Further Investigation of Ethylene (C$_2$H$_4$) as Amplification Agent with PeRCA Method

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Introduction

- Peroxy radicals: $RO_2^* = HO_2 + \sum RO_2$, where R stands for any organic chain (CH_3, CH_3CH_2, ...)

- Very low concentration, short life time and very reactive;

(Jynto, 2011)

- A key intermediates in most atmospheric oxidation reactions;

- Important trace gas to study the oxidation mechanisms in the atmosphere;

- IUP TROLAS has long term experience with the work with peroxy radicals.
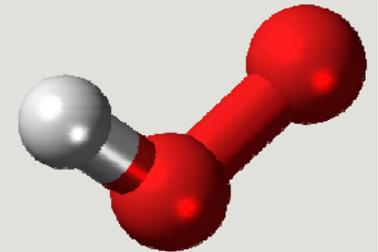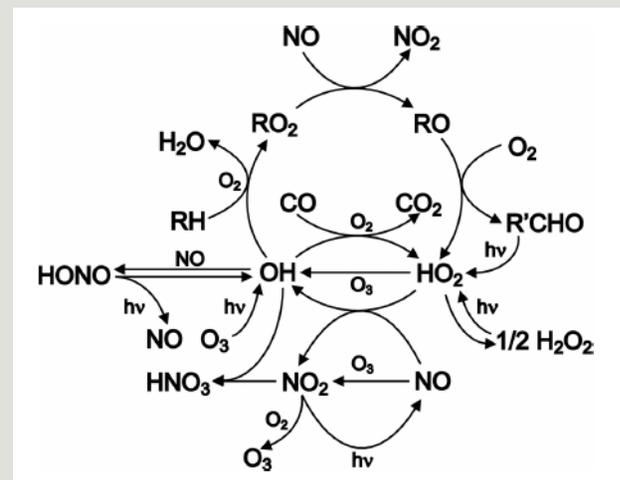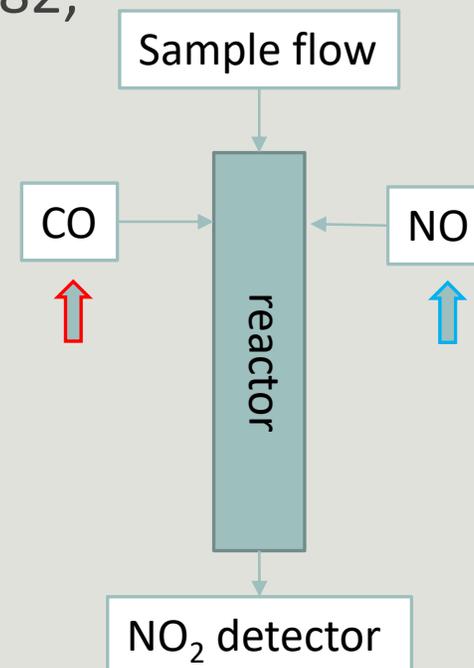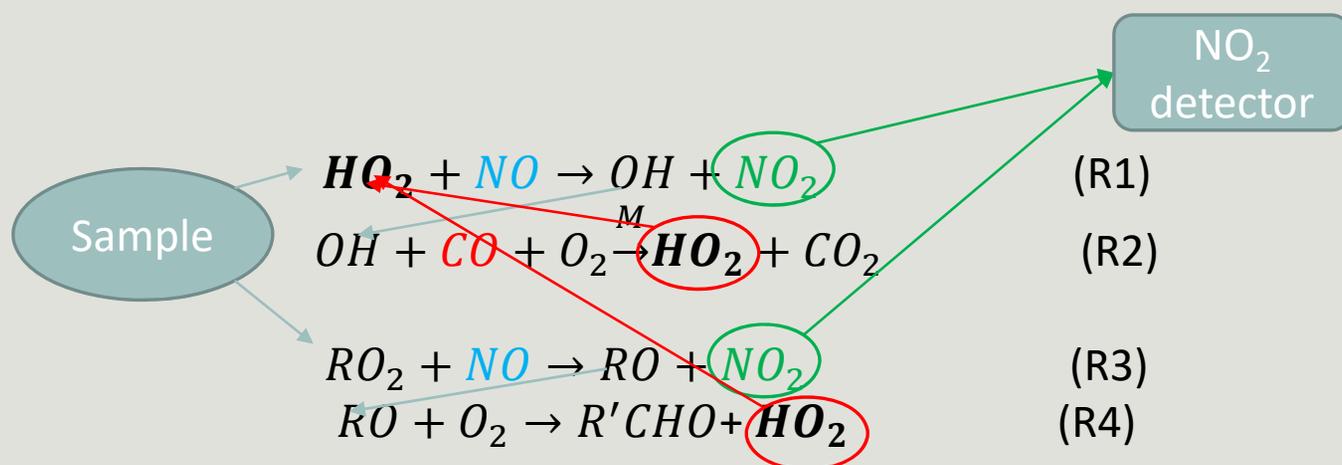
(Fuchs, 2006)

Peroxy Radical Chemical Amplification (PeRCA)

- Indirect measurement technique;

- First introduced by Cantrell and Stedman in 1982;

- RO_2^* measurement;

$$HO_2 + NO \rightarrow OH + NO_2 \quad (R1)$$

$$OH + CO + O_2 \xrightarrow{M} HO_2 + CO_2 \quad (R2)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (R3)$$

$$RO + O_2 \rightarrow R'CHO + HO_2 \quad (R4)$$

Sample

NO$_2$ detector

Sample flow

CO

NO

reactor

NO$_2$ detector

CO is the amplification agent in this chain reaction

Motivation

- Airborne measurements (vertical distribution, characterize photochemical activity);

- Adapt the measurement techniques for airborne measurement;

- Safety regulations for airborne measurements are very strict;

- Use of toxic and dangerous gases on board very restricted.

CO – the trouble maker

- Secondary containment needed in aircraft;

- Special alarm systems needed;

- Lots of paper work, certifications, etc.;

- Logistics problems as dangerous goods;

- OMO-EU: couldn't get certification for CO on board on time;

- EMeRGe campaign: CO logistics are causing a lot of problems;

Money, mood, and time.
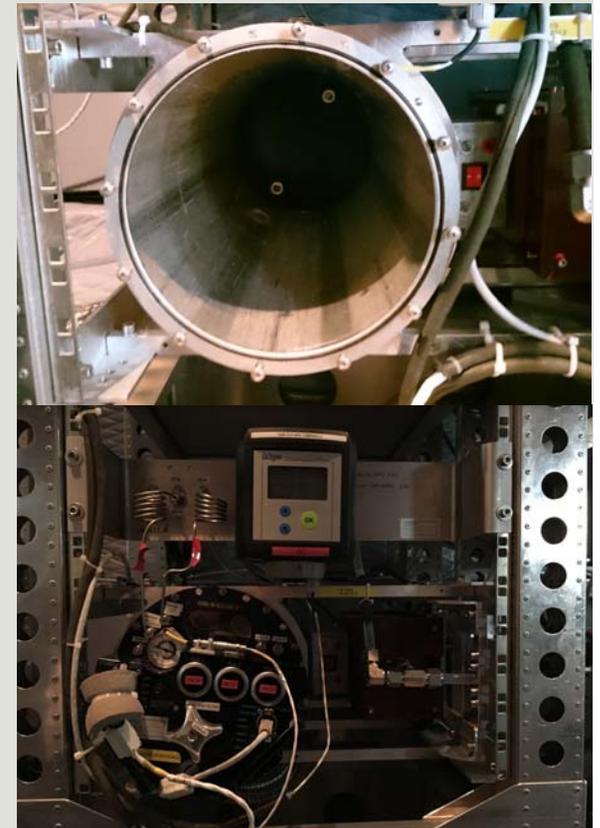
CO Alternative

Criteria for the gases on board:

- Could be transported in bottles

- Under toxicity limit

- None flammable/explosive (below of LFL/LEL)

- Do not require extra certification

- Can amplify our signal.

(VINTECH, 2011)

Candidates:
Ethylene (C_2H_4) 2% in N_2

But before talking about ethylene

PeRCA in Practice

Sample flow		Sample flow	

N$_2$	reactor	NO		CO	reactor	NO

OR

| CO | | | N$_2$ | | |

NO$_2$ detector		NO$_2$ detector

$[NO_2]_{background}$

$[NO_2]_{amplification}$

Background mode

Signal mode

"switching"

NO$_2$ signal
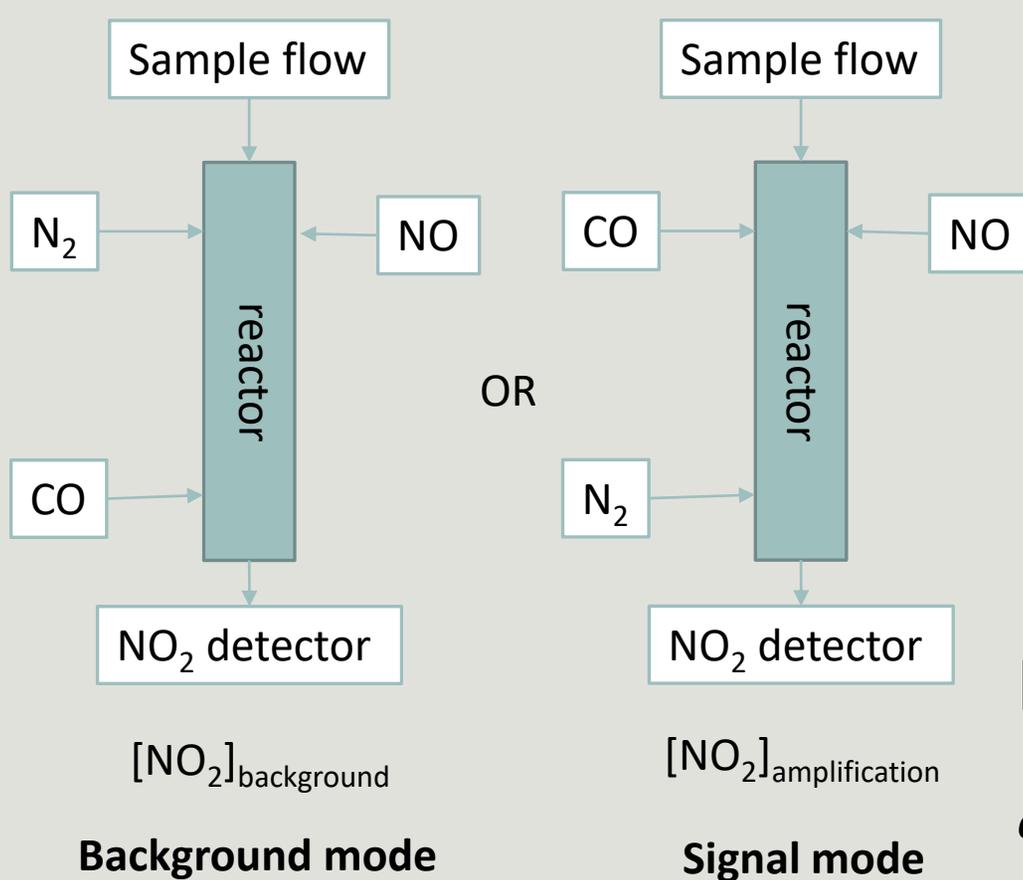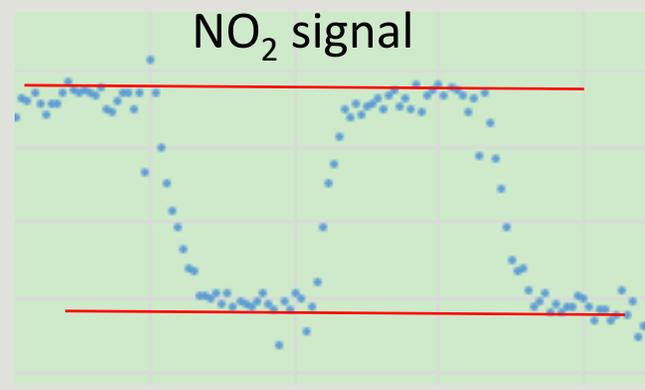
$$[RO_2^*]=\frac{[NO_2]_{amplification}-[NO_2]_{background}}{eCL}$$

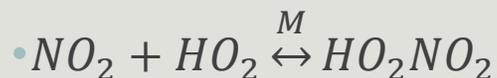*eCL, effective chain length, is determined from series of calibrations.*

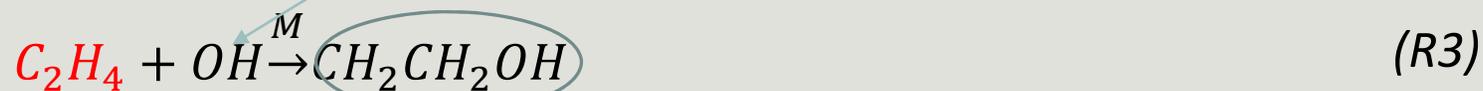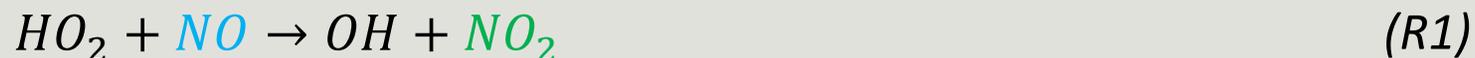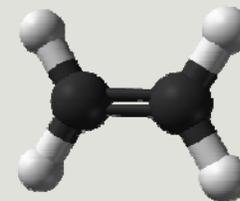# PeRCA in Practice

Total NO_2 measurements:

- NO_2 from the chain reaction of total peroxy radicals (RO_2^*);

- NO_2 in the sample air;

- NO_2 as reaction product from NO and O_3;

Chain reaction termination:

- Wall loss: OH, RO, HO_2, RO_2 reach the wall and create non radical products;
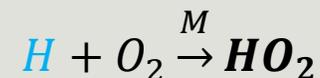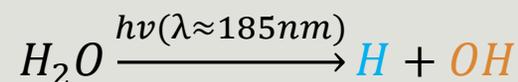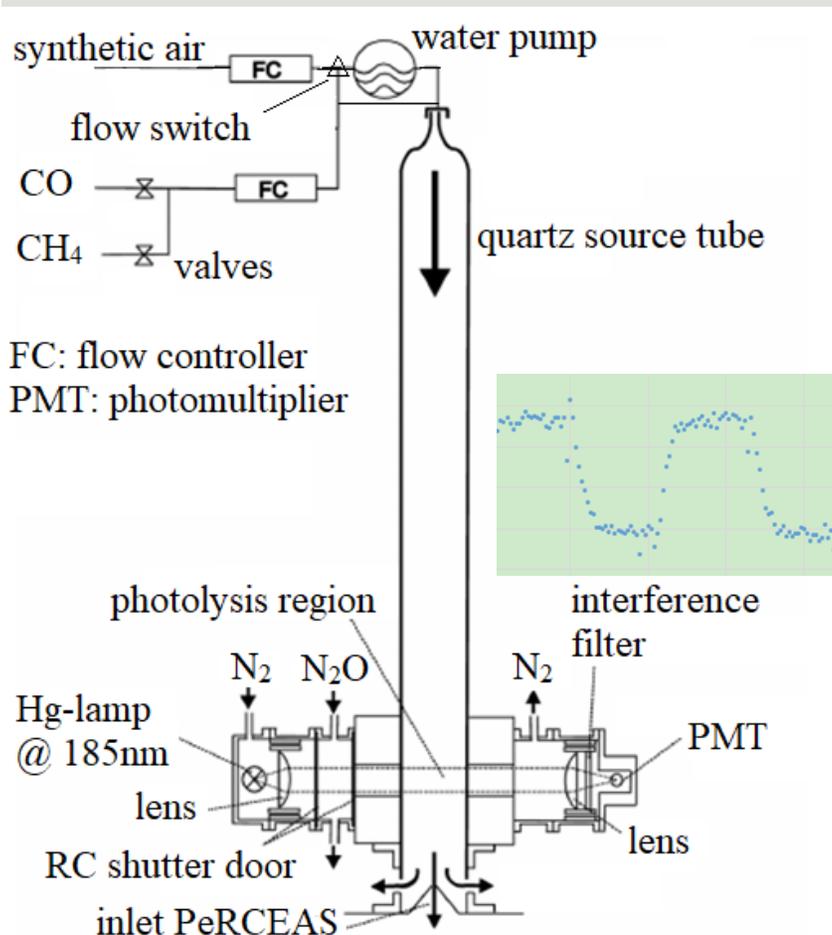
- Radical-radical reactions

- $OH + NO \xrightarrow{M} HONO$

- $OH + NO_2 \xrightarrow{M} HNO_3$

- $NO_2 + HO_2 \overset{M}{\leftrightarrow} HO_2NO_2$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R1)$$
$$OH + CO + O_2 \xrightarrow{M} HO_2 + CO_2 \qquad (R2)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (R3)$$
$$RO + O_2 \rightarrow R'CHO + HO_2 \qquad (R4)$$

Amplifier Ethylene

$$HO_2 + NO \rightarrow OH + NO_2 \qquad \text{(R1)}$$

$$C_2H_4 + OH \xrightarrow{M} CH_2CH_2OH \qquad \text{(R3)}$$

$$CH_2CH_2OH + O_2 \rightarrow CH_2CHOH + HO_2 \qquad \text{(R4)}$$

$$CH_2CH_2OH + O_2 \rightarrow CH_2CH_2O + HO_2 \qquad \text{(R5)}$$

$$CH_2CH_2OH + O_2 \xrightarrow{M} CH_2(OH)CH_2O_2 \qquad \text{(R6)}$$

$$CH_2(OH)CH_2O_2 + NO \rightarrow CH_2(OH)CHO + NO_2 \qquad \text{(R7)}$$
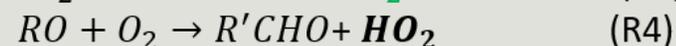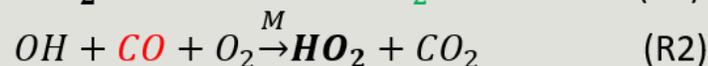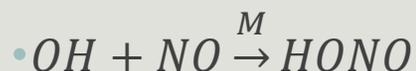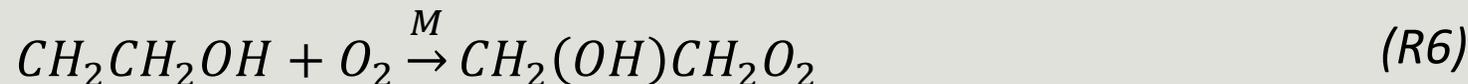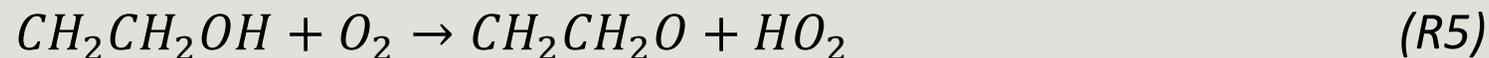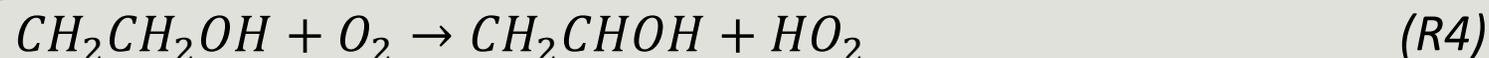
Theory okay, what about practically?

(Mills, 2009)

Radical source for eCL determination

synthetic air — FC

flow switch

water pump

CO — ⊠ — FC

CH₄ — ⊠ — valves

quartz source tube

FC: flow controller
PMT: photomultiplier

photolysis region

interference filter

N₂ N₂O   N₂

Hg-lamp @ 185nm

lens

RC shutter door

inlet PeRCEAS

PMT

lens

$$H_2O \xrightarrow{hv(\lambda \approx 185nm)} H + OH$$

$$H + O_2 \xrightarrow{M} HO_2$$

OH can be saved by adding CO to the source so that pure HO$_2$ radicals are generated:

$$CO + OH + O_2 \rightarrow HO_2 + CO_2$$
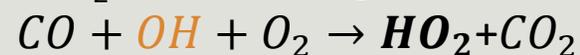
Alternatively, add CH$_4$ to the source can generate the mixture of radicals HO$_2$ and CH$_3$O$_2$:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2$$

In the meanwhile,

$$O_2 \xrightarrow{hv(\lambda \approx 185nm)} 2O$$
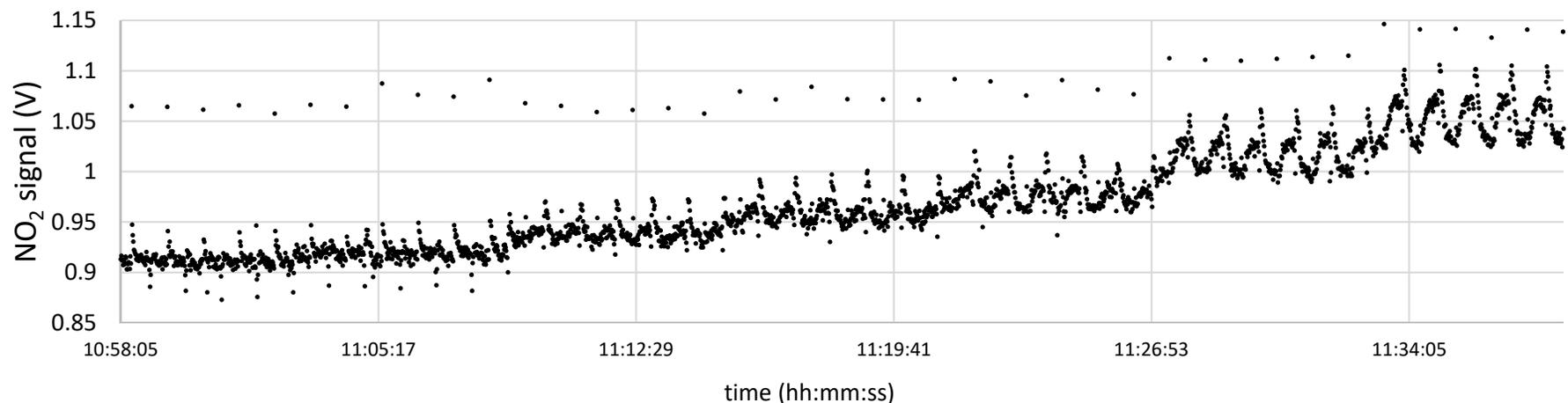
$$O_2 + O \rightarrow O_3$$

$$O_3 + NO \rightarrow O_2 + NO_2$$
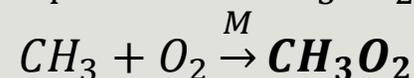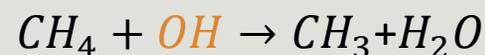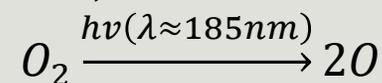
Amplifier Ethylene previous

Amplification modulations observed, even without radicals at the source.

In another meanwhile,

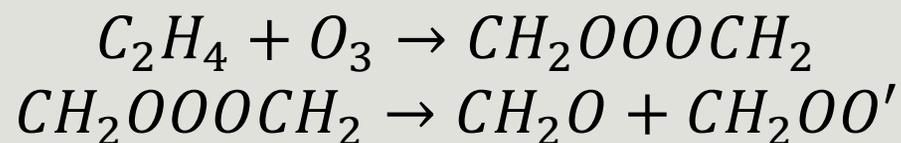$$O_2 \xrightarrow{hv(\lambda \approx 185nm)} 2O$$

$$O_2 + O \rightarrow O_3 \quad \longrightarrow \quad O_3 + C_2H_4 \rightarrow peroxy\ radicals$$

$$O_3 + NO \rightarrow O_2 + NO_2$$
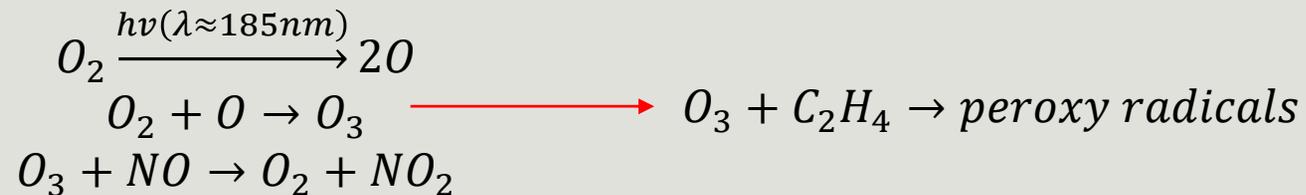
Chain length calibration without HO_2 generated from the source

Ethylene Interference

$$C_2H_4 + O_3 \rightarrow CH_2OOOCH_2$$
$$CH_2OOOCH_2 \rightarrow CH_2O + CH_2OO'$$

Criegee Intermediate

CH_2OO' will then go to complex pathways and create peroxy radicals which will be amplified by C_2H_4 in addition to the peroxy radicals generated at the radical source.

Criegee Intermediate
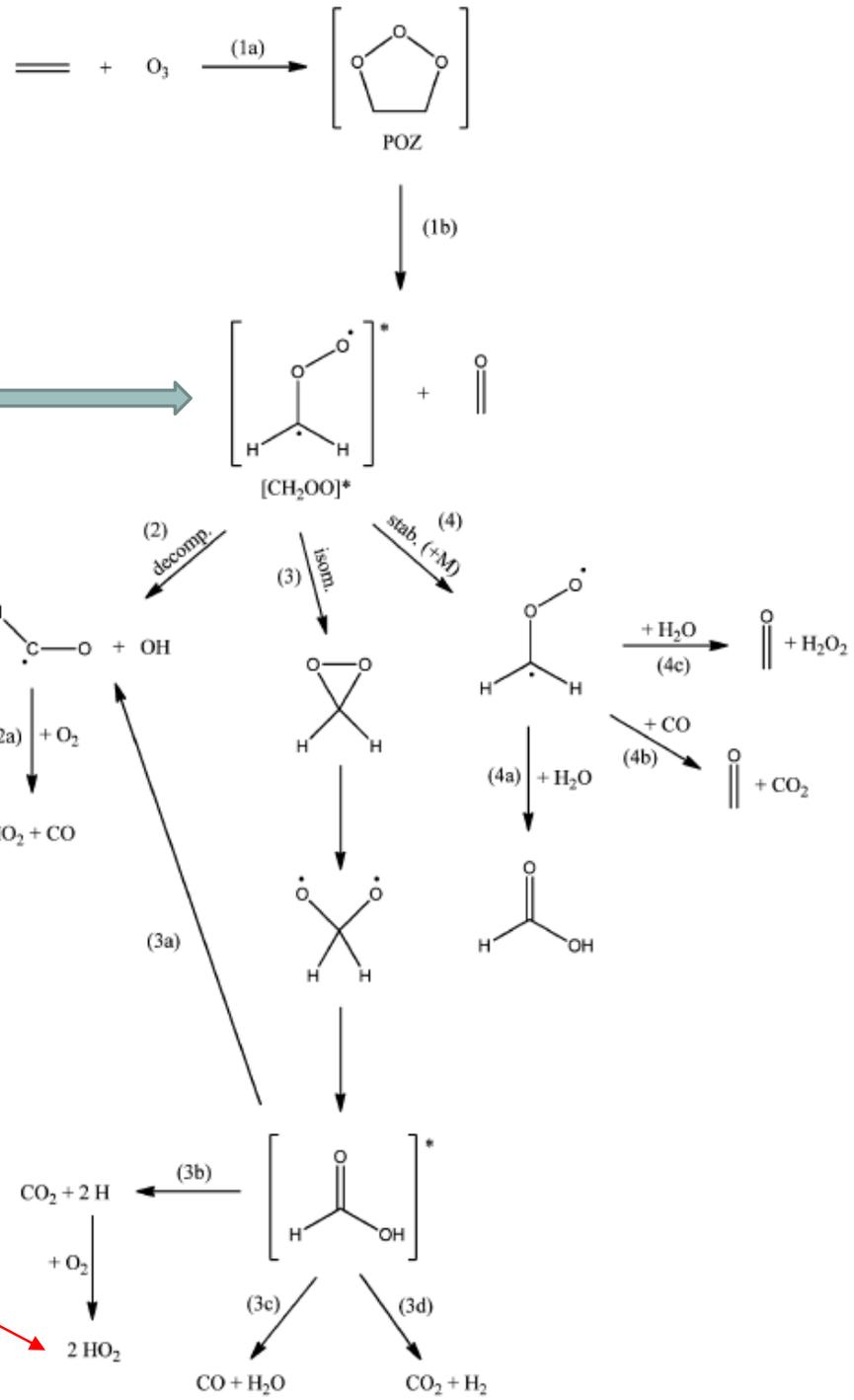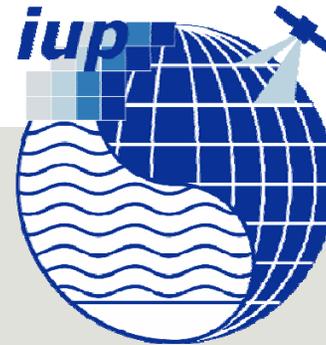
Ethylene amplifier

Reaction	Rate constant $k(298K), [cm^3 \cdot molec^{-1} \cdot s^{-1}]$
$O_3 + NO \rightarrow NO_2 + O_2$	1.9×10^{-14}
$O_3 + C_2H_4 \rightarrow product$	1.7×10^{-18}

@298K, ambient pressure for NO=7.78×10^{13} molec.cm^{-3}, NO=1.4×10^{14} molec.cm^{-3}, NO=2.25×10^{14} molec.cm^{-3} (3ppmv, 6ppmv, and 9ppmv) and 2% C$_2$H$_4$ in N$_2$ competing reactions with 1.0×10^{11} molec.cm^{-3} (4ppbv) O$_3$
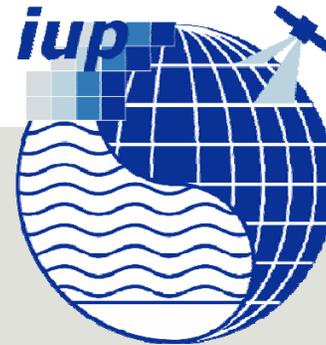
Ethylene's previous conclusion

- More NO, less interference;

- The tests stopped until NO at 9ppmv under ambient pressure condition;

- NO_2 detector-> Chemiluminescence reaction of NO_2 with Luminol (3-aminophthalhydrazide: $C_8H_7N_3O_2$), and is strongly influenced by NO presence. Higher NO, lower sensitivity.

It will be interesting to try with different pressure and conditions to see the competition reactions. New NO_2 detector.

PeRCEAS instrument

- **Peroxy radical chemical enhancement and absorption spectroscopy;**

- Airborne instrument;

- CRDS NO$_2$ detector.
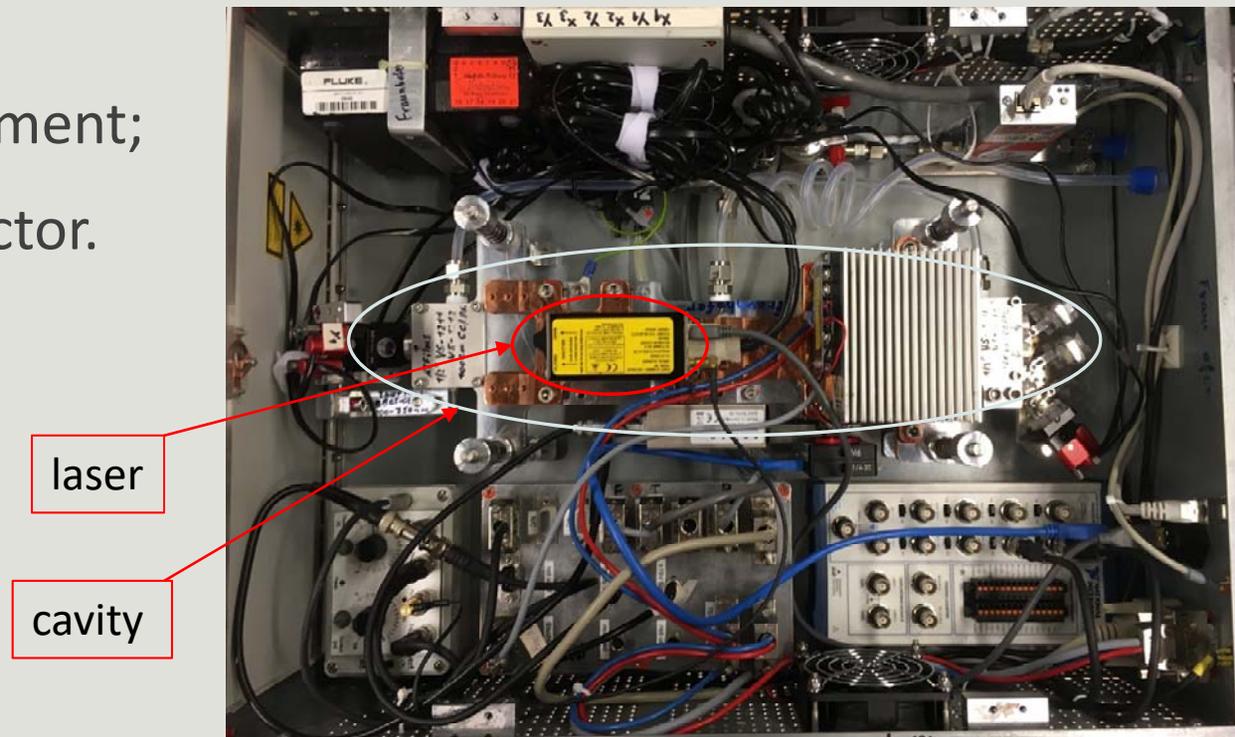
laser

cavity

NO$_2$ detection using CRDS Technique

Cavity Ring-down spectroscopy:

- Blue diode laser at 409nm;

- V-shaped resonator;

- Measure the decay time, aka. the ring-down time

- Highly sensitive;

- Do not effect by NO.
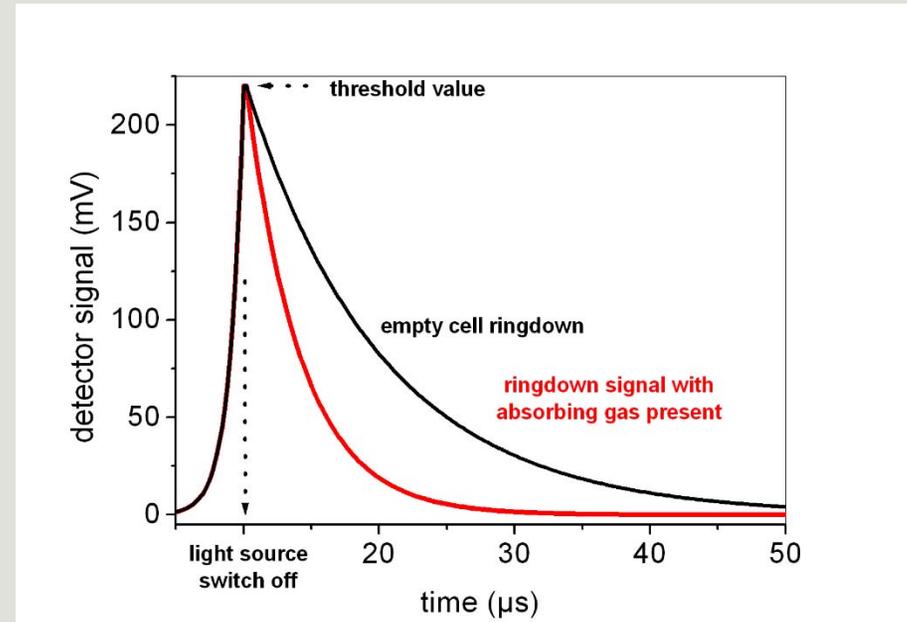
CRDS NO$_2$ detection

The absorption coefficient α of an absorber:

$$\alpha = \frac{n}{c_0} \times \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right),$$

where **n** is the index of refraction of sample air, **c$_0$** is the speed of light in vacuum, **τ** is the ring-down time signal, **τ$_0$** is the ring-down time background.
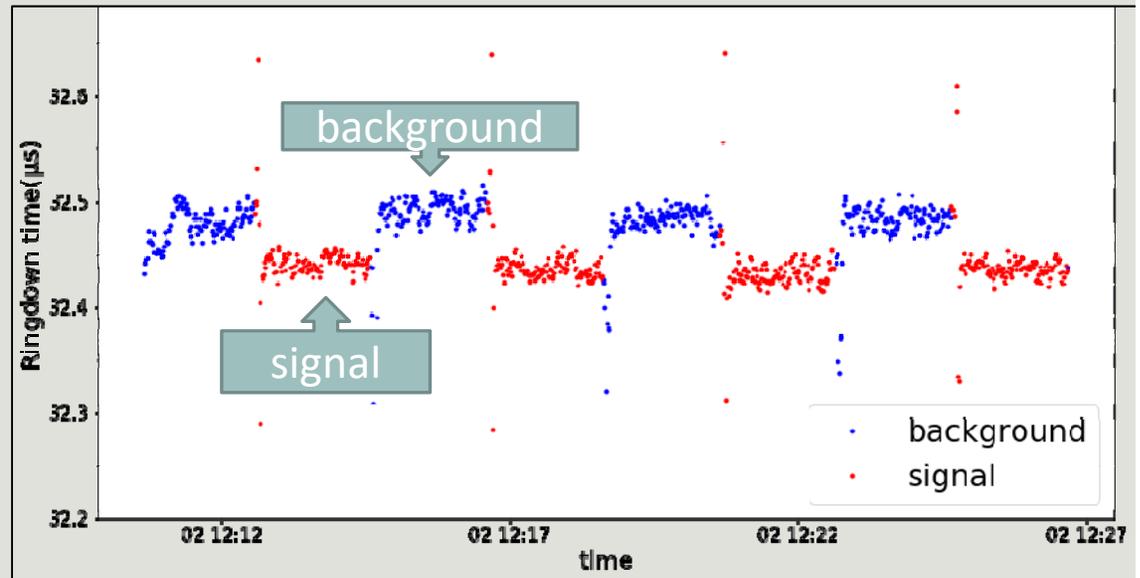
$$\alpha = \frac{N}{V} \times \sigma^{\lambda}_{absorber}$$

Where N is the number of molecules, V is the volume, and $\sigma^{\lambda}_{absorber}$ is the absorption cross section at wavelength λ.

Instrument setups
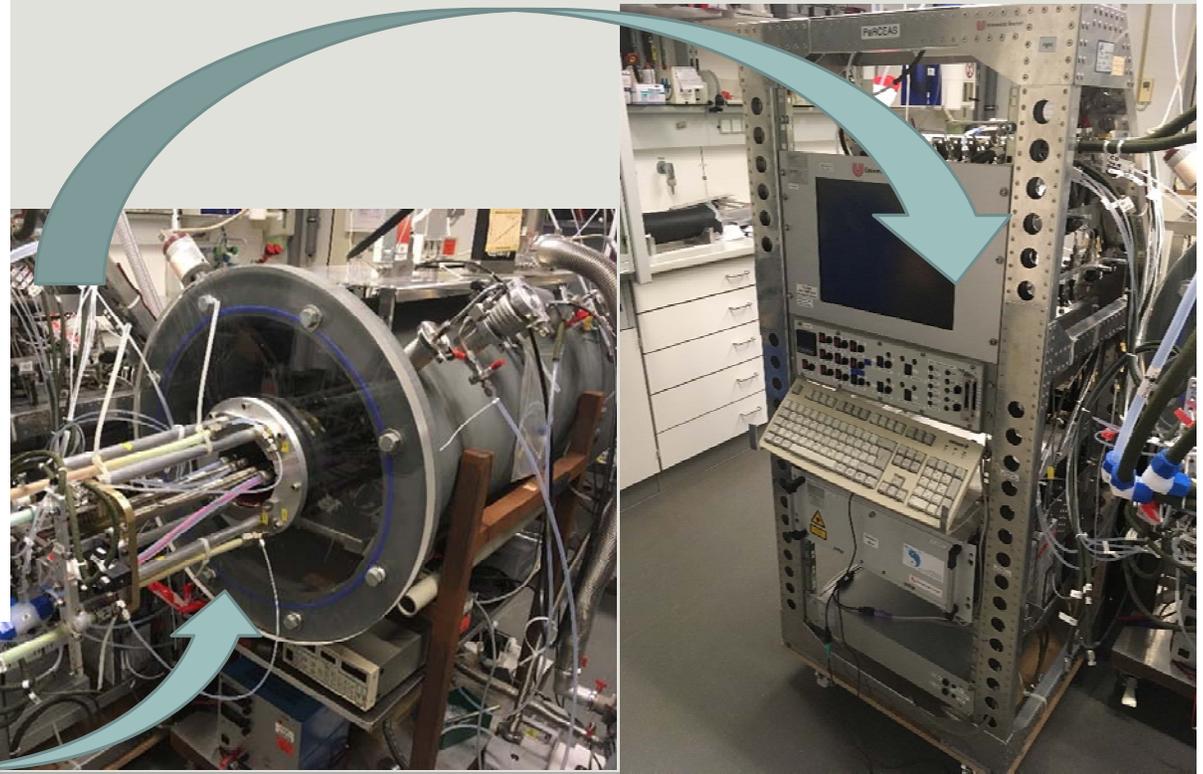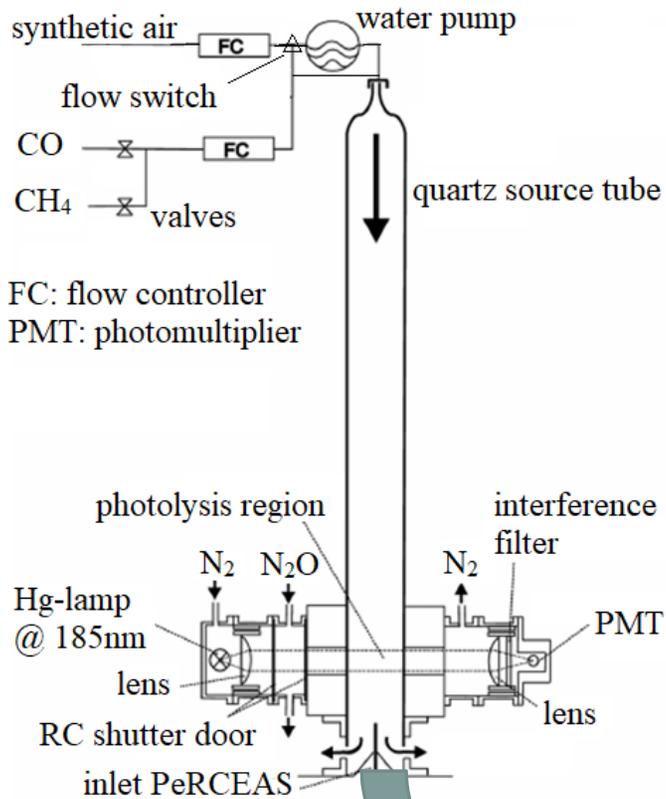
Results

▪Test conditions: Inlet pressure=160mbar, sample flow=500ml/min, NO= 1.17×10^{14} molec.cm^{-3}(30ppmv), C_2H_4/N_2 flow =45ml/min, chamber pressure=500mbar

No modulation!

No interference?

Interference test mode

Sample flow → | N$_2$ → [ ] ← NO | C$_2$H$_4$ → [ ] ← NO
C$_2$H$_4$ → [ ] → NO$_2$ detector

[NO$_2$]$_{background}$

Background mode

OR

Sample flow → | C$_2$H$_4$ → [ ] ← NO | N$_2$ → [ ] → NO$_2$ detector

[NO$_2$]$_{amplification}$
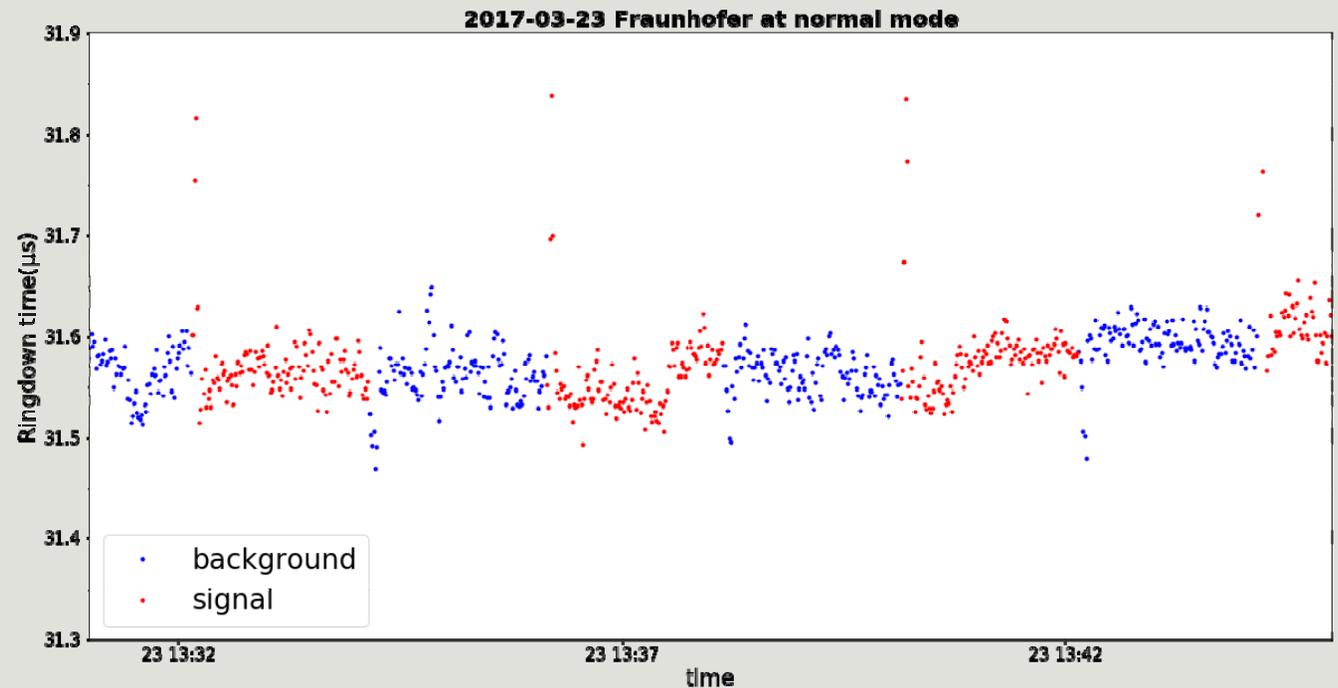
Signal mode
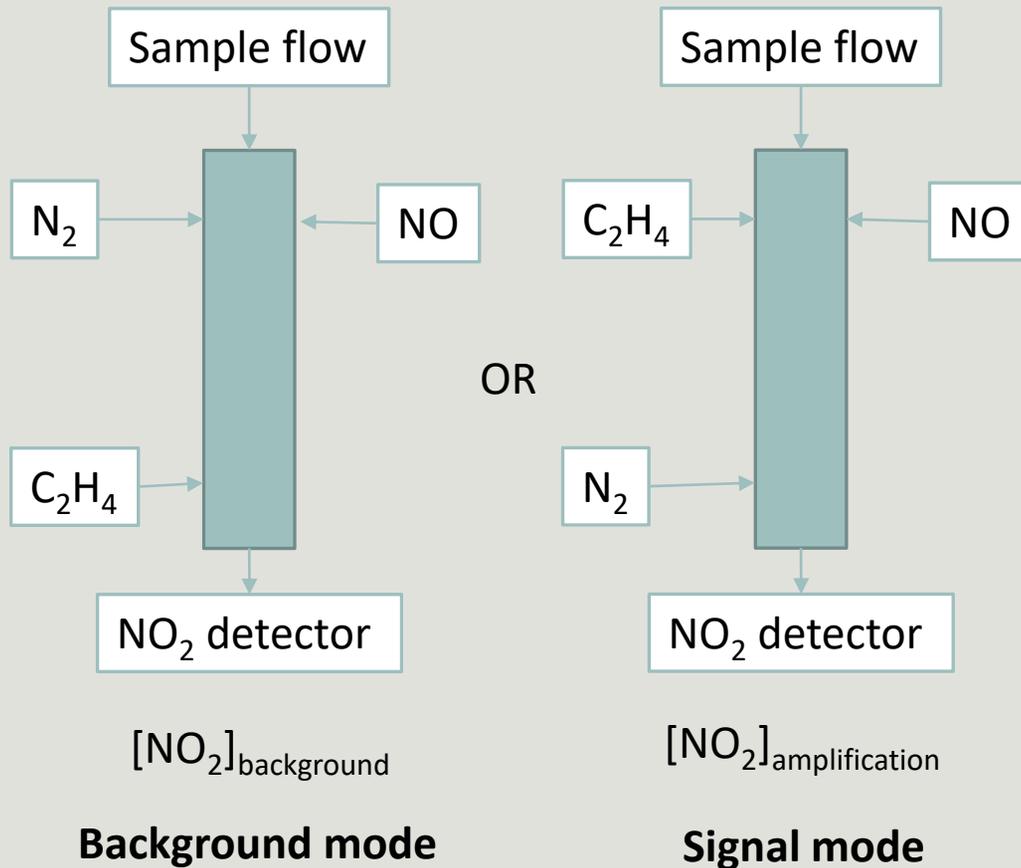
- Can remove the interference from C$_2$H$_4$ totally;
- Prolong the reaction time, by taking the advantage of using the tubes until the NO$_2$ detector.

Interference test with Ethylene

2017-03-23 System 2 at interference mode
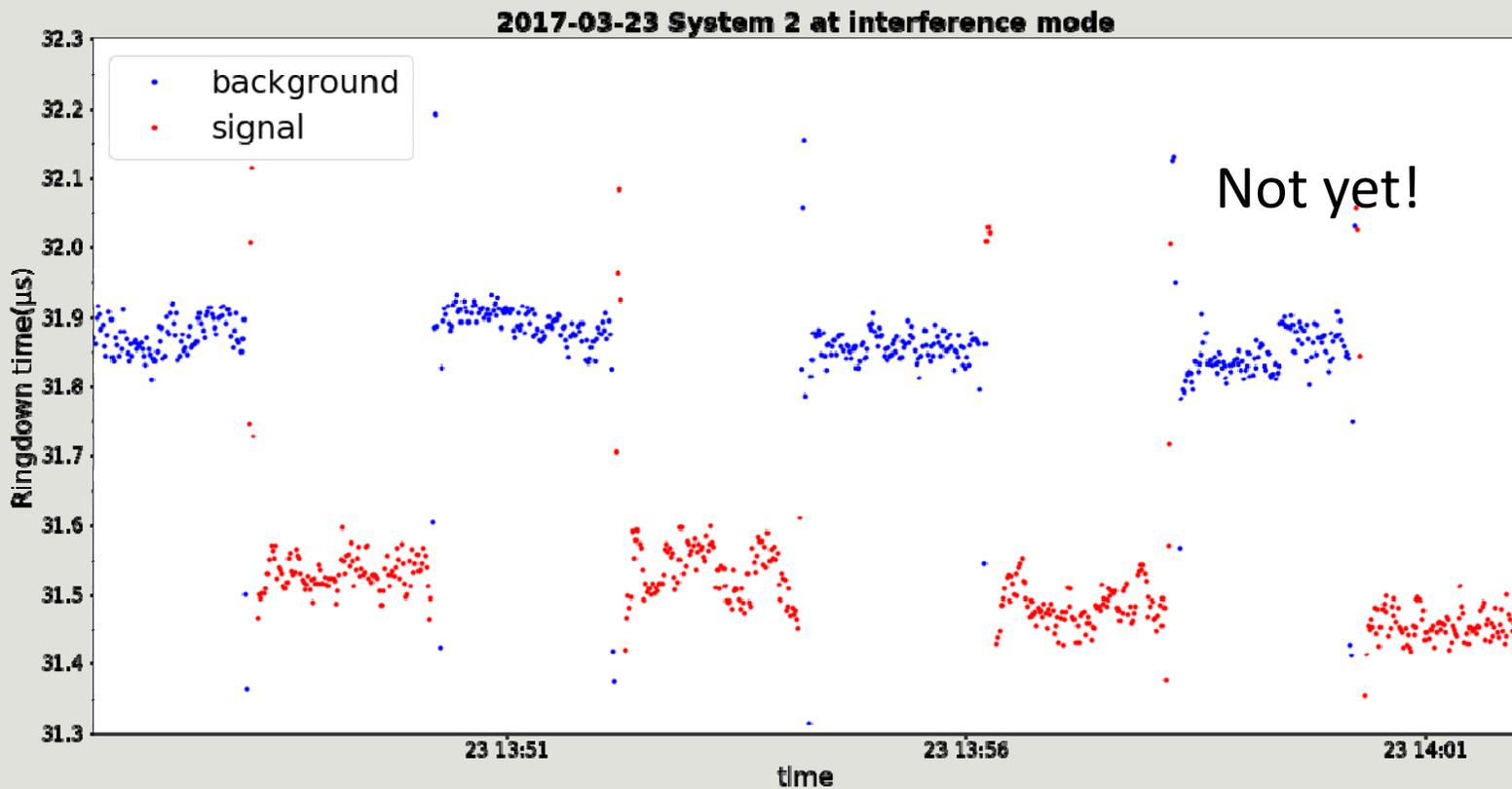
Interference test with CO
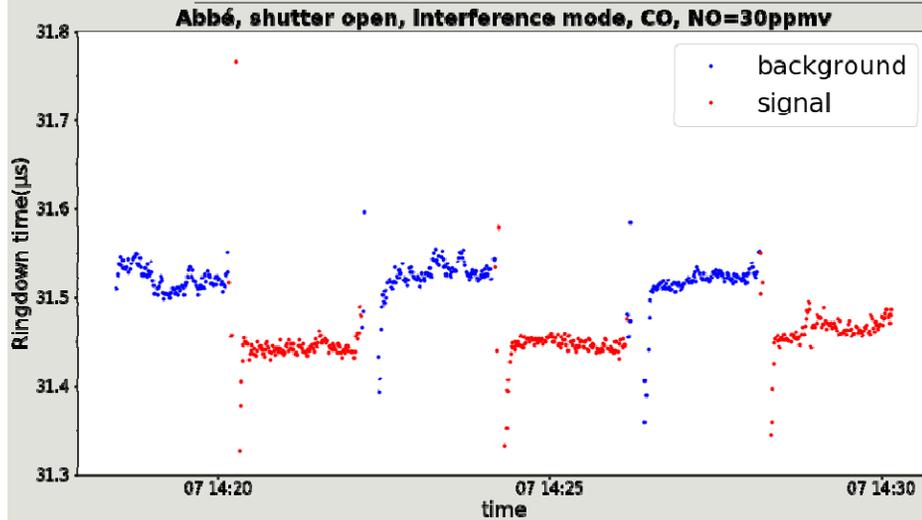
The molecules inside the cavity are changing, therefore, the scattering is different causing the change of ring-down time.
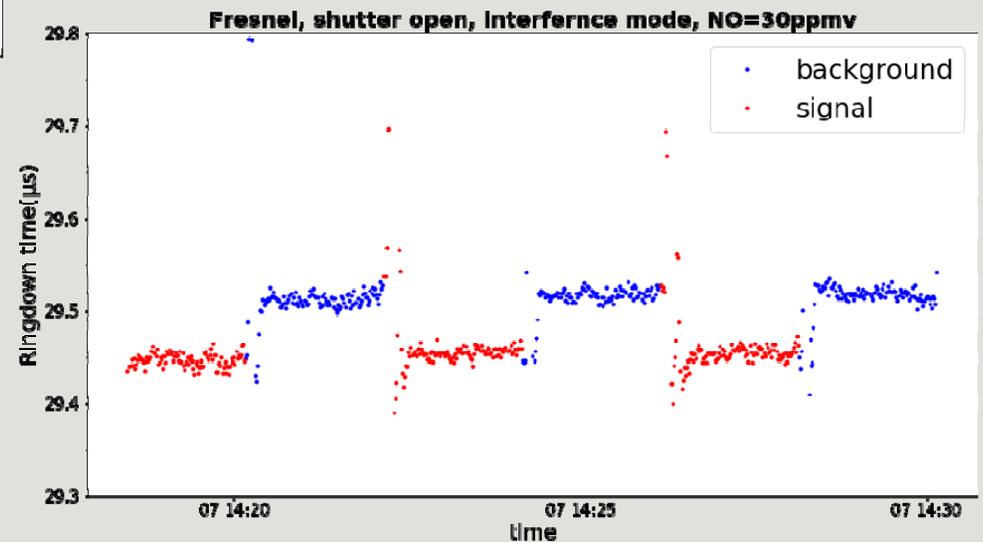
Back to Ethylene

- The detection limits increased, able to see smaller modulations.

- Test conditions: Inlet pressure=160mbar, sample flow=500ml/min, C_2H_4/N_2 flow =45ml/min, chamber pressure=500mbar

- NO=7.78×10^{13} molec.cm^{-3}(20ppmv), 1.17×10^{14} molec.cm^{-3}(30ppmv), 1.75×10^{14} molec.cm^{-3}(45ppmv), or 2.33×10^{14} molec.cm^{-3}(60ppmv), .

- Two systems working simultaneously under similar conditions.

Results from "switching tests"

System 1 at NO 20ppmv, 30ppmv, 45ppmv
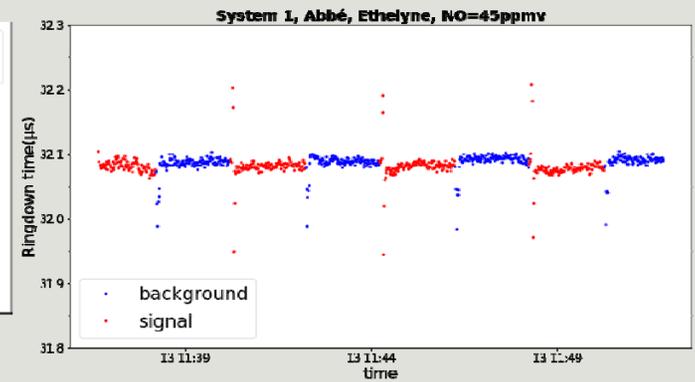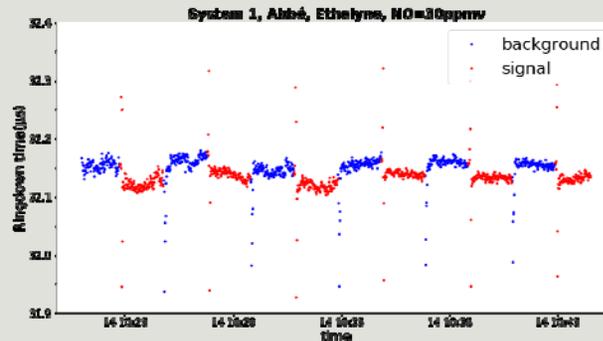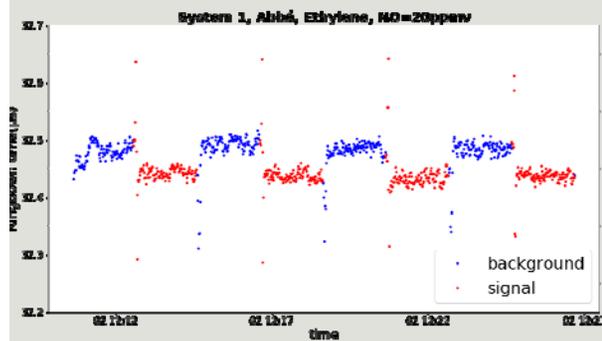
System 2 at NO 20ppmv, 30ppmv, 45ppmv
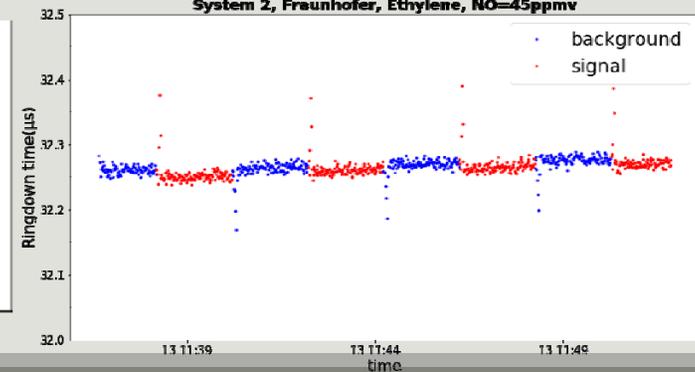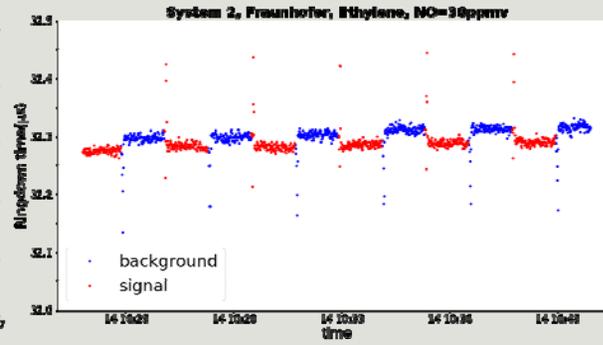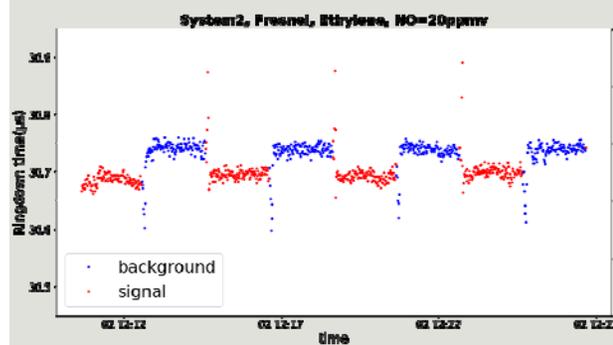
Identify the interference using ozone calibration

System 1, Abbé, ozone calibration, background

Shutter close

Shutter open
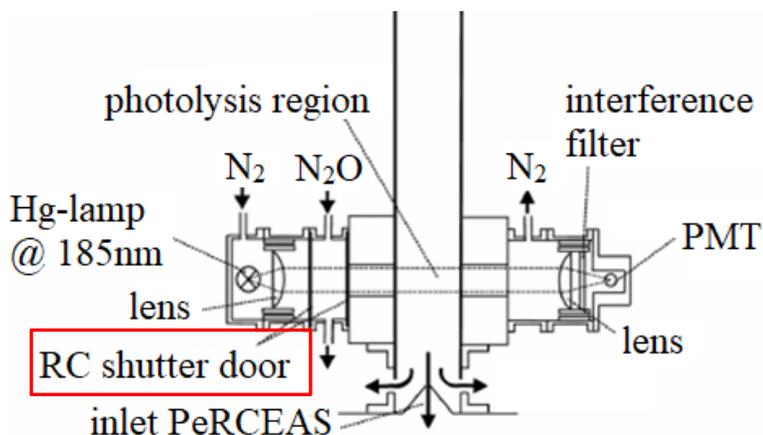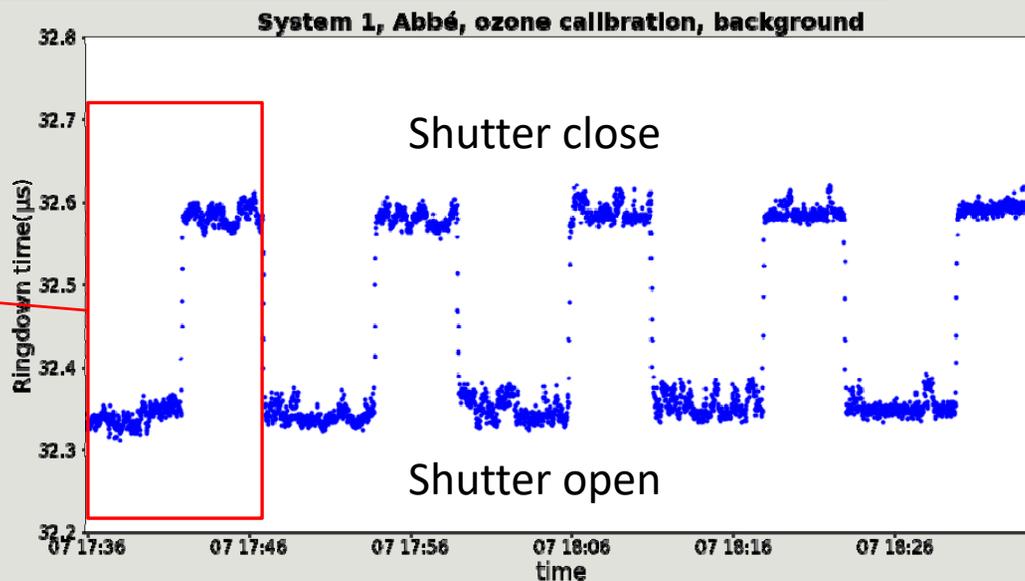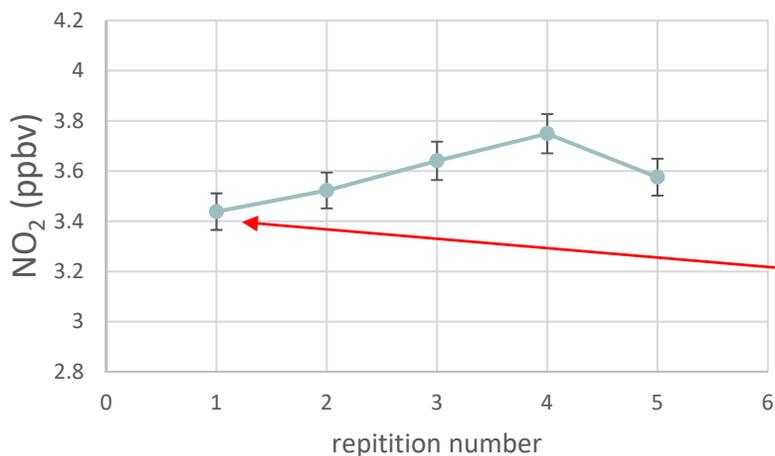
$[NO_2] \rightarrow NO$ react with O_3
+ interference of C_2H_4 react with O_3

Comparable with the "switching" tests

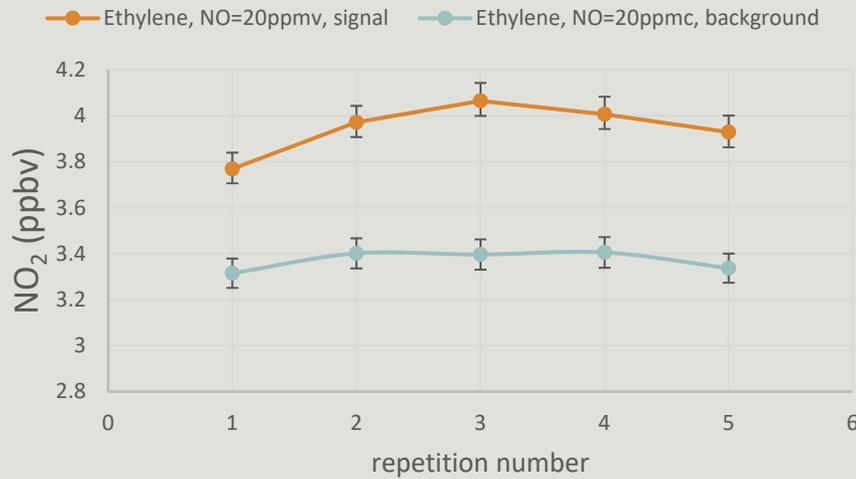# Results at NO=20ppmv, sys1

System 1, Abbé

Ethylene, NO=20ppmv, signal • Ethylene, NO=20ppmv, background

2017-12-02, interference test, System 1, shutter open, NO=20ppmv

τ_{sig}=32.44±0.03μs
τ_{bck}=32.48±0.03μs
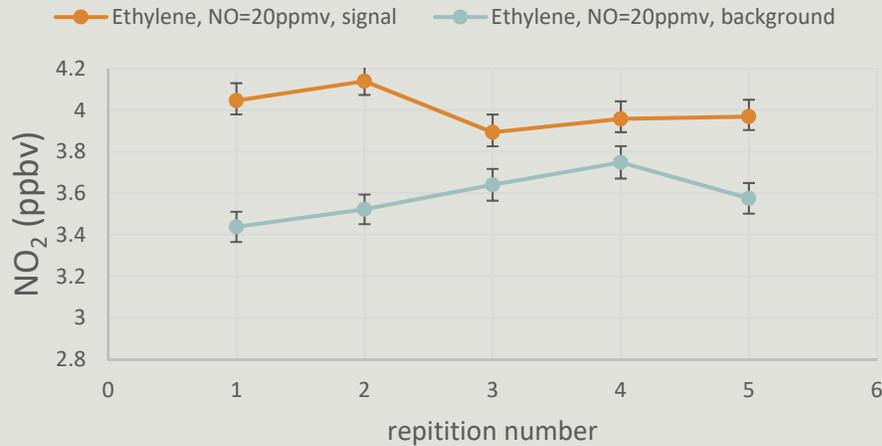
Delta NO_2=420±69(pptv)
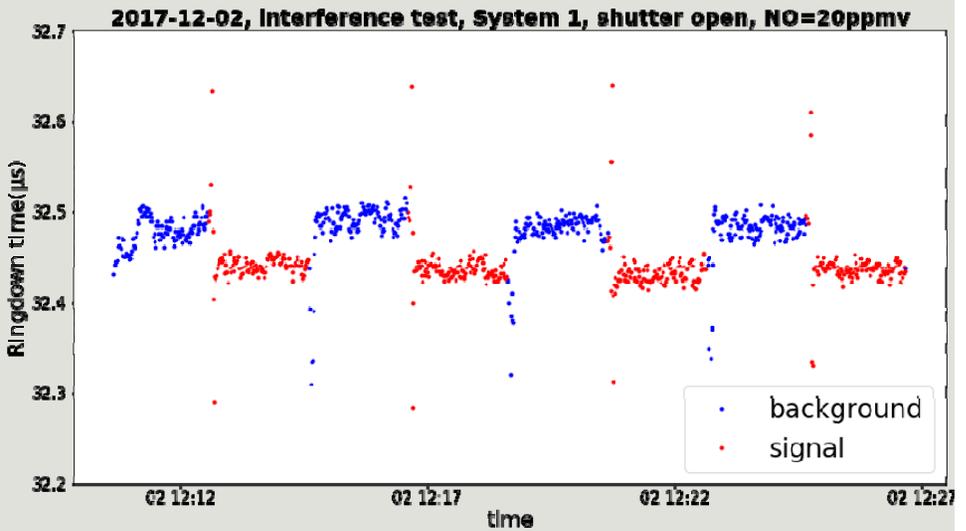
Delta NO_2=631±189(pptv)

Results at NO=20ppmv, sys2

System 2, Fraunhofer

Ethylene, NO=20ppmv, signal — Ethylene, NO=20ppmc, background

2017-12-02, Interference test, System2, shutter open, NO=20ppmv

τ_{sig}=30.70±0.02μs
τ_{bck}=30.73±0.02μs

Delta NO_2=597±34(pptv)
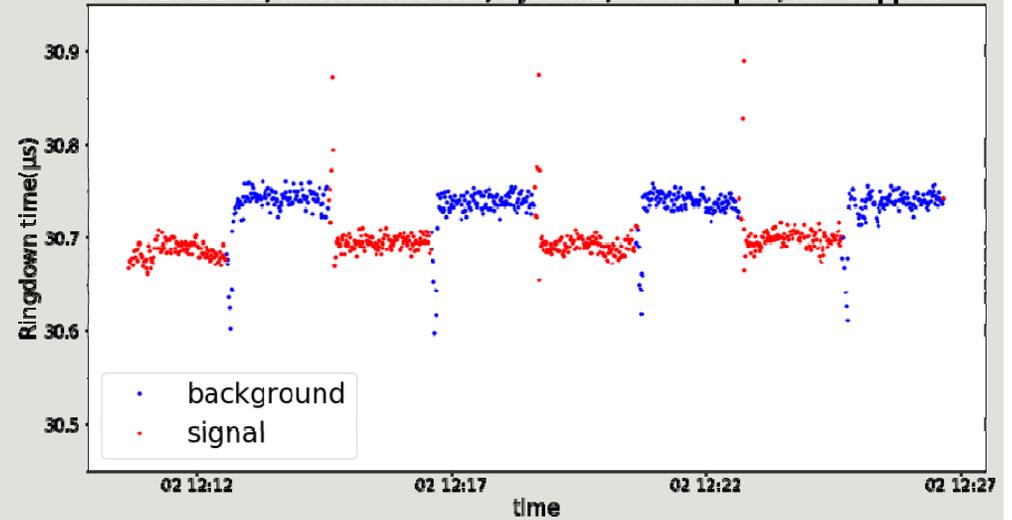
Delta NO_2=651±186(pptv)

Results at NO=30ppmv, sys1

System 1, Abbé
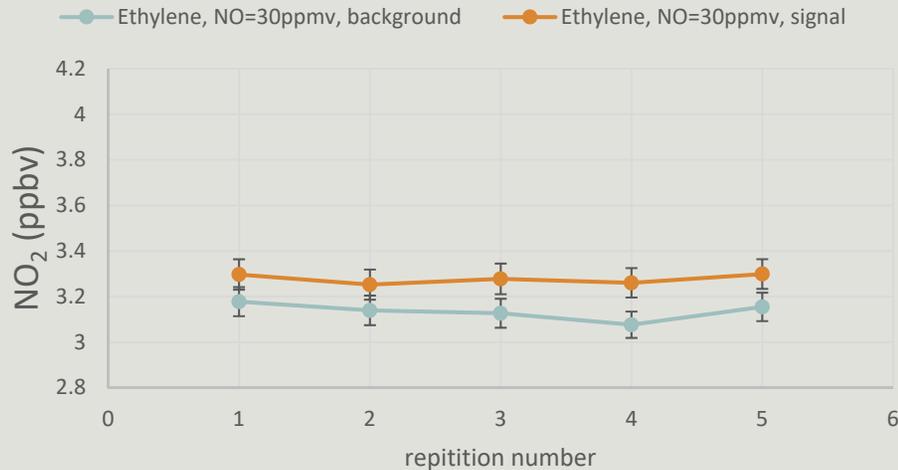
Delta NO_2=149±31(pptv)

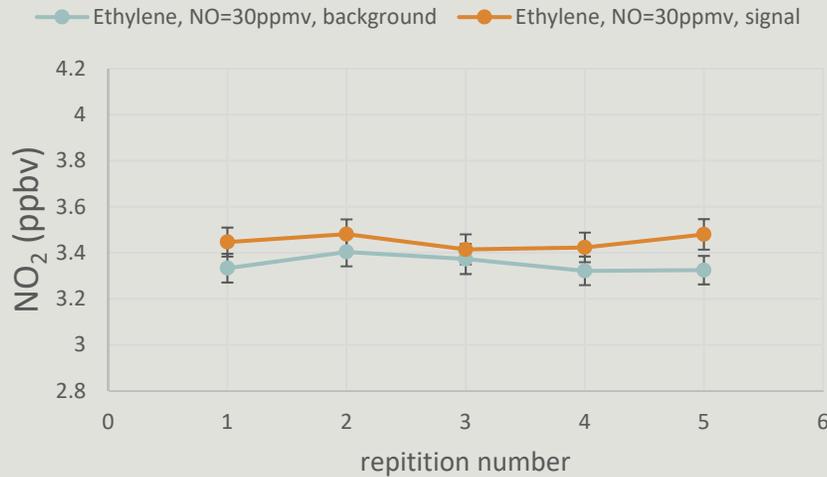Interference test, System 1, shutter open, Ethelyne, NO=30ppmv

τ_{sig}=32.13±0.03μs
τ_{bck}=32.15±0.03μs

Delta NO_2=264±194(pptv)

Results at NO=30ppmv, sys2
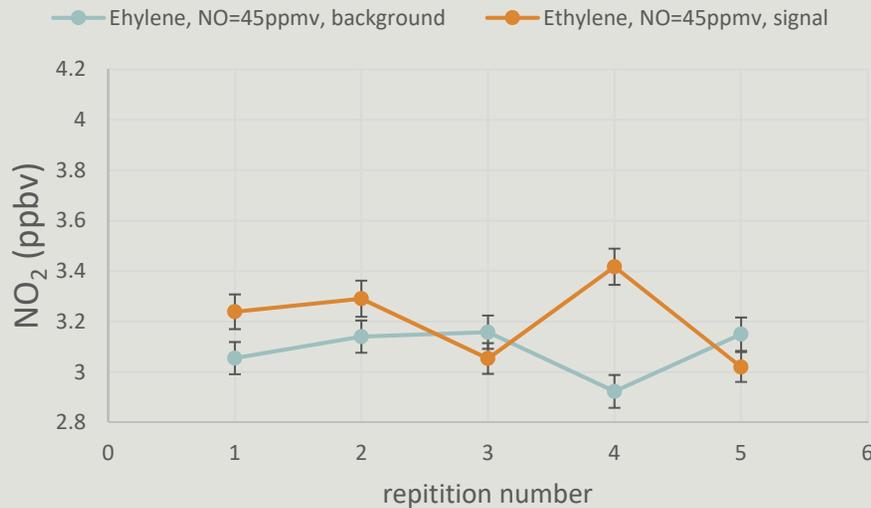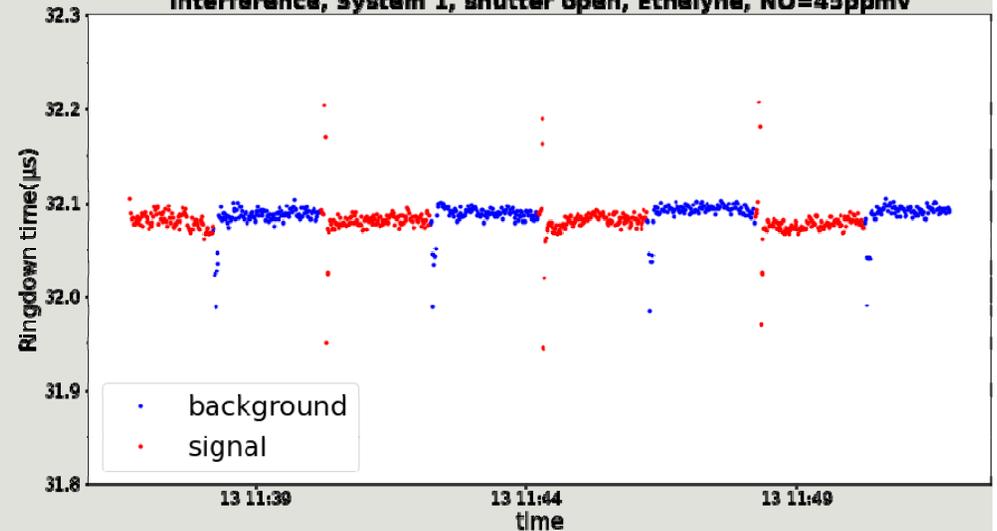

System 2, Fresnel

Delta NO_2=136±30(pptv)
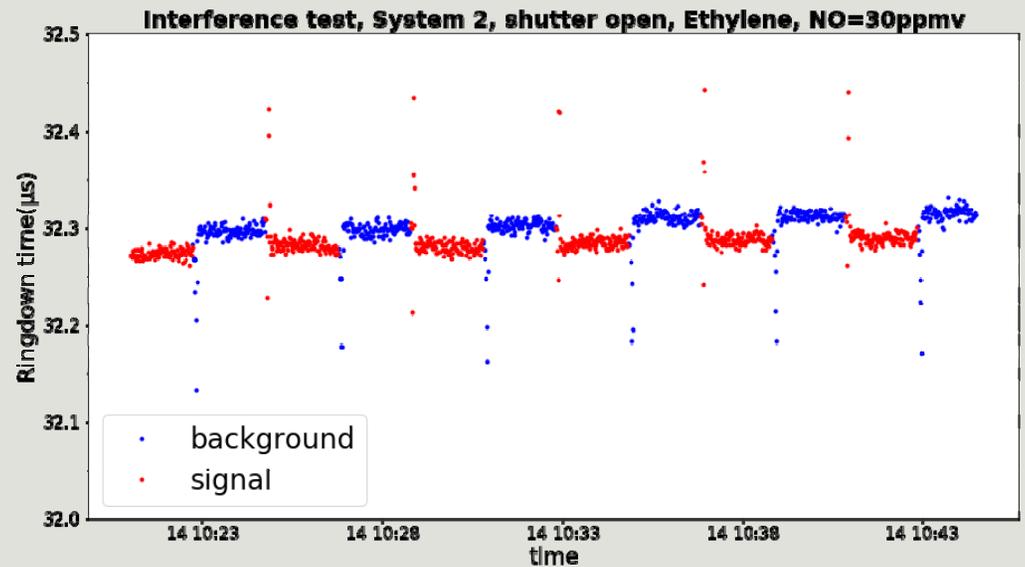
τ_{sig}=32.29±0.02μs
τ_{bck}=32.30±0.02μs

Delta NO_2=214±195(pptv)

Results at 45ppmv, sys1

System 1, Abbé

Delta NO_2=119±56(pptv)

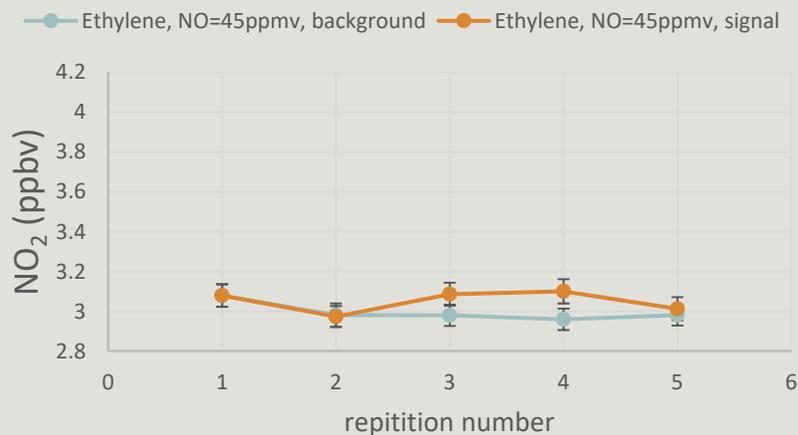Interference, System 1, shutter open, Ethelyne, NO=45ppmv

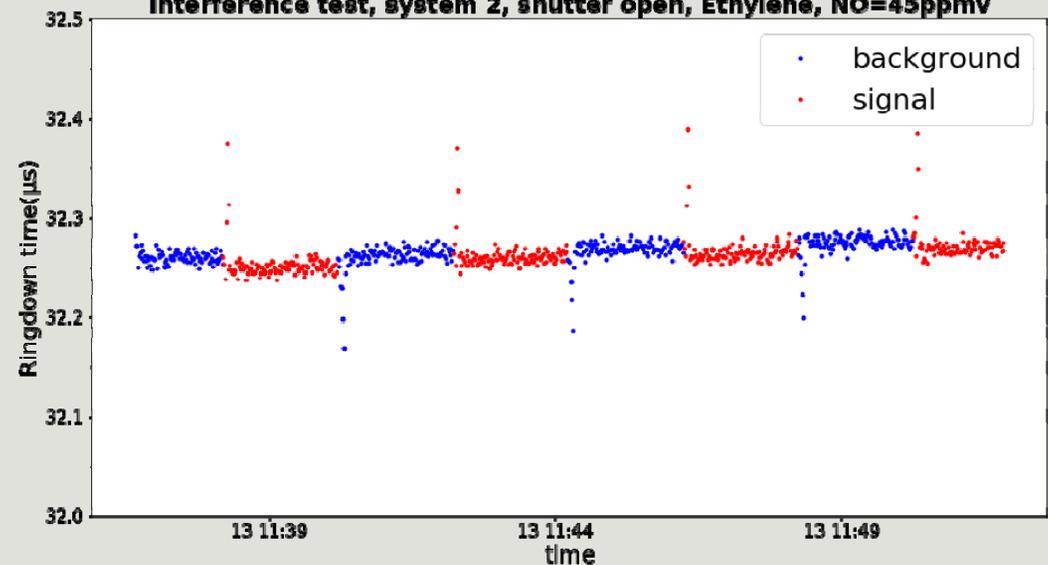τ_{sig}=32.08±0.03µs
τ_{bck}=32.09±0.02µs

Delta NO_2=91±186(pptv)

Results at 45ppmv, sys2

System 2, Fraunhofer

Interference test, system 2, shutter open, Ethylene, NO=45ppmv

τ_{sig}=32.08±0.03μs
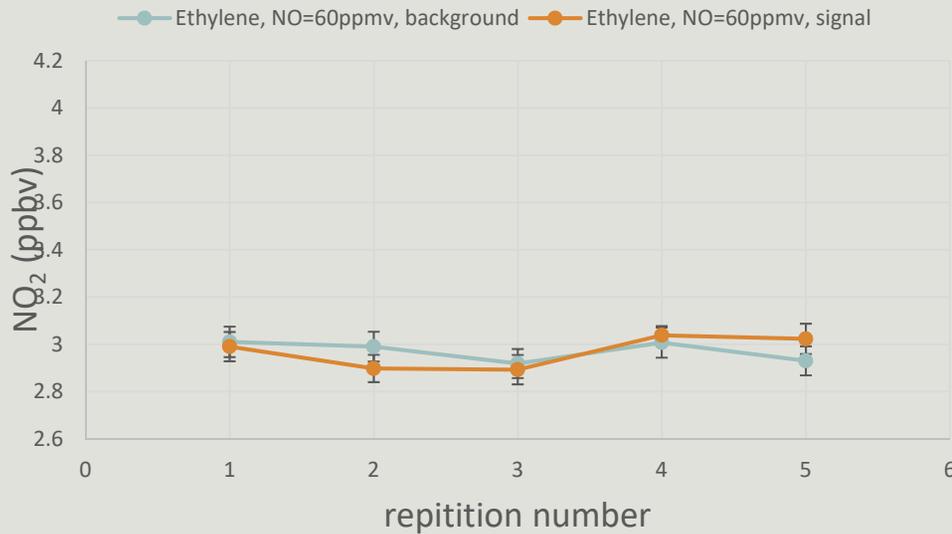τ_{bck}=32.09±0.02μs

Delta NO_2=54±31(pptv)   Delta NO_2=56±173 (pptv)
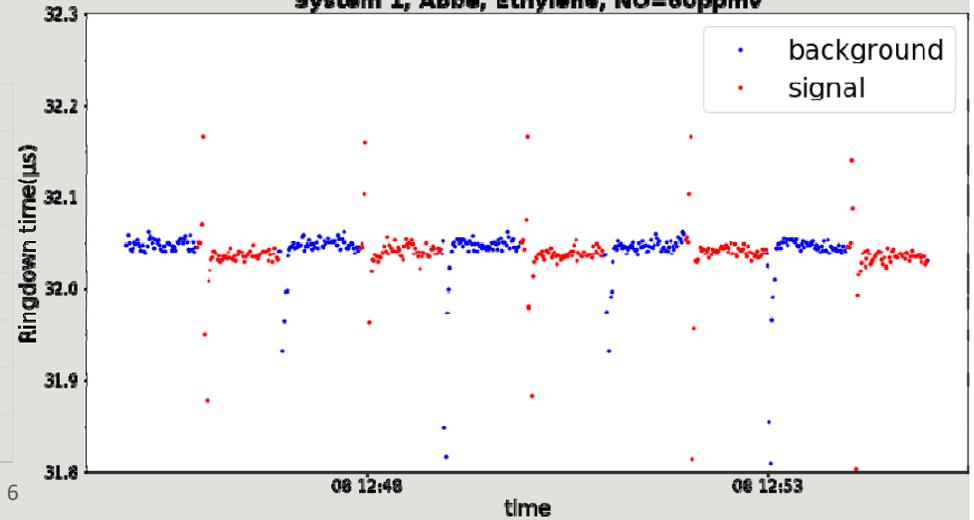
Results at 60ppmv, sys1

System 1, Abbé

Delta NO_2=-3±28(pptv)

System 1, Abbé, Ethylene, NO=60ppmv

τ_{sig}=32.08±0.03μs
τ_{bck}=32.09±0.02μs

Delta NO_2=100±191 (pptv)

Interference results

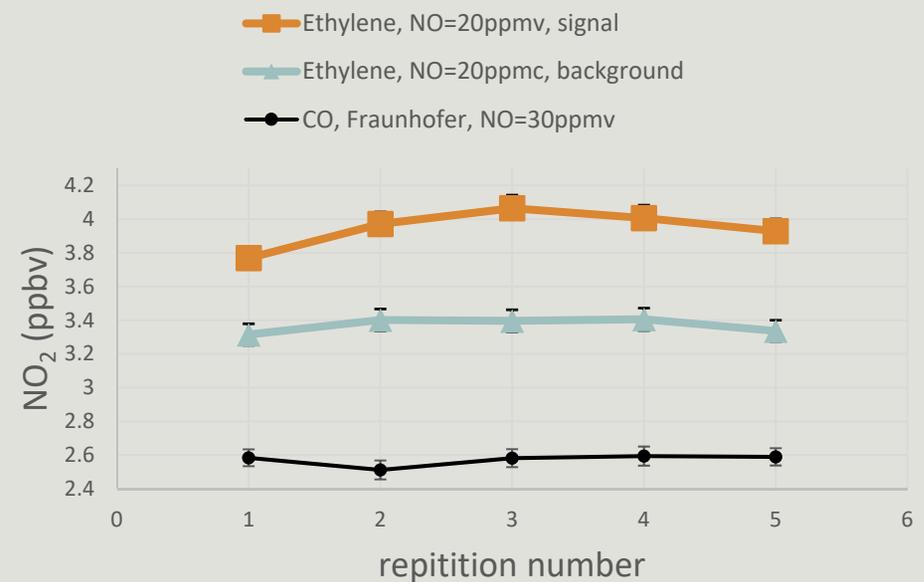| NO[ppmv]	NO_2 in [pptv]			
	Interference obtained from ozone calibration		Interference obtained from "switching"	
	System 1	System 2	System1	System 2
20	420±69	597±34	631±189	651±186
30	149±31	136±30	264±194	214±195
45	119±56	54±31	91±186	56±173
60	-3±28		100±191	

Interference results
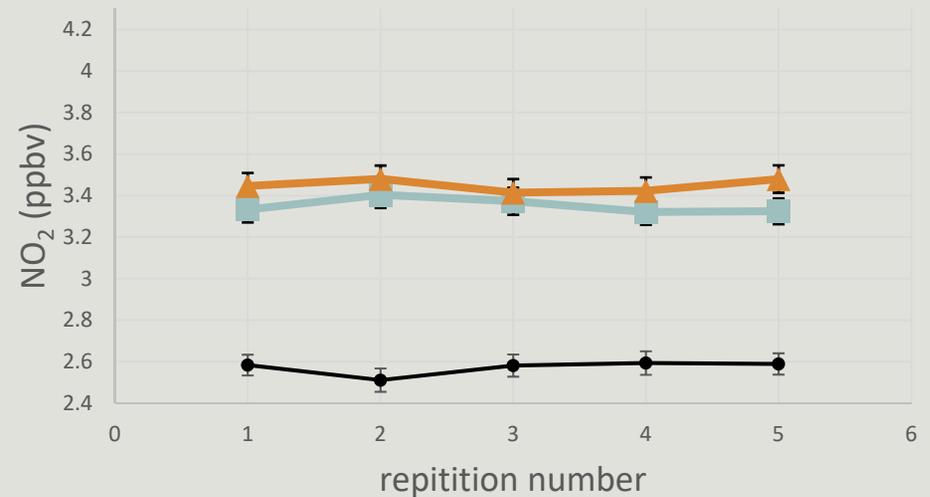# NO 20ppmv

Interference results
NO 30ppmv

System1, Abbé

- Ethylene, NO=30ppmv, background
- Ethylene, NO=30ppmv, signal
- CO, Abbé, NO=30ppmv
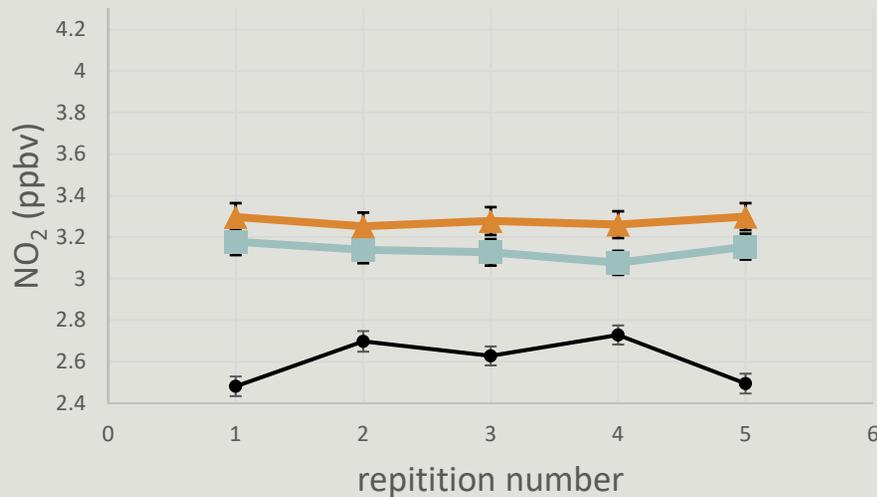
System2, Fresnel

- Ethylene, NO=30ppmv, background
- Ethylene, NO=30ppmv, signal
- CO, Fraunhofer, NO=30ppmv

Interference results NO 45ppmv

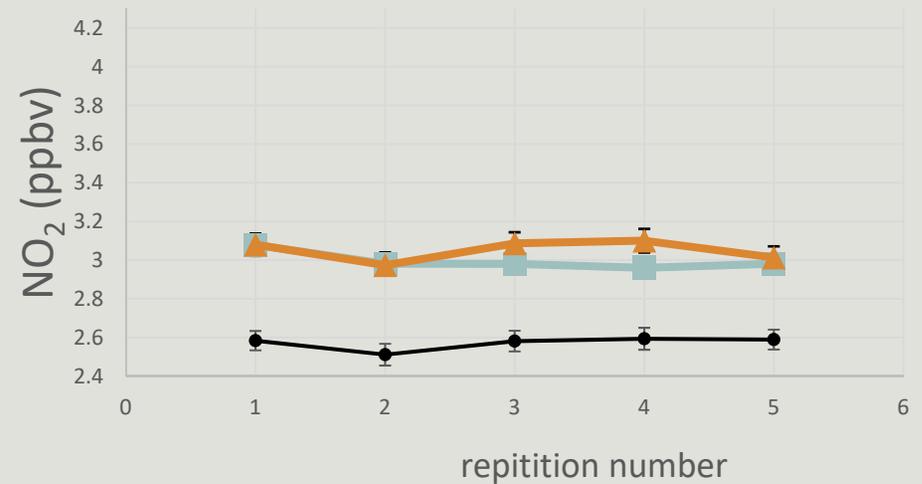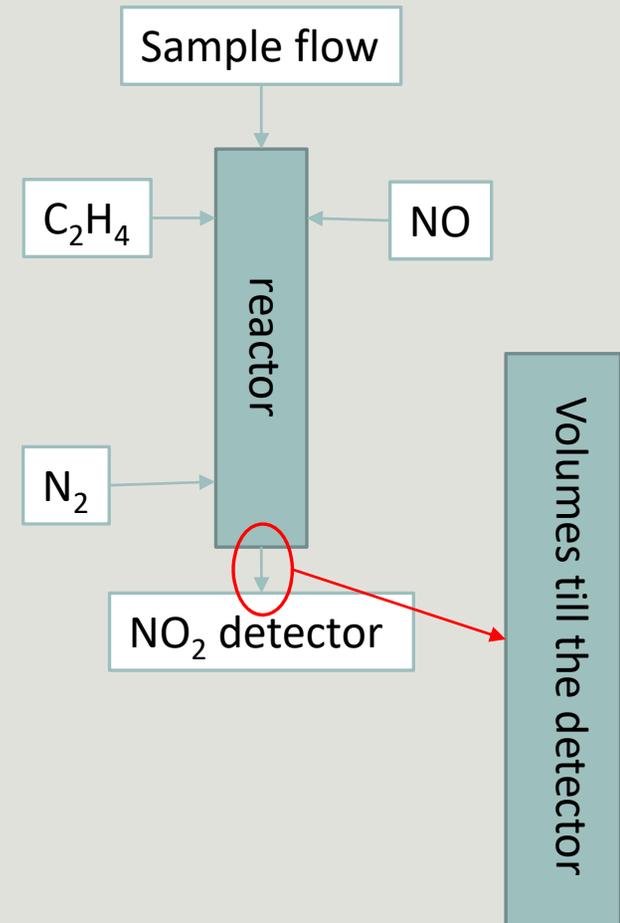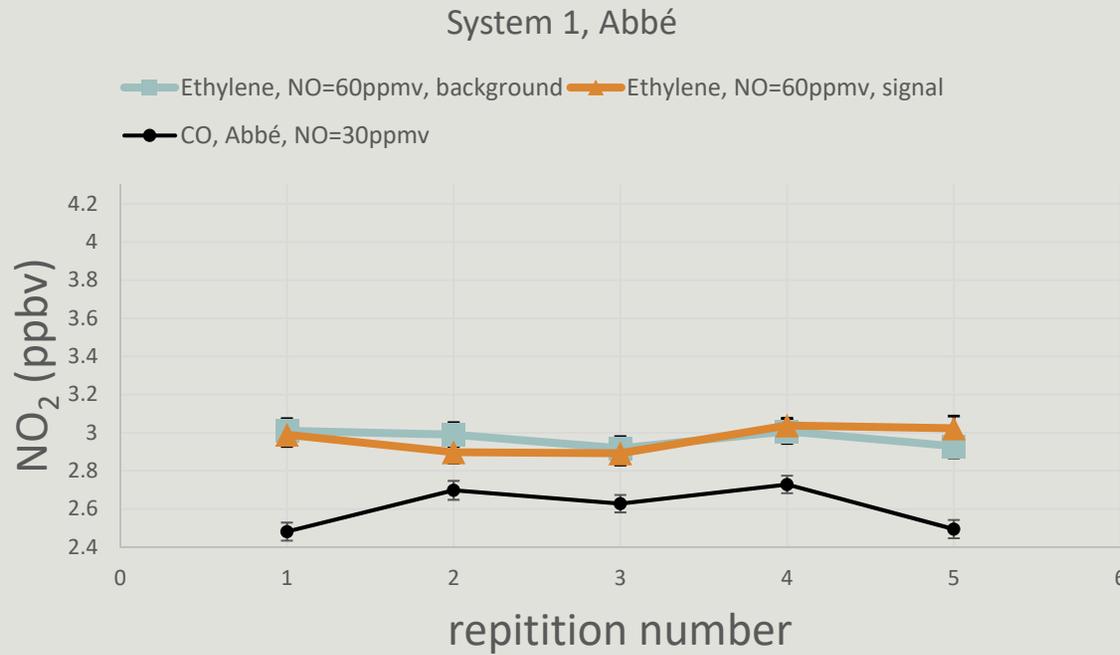# Results at 60ppmv, sys1

System 1, Abbé

— Ethylene, NO=60ppmv, background   — Ethylene, NO=60ppmv, signal

— CO, Abbé, NO=30ppmv

NO$_2$ (ppbv)

repitition number

Sample flow

C$_2$H$_4$ NO

reactor

N$_2$

NO$_2$ detector

Volumes till the detector
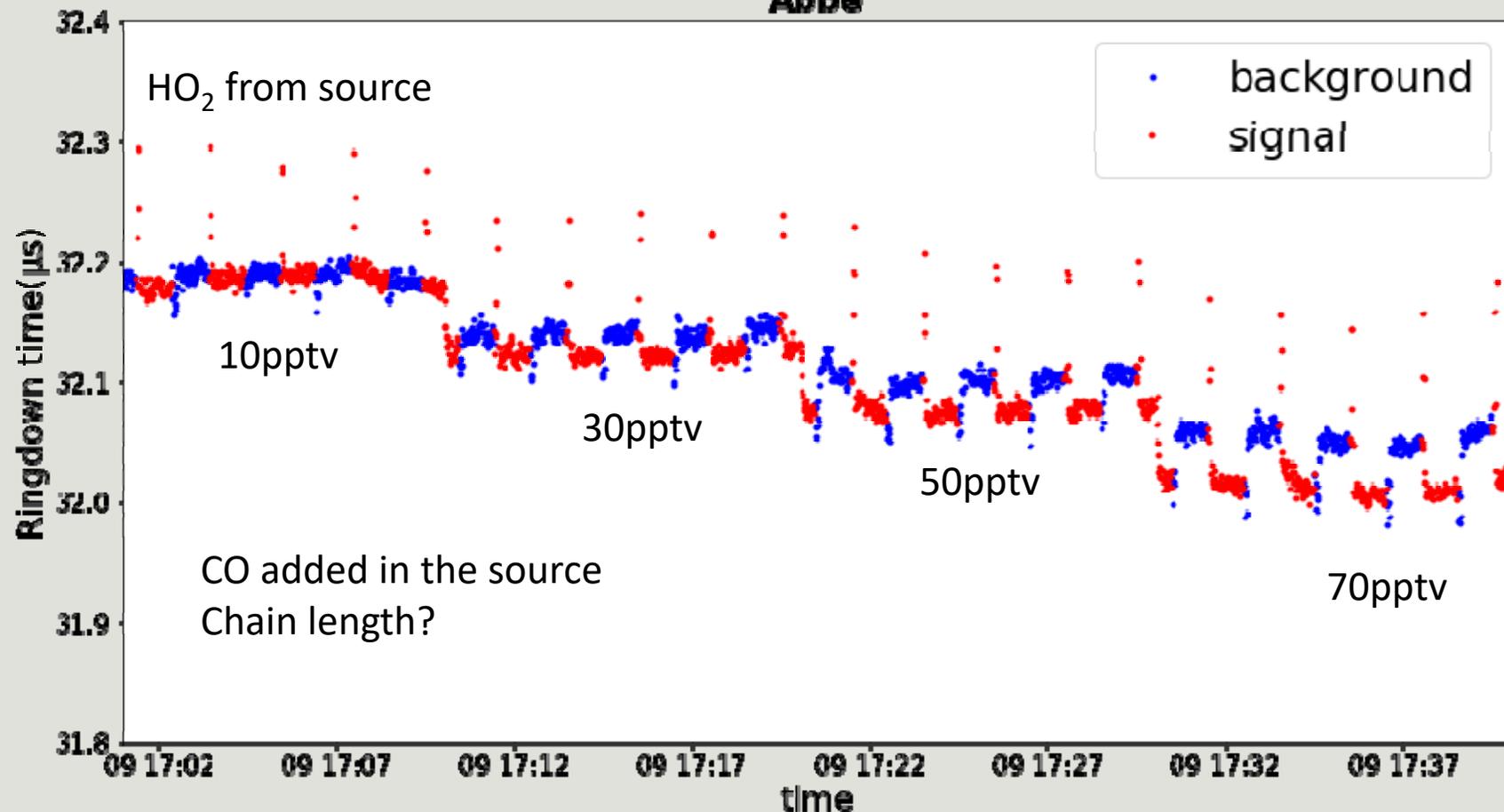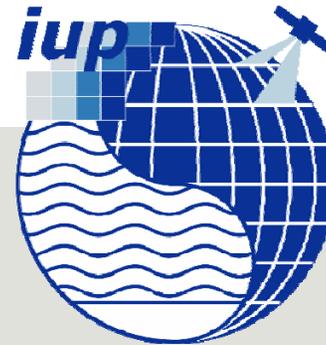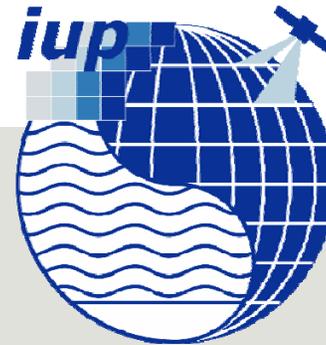
The chain length determination

Summary

- It was possible to identify interference with the improvement of the instruments at low pressures and longer reaction time;

- With higher NO the interference from C_2H_4 is decreased;

- The competing interference reactions is taken place from the inlet of the reactor till it reach the NO_2 detector.

Outlook

- Investigate and compare the chain length with CO under mixture source of radicals with C_2H_4, determine the chain length with C_2H_4 under controlled radical source;

- Further investigation at higher O_3 conditions and to simulate the OMO-EU flight conditions;

- Therefore, analyze the data from OMO-EU

Reference

Fuchs, H.: Measurement of Peroxy Radicals using Laser-Induced-Fluorescence Technique, PhD dissertation, University of Humboldt, 2006.

Horstjann, M., Andrés Hernández, M. D., Nenakhov, V., Chrobry, A., and Burrows, J.P.: Peroxy radical detection for airborne atmospheric measurements using absorption spectroscopy of NO2, Atmos. Meas. Tech., 7, 1245-1257, doi: 10.5194/amt-7-1245-2014, 2014.

Jynto, Ball-and-stick model of the hydroperoxyl radical, Wikimedia, https://commons.wikimedia.org/wiki/File:Hydroperoxyl_radical_ball.png, last access date: 14.12.2017.

Mills, Ball-and-stick model of the ethylene (ethene) molecule, C_2H_4 Wikimedia, https://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-3D-balls.png, last access date:14.12.2017.

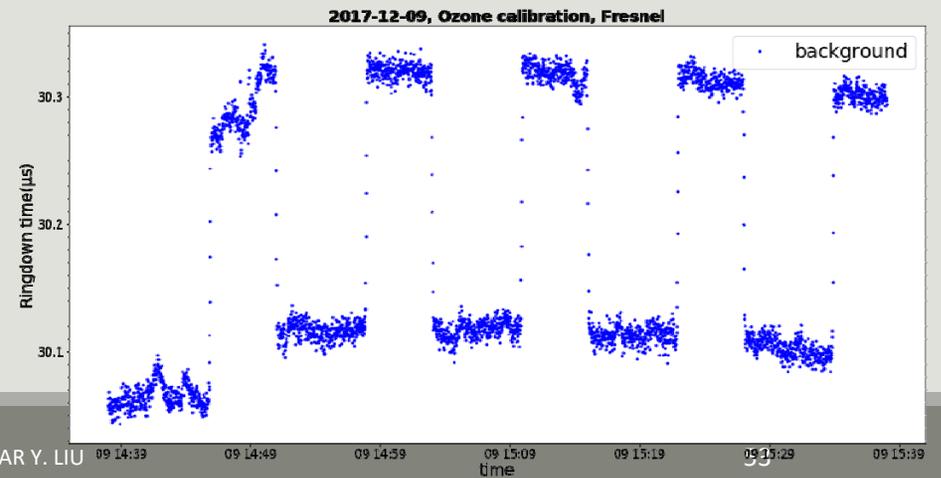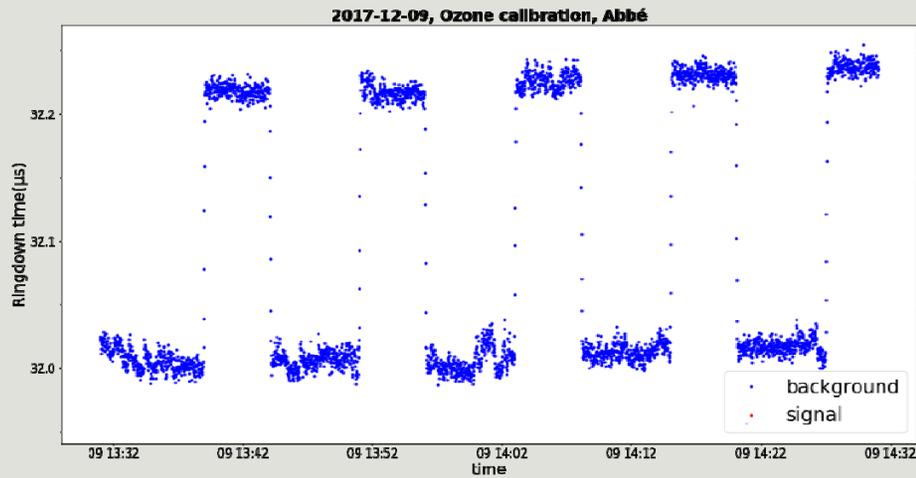VINTECH, Carbon Monoxide, the Invisible Threat, VINTECH, http://vintechnology.com/2011/02/17/carbon-monoxide-the-invisible-threat/, last access date:14.12.2017

Thank you!

2017-12-09
NO(sys1)=60ppmv
NO(sys2)=45ppmv