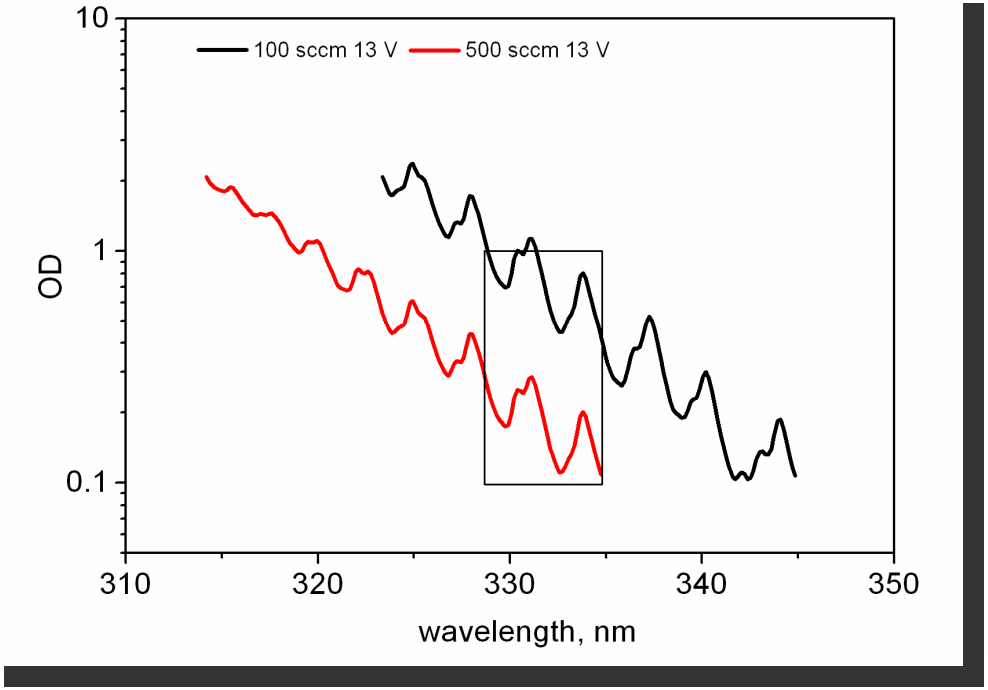
Partial spectrum quality
10 spectra averaged (293 K, 100 mbar)

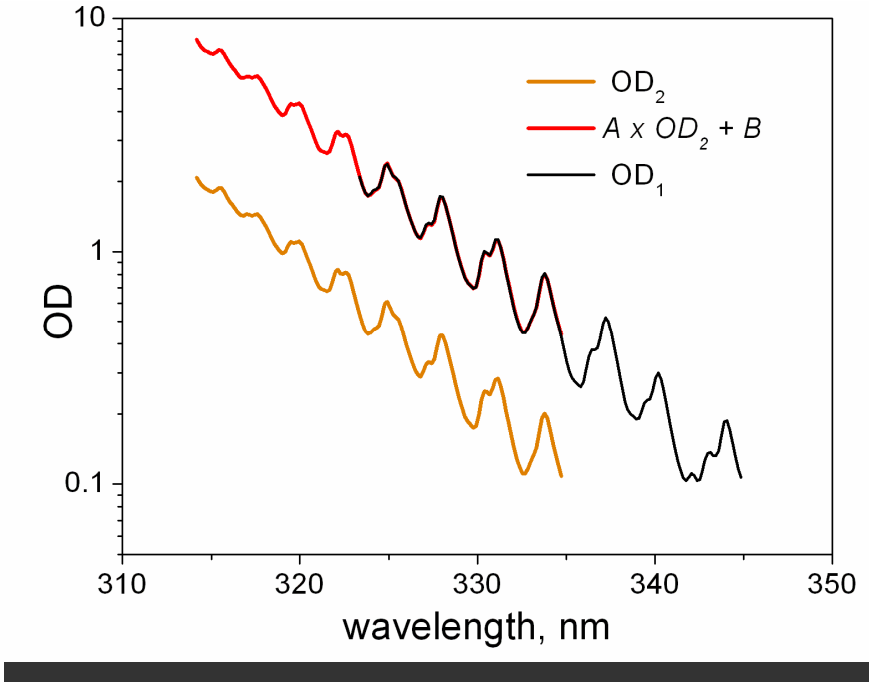


Scaling: overlap



Scaling:
overlaped and glued

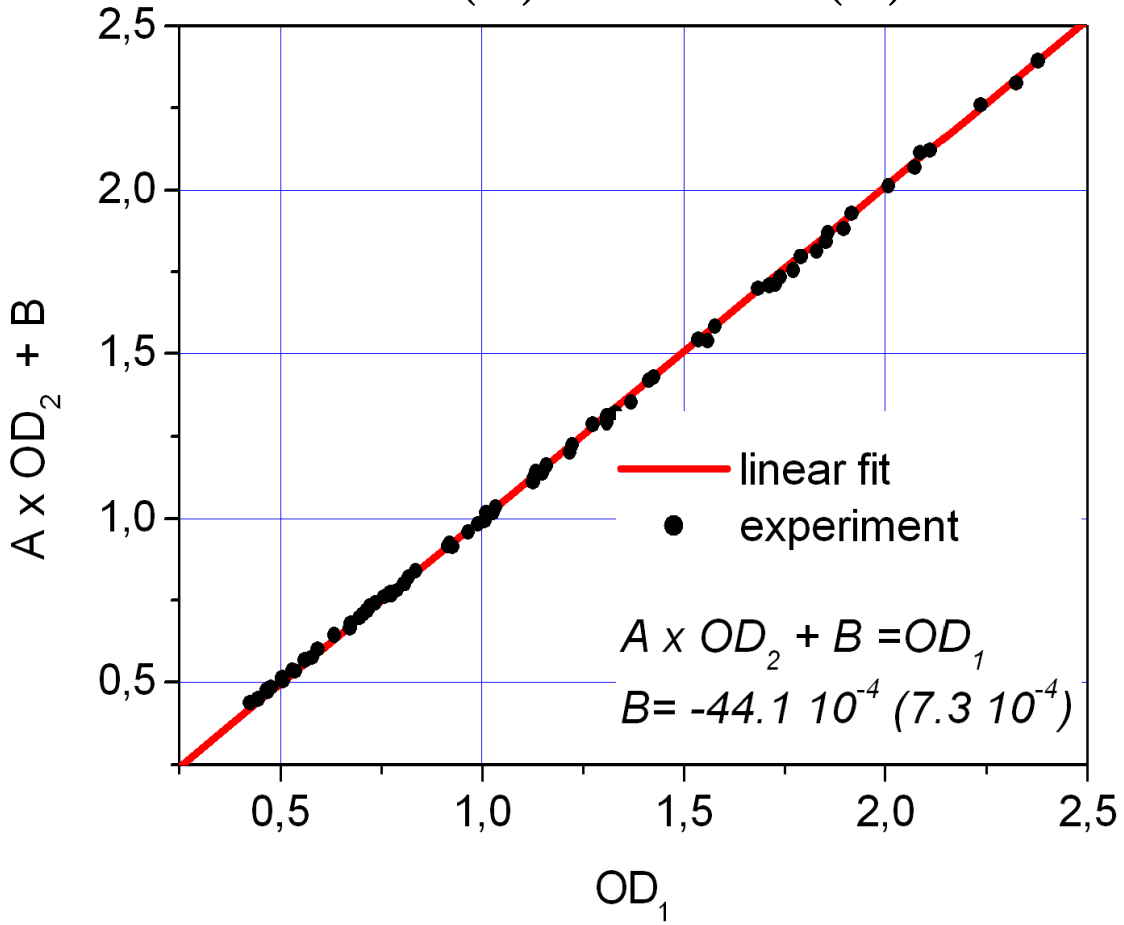




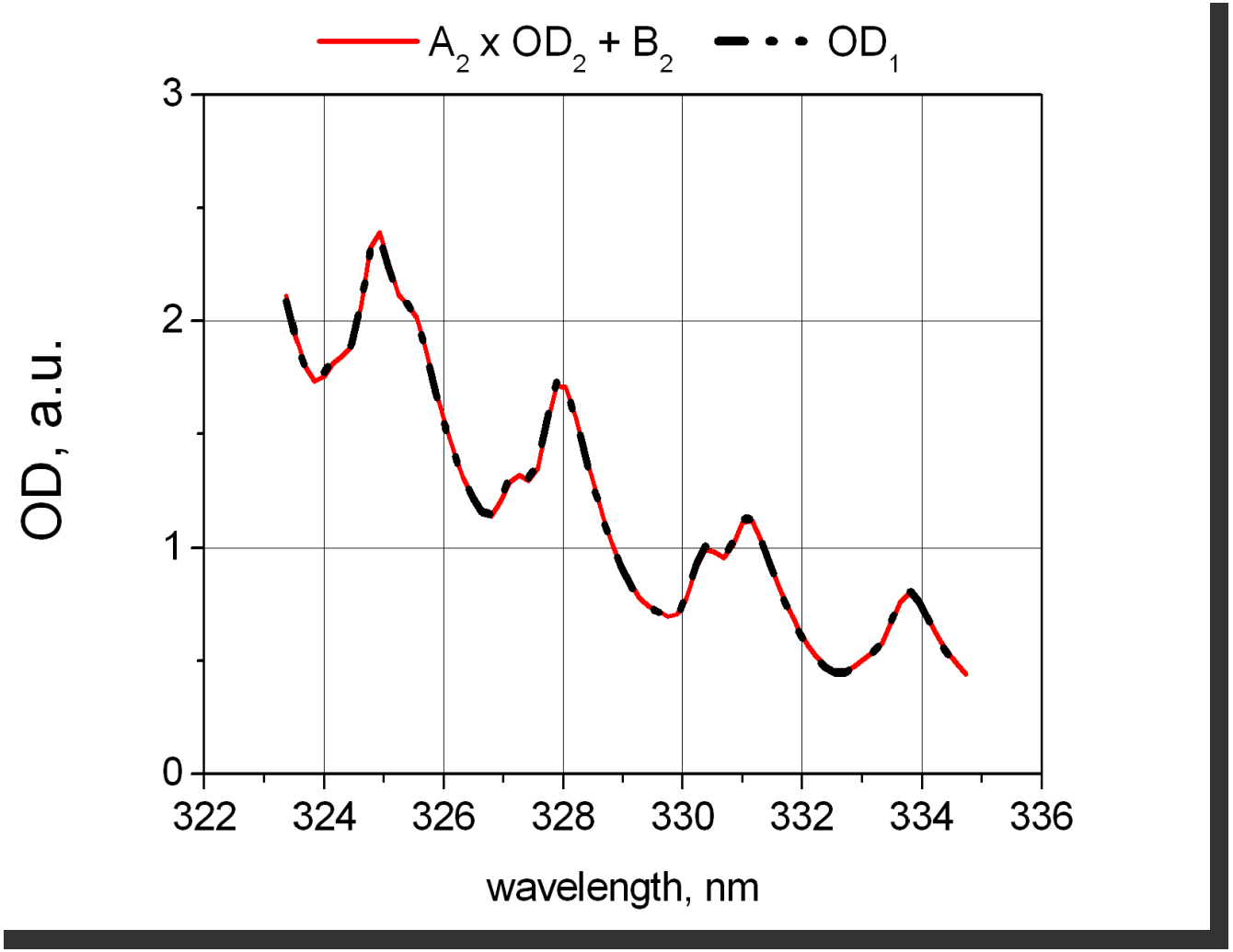
293 K, 100 mbar

Scaling:
least squares fit with non-zero off-set

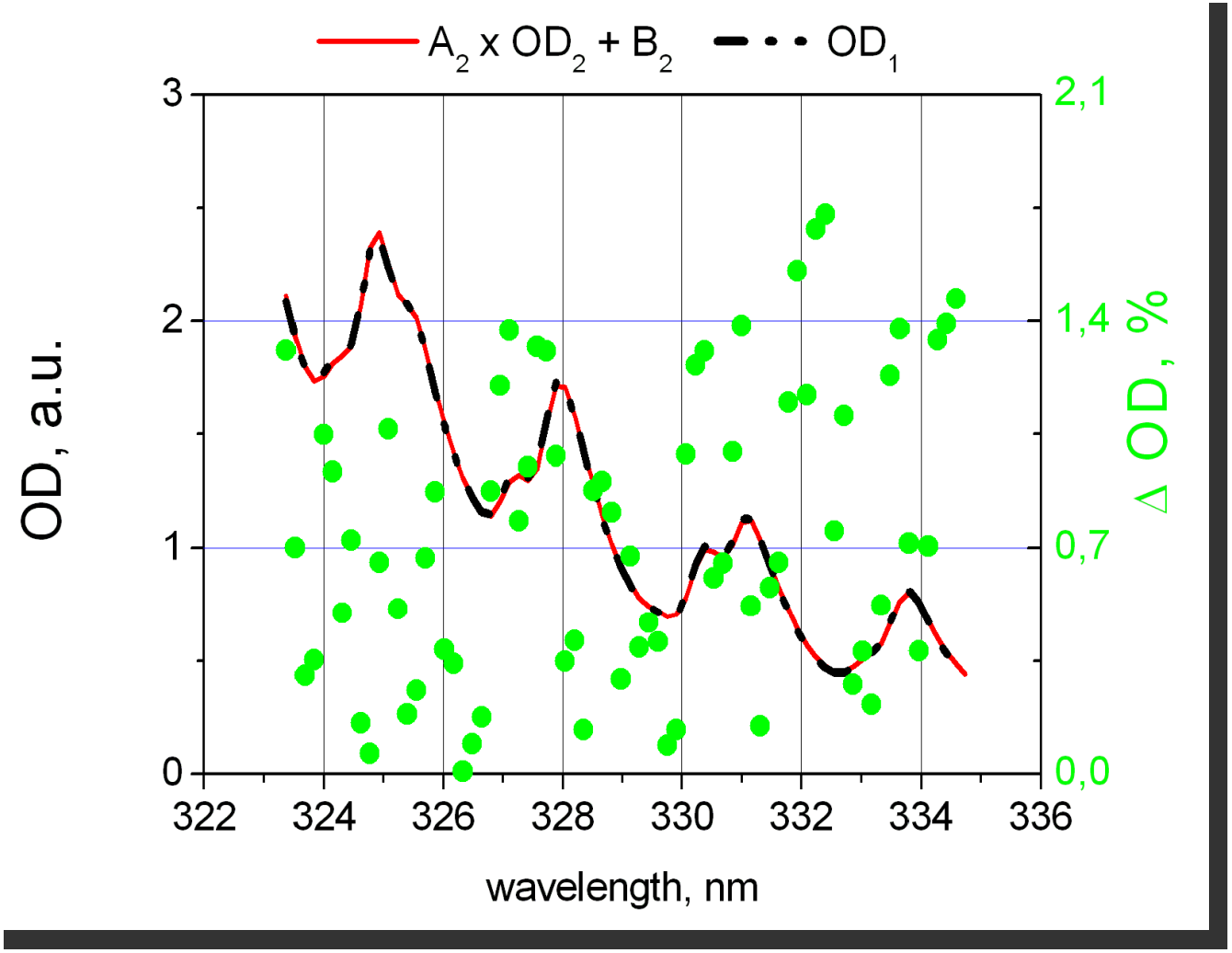
$$OD(\lambda) = N \cdot L \cdot \sigma(\lambda)$$



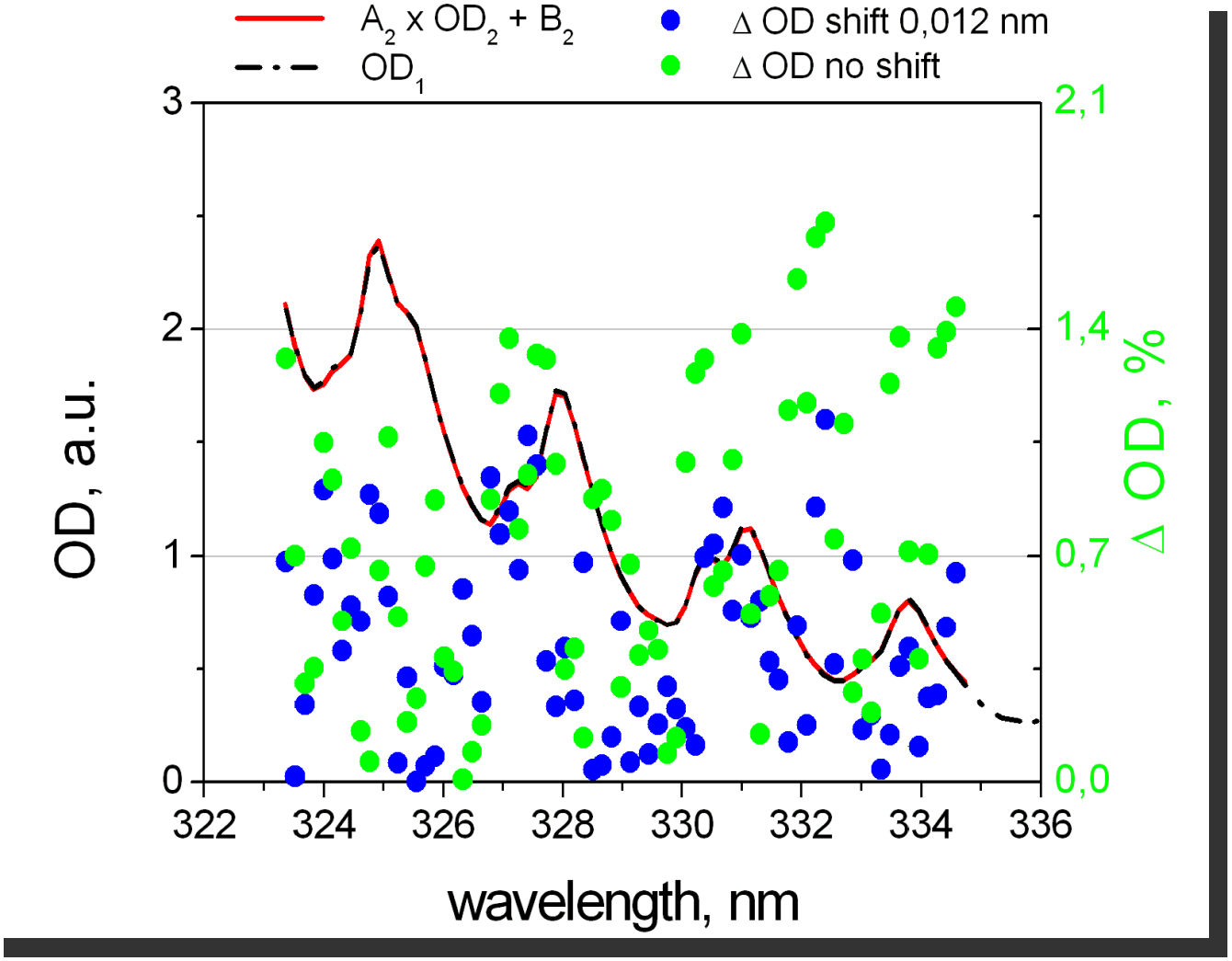
Scaling: scaled and initial spectra at 293 K, 100 mbar



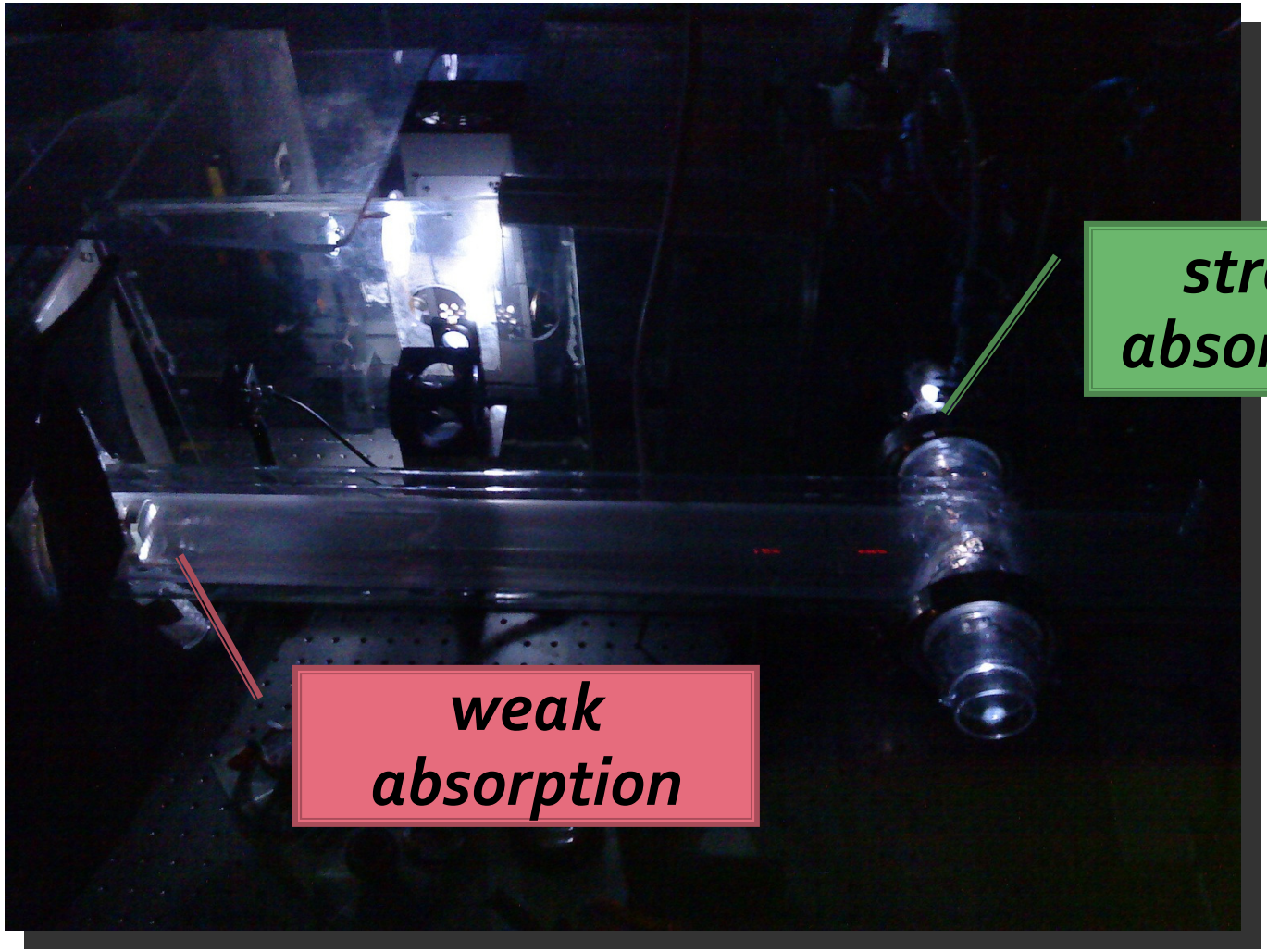
Scaling: scaled and initial spectra at 293 K, 100 mbar



Error source III: wavelength shift 0.012 nm



Modification of experimental set-up: cross-path



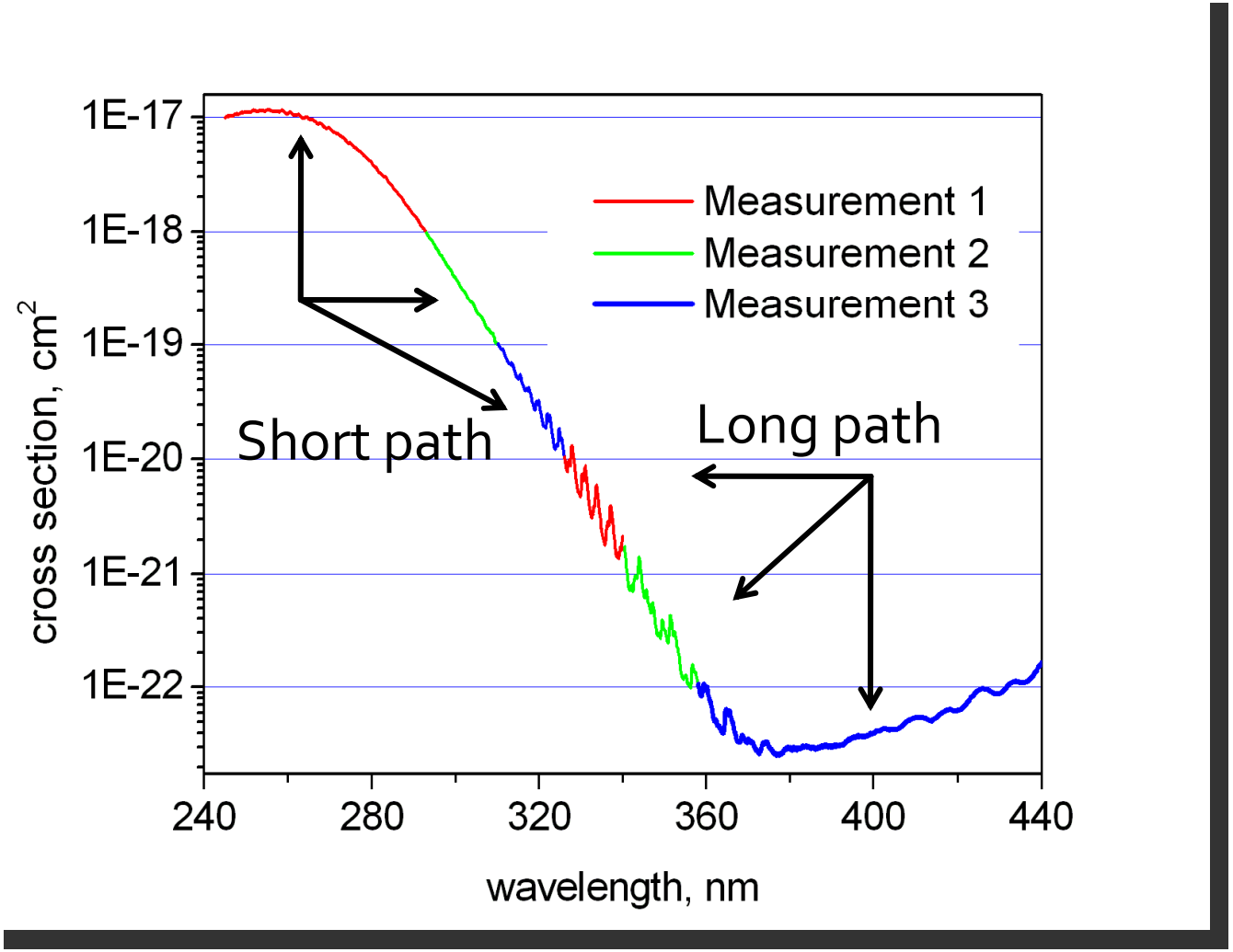
Modification of experimental set-up: cross-path

- ✓ Quasi-**Simultaneous** measurement:
  - ✓ Short path L_{cross} ~5 cm for high σ,
  - ✓ Long path L_{multi} ~ 30 m for low σ,
  - ✓ Factor 600 in optical density.

- ✓ Source: the **same Xenon lamp** – same baseline drift
- ✓ Detector: **same spectrometer and CCD** - same sensitivity, spectral response and resolution

- ✓ **Less conditions** to realize;
- ✓ **Less spectra** to glue.
- ✓ Thermal stability of the cell

Two paths measurements:
3 measurements to combine



Summary and outlook

- Analysis performed for
  - Set-ups resolution and stability;
  - Wavelength calibration;
  - Error sources;
  - Conditions sets;
  - Procedure for gluing of spectra .
- Test spectrum obtained for 250- 340 nm region at mid resolution

- Light source improvement
- Two paths measurement
- Cross- section temperature dependence (mid resolution)
- Resolution: FTS set-up

Nothing is difficult...
until you want to do
it accuratly