Faraday Rotation Spectroscopy with an External Cavity Quantum Cascade Laser for the Ultra-Sensitive Detection of NO_2

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Contents

Motivation – why NO_2?

- toxic pollutant in the atmosphere
  - knowing the concentration desired
- produced in combustion devices

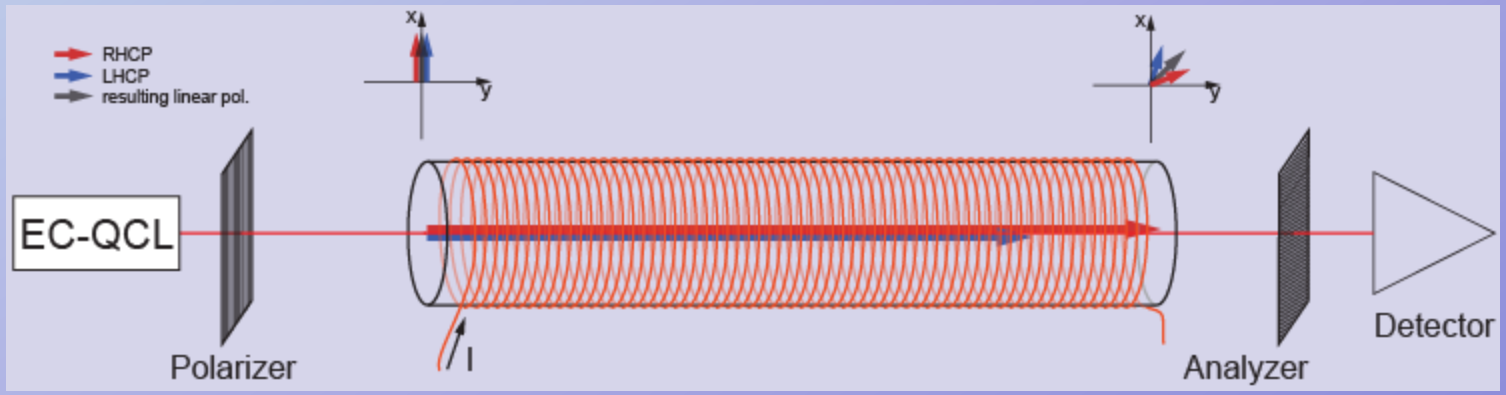
- => understand and control the formation processes

Motivation – why FRS?

- high sensitivity
  - needed for atmospheric measurements
  - typical values in single ppb range
- background free
- high selectivity
- no signal by non-paramagnetic molecules
  - e.g. H_2O and CO_2 do not restrict sensitivity

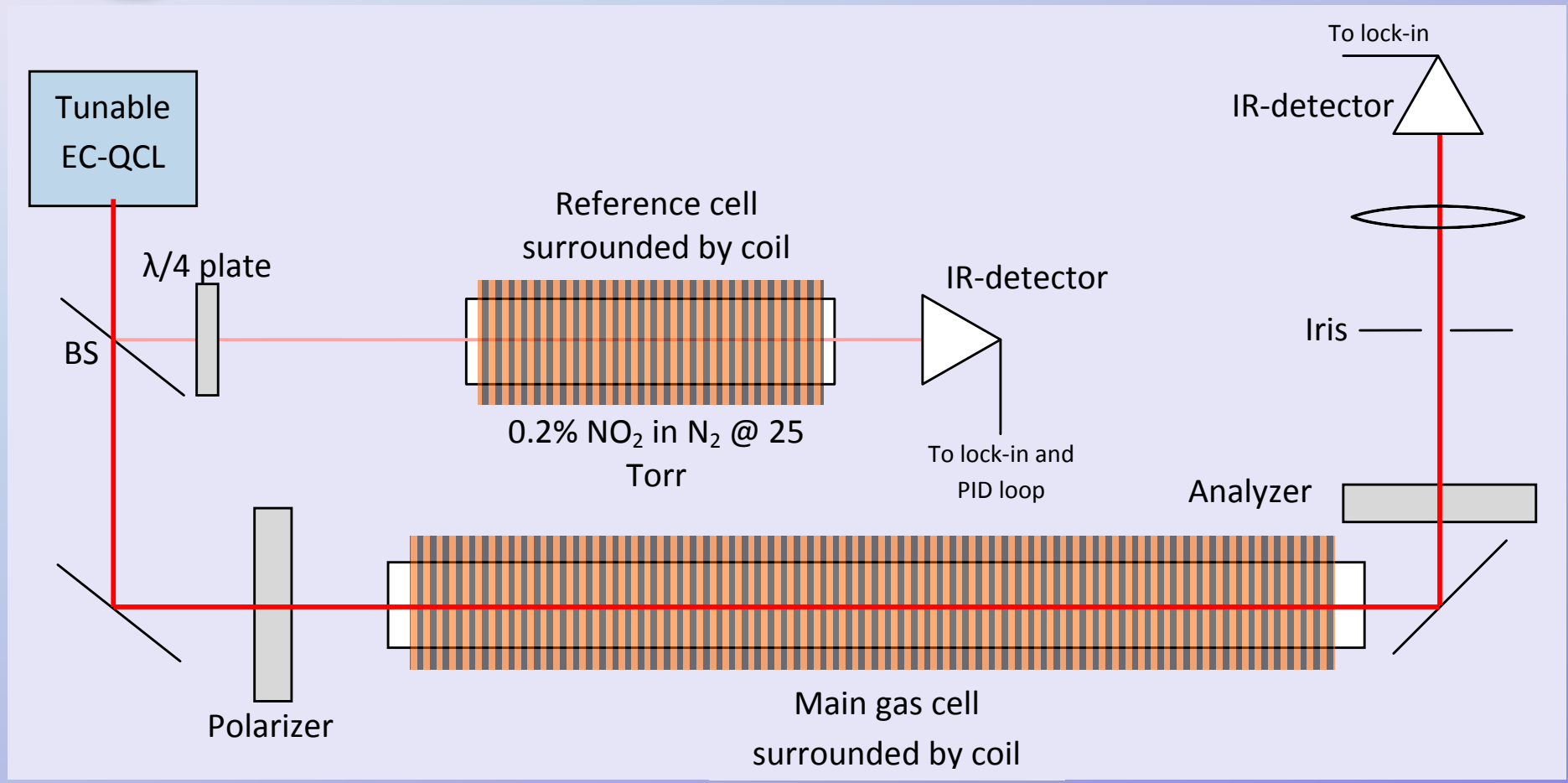
Theory of FRS [1, 2]

- paramagnetic molecules (such as NO_2) observe Zeeman splitting under the influence of an external magnetic field
- => LHCP and RHCP light couples to $\Delta M_J = -1$ or $\Delta M_J = +1$ respectively
- => difference in refractive indices $\Delta n = n_{LHCP} - n_{RHCP}$ of the LCHP and RHCP
- => linear polarized beam (= superposition of LHCP and RHCP) observes birefringence
- => linear polarization is rotated and rotation angle is proportional to the NO_2 concentration



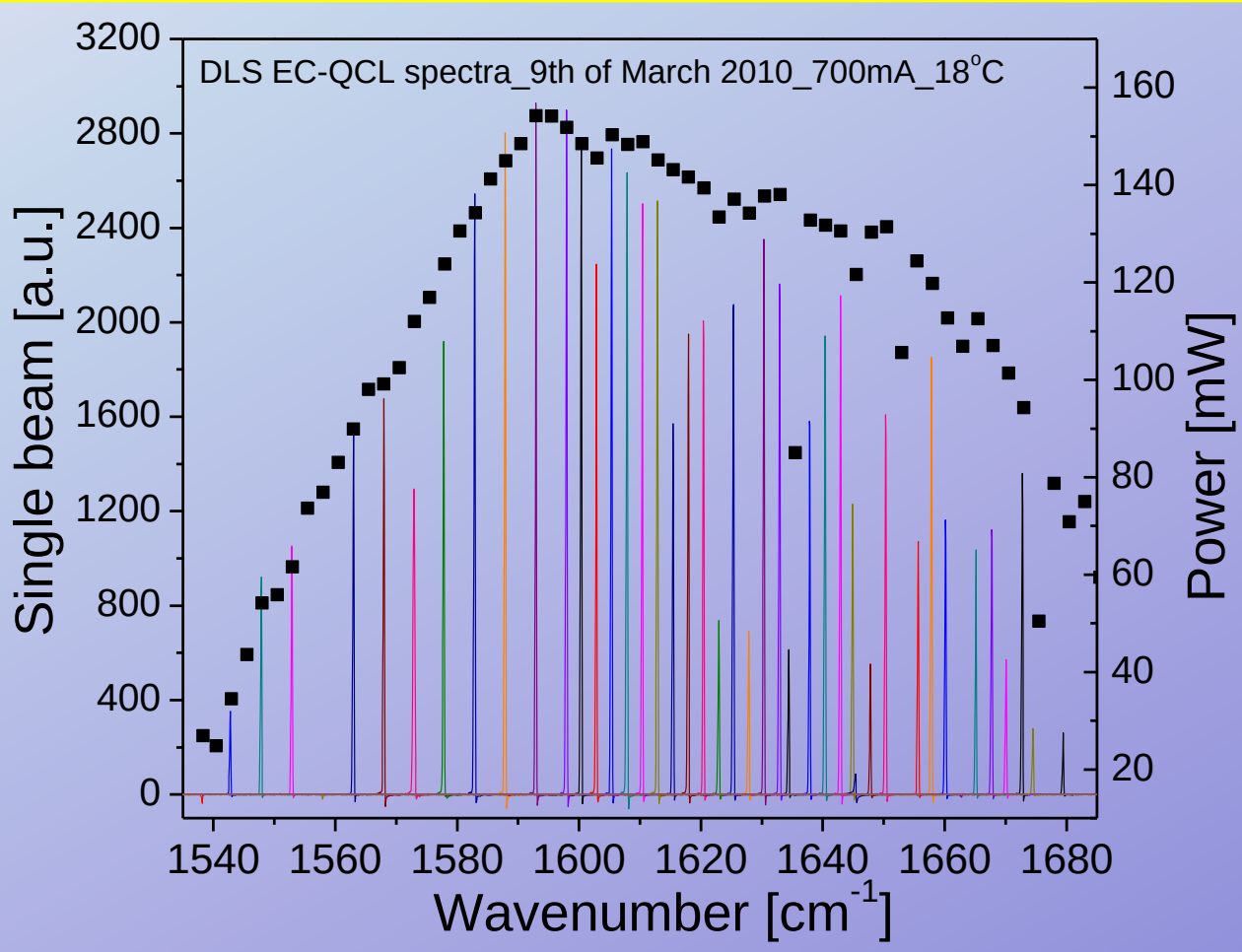
[1]: Liftin, Pollok, Curl, Tittel; J. Chem. Phys.; 1980
[2]: Lewicki, Doty, Curl, Tittel, Wysocki; PNAS; 2009

Experimental setup – overview



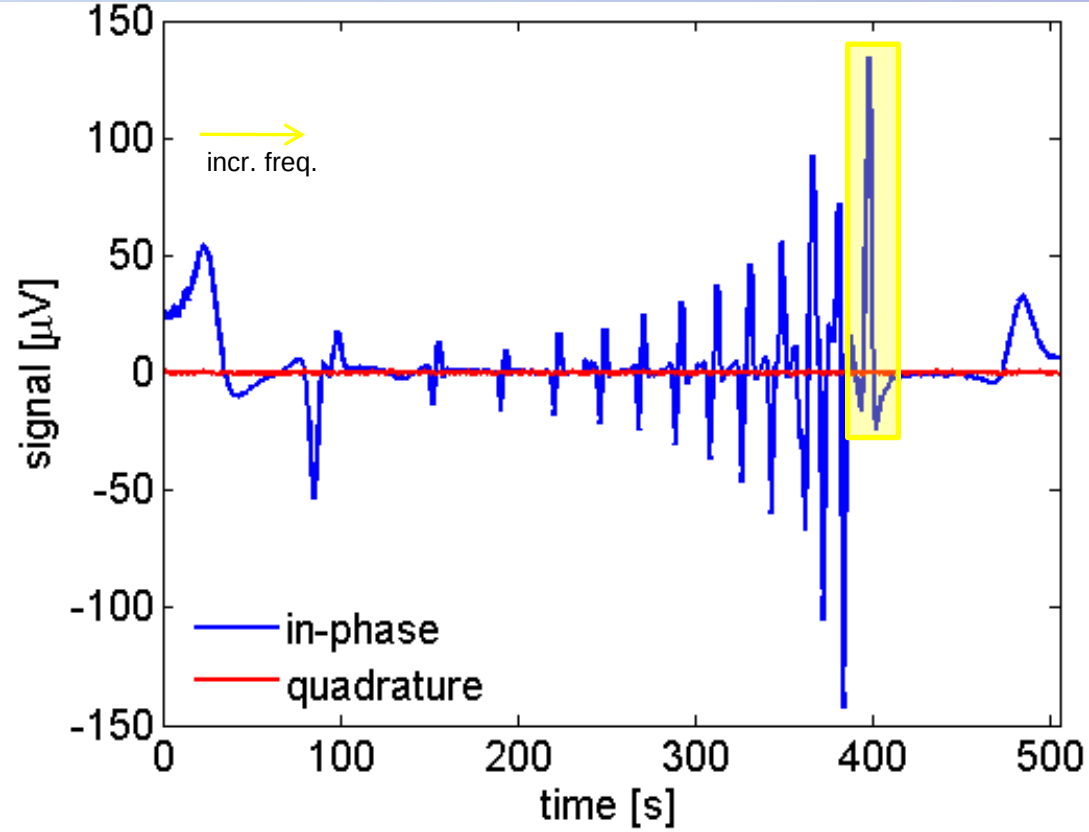
Experimental setup – EC-QCL

- mode-hop free:
  1600 cm^{-1} to 1650 cm^{-1}
- targeted range:
  1613.25 cm^{-1}
- power at 1613.25 cm^{-1}:
  ≈140 mW



Results – line scanning

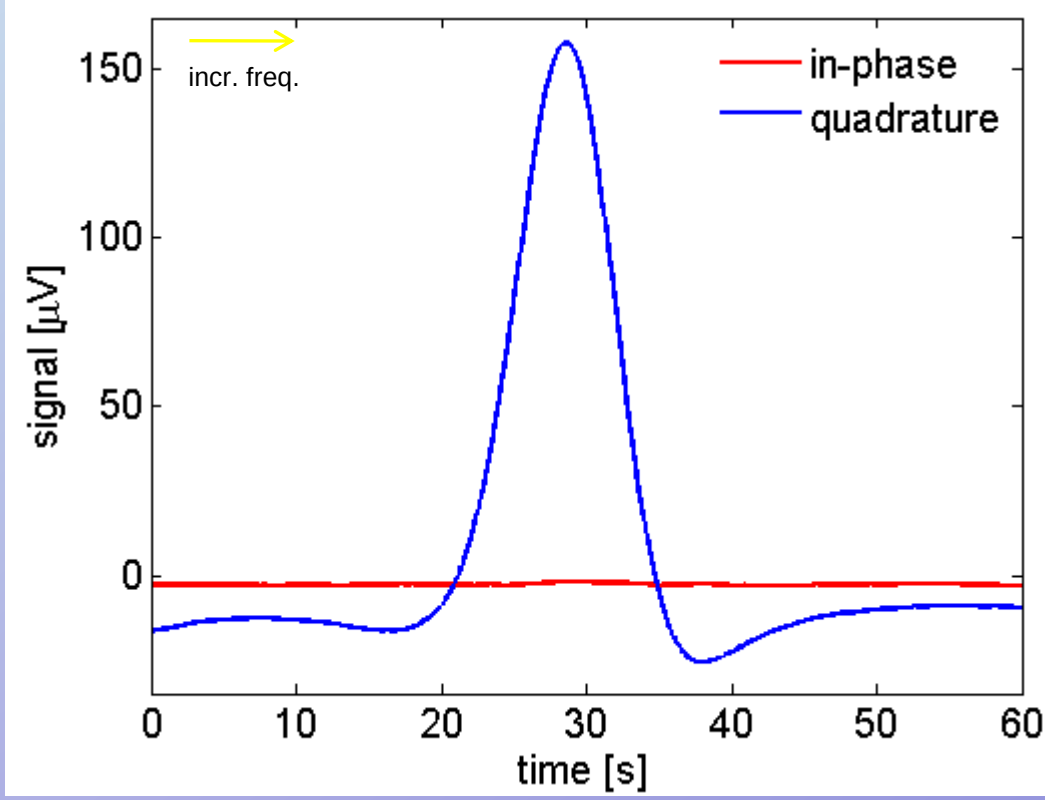
- 2 ppm NO_2 @ 30 Torr;
- magnetic field 180 G_{rms} @ 830 Hz;
- piezo scan: ΔV=64 V @ 1 mHz (sine);
- covered range: ≈1612.5 – 1613.3 cm^{-1}
- lock-in: TC 300 ms, sens. 200 µV;
- polarizer angle: 2° from crossed position;



- Best line: Q-branch 4_{41}<-4_{40} at 1613.25 cm^{-1}
  - strongest signal
  - best distinguishibility (3-f signal)

Results – line scanning

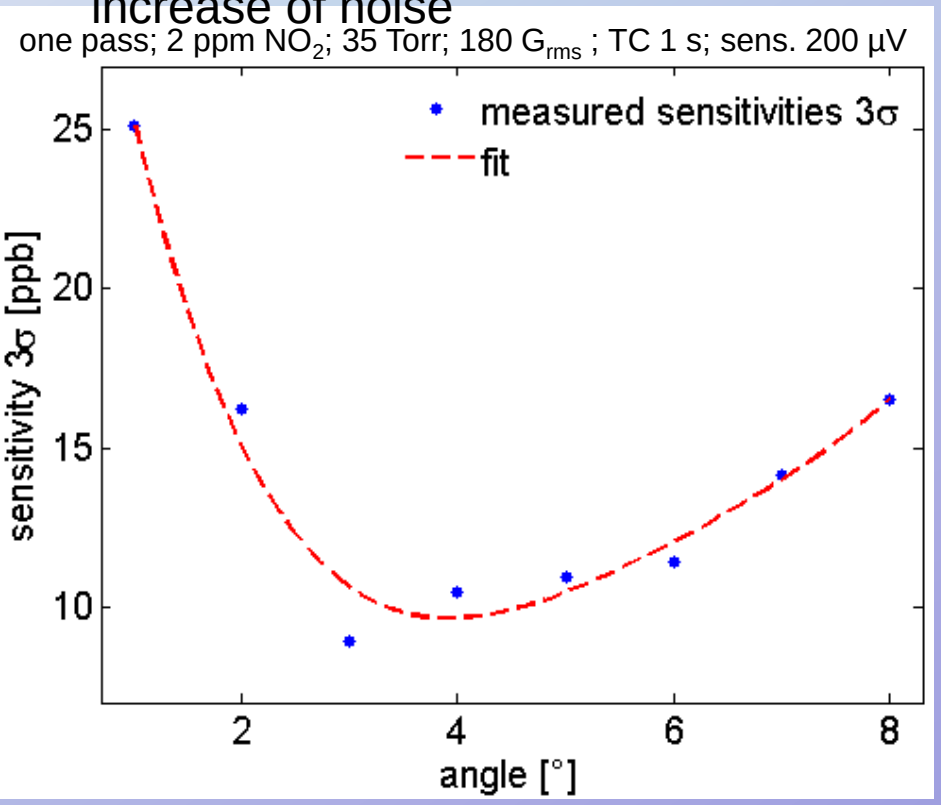
- 2 ppm NO_2 @ 35 Torr;
- magnetic field: 200 G_{rms} @ 830 Hz;
- piezo scan: ΔV=3 V @ 20 mHz (sine);
- lock-in: TC 1 s, sens. 200 μV;
- polarizer angle: 4° from crossed position;

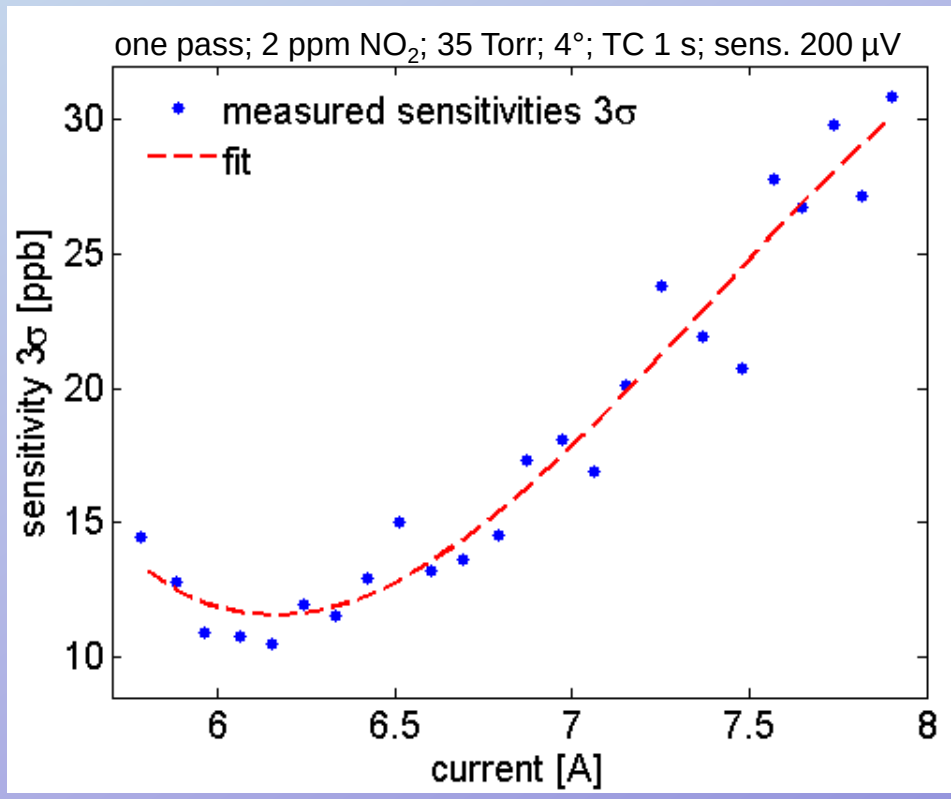


- Minimum sensitivity: **3.5 ppbV** (1σ)

Results – sensitivity optimization

- optimum magnetic field for line scanning operation: ≈ 200 G_{rms} (≈ 6.2 A_{rms})
- increase of sensitivity caused by increase of noise

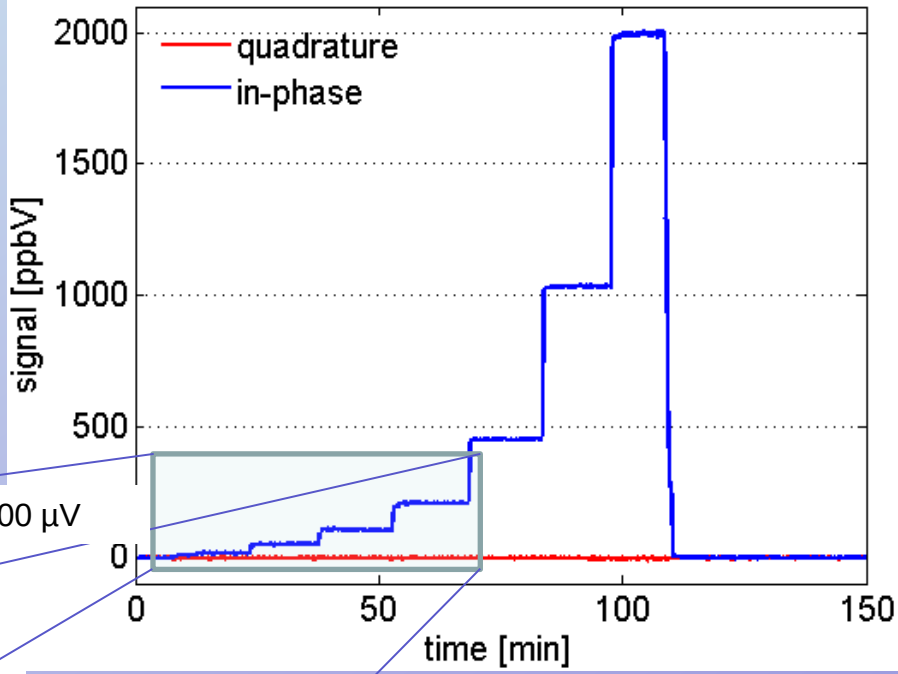




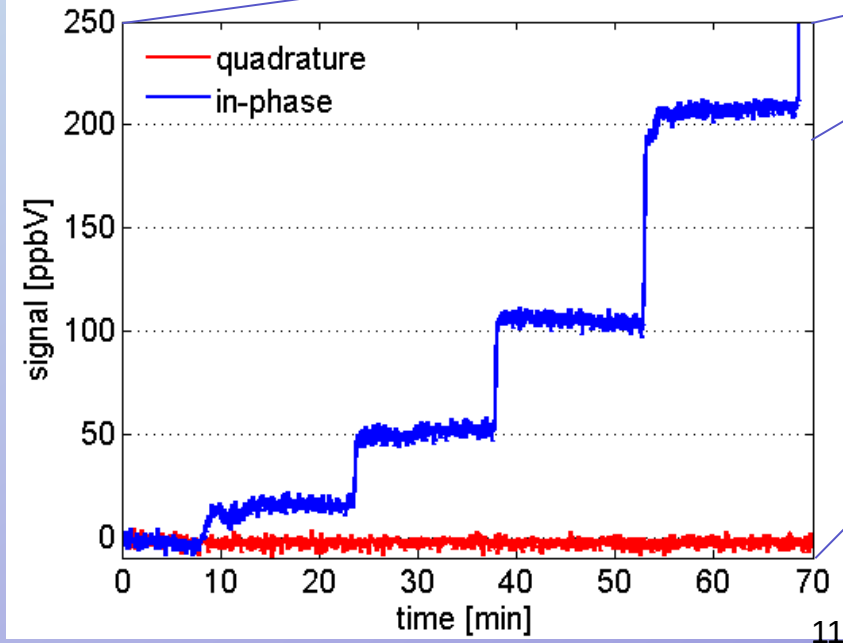
- optimum analyzer angle for line scanning operation: ≈ 3°

Results – line-locked operation

- line-locking with reference cell and software based 3-f PID loop



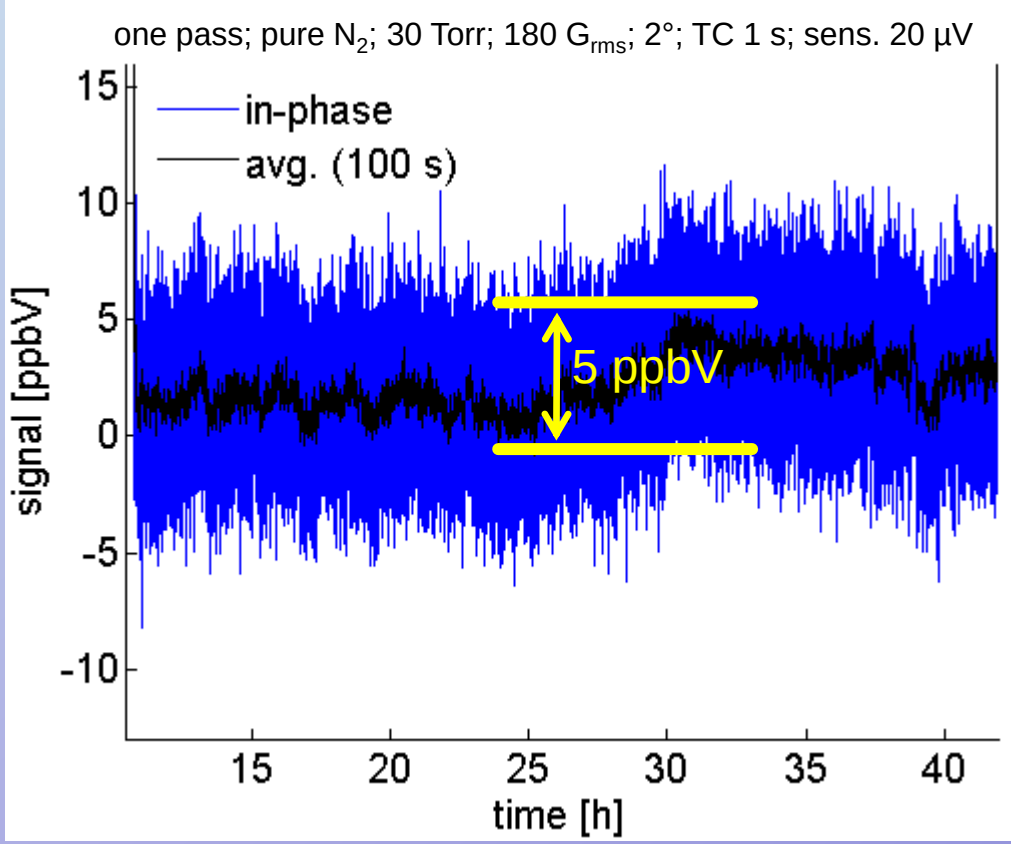
one pass; 2 ppm NO_2; 30 Torr; 180 G_{rms}; 2°; TC 1 s; sens. 200 µV



Targeted [ppbV]	Measured [ppbV]
20	16.5
50	53.6
100	105
200	207
500	450
1000	1030
2000	2000 (calibration)

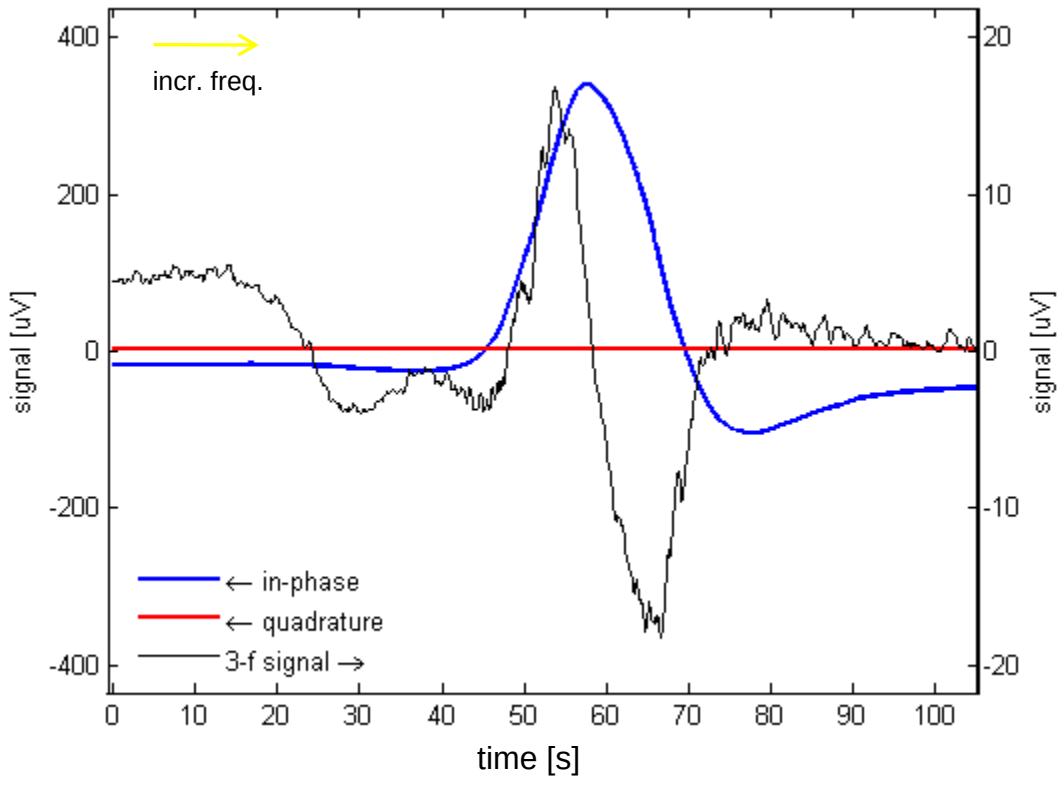
Results – long-term measurement

- long-term background measurement with pure N_2 in line-locked operation mode
- calibrated with 2000 ppbV NO_2
- long-term fluctuations in the order of 5 ppbV
- => to high for atmospheric NO_2 concentration monitoring (single ppbV required)



Results – double pass cell

- 2 ppm NO_2 @ 30 Torr;
- **two pass cell**
- magnetic field: 180 G_{rms} @ 830 Hz;
- piezo scan: ΔV=3 V @ 5 mHz (sine);
- lock-in: TC 1 s, sens. 500 µV;
- polarizer angle: 2° from crossed position;



- Minimum sensitivity: **1.1 ppbV** (1σ)

Conclusion

- achieved NO_2 detector based on FRS using an EC-QCL
- line scanning operation:
  - optimized experimental parameters
  - single ppbV sensitivity (double pass cell)
- system suitable for real-time NO_2 monitoring:
  - line-locking stable over several days
  - sensitivity 5 ppbV (one pass cell)

Outlook

- implement line-locking for double pass cell
  - expected long-term sensitivity: 2.5 ppbV
- increase long-term stability:
  - identify source of fluctuations
  - optimize double pass cell for stability
- increase path length through cell with multi-pass cell
- perform atmospheric NO_2 measurements