KIT, Karlsruhe, 06-06-2019| Workshop: Gas cleaning, experiences, new developments, analytics and diagnostics

On line UV/IR measurements of tars and other gas compounds

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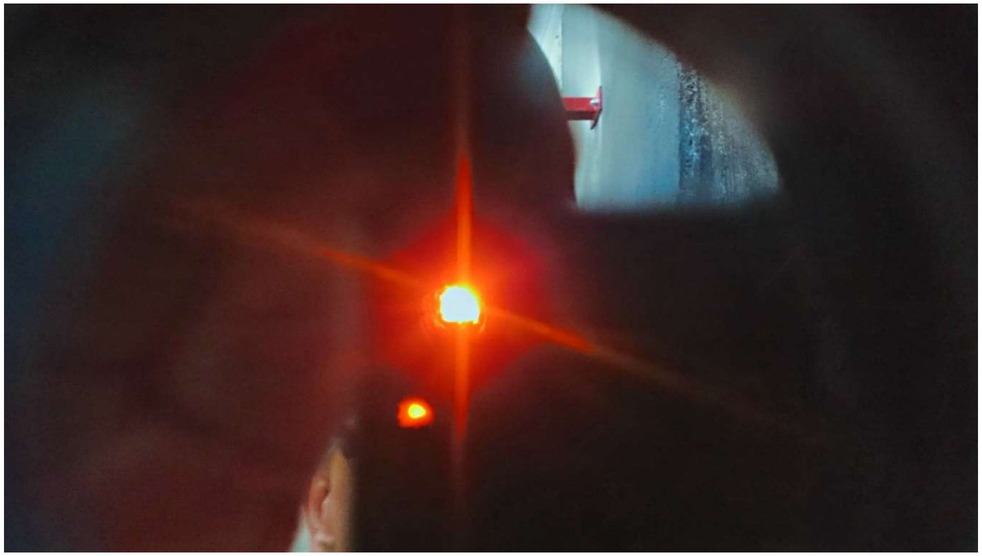
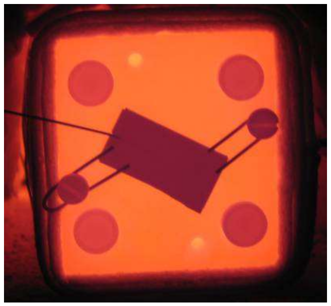


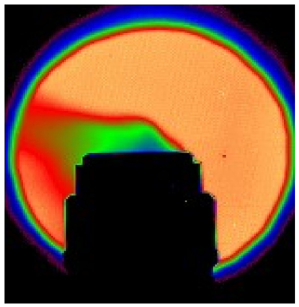
DTU Chemical Engineering | Optical Diagnostics Group

Activities



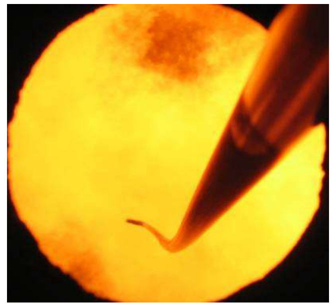
Emission from surfaces

Heat transfer, energy balance in solids



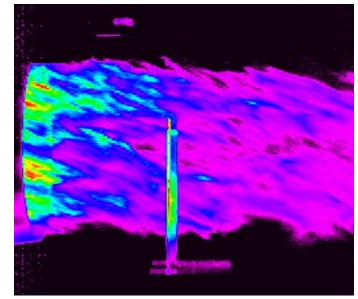
Leak valve bottle

IR gas/particles fast imaging with LED



Extractive/*in situ*/*on line*

Gas composition, (non-contact) gas/particle temperature, RHT modeling in gases



Exhaust aircraft engine

Mixing, flows and properties

At one glance:

- Two men show: Alexander Fateev and Sønnik Clausen, both Senior Scientists (Risø National Lab, then DTU)
- A track record in harsh industrial measurements: power plants, waste incinerators, ship/aircraft engines
- A track record in collaboration with industry in DK, SE, DE (energy, bio-medical, environment)
- Participation in various national and EU-funded projects
- Instrumentation: gas cells (<1500C), spectrometers: from 120 nm (far UV) to 20 cm^{-1} (far IR)
- Spectroscopic (HITRAN/HITEMP/ExoMol) databases validation/development/spectra modeling
- Sensor development (NG quality (C1-C5), wood stoves (soot, PAH), fast particle imaging with LED's)

Outline

Not fancy at all: broadband Optical Absorption Spectroscopy/DOAS

- ❑ Choice of spectral range: IR vs UV/far-UV
- ❑ Re-born of oldies: VUV as far-UV without vacuum: a practical approach

In the lab:

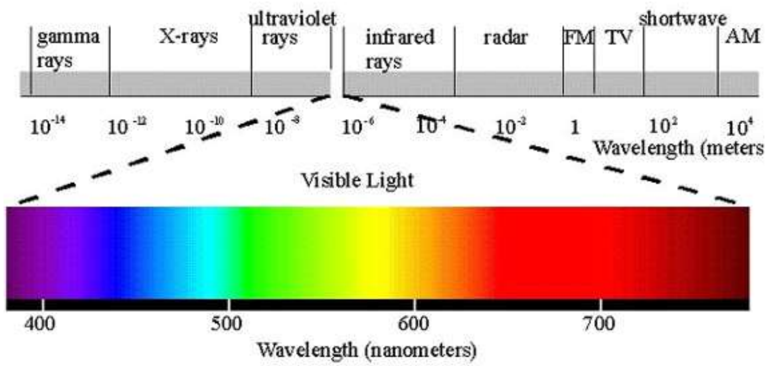
- ❑ gas cells for wide-range of P/T's: 20-1500C/1-200bar
- ❑ temperature-dependent Absorption Cross-Sections Databases or line-lists databases

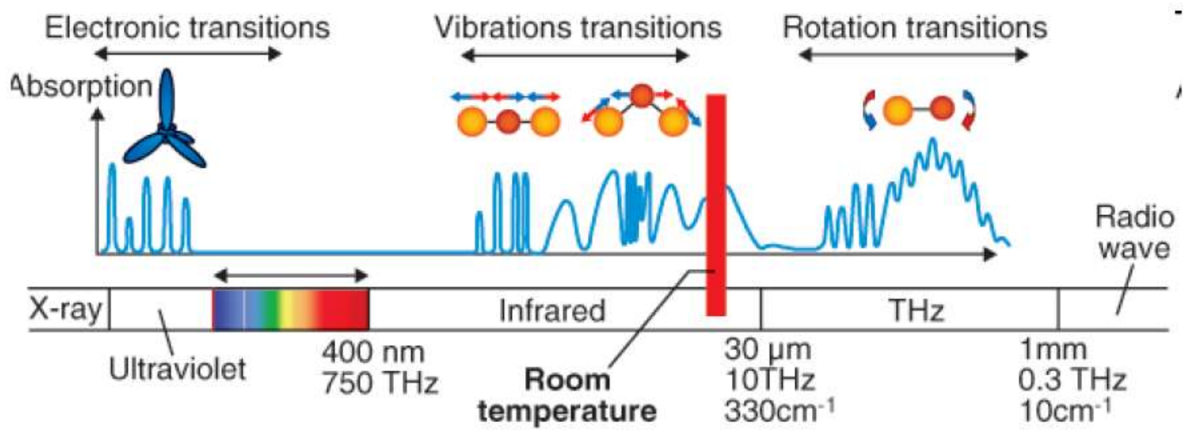
In the field:

- ❑ From 100kW to 6MW gasification
- ❑ Measurements in stack gases (combustion)

Conclusions

Choice of spectral range: depends on…





IR (MIR: 600-8000cm-1):

- Classic tool for H2O, CO2 and HxCy+
- Databases available (HITRAN, PNNL)
- in situ or on-line measurements

UV (200nm<λ):

- superb sensitivity for (complex) organics
- (very) strong light absorption
- in situ or on-line measurements

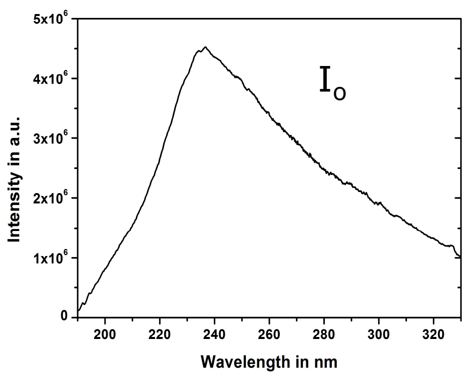
Special for gasification: no O_2

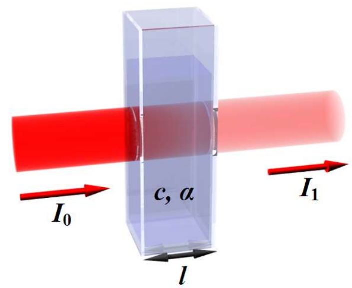
- ❑ possibility to go further down (120nm<λ): far-UV
- ❑ superb sensitivity for major/minor gas components
- ❑ compact system
- ❑ in situ or on-line measurements

Optical Absorption Spectroscopy/DOAS

Spectrum w/o absorption

1





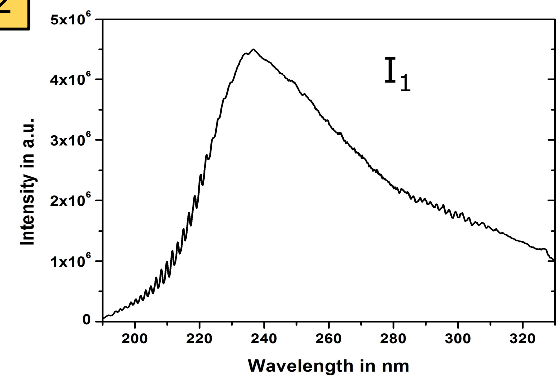
Lambert Beer Law:

$$\frac{I_1}{I_0} = e^{-\alpha \cdot l} = e^{-\sigma \cdot N \cdot l}$$

$$\ln \frac{I_0}{I_1} = \sigma \cdot N \cdot l$$

Spectrum with absorption

2



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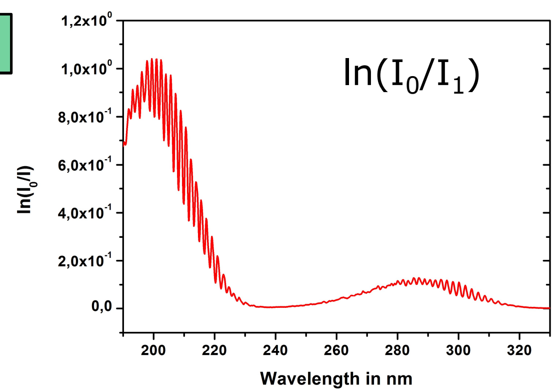
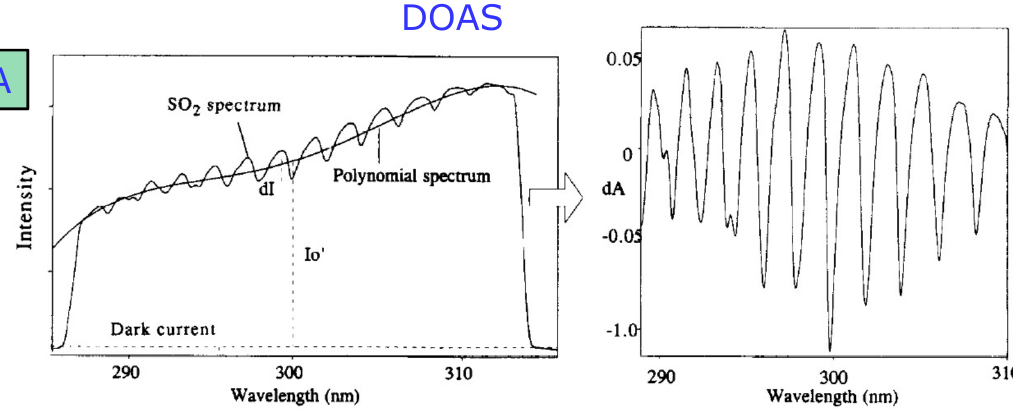


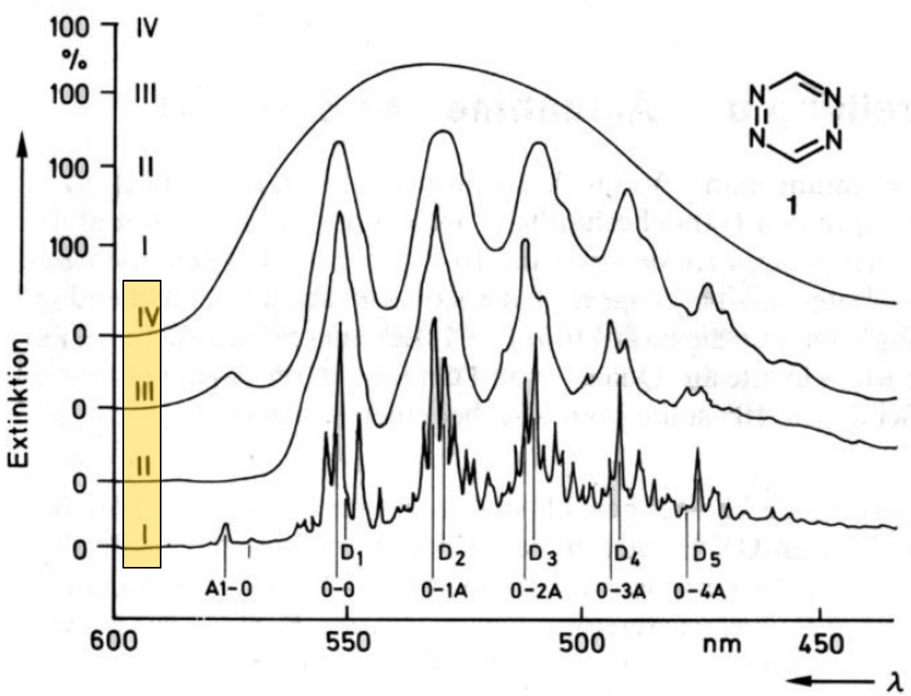
DOAS

2A



Choice of medium

Example: 1,2,4,5-tetrazine



- I Gas phase, room temperature
- II In isopentane-methylcyclohexane matrix, 77K
- III In cyclohexane, room temperature
- IV In water, room temperature

- ❑ Molecules have their own “fingerprints” in IR/UV
- ❑ Vibrational fine structure disappears in solutions but not in the gas phase
- ❑ Fine structure degrades with temperature

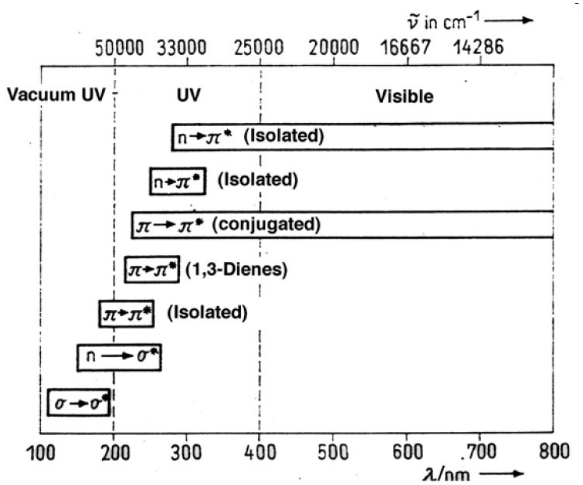
Re-born of oldies: VUV as far-UV

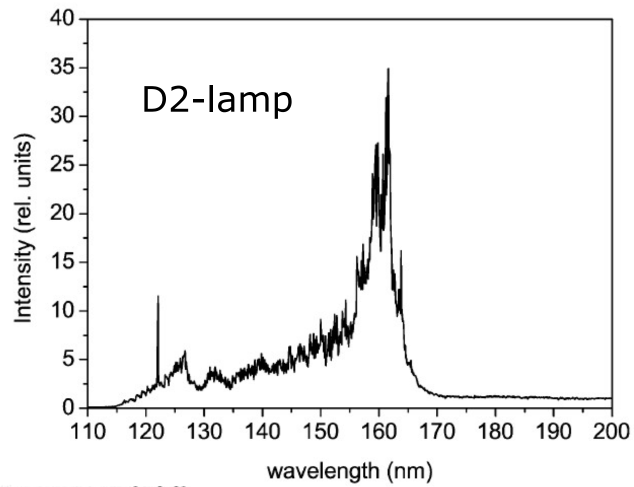
- Classical VUV definition: λ < 200 nm (when O2 absorption matters)
  - 4 main "-":
    - forced use of HV-pump
    - light source availability (synchrotron the best)
    - spectrometer/optics performance drop at λ < 110 nm
    - windowless system design (i.e. coupled system)

- Far UV definition: 110 nm < λ (defined by MgF2 cut off)
  - 4 main "+":
    - MgF2: good robust optical material (H2O/T) (i.e. de-coupled system)
    - No need for use HV-pumps: N2 or Ar purge is enough
    - VUV D2-lamp: affordable light-source with good *costs:performance* ratio
    - transportable system (flight-case scenario) for lab/field measurements

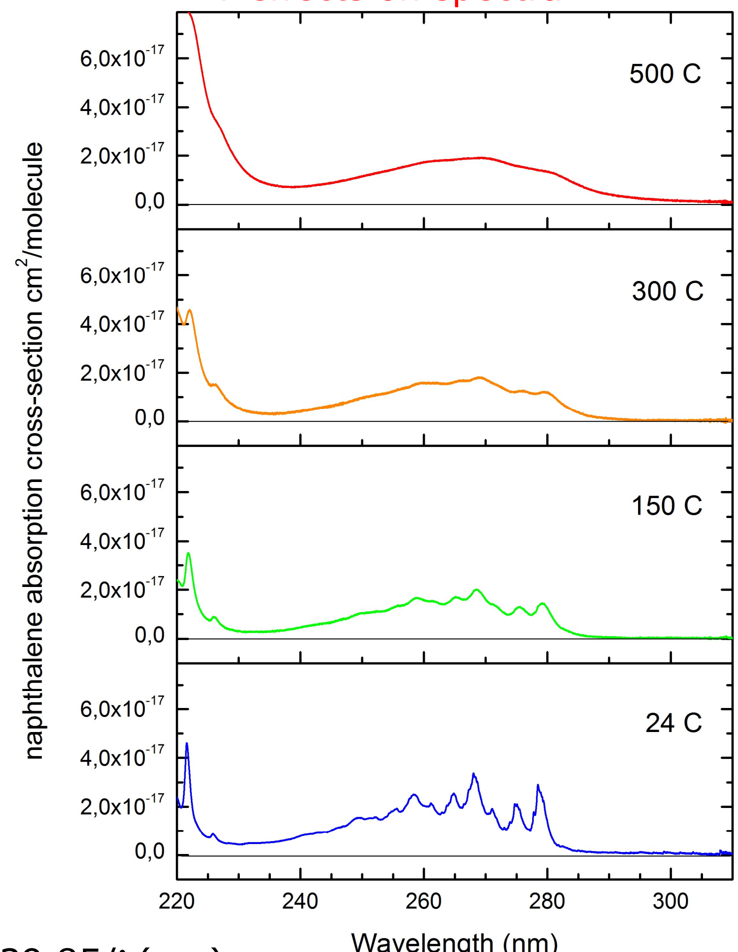
- Rydberg state spectroscopy below ionization limit
  - large absorption cs (i.e. short absorption pathlengths)

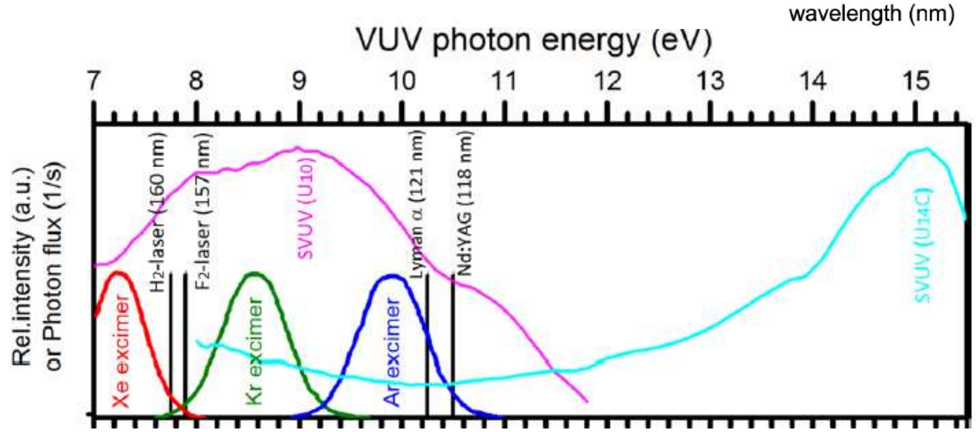
Re-born of oldies: VUV as far-UV in pictures





T-effects on spectra



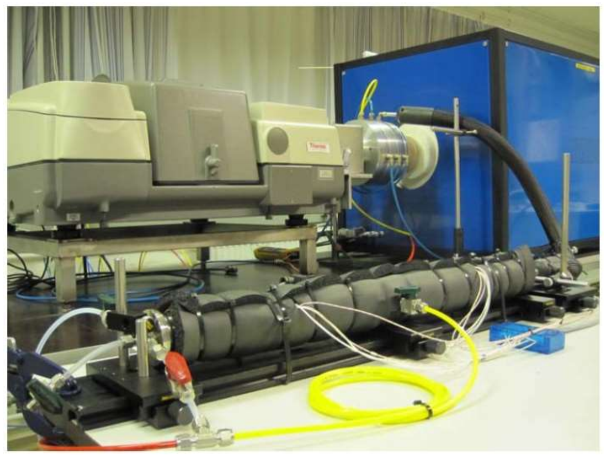


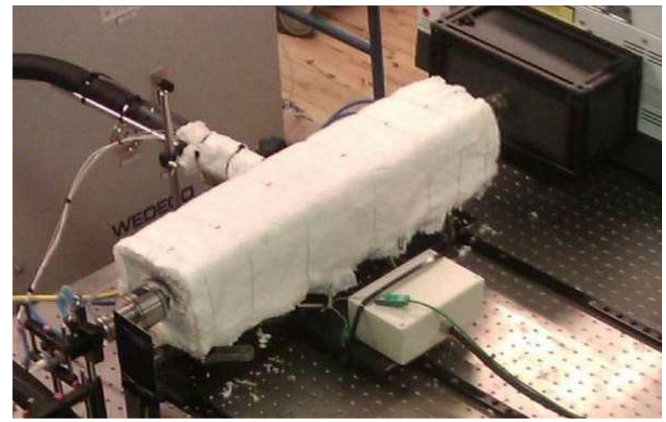
177 nm

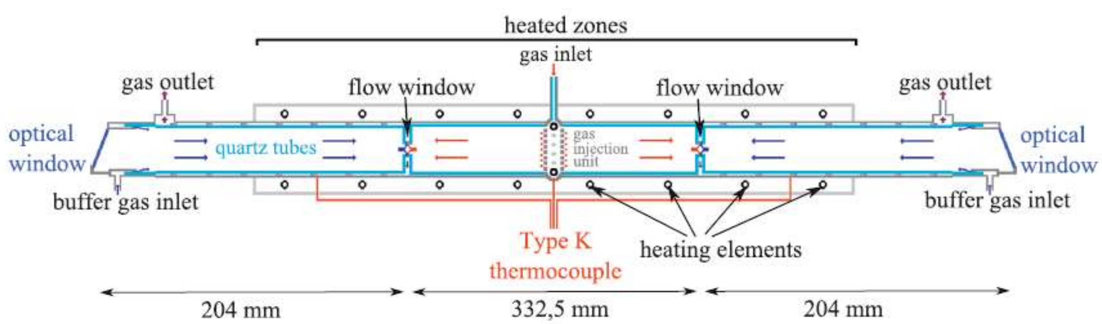
$E(eV)=1239.85/\lambda(nm)$

Experimental facilities

- ✓ High Temperature Gas Cell (max 1600C): CO, O2, NO, CO2, H2O, CH4,…
- ✓ Quartz Gas Cell for reactive gases (max 525C): NH3, SO3, SO2, PAH (phenol, naphthalene),…
- ✓ 0.39 cm, 5.1 cm (max 300C), 50cm, 1m, 5.7 m (max 200C) gas cells for lab/field measurements





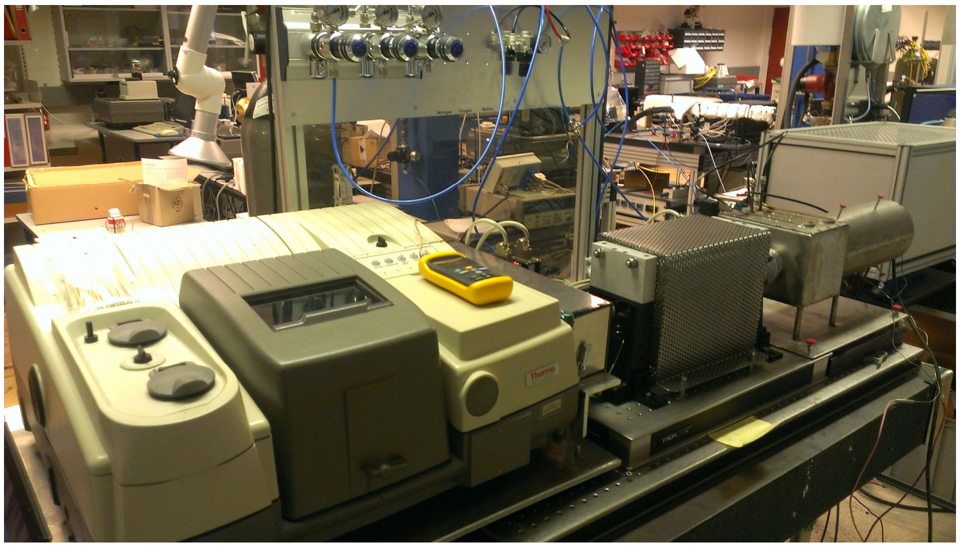


Replaceable outer windows:

- ❑ no reactive gas contact with windows
- ❑ **far UV to μw coverage**

Experimental facilities: special case

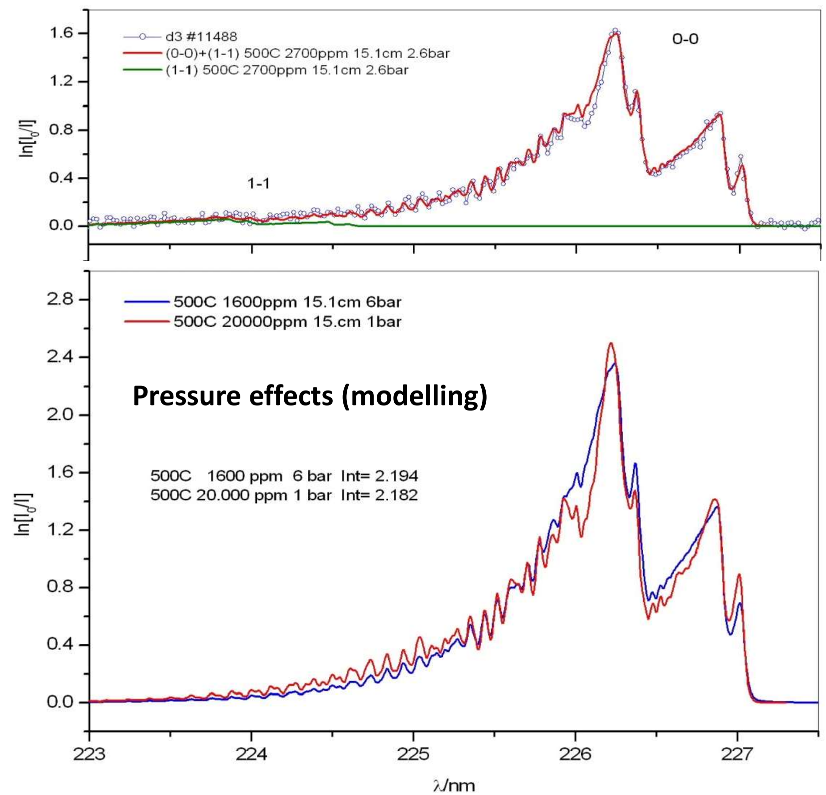
- high-pressure (up to 1000°C)/high pressure (up to 200 bar) flow gas cell



- ❑ sapphire windows:
- ❑ far UV to mid IR: CO_2, CO, O_2, NO, H_2O

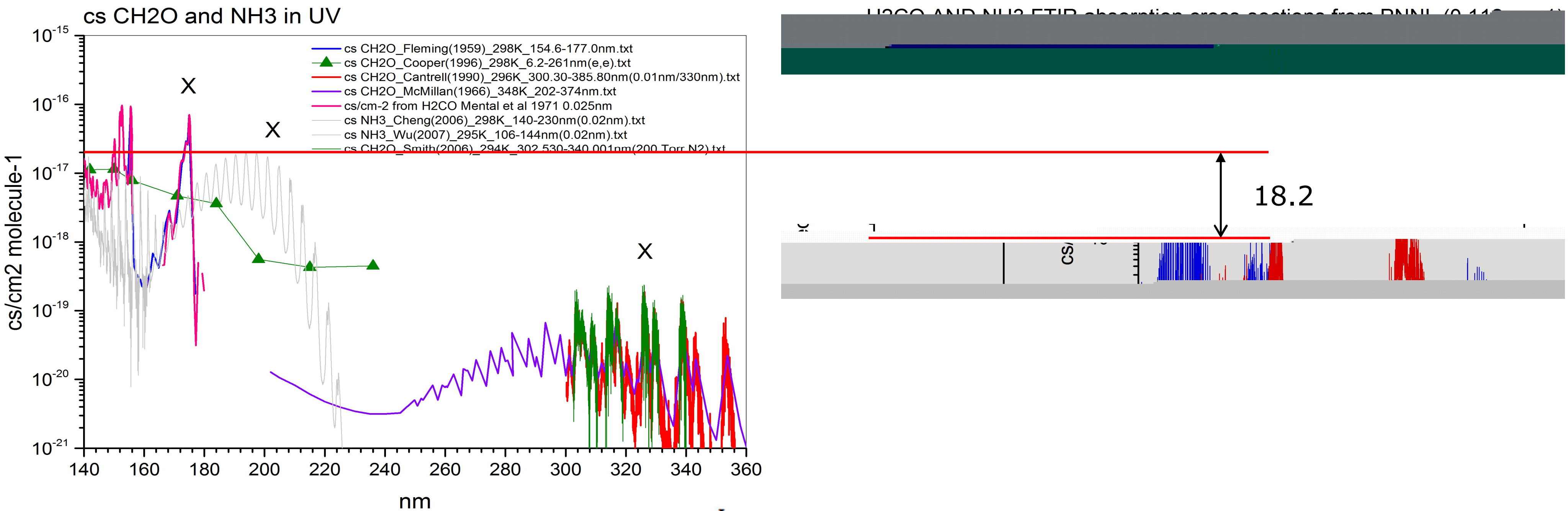
UV NO band:

fast *in situ* measurements (blue) vs. modelling (red)



Spectroscopy of NH3 and H2CO

What shall I choose: far UV, UV or IR?



$$\ln\frac{I_0}{I_1} = \sigma \cdot N \cdot l$$

l in cm/mm or meters?

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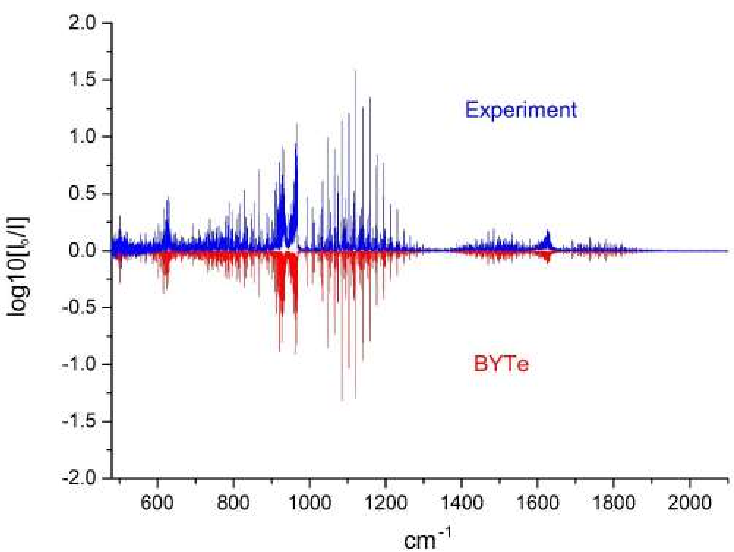
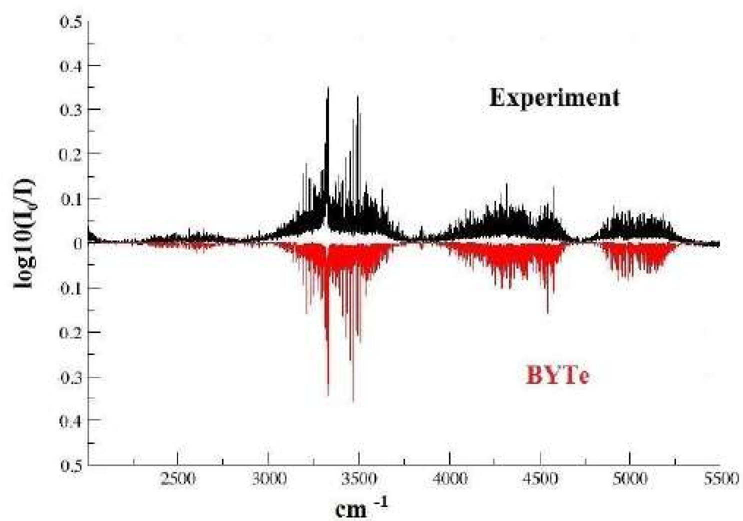
IR spectroscopy of NH3

500 - 2100 cm^{-1} 500^0C NH_3 = 1%

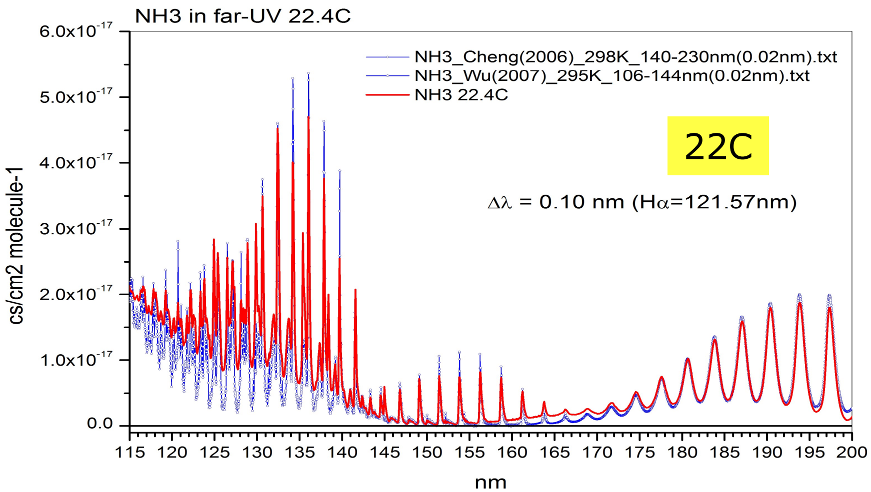


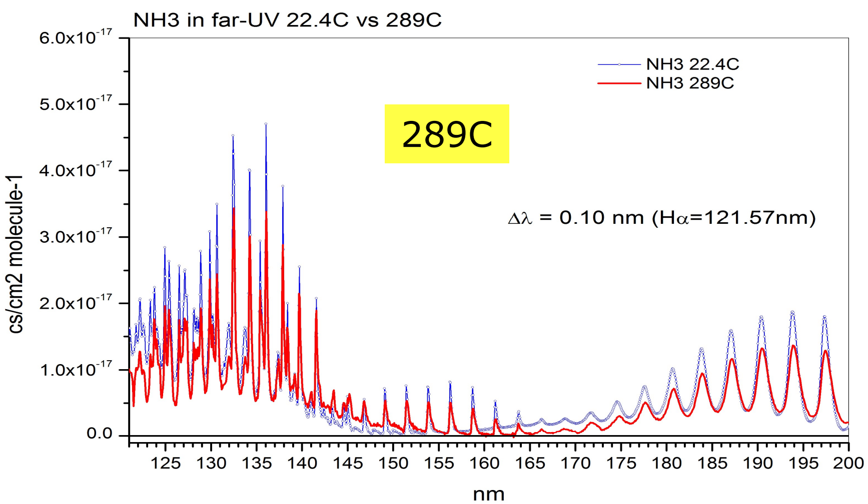
2100 - 5500 cm^{-1} 1027^0C NH_3 = 10%

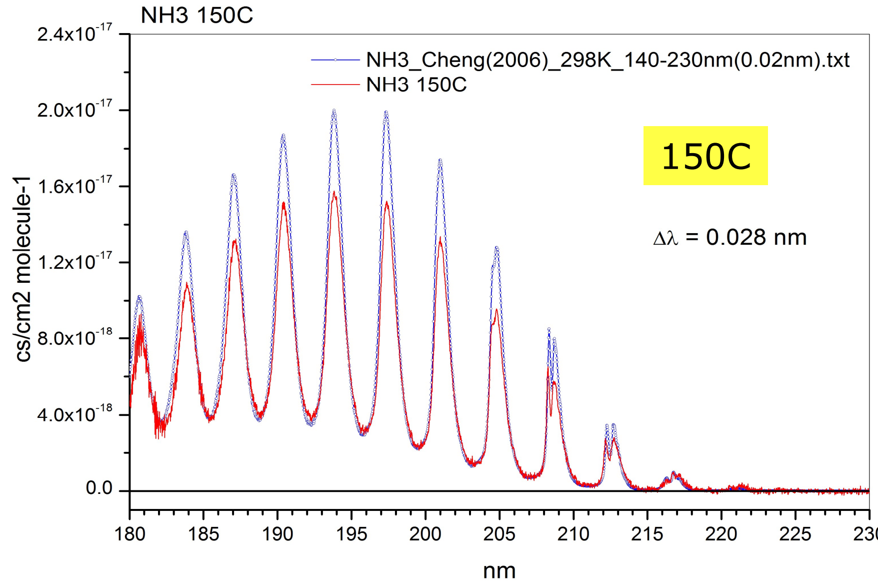


- ❑ Updated NH3 line-list database available at ExoMol web site
- ❑ Can be used for NH3 spectra modeling up to 1500C

Far-UV spectroscopy of NH3







- Difficult molecule to deal with
- Most reliable data: 180 < λ

NH3 spectra analysis:

Wo et al (2007): 110-144 m: (synchrotron)

Cheng et al (2006): 140-220 nm (synchrotron)

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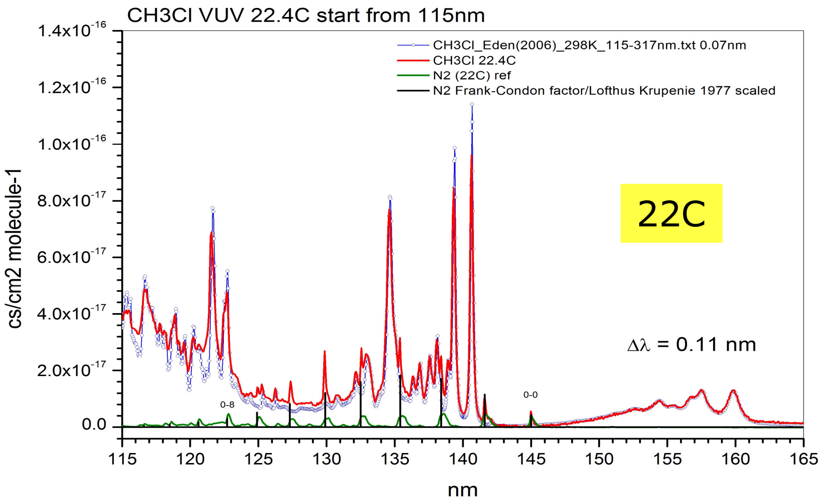
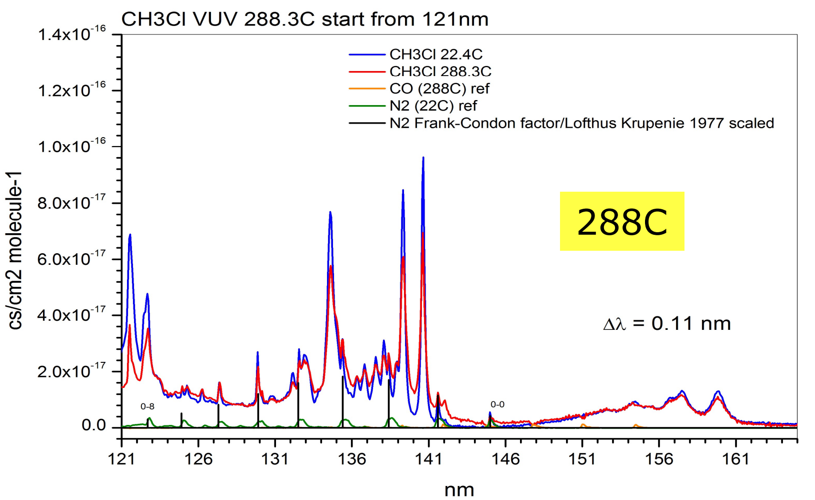
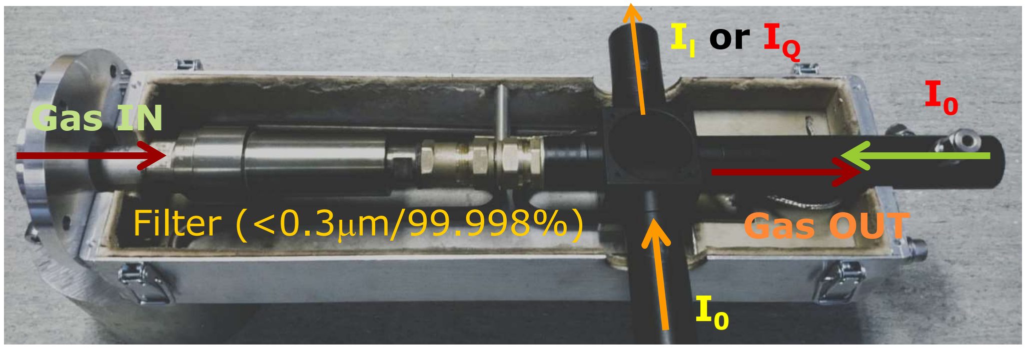
Far-UV spectroscopy of CH3Cl and C2H4

DTU







4

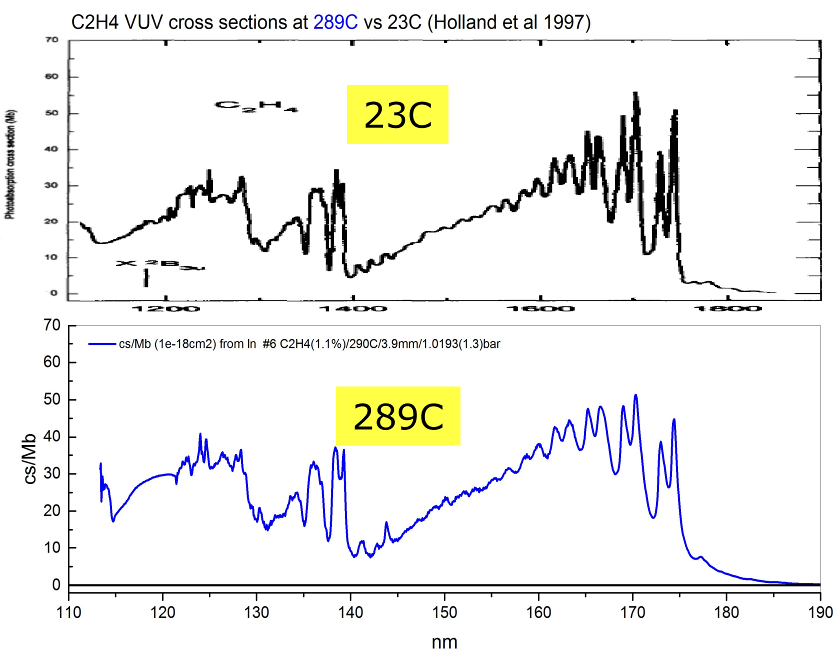
Measurements on 0.39 cm gas cell (up to 300C)

(λ-calibration with NH3 spectrum)

Lower end limited by MgF2 cut off (temperature depended)

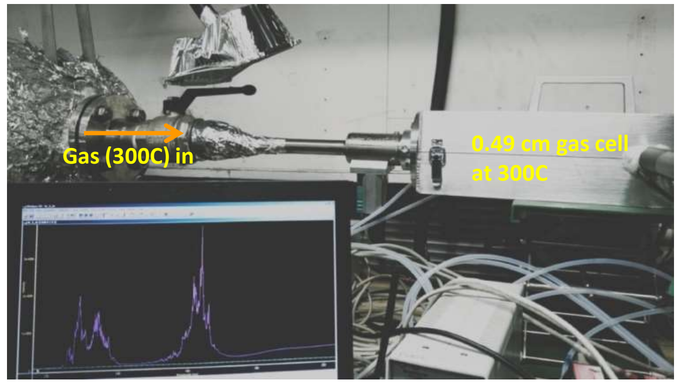
Detailed CH3Cl spectra analysis (320-115 nm): Eden et al (2007) (synchrotron)

Ethylene spectra analysis : Holland et al (1997) (synchrotron)

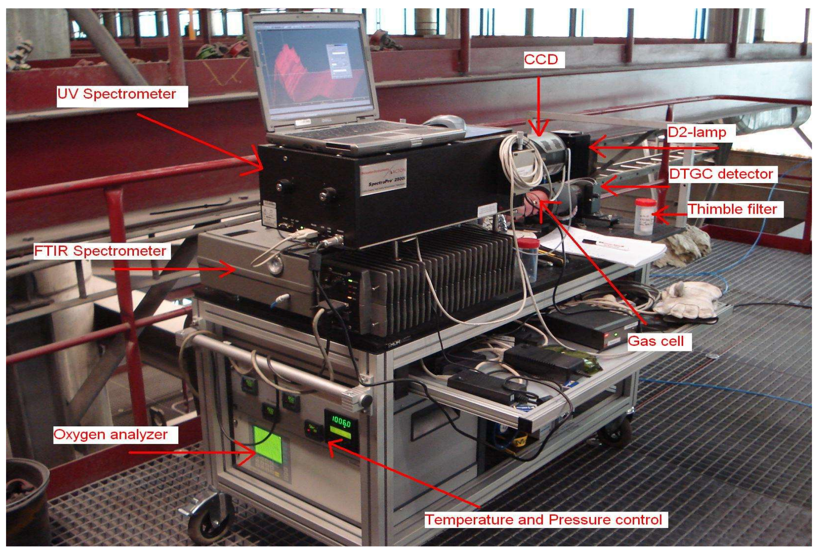


Field measurements: on-line vs in situ



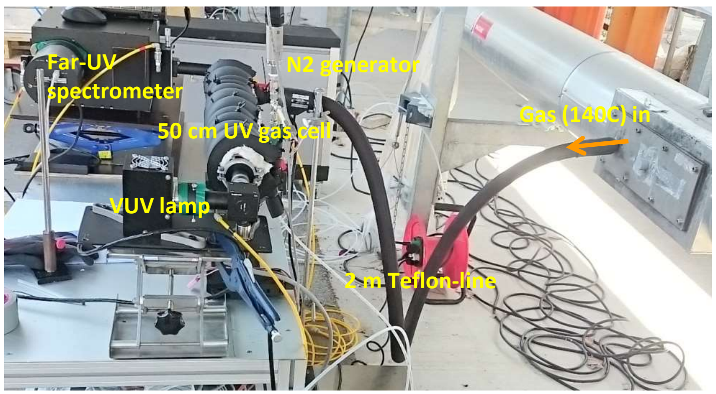


- UV/IR Light through
- Ti-probe at 300C, gas cell at 300C (far-UV)
- No tar condensation issues

- Removing heavy tar with tar trapper
- UV/IR dedicated measurements at 150C: only limited by optics (windows)

Field measurements: NH3 in stack gas



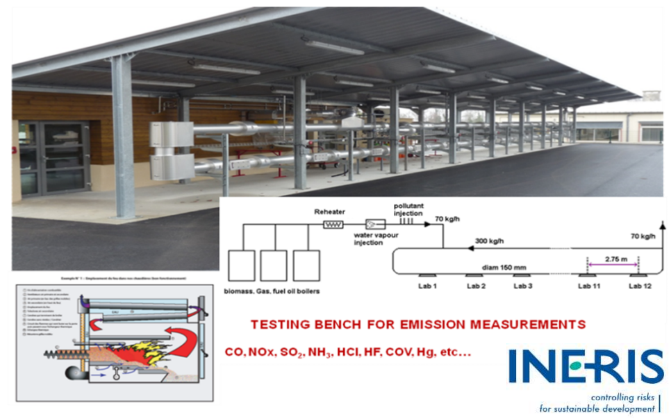
Combustion cases:

- natural gas (EL, power)
- biomass (wood pellets, heating)
- diesel (cars)

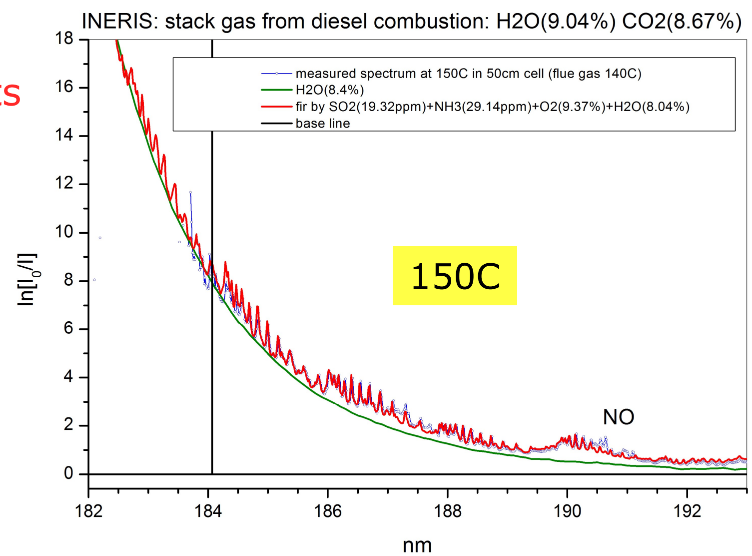
On-line measurements at 150C

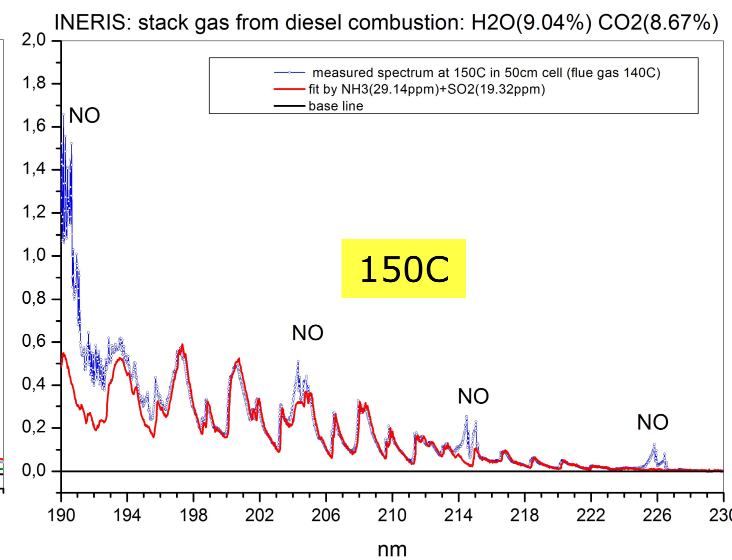
- above stack gas temperature 130-140C

Relevant for gas cleaning process

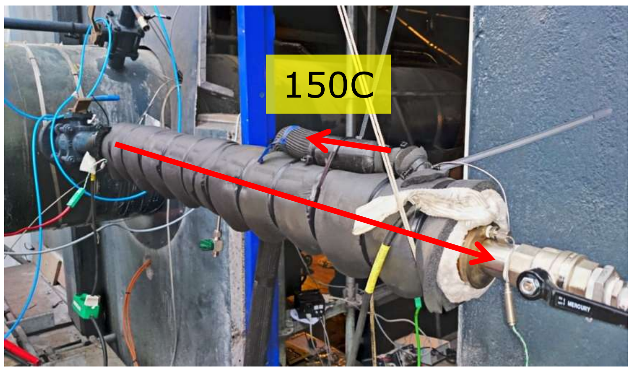


✓In situ/on line measurements
✓Limited by H2O (50cm)
✓Excellent sensitivity to
NH3, SO2, O2, H2O, NO

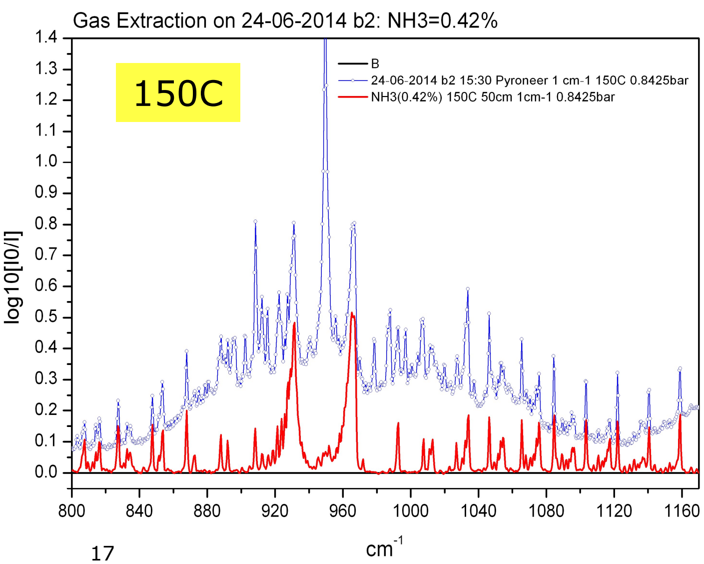


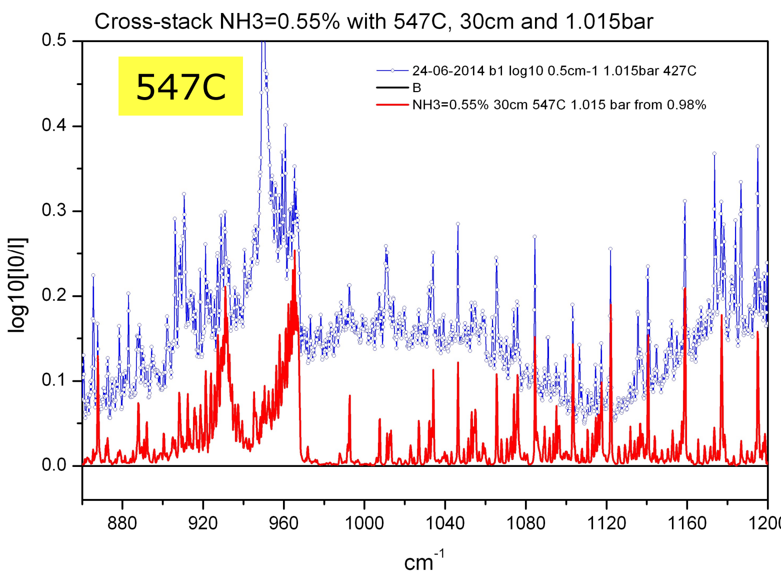


Field measurements: 6MW demonstration plant



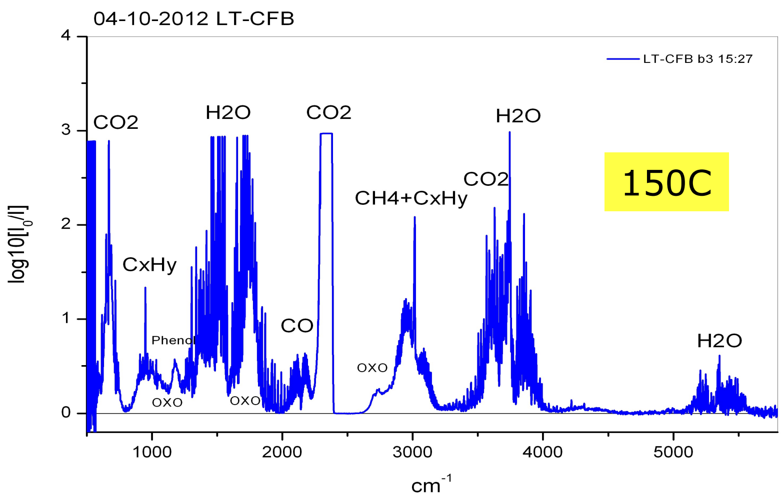
- Straw gasification
- Gas feed into burner
- Target: NH3, HCN, NO and H2O
- In situ (cross-stack) and gas extraction: same H2O





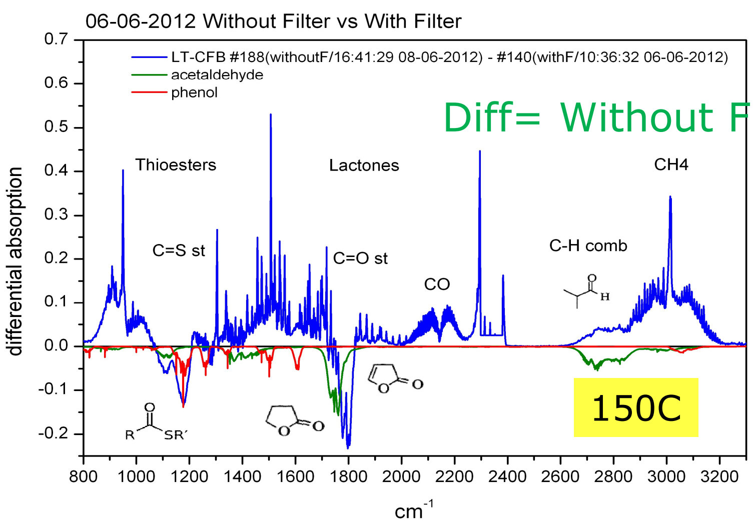
- NH3 extraction: ca. 24% less than in situ
- NH3 trapping by condensing acids/tars

Field measurements: LT-CFB (LT-gasification, 100kW)



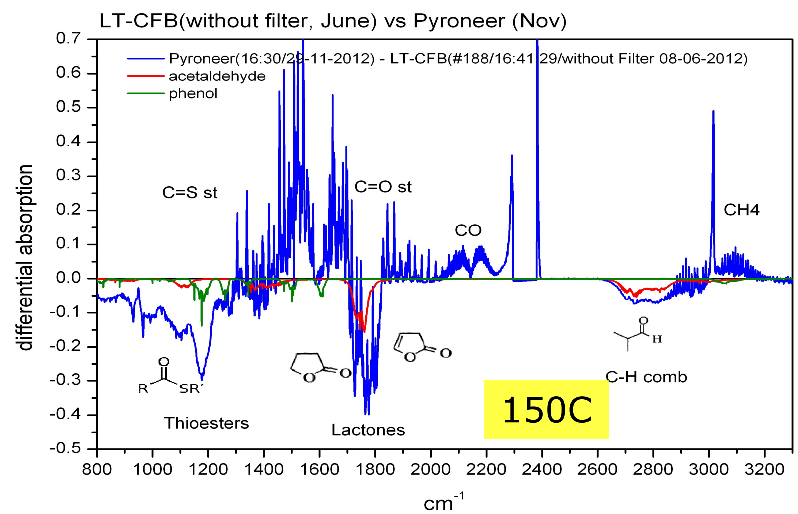
- Straw gasification
- Gasifier with (330C) and without (504C) particle filter: "base line" check (=process monitoring)
- thioesters and lactones: precursors of more simple HC
- Higher T → cleaner gas

Diff= 6MW(547C) –100kW(504C)

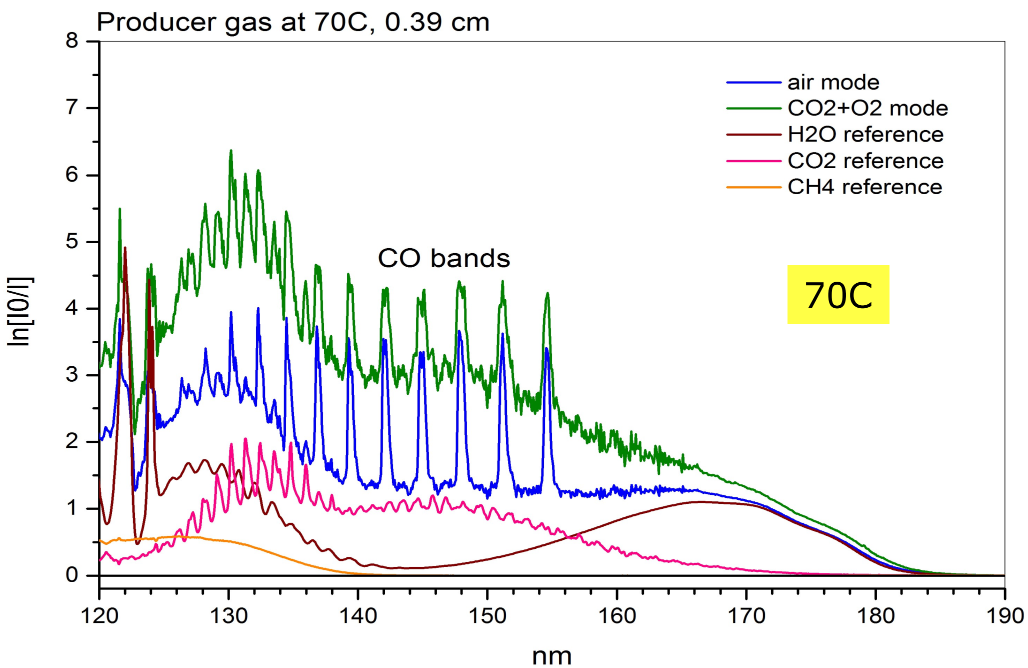


Diff= Without F(504C) –with F(310C)

Process monitoring: IR



Field measurements: Viking (HT-gasification)



- ❑ Very clean gas
- ❑ Traces of NH3 and other organics

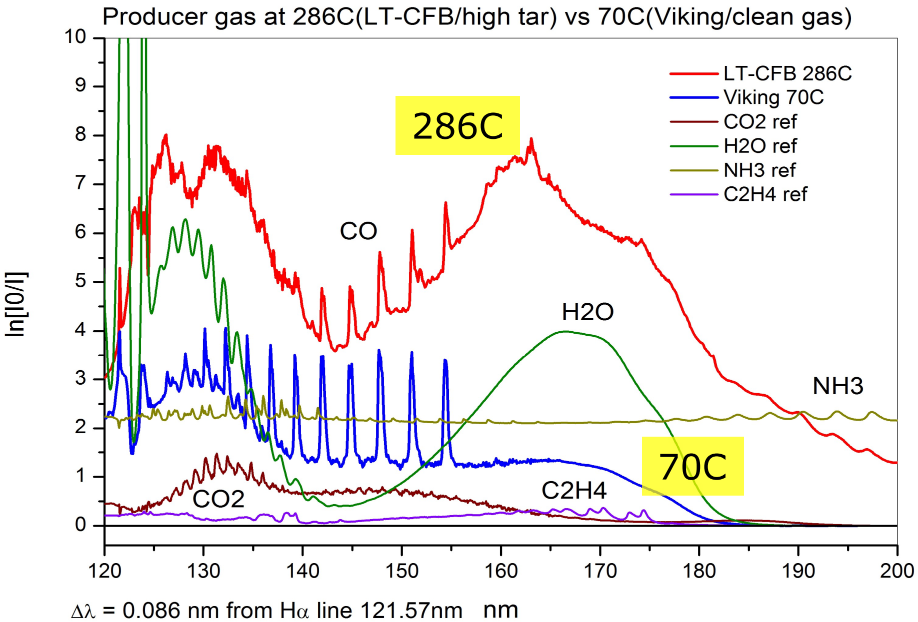
Viking	Air ***	O_2-CO_2 1st run ***	O_2-CO_2 2nd run***
CH_4	0.433%	0.866%	1.028%
CO_2	12.2%	31.08%	24.42%
H_2O	2.74%	2.82%	2.8%
O_2	0.354%	0.885%	0.955%
CO	8%	14%	14%
N_2	77%	0%**	0%**
NH_3	33ppm	0ppm**	0ppm**
C_6H_6	0ppm**	22ppm	22ppm
CH_3CHO*	0pmm**	100ppm	100ppm
OCS, CH_3Cl, HCl	0ppm**	0ppm**	0ppm**

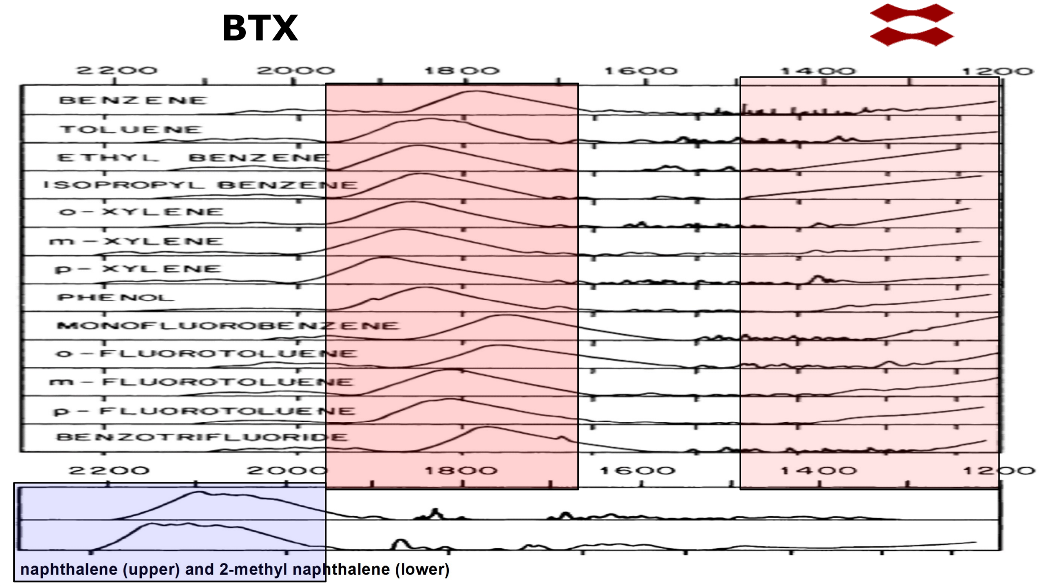
*) Aldehydes in CH_3CHO equivalent

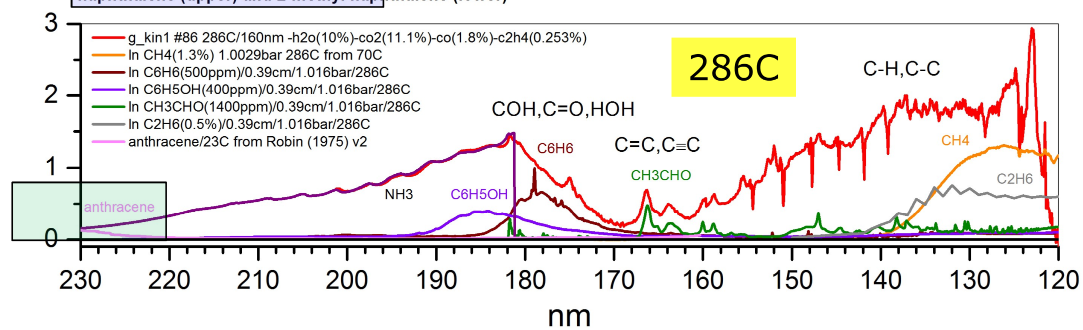
**) below detection limit

***) concentrations calculated from spectra measured over 10 min measurement time

Field measurements: LT-CFB (LT-gasification, 100kW)





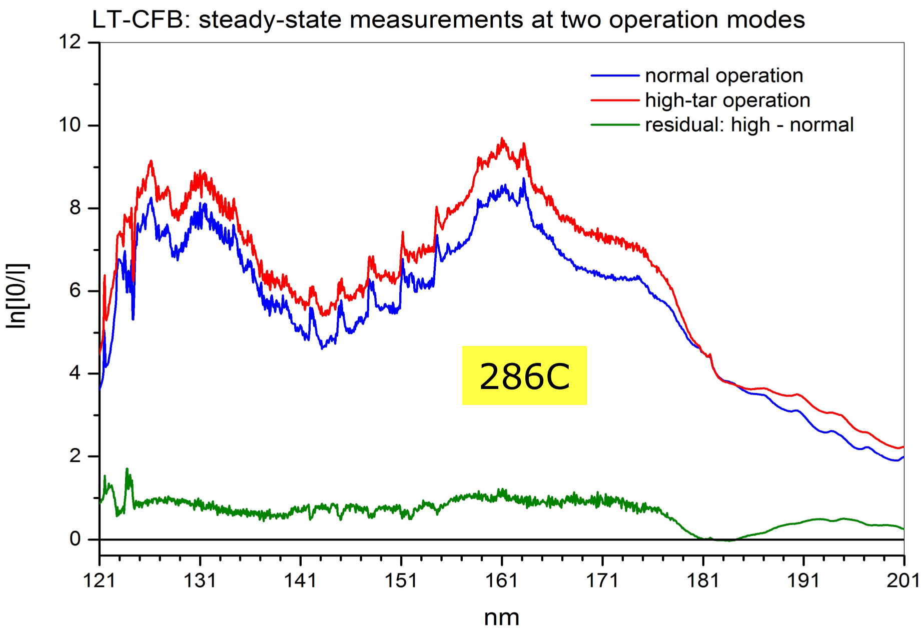


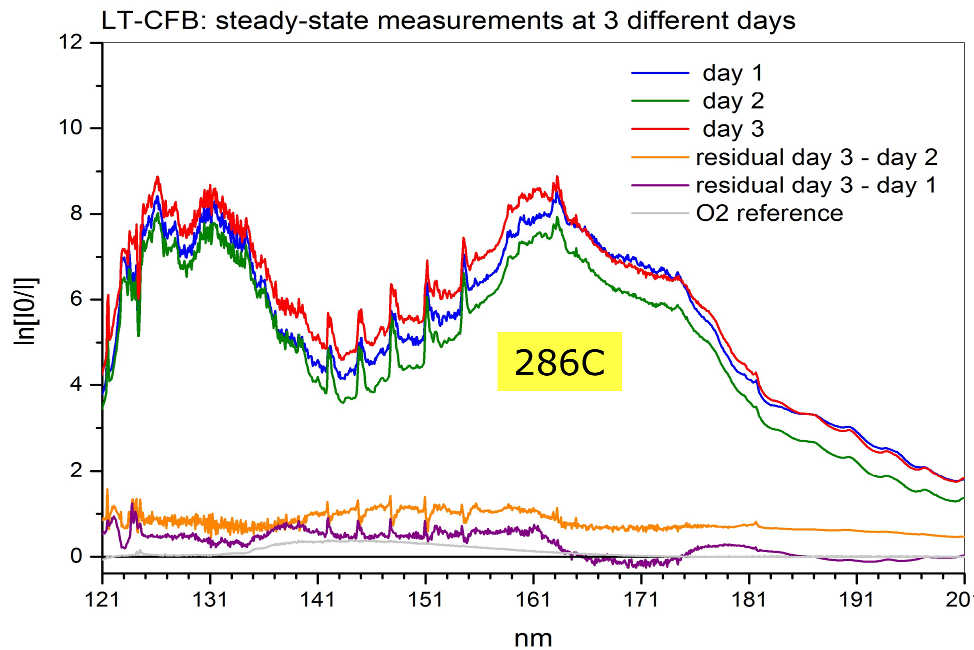
Typical residual spectrum after $H_2O+CO_2+CO+C_2H_4$ subtraction

Tar (PAH) contribution to the total absorption:

- High: BTX (170-190nm)
- Medium: "light tar" (naphthalene$^+$) (190-220nm)
- Low: "heavy tar" (anthracene$^+$) (λ>220nm)

Field measurements: LT-CFB (LT-gasification, 100kW)





Process monitoring: far UV

- "high-tar" operation mode: less BTX(181 nm), more tar (<170nm) and less NH3(185-200nm)
- "normal" operation mode: no change in BTX and minor O_2 changes in the gas over few days

Conclusions

- Broad-band absorption spectroscopy is a powerful and robust tool for tar and major/minor gas components *in situ* and *on line* measurements and process monitoring: buy all for 1 price concept
- T-dependent cross section databases can be generated on request (support instrument/sensor development
- Successful demonstration of in situ/on line approaches in measurements in various environments (low/high temperature gasification and combustion)
- Far-UV (160nm<) can be used for tar/BTX in situ measurements (absolute or relative) by simple weighting of the 195-230 nm and 170-200 nm areas under an absorption spectrum
- Ability unexpansive far UV small spectrometers opens possibility for a new in situ tar/BTX sensor development when a complex tar/BTX sampling can be avoided.

Acknowledgments

- Energinet.dk: projects No. 2013-12027 and 2011-1-10622

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Thank You

Questions? Comments?

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+45 23 65 2906

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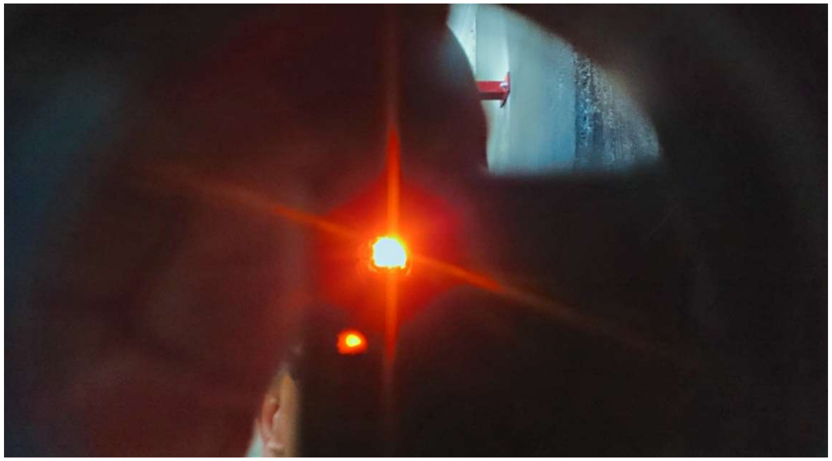

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