Wavelength modulation spectroscopy on traces of carbon monoxide using quantum cascade lasers

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Bachelor internship Physics & Astronomy

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Institute for
Molecules and Materials
Radboud University

Personal introduction

- BSc student* Physics & Astronomy, and Mathematics
- MSc student Physics of Molecules and Materials

- Love combining advanced physics with applications that matter

Life Science Trace Gas Research Group

*waiting for diploma approval

Goals of the presentation

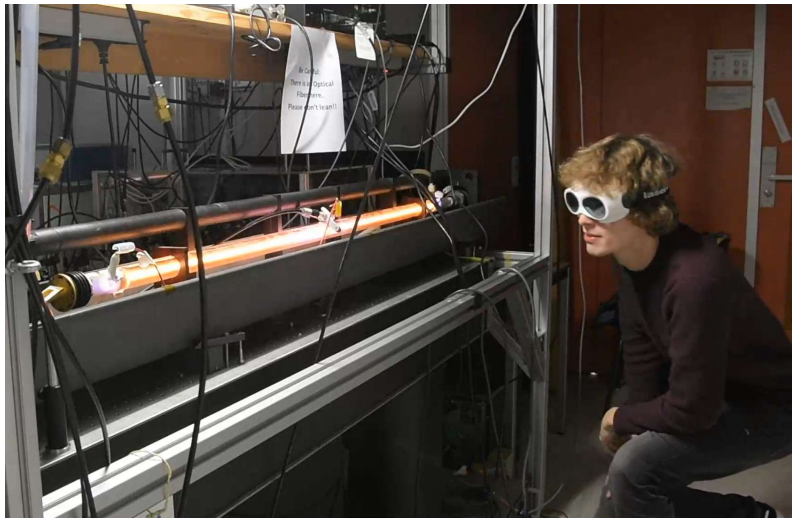
- Understand the motivation behind the research
- Roughly understand the presentation title
  - "Wavelength modulation spectroscopy on traces of carbon monoxide using quantum cascade lasers"
- See what I've done

Why look at carbon monoxide

eCO as biomarker

2.0 ppmv healthy
> 2.7 ppmv cystic fibrosis [1]

Conversion of CO_2
into value-added chemicals



0.1 – 5% [2]

[1] https://link.springer.com/article/10.1007/s00340-018-7030-x
[2] https://pubs.rsc.org/en/content/articlelanding/2017/cs/c6cs00066e

Why normal methods fail

Normal absorption

Trace gas absorption

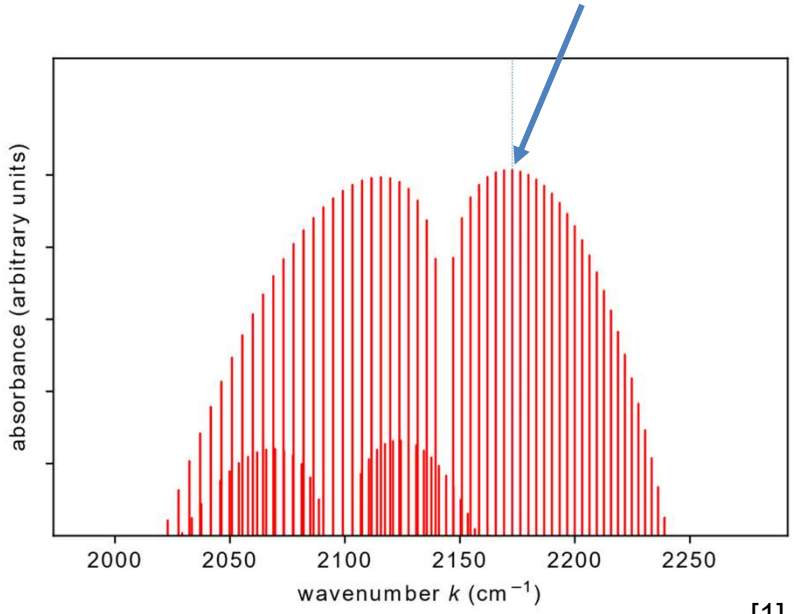
Idea

- Separate the absorption signal from the noisy signal

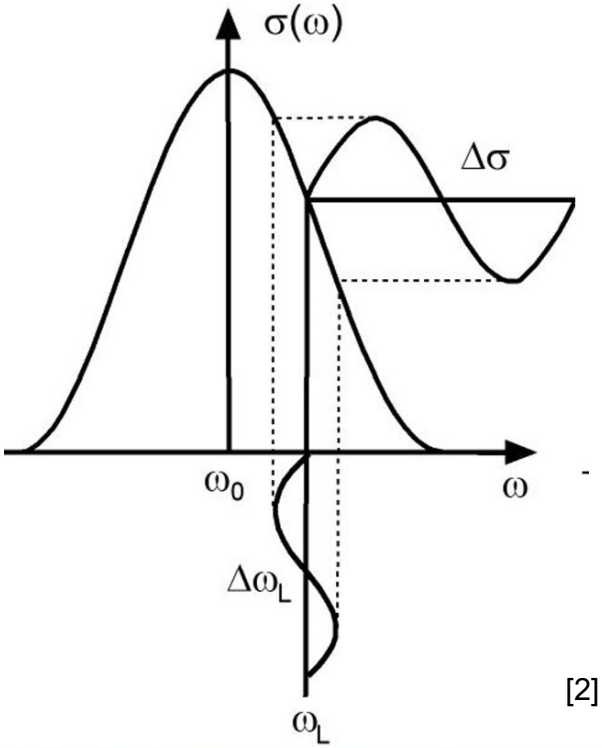
- How?
  - Introduce periodic time variation to the signal strength
  - Make use of light color dependent absorption
  - Extract signal with lock-in amplifier
  - Relate the extracted quantity to the concentration

Wavelength dependent absorption

$$k = 2170\ cm^{-1}\ or\ \lambda = \frac{1}{k} = 4.6\ \mu m$$



[1]

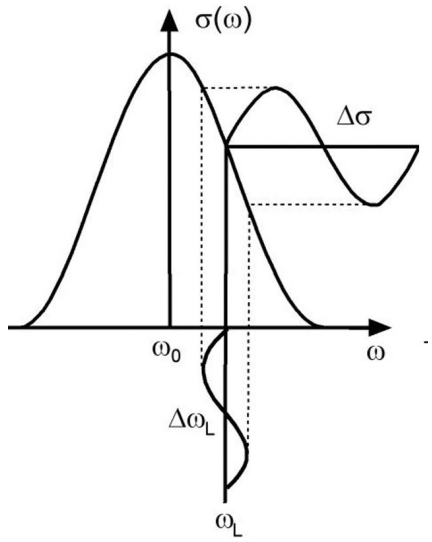


[2]

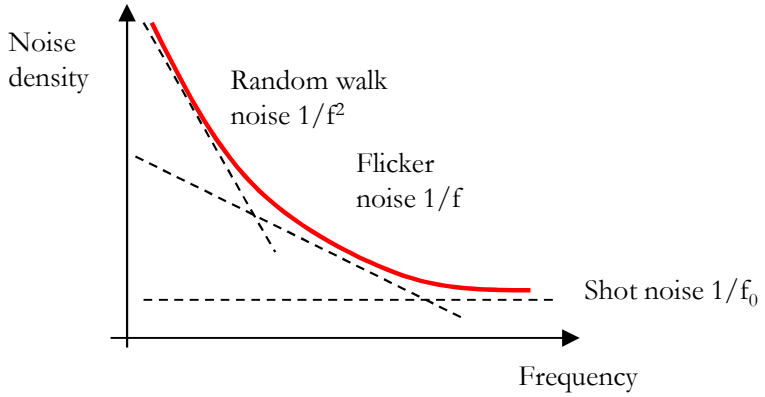
[1] The HITRAN2016 molecular spectroscopic database
[2] https://webdoc.ubn.ru.nl/mono/m/moeskops_b/specdeoft.pdf

Wavelength modulation

- Modulate the wavelength
- Extract the harmonics via lock-in amplification



- Benefits:
  - Reduction of noise

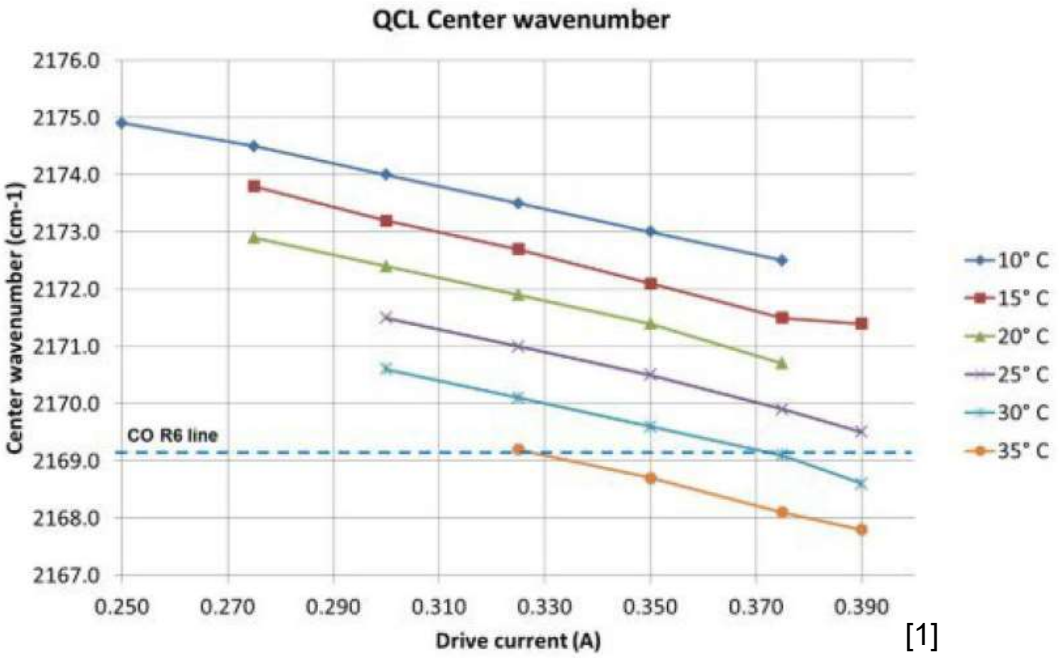


  - Zero baseline

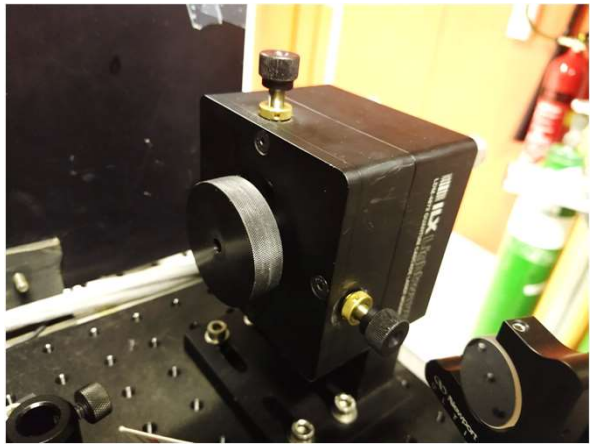
[1]

[1] Lecture slide Spectroscopy course, Frans Harren 2016

Quantum cascade laser

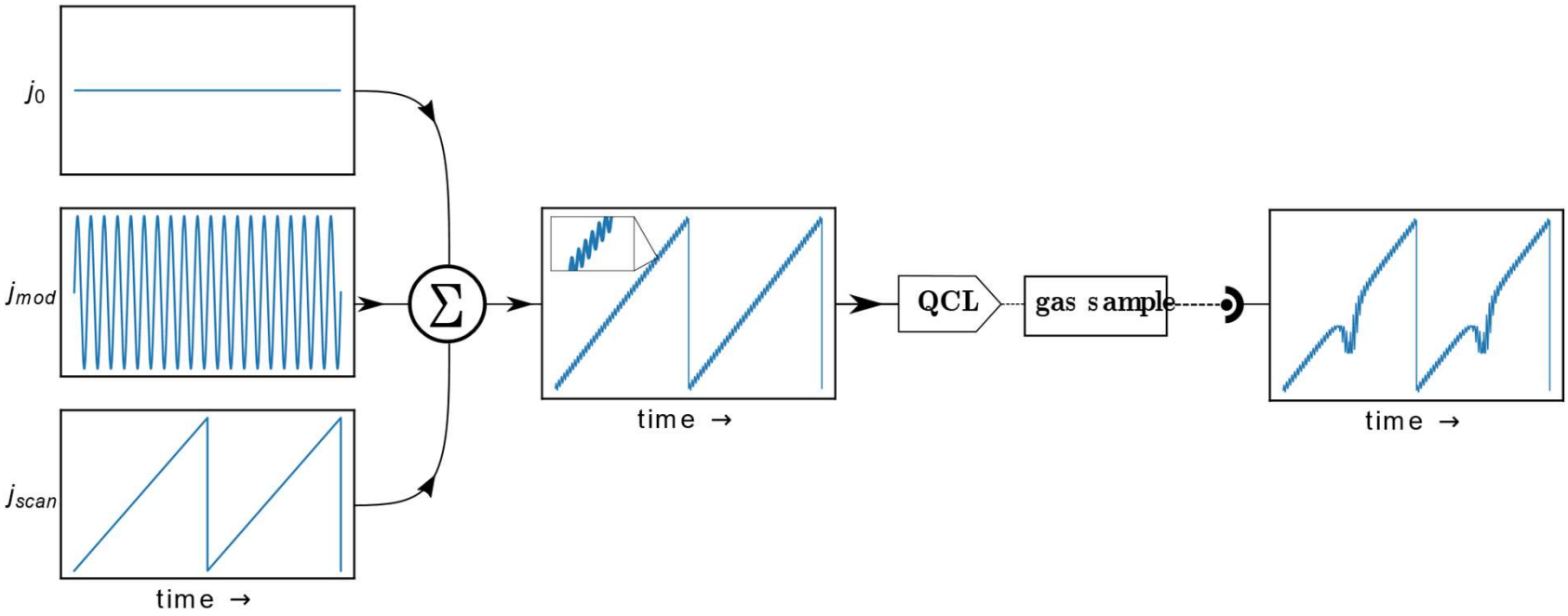


[1]

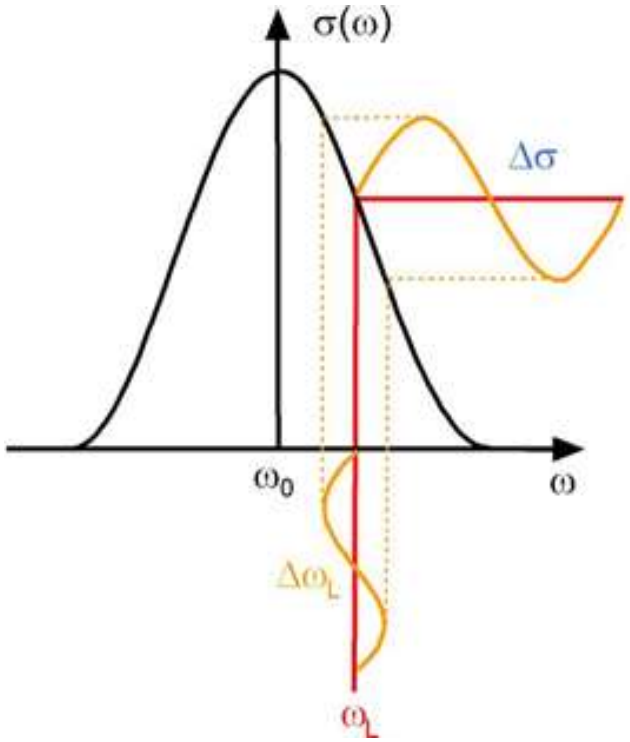


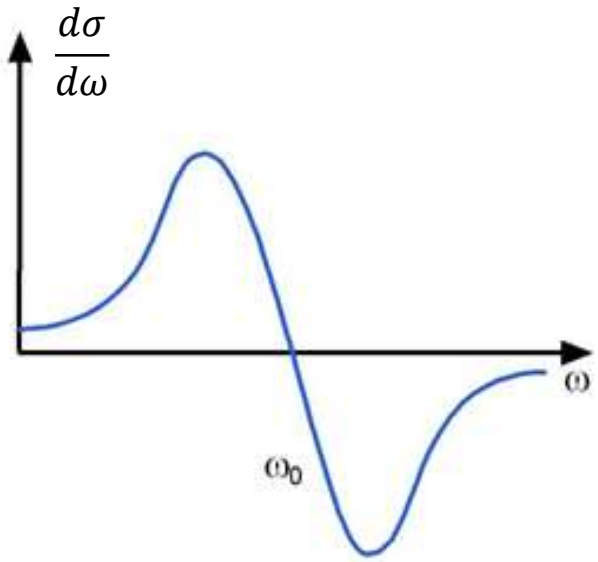
[1] https://www.yumpu.com/en/document/read/6185299/a-compact-low-power-quantum-cascade-laser-based-co-sensor

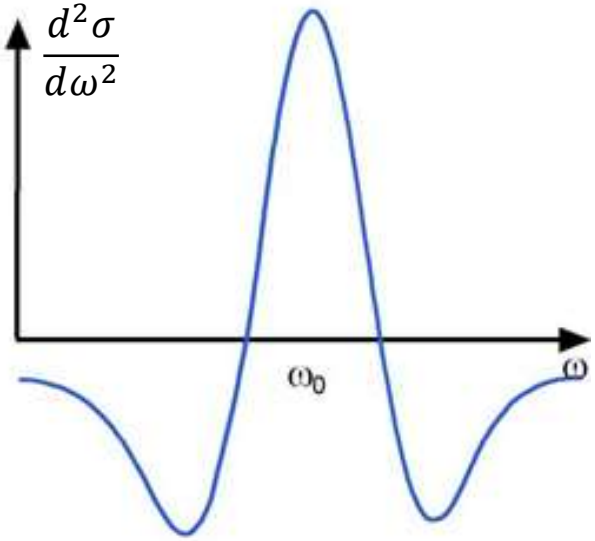
Scanning the wavelength



Extract the 1f and 2f signals







[1]

[1] Lecture slide Spectroscopy course, Frans Harren 2016

And what is the concentration, then?

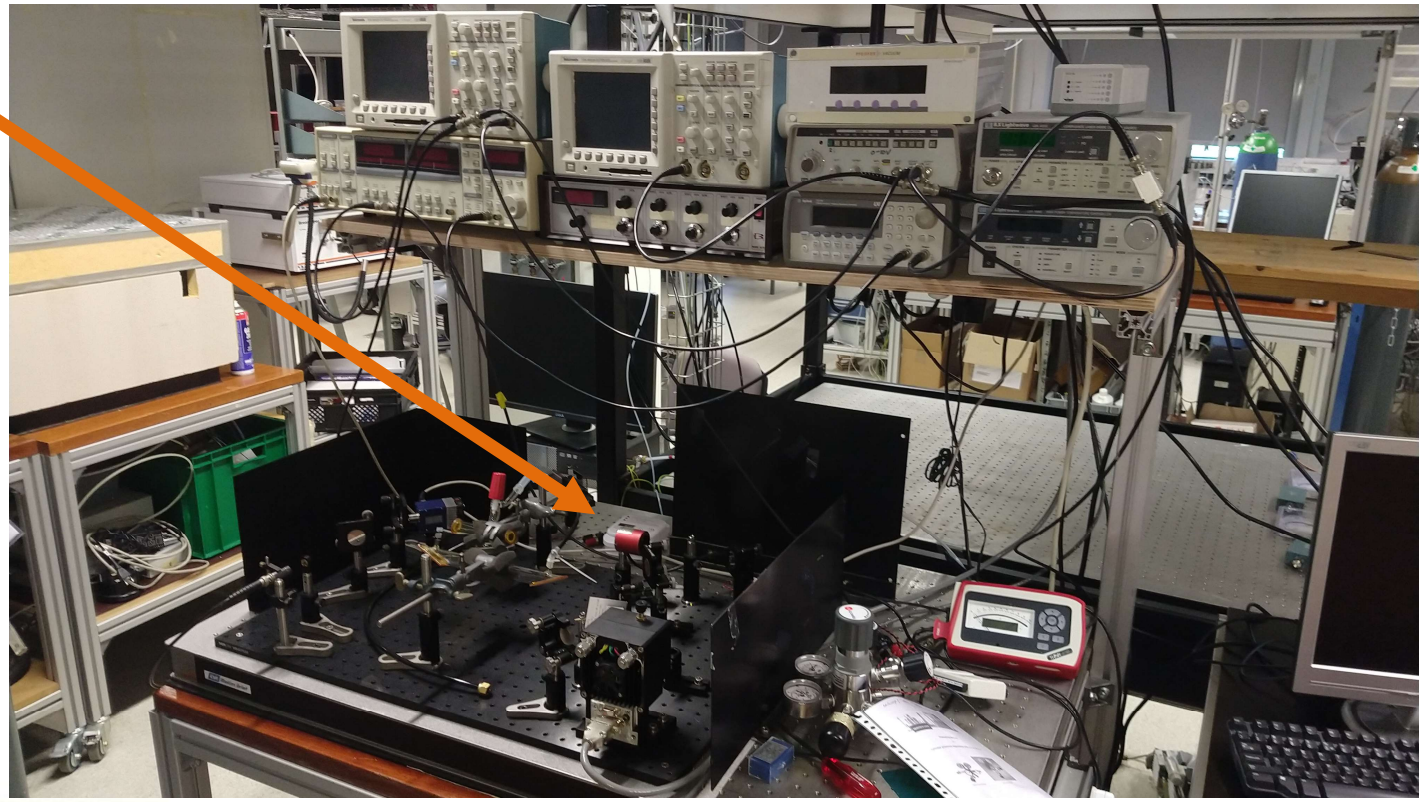
$$X_{1f} \approx G I_0$$

$$X_{2f} = \frac{G}{4} I_0 \ell n (\Delta\omega)^2 \left|\frac{d^2\sigma}{d\omega^2}\right|_{\omega=\omega_L}$$

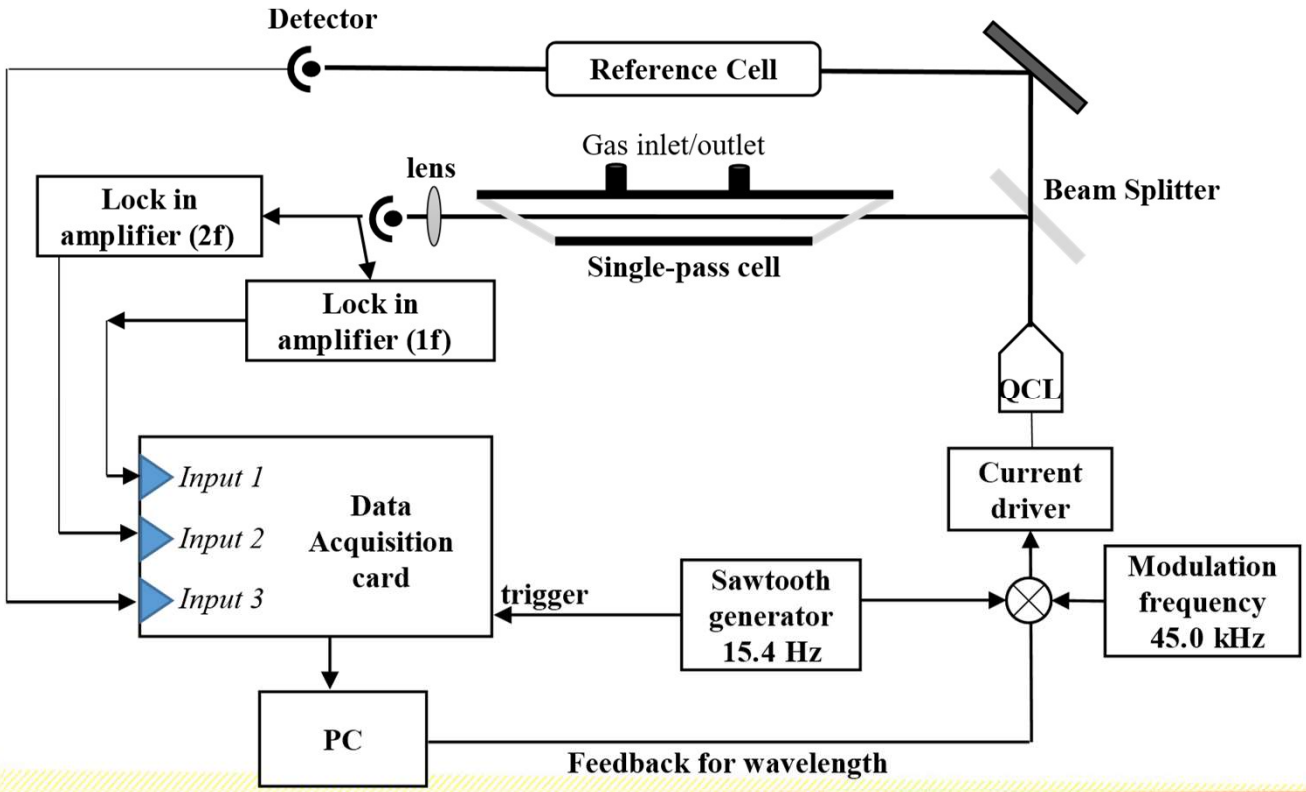
$$\frac{X_{2f}}{X_{1f}} = \frac{1}{4} \ell n (\Delta\omega)^2 \left|\frac{d^2\sigma}{d\omega^2}\right|_{\omega=\omega_L}$$

G = gain factor of the system
I_0 = initial laser intensity
ℓ = optical path length
n = CO concentration
$\Delta\omega$ = modulation amplitude

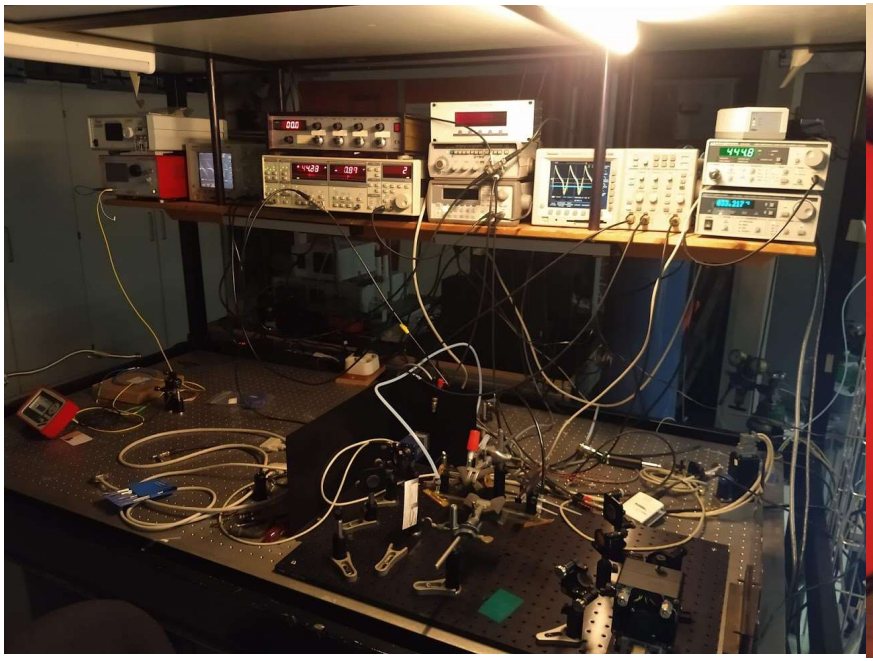
Experiment

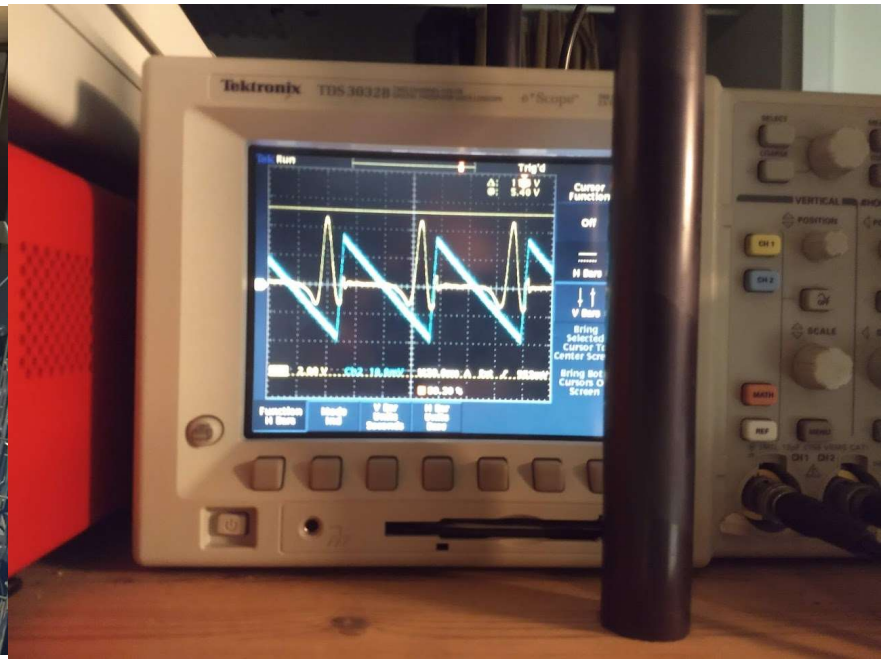


Schematic setup



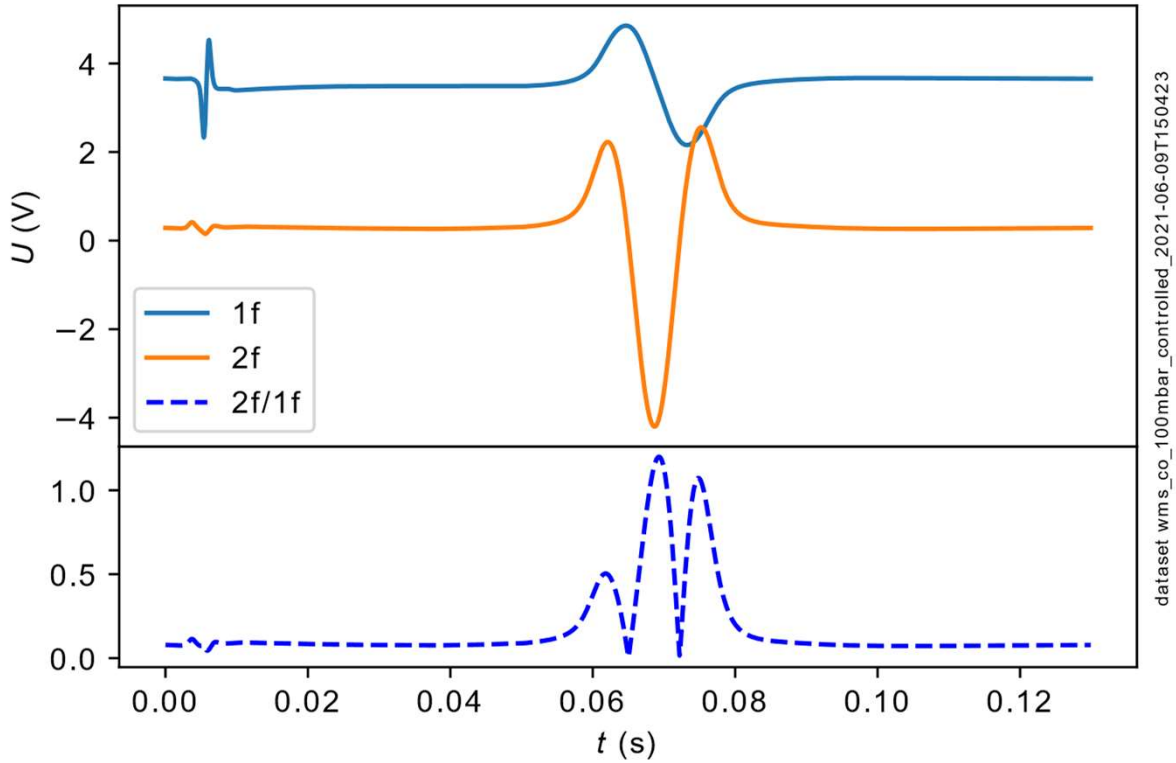
Experiment





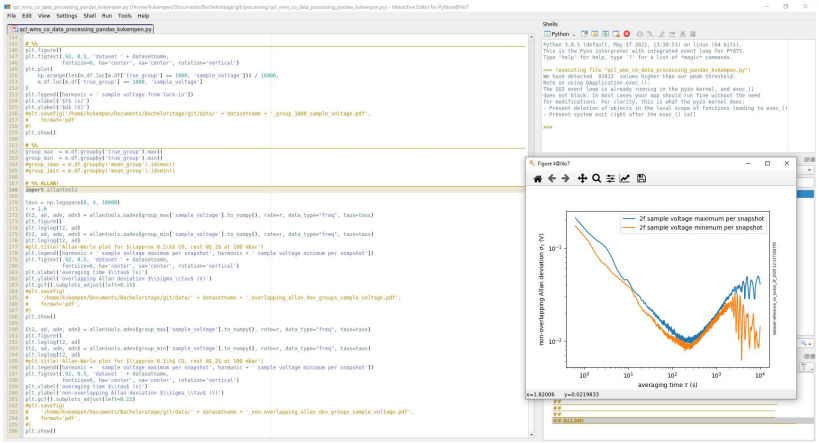
Photos found in my own archive by searching for `oscilloscope` in Google Photos, which somehow works.

Averaged scan of the absorption line

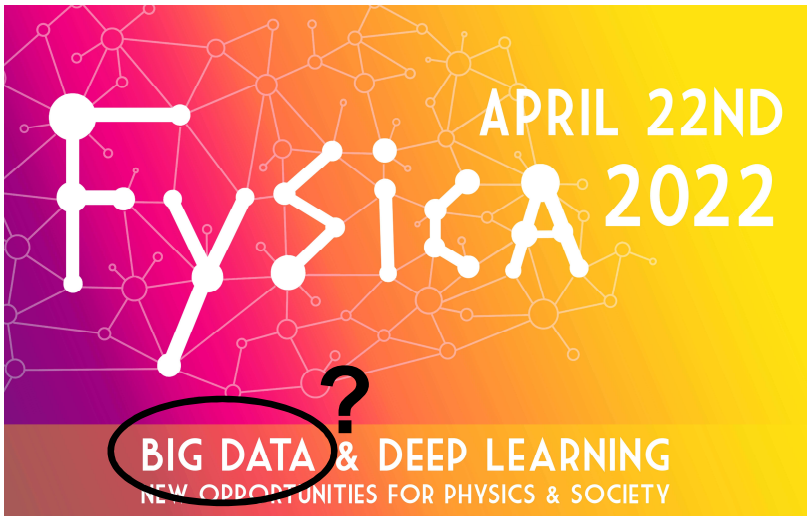


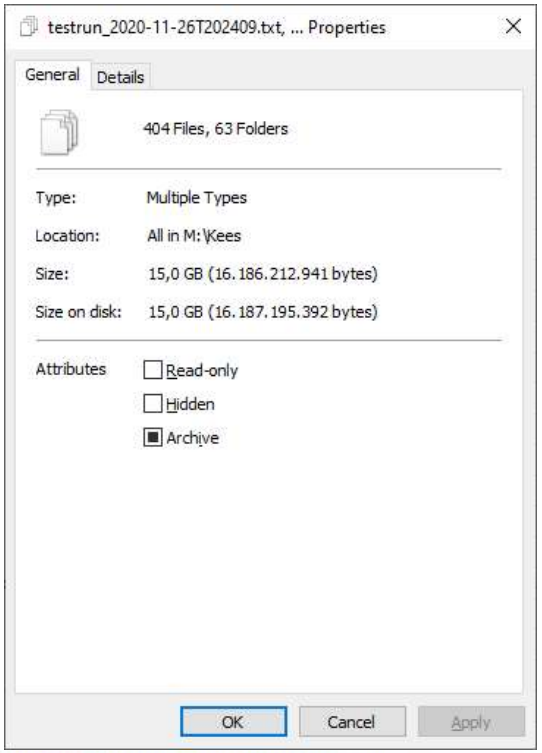
Data recording and processing

```
# Recorded with `qcl_wms_co_v3_plaintxt` on computer `MLF-PC-
KEES` at starttime `2020-12-14T14:40:00`
# Settings: sample_rate = 16000, actual_sample_rate = 16000,
buffersize = 1600
# volt  volt    volt
reference_voltage       sample_voltage  scanning_voltage
0.000984        6.944711        0.011684
-0.002839       7.079801        0.019580
-0.000290       7.218714        0.020472
0.000984        7.335962        0.012958
0.003533        7.440466        0.005317
0.003533        7.529676        0.007991
...
```



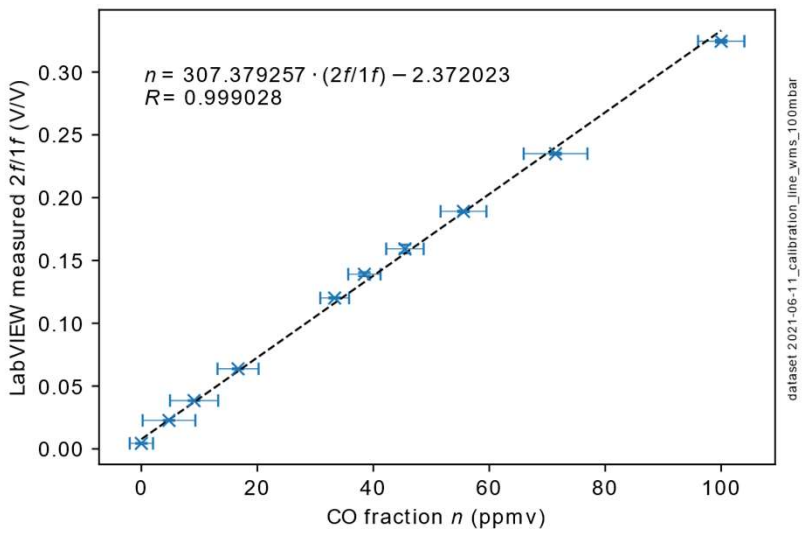
Fysica 2022: connection to the theme



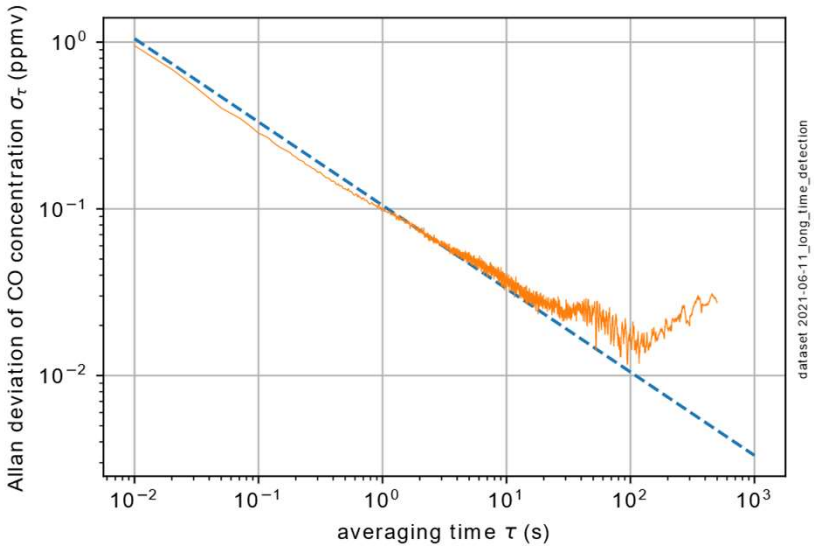


Results

Calibration of the system



Allan-Werle plot of the 2f/1f signal



Detection limit:

- 700 ppbv @ 100 ms 100 ppbv @ 1 s 10 ppbv @ 100 s

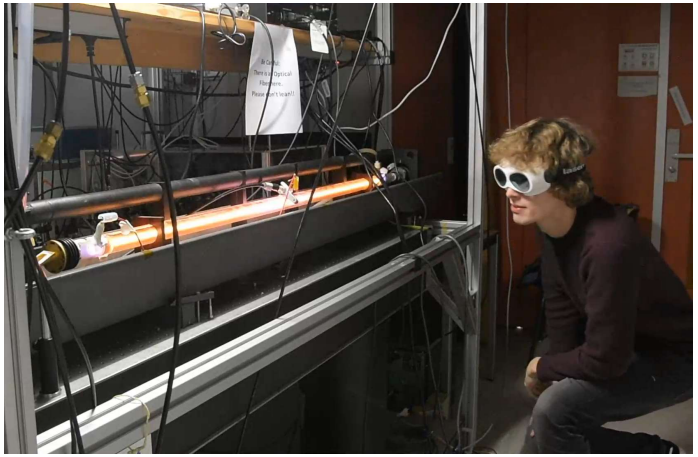
Applications

700 ppbv @ 100 ms 100 ppbv @ 1 s 10 ppbv @ 100 s

Non-invasive medical diagnostics

> 2.7 ppmv cystic fibrosis [1]

Plasma-catalytic conversion of CO_2



0.1 – 5% [2]

Outlook

- Reduce drift in the system
- Simplify and shrink setup [1]
- More applications:
  - Different gases (CO with ^{14}C, or with another laser CO_2, ethylene [2], …)
  - Investigate other organisms

[1] A Raspberry Pi-based field-deployable tunable diode laser spectroscopy system for the detection of CO2 at 2003.5 nm (https://ieeexplore.ieee.org/document/7408713)
[2] Ethylene, an early marker of systemic inflammation in humans (https://www.nature.com/articles/s41598-017-05930-9)

Acknowledgements

- Trace Gas Research group
  - Now Trace Detection Laboratory
  - Frans Harren & Amir Khodabakhsh
  - Ningwu Liu & Roderik Krebbers
  - Fleur for the last-minute presentation input

- All others, please see the thesis!

Summary

- Prior goals reached (I hope)
  - ✓ Understand the motivation behind the research
  - ✓ Roughly understand the presentation title
    - "Wavelength modulation spectroscopy on traces of carbon monoxide using quantum cascade lasers"
  - ✓ See what I've done
- Trace gas detection (of CO) has important applications
- WMS is a good detection method
  – Sensitivity, specificity, fast in time

- Want to read more or look a little slower to the slides?
  https://keesvankempen.nl/physics/fysica-2022/

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Carbon monoxide concentrations

CO concentration	Description
7 000 – 100 000 ppmv	Car exhaust (without catalytic converter) [1, 2]
30 000 ppmv (3%)	Undiluted cigarette smoke without filter [2]
5 000 ppmv	Household wood fire chimney [2]
3 200 ppmv	Immediate death [5]
800 ppmv (0.08%)	Headache, dizziness, nausea, convulsions; insensibility in two hours [5]
700 ppmv	Atmosphere of Mars [1]
25 – 100 ppm (0.0025 – 0.01%)	Dangerous levels for prolonged exposure [2, 4, 5] (will trigger CO alarms)
5 – 15 ppmv	Car exhaust (with modern catalytic converter) [1]
10 ppmv	Air in urban areas [3]
< 1 ppmv	Trace gases

[1] https://en.wikipedia.org/wiki/Carbon_monoxide#Occurrence
[2] https://web.archive.org/web/20081225113654/http://www.gi.alaska.edu/ScienceForum/ASF5/588.html
[3] https://scied.ucar.edu/learning-zone/air-quality/carbon-monoxide
[4] https://www.ilo.org/dyn/icsc/showcard.display?p_lang=en&p_card_id=0023
[5] https://en.wikipedia.org/wiki/Carbon_monoxide_poisoning

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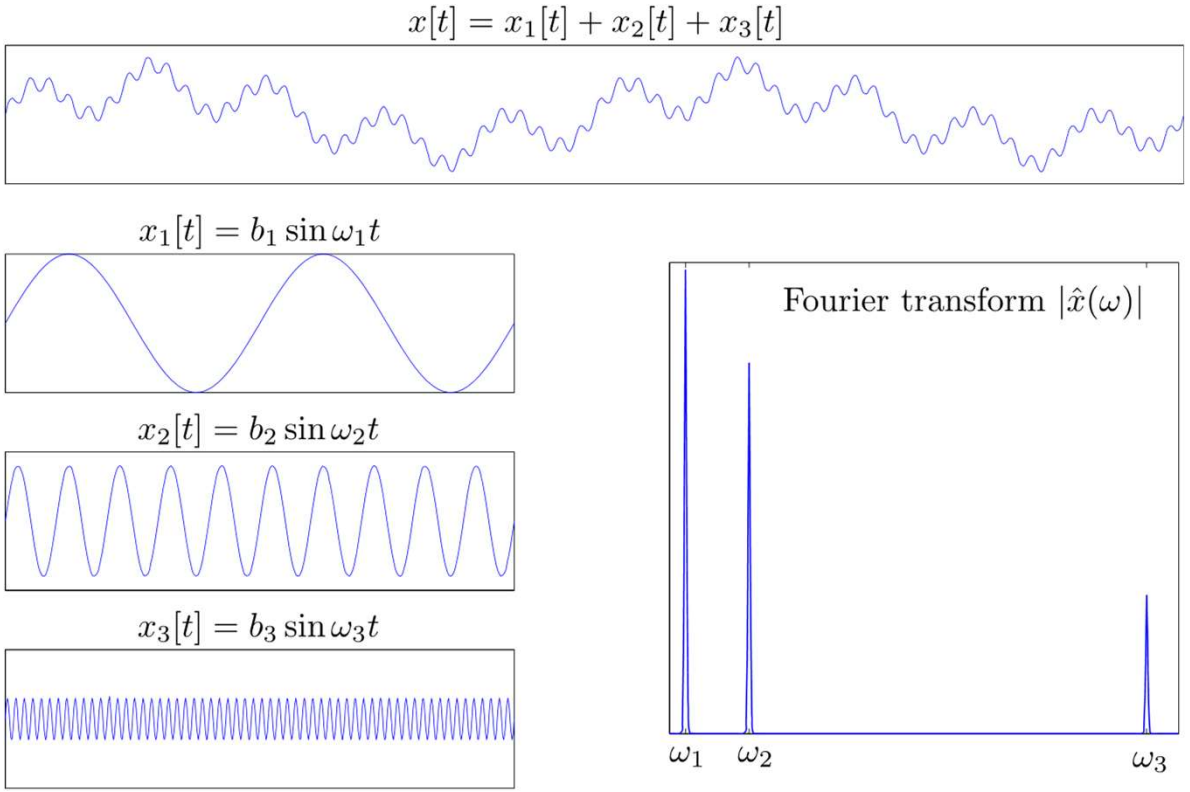
Why look at carbon monoxide?

- eCO as biomarker [1]
- Conversion of CO_2 into value-added chemicals [2]

CO concentration	Description
2.7 – 4.8 ppmv	Inflammation patients with cystic fibrosis [3]
2.0 ppmv	Exhaled breath healthy person [3, 4]
0.5 ppmv	Troposphere of Earth [5]
7 ppbv	Detection limit of previous WMS setup Trace Gas Facility [4]
0.1 – 5%	Plasma reactor/combustion engine [6, 7]

[1] https://link.springer.com/article/10.1007/s00340-018-7030-x
[2] https://pubs.rsc.org/en/content/articlelanding/2017/cs/c6cs00066e
[3] https://thorax.bmj.com/content/55/2/138
[4] https://link.springer.com/article/10.1007%2Fs00340-015-6294-7
[5] https://en.wikipedia.org/wiki/Carbon_monoxide#Occurrence
[6] https://doi.org/10.1051/epjconf/201818900010
[7] https://www.osapublishing.org/ao/abstract.cfm?uri=ao-48-29-5546

Harmonic analysis



[1]

[1] https://www.researchgate.net/publication/237061998_time-freq

Lock-in amplification

$$U_{psd} = U_{sig} sin(\omega t + \varphi_{sig})\, U_L \sin(\omega t + \varphi_{ref})$$
$$= \frac{1}{2} U_{sig} U_L [\cos(\varphi_{sig} - \varphi_{ref}) - \cos(2\omega t + \varphi_{sig} - \varphi_{ref})]$$

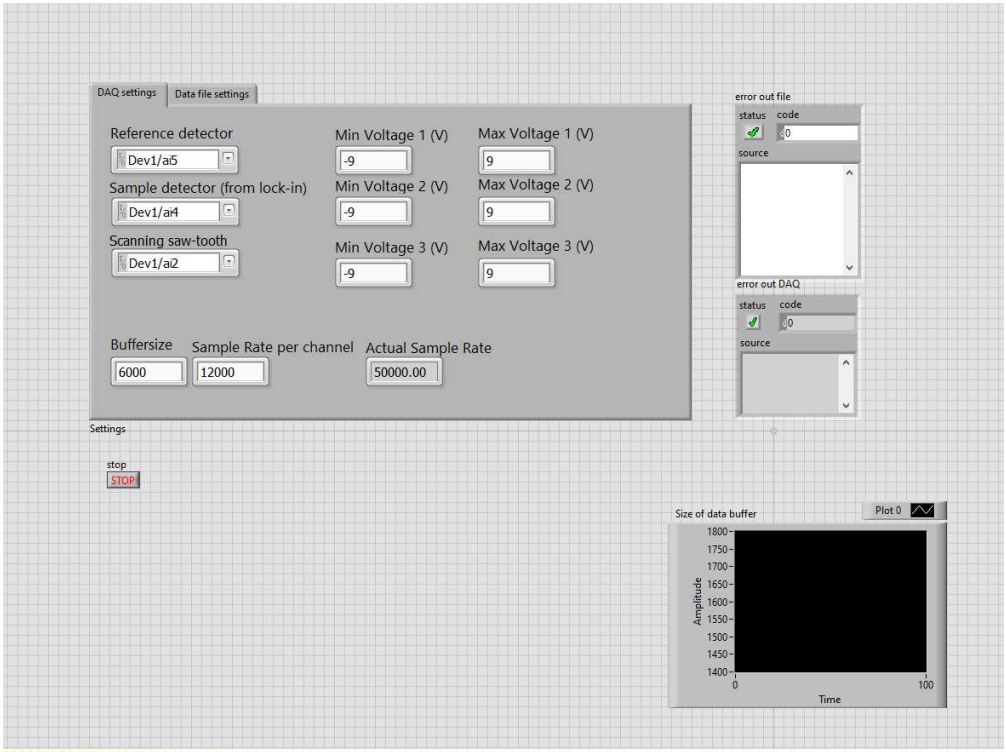
Set $\varphi_{sig} = \varphi_{ref}$ *and average over time* τ:

$$X(t) = \frac{1}{\tau} \int_{t-\tau}^{t} U_{psd}(s) ds$$
$$= \frac{1}{2\tau} \int_{t-\tau}^{t} U_{sig} U_L [1 - \cos(2\omega s)] ds$$
$$= \frac{1}{2} U_{sig} U_L$$

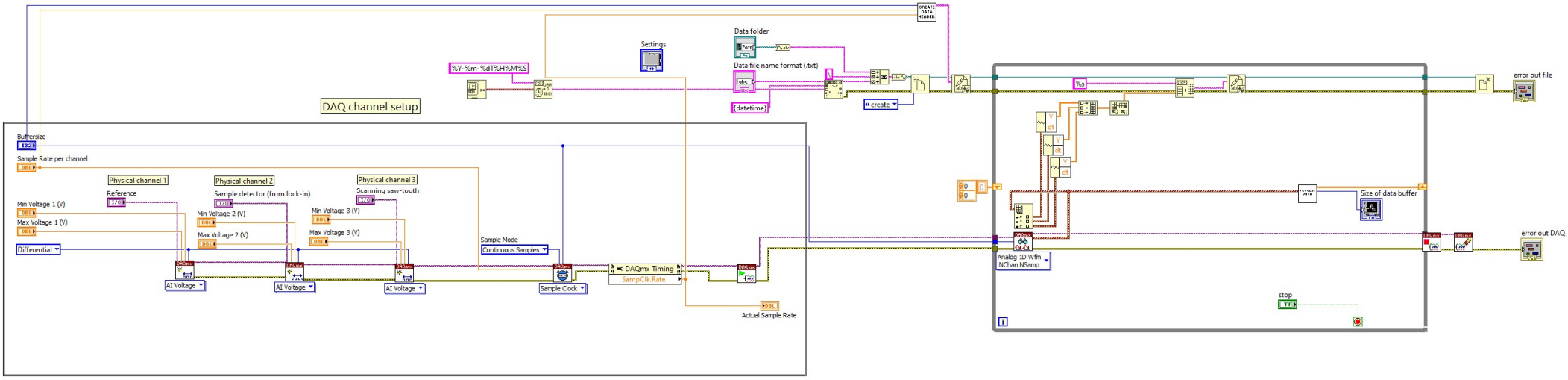
[1]

[1] Stanford Research Systems SR830 manual

LabVIEW front panel



LabVIEW block diagram



Data file

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# volt  volt    volt
reference_voltage       sample_voltage  scanning_voltage
0.000984        6.944711        0.011684
-0.002839       7.079801        0.019580
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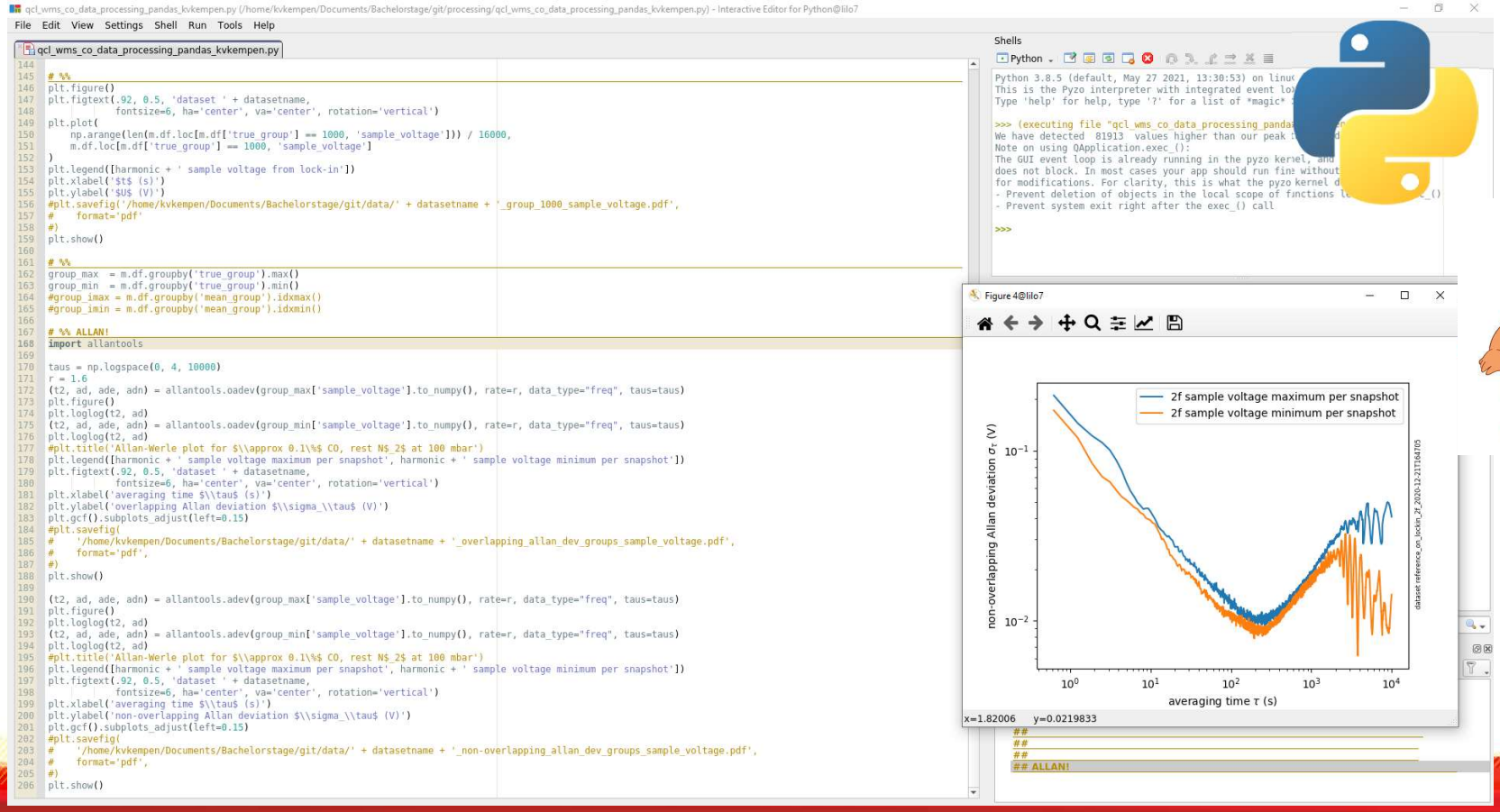
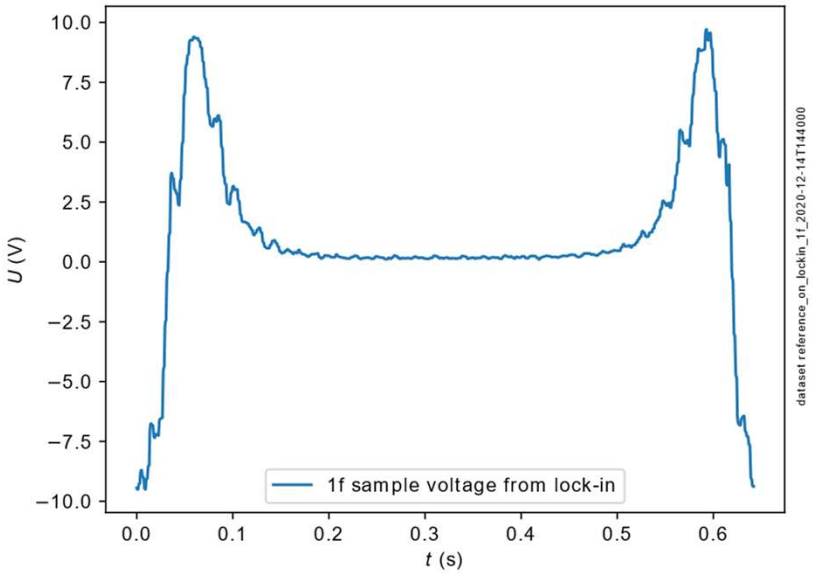
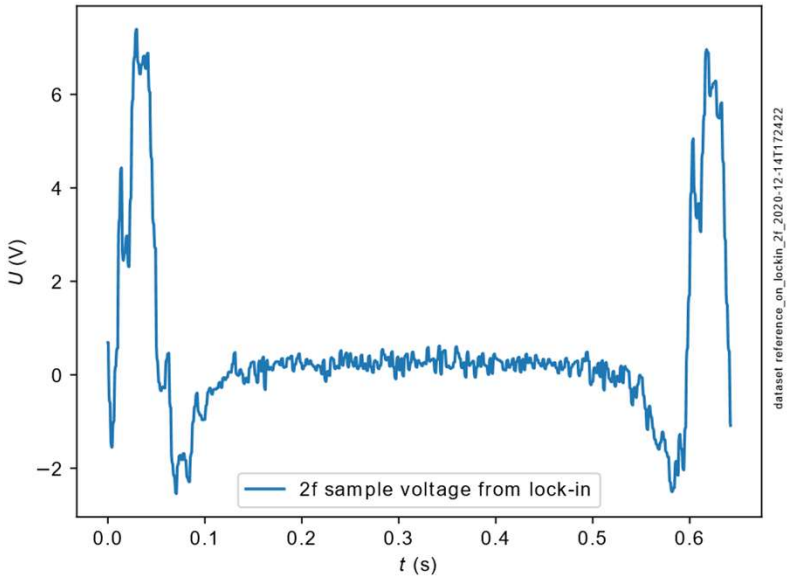
0.000984        7.335962        0.012958
0.003533        7.440466        0.005317
0.003533        7.529676        0.007991
...
```

Processing

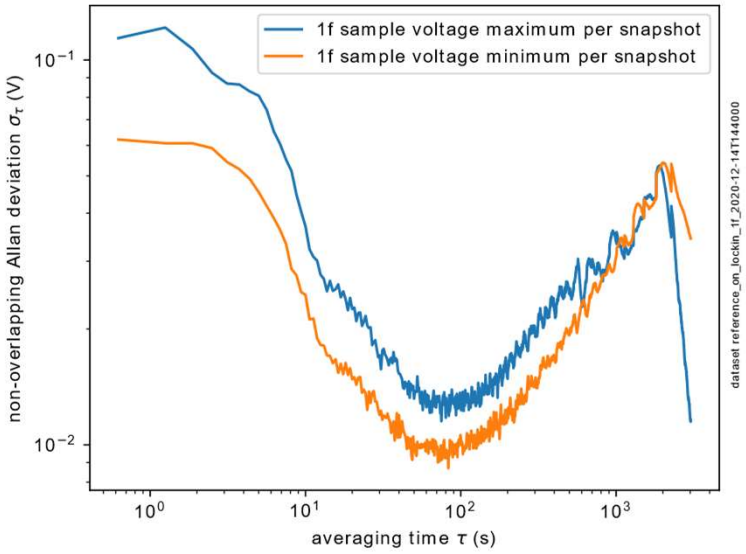

qcl_wms_co_data_processing_pandas_kvkempen.py (/home/kvkempen/Documents/Bachelorstage/git/processing/qcl_wms_co_data_processing_pandas_kvkempen.py) - Interactive Editor for Python@lilo7
File Edit View Settings Shell Run Tools Help
qcl_wms_co_data_processing_pandas_kvkempen.py
Shells
Python
Figure 4@lilo7
2f sample voltage maximum per snapshot
2f sample voltage minimum per snapshot
non-overlapping Allan deviation σ_τ (V)
averaging time τ (s)
x=1.82006 y=0.0219833
ALLAN!

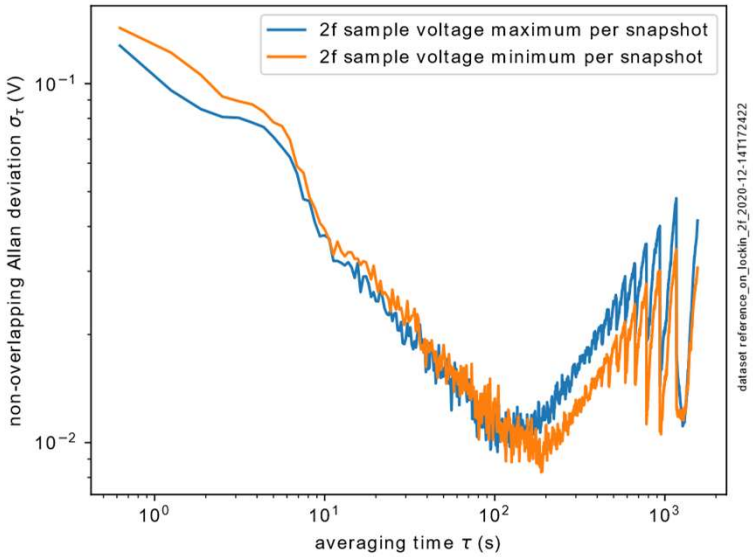
Results


10.0
7.5
5.0
2.5
0.0
−2.5
−5.0
−7.5
−10.0
U (V)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
t (s)
1f sample voltage from lock-in
dataset reference_on_lockin_1f_2020-12-14T144000

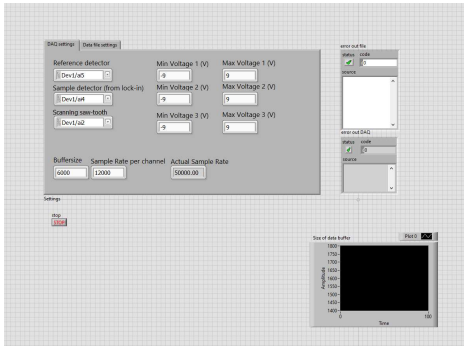

6
4
2
0
−2
U (V)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
t (s)
2f sample voltage from lock-in
dataset reference_on_lockin_2f_2020-12-14T172422

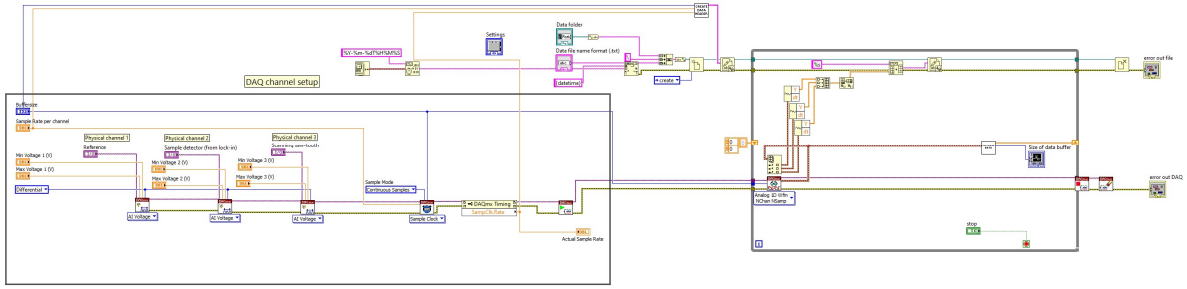
Results


1f sample voltage maximum per snapshot
1f sample voltage minimum per snapshot
non-overlapping Allan deviation σ_τ (V)
averaging time τ (s)
dataset reference_on_lockin_1f_2020-12-14T144000


2f sample voltage maximum per snapshot
2f sample voltage minimum per snapshot
non-overlapping Allan deviation σ_τ (V)
averaging time τ (s)
dataset reference_on_lockin_2f_2020-12-14T172422

LabVIEW


DAQ settings
Data file settings
Reference detector
Sample detector (from lock-in)
Scanning saw-tooth
Min Voltage 1 (V)
Max Voltage 1 (V)
Min Voltage 2 (V)
Max Voltage 2 (V)
Min Voltage 3 (V)
Max Voltage 3 (V)
Buffersize
Sample Rate per channel
Actual Sample Rate
error out file
error out DAQ
Size of data buffer
Amplitude
Time


DAQ channel setup
Data folder
Settings
Physical channel 1
Physical channel 2
Physical channel 3
Reference
Sample detector (from lock-in)
Min Voltage 1 (V)
Max Voltage 1 (V)
Min Voltage 2 (V)
Max Voltage 2 (V)
Min Voltage 3 (V)
Max Voltage 3 (V)
Sample Mode
Continuous Samples
Sample Clock
Actual Sample Rate
Size of data buffer
error out file
error out DAQ