Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

FTIR-based spectral line data of the ν_3 band of NO_2 at 6.3 µm and multi-component impurity analysis of NO_2 reference gases within the scope of the EMPIR MetNO2 project

EGU GA 2020 web presentation – Session AS5.11 Atmospheric gases and particles: metrology, quality control and measurement comparability

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Overview

1. **Experimental setup**
2. **Result of static measurements**
3. **Results of dynamic measurements**
4. **Future work**

PTB activities in the MetNO2 project

FTIR method for impurity analysis in NO_2 standards

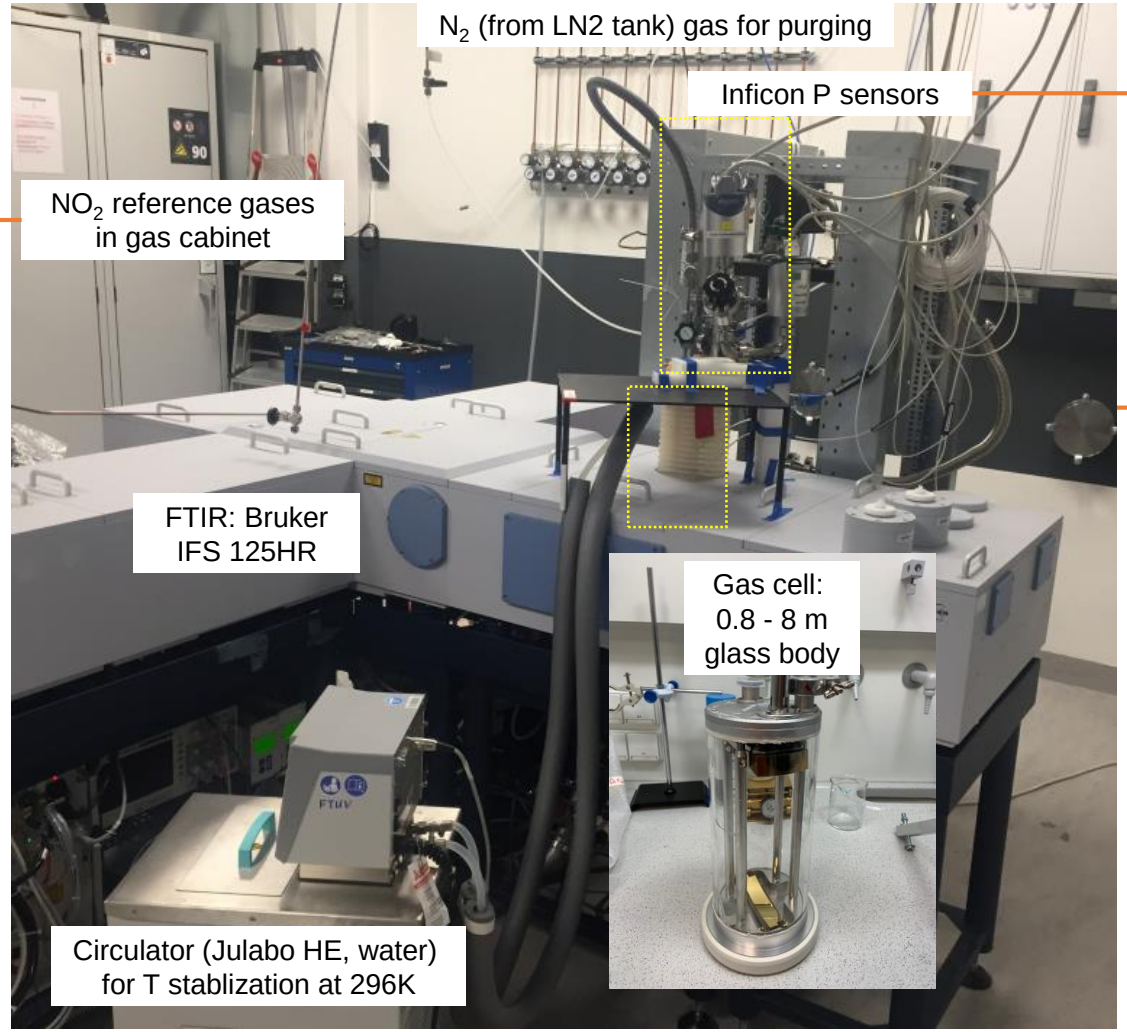
Description
Fully characterise the major impurities in the NO_2 reference gas standards (NOy compounds - especially HNO3, NO, water vapour).

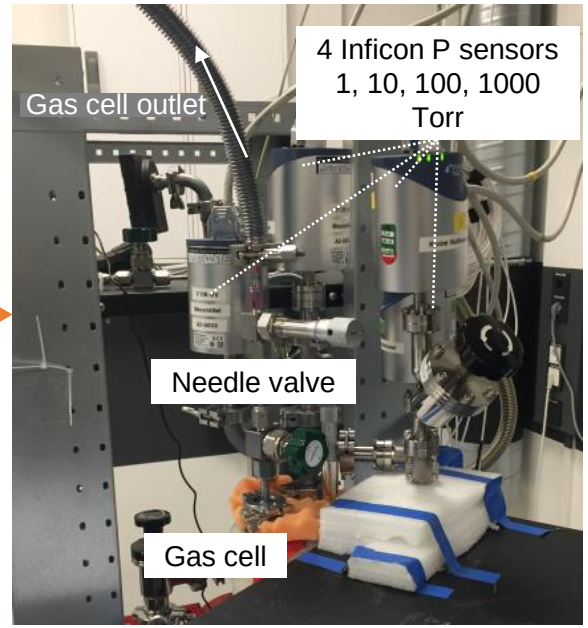
NO_2 line data measurements

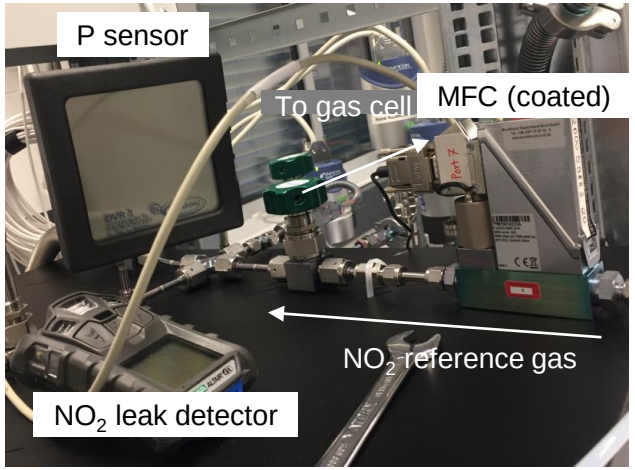
Description
Measure NO_2 line data at the wavelength range selected in A3.1.3 to support accurate NO_2 amount of substance fraction measurements and the development of spectroscopic transfer standards.

Experimental setup: Flow measurements

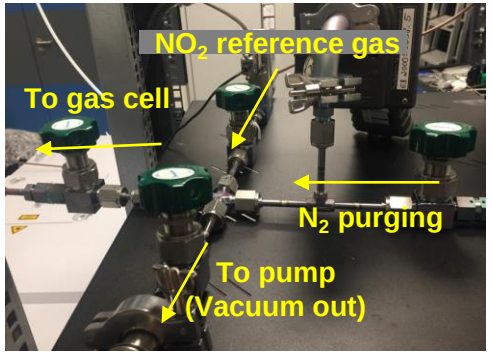
NO_2
CRM gas
Linde



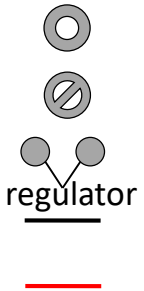




Silconert® coated components



Dynamic measurement: gas flow chart



Needle valve

On/off valve

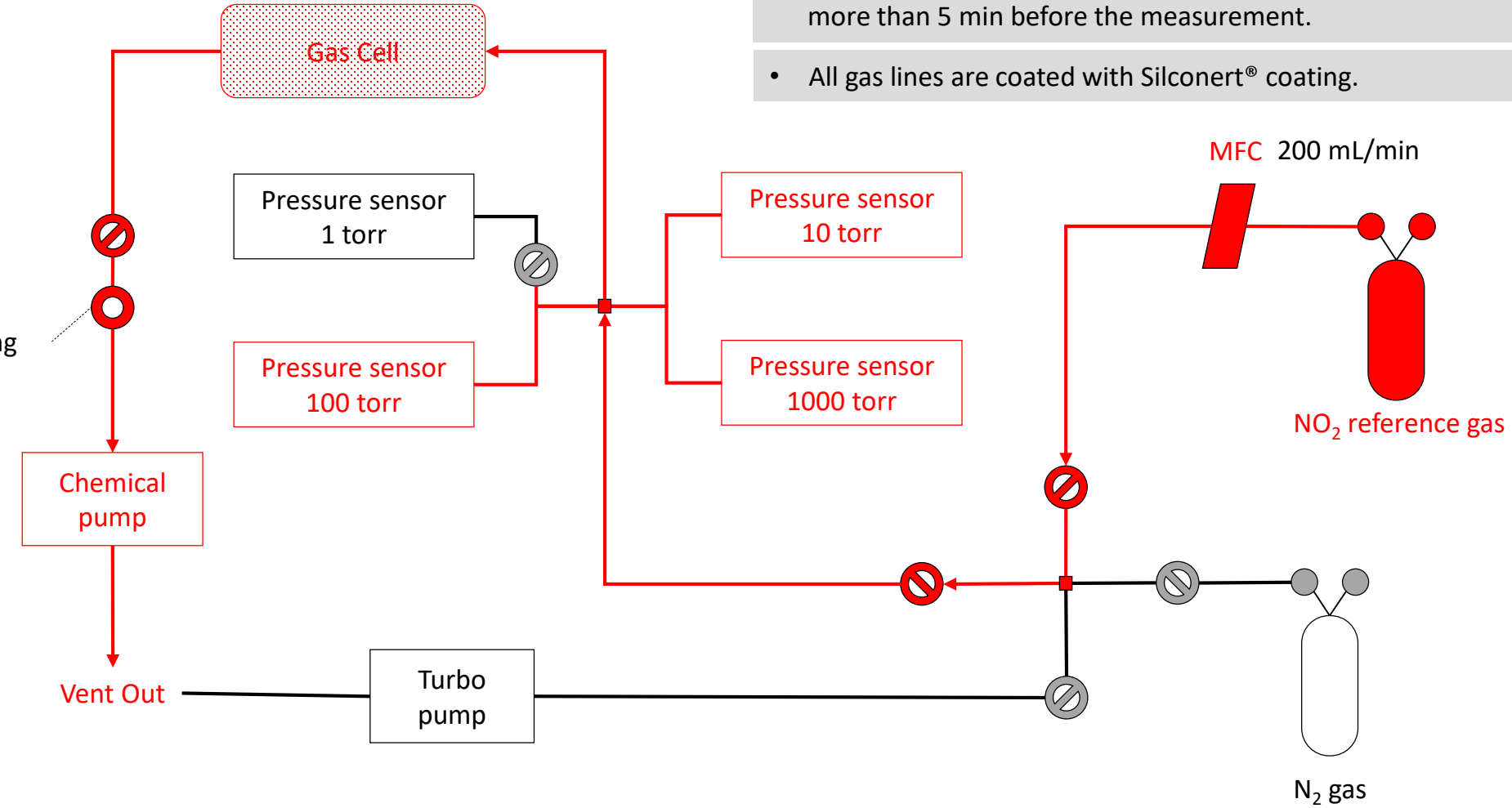
Cylinder pressure

Deactivated & Close

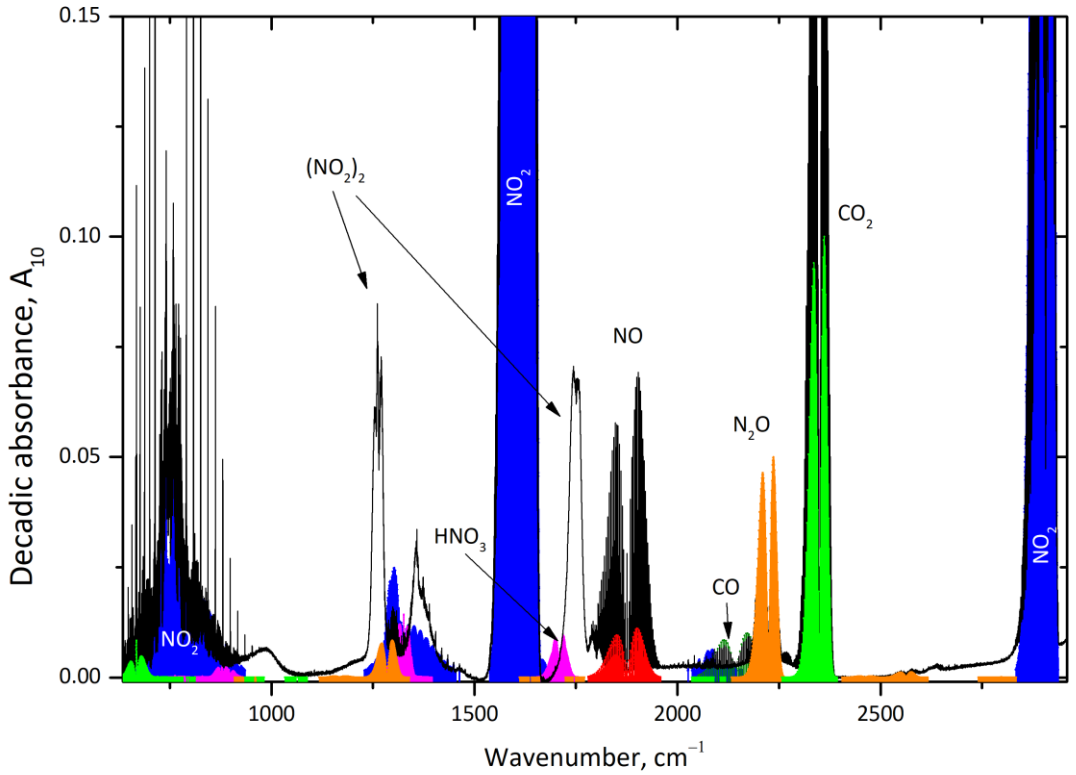
Activated & Open

Gas cell pressure was controlled precisely using a needle valve.

- To achieve fast equilibrium state, gas cell and sampling lines were flushed using NO_2 reference gas at 500 mL/min for more than 5 min before the measurement.
- All gas lines are coated with Silconert® coating.



Static measurements: impurities



Black: FTIR spectrum of 979 µmol/mol NO_2 in air at 807 mbar at 296 K in a 6.4 m absorption path after a day from initial filling.

Colour: Simulation of NO_2 and impurities using the HITRAN database.

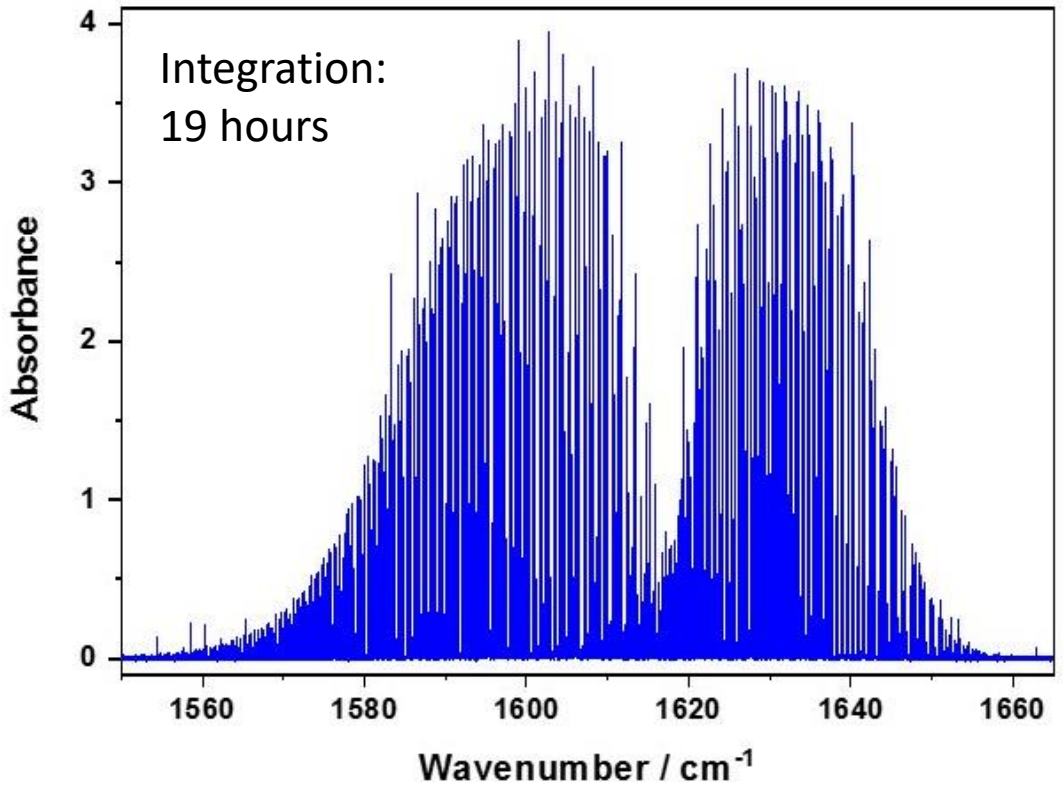
Impurities change dramatically with time in static measurements.

Impurities reconstructed to t=0

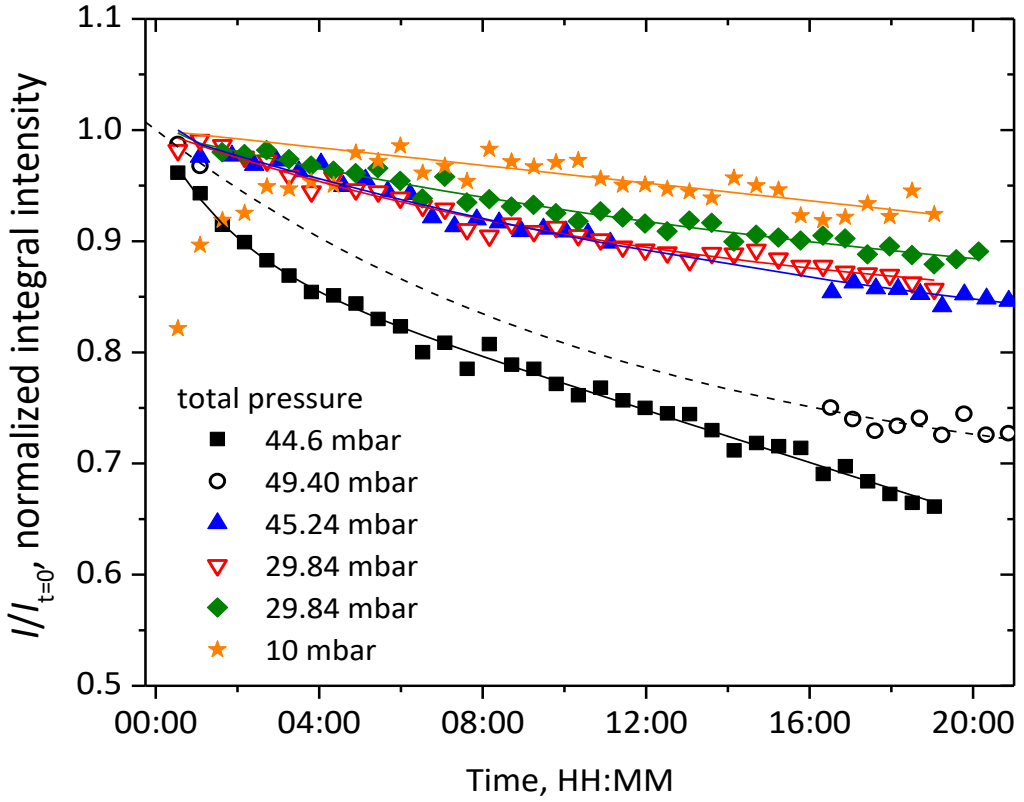
N	Molecule	Amount Fraction (µmol/mol)	Spectral band	CCQM-K74-2018* (µmol/mol)
1	NO_2	990(15); certified value from AirLiquide 979(20)	{ $\nu_1+\nu_3$, $\nu_1+2\nu_2$}, 2900 cm^{-1}	10.119(16) MY9743_7
2	NO	Not found in spectrum	Fundamental, 1880 cm^{-1}	-
3	N_2O	0.790(40)	ν_3, 2224 cm^{-1}	0.027(5) MY9743_7
4	HNO_3	0.430(80)	ν_2, 1709.5 cm^{-1}	0.108(36) Cyn. 614632 0.588(73) BIPM cyn.
5	CO_2	0.160(20)	ν_3, 2349 cm^{-1}	0.110(92) MY9743_7
6	CO	Not found in spectrum	Fundamental, 2143 cm^{-1}	0.0141(19) MY9743_7
7	H_2O	Not found in spectrum	ν_2, 1595 cm^{-1}	0.0105(87) MY9743_7
8	N_2O_5	Not found in spectrum	X-sections from HITRAN 1750 cm^{-1}	-

*Value from multiple cylinders, using GC, FTIR

Static measurements: NO_2 line intensity at 1600 cm^{-1} band



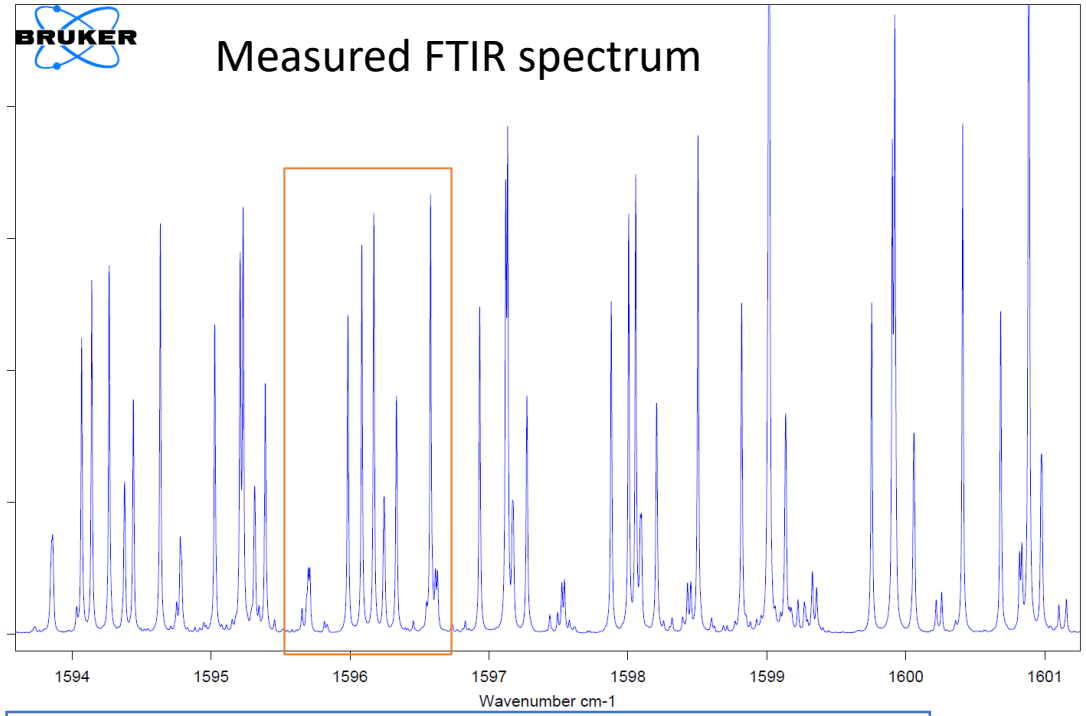
FTIR spectrum of 979 µmol/mol NO_2 in air.

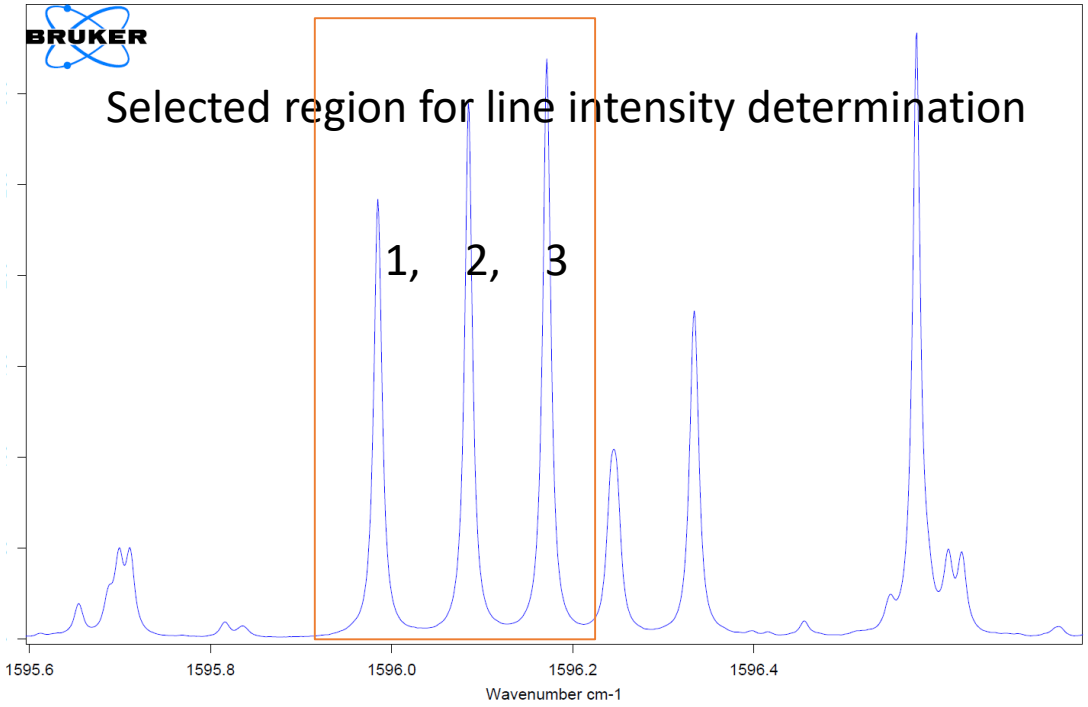


Relative changes of the **integral band intensity** as a function of time.

Intensity decrease dramatically with time in an unpredictable way.
Static measurement is not suitable for accurate line intensity determination.

Dynamic measurements: spectra

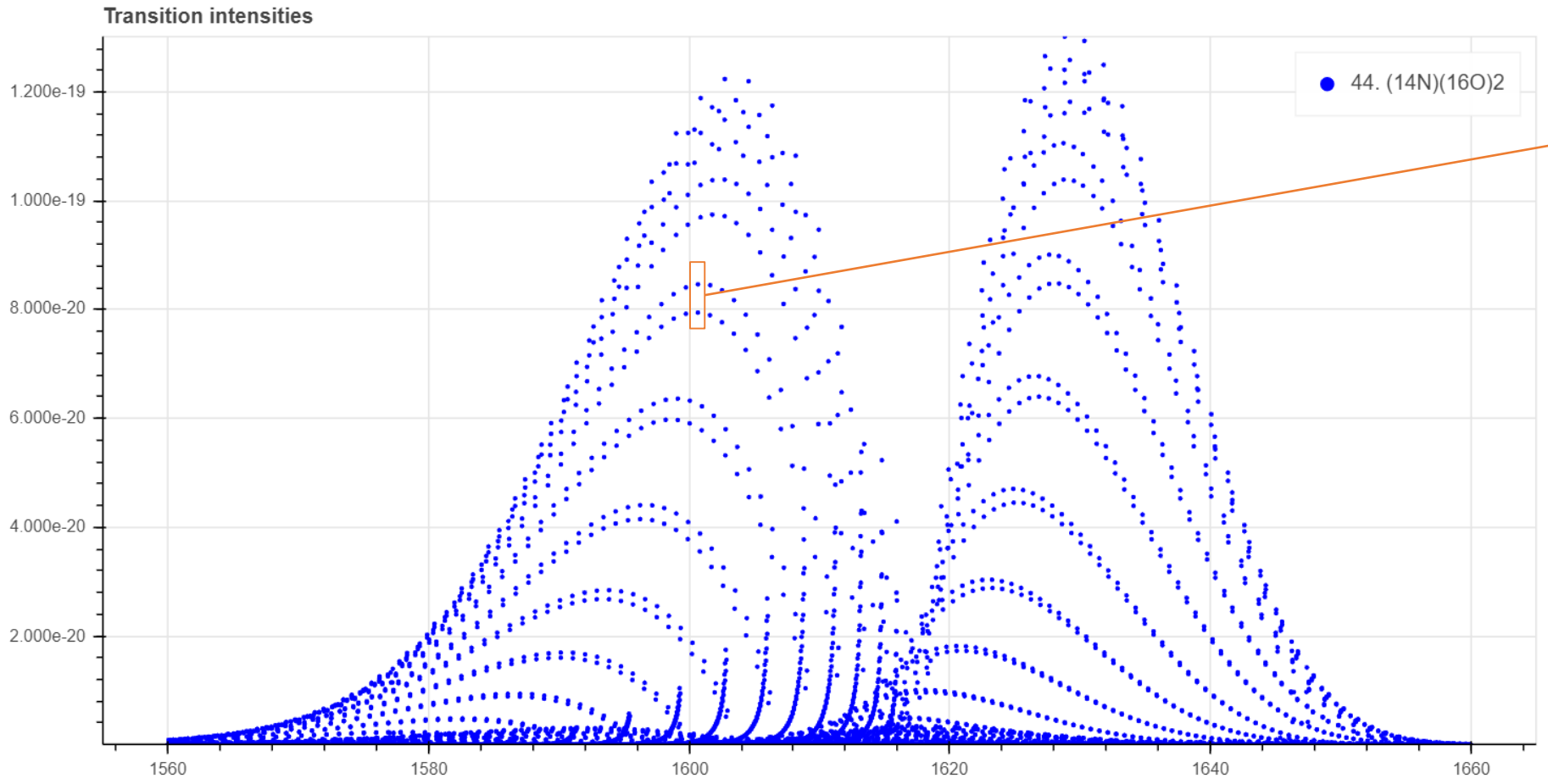




Spectrometer:	Bruker IFS125HR
Resolution:	0.005 cm^{-1}
SNR:	>1000
Source:	Globar
Detector:	MCT
Band pass filter	400 – 1880 cm^{-1}
Path length:	0.85 m, 1.66 m, 4.89 m

Flow rate:	200 sccm
Integration time:	9 hours
Signal stability:	no change within 9h
Pressure uncertainty:	0.3% (k=2)
Path uncertainty:	0.08% to 0.25%
T inhomogeneity:	0.15 K

The HITRAN database: NO_2



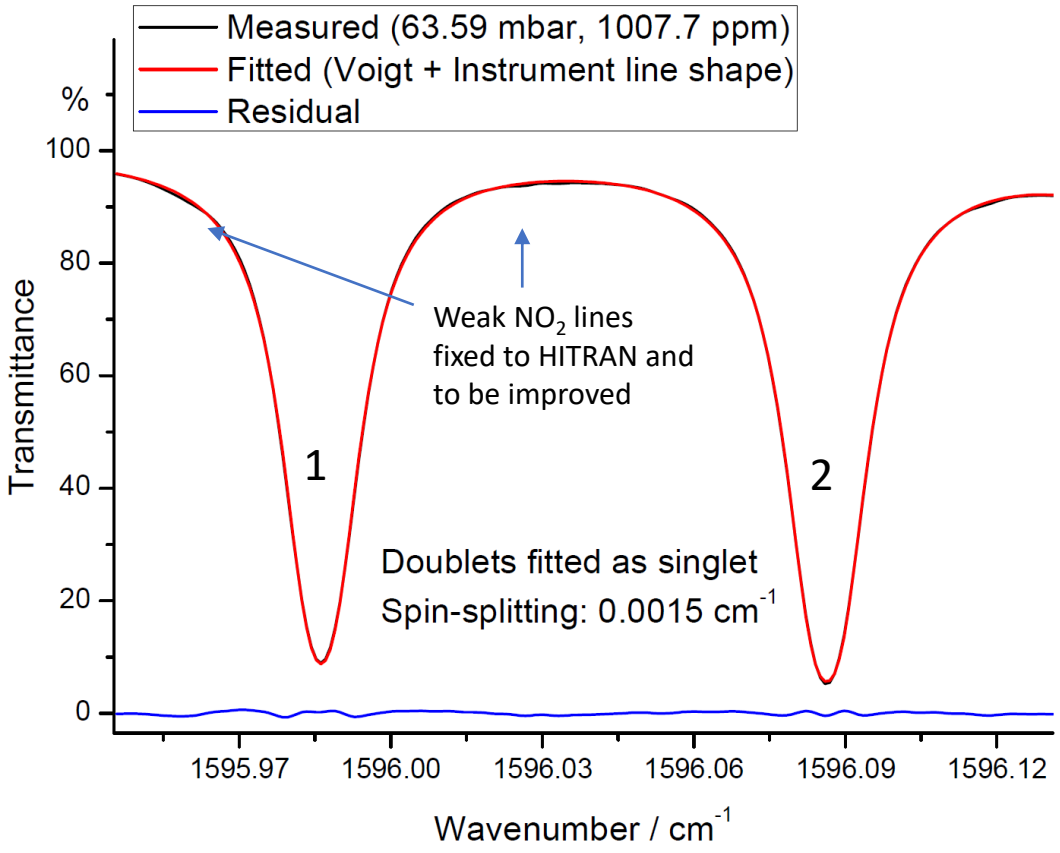
Doublets with spin-splitting typically around 0.002 cm^{-1}.

NO_2 line intensity in HITRAN is unchanged since HITRAN96, which is based on Ref. 2.

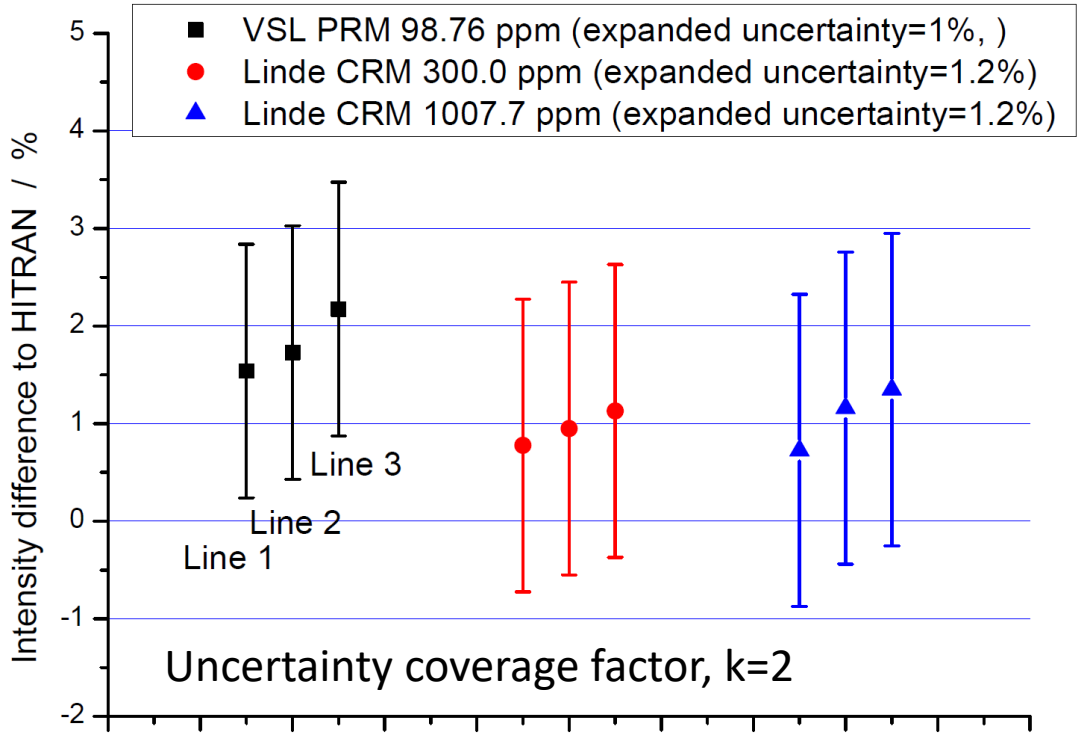
Intensity uncertainty given by HITRAN 2-5%.

[2] A. Perrin et al. Journal of Molecular Spectroscopy 154, 391-406 (1992).

Dynamic measurements: NO_2 line intensity at 1600 cm^{-1} band



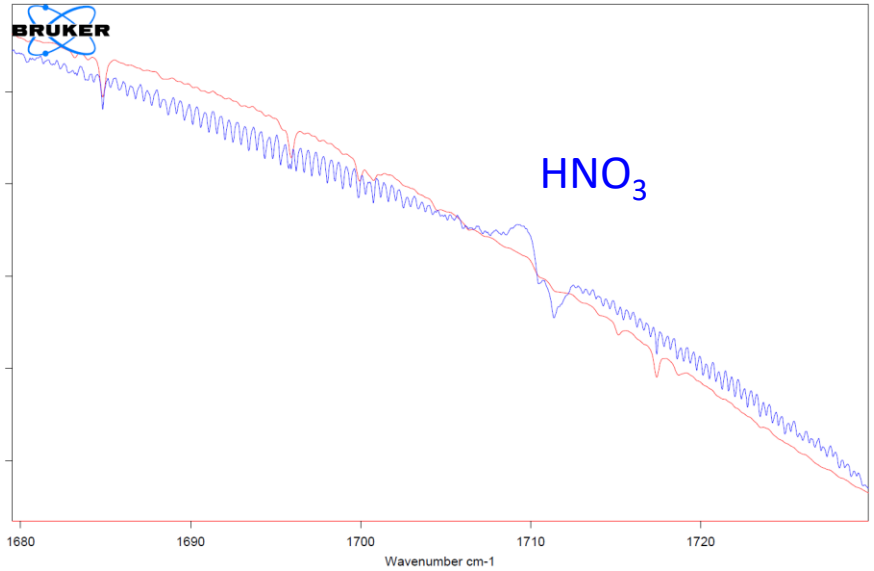
Example Voigt⊗ILS fit using PTB program



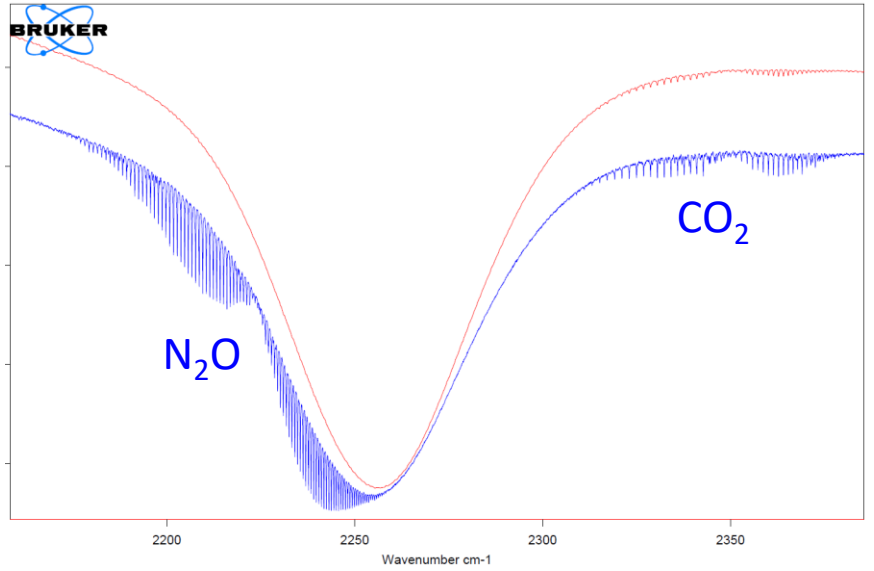
Major uncertainty components:
Amount fraction: 1%, P: 0.3%, L: 0.2%, ILS: 0.1%, Area: 0.1%
Note: HITRAN uncertainty 2-5%.

Dynamic measurements: Impurities and dimer

Two gases: Red: 98.76 ppm VSL PRM, Blue: 1007.7ppm Linde CRM



4.89 m path length
994 mbar
250 scans
Resolution: 0.2 cm^{-1}
Flow rate: 200 sccm



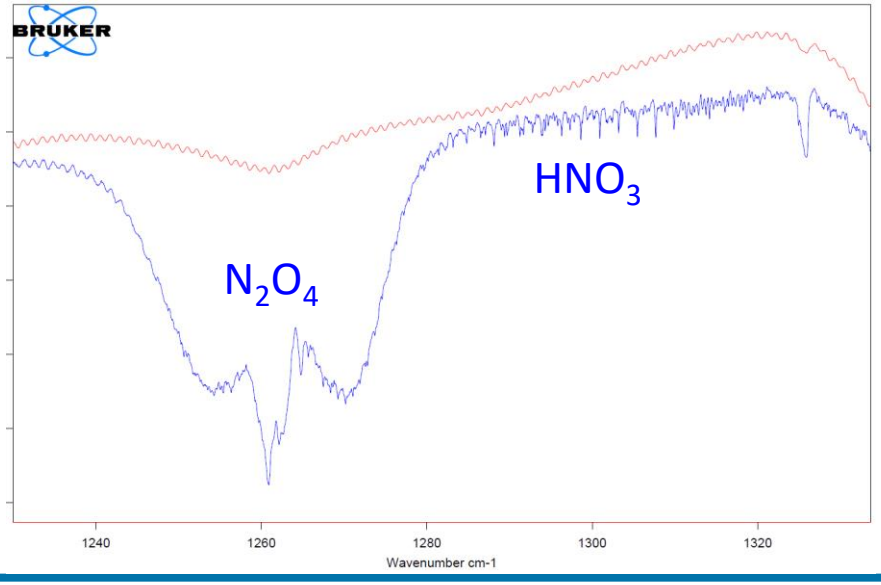
Ongoing work: quantitative results come later

" 100" ppm VSL PRM:

No sign of N_2O and CO; H_2O band; HNO_3 band, trace amount of CO_2

- "1000" ppm Linde CRM

Clear N_2O band at 2225 cm^{-1}, No H_2O in sample (but inside spectrometer), clear HNO_3 band at 1710 cm^{-1} and 1325 cm^{-1}, trace amount of CO_2



Future work and acknowledgement

Future work

- To improve accuracy of the NO_2 line intensities in the v3 band.
- To quantify impurity in the 1 ppm NPL PRM, using the 40 m silconert coated ICL multipass cell.
- To repeat measurements to check the stability of cylinder, re-assuring line intensity accuracy.

Acknowledgement

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EMPIR EURAMET

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