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Spectroscopy for Industrial Applications: High-Temperature Processes

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DTU Chemical Engineering
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Outline

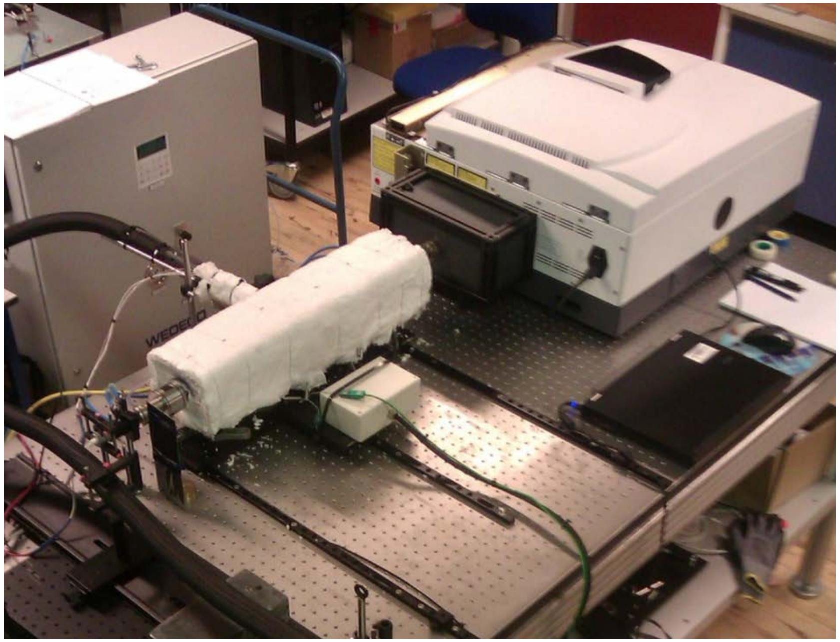
- Hot flow gas cell and FTIR/UV optical set up
- A road to In Situ measurements:
  - NH3 spectroscopy at high-temperatures: band assignment and spectra modelling
  - NH3/H2O field measurements at a pilot scale 6MW gasifier

  - Phenol –major trace gas from PAH's in low temperature gasification
  - Temperature-dependent UV absorption cross-sections
  - Why In Situ measurements are important: comparison with "standard" tools

- How planets meet the Earth

- Conclusions

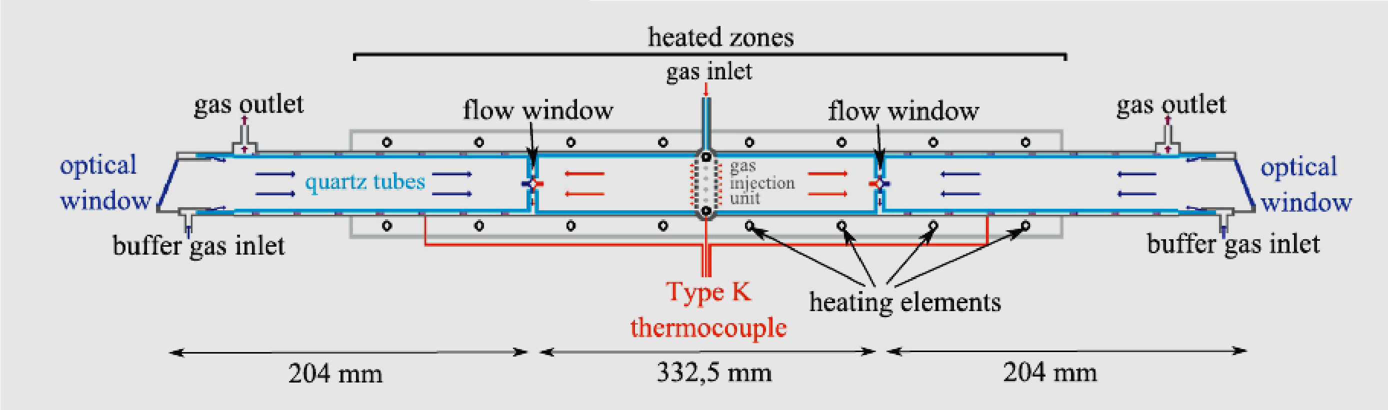
NH3/Phenol: experimental set up



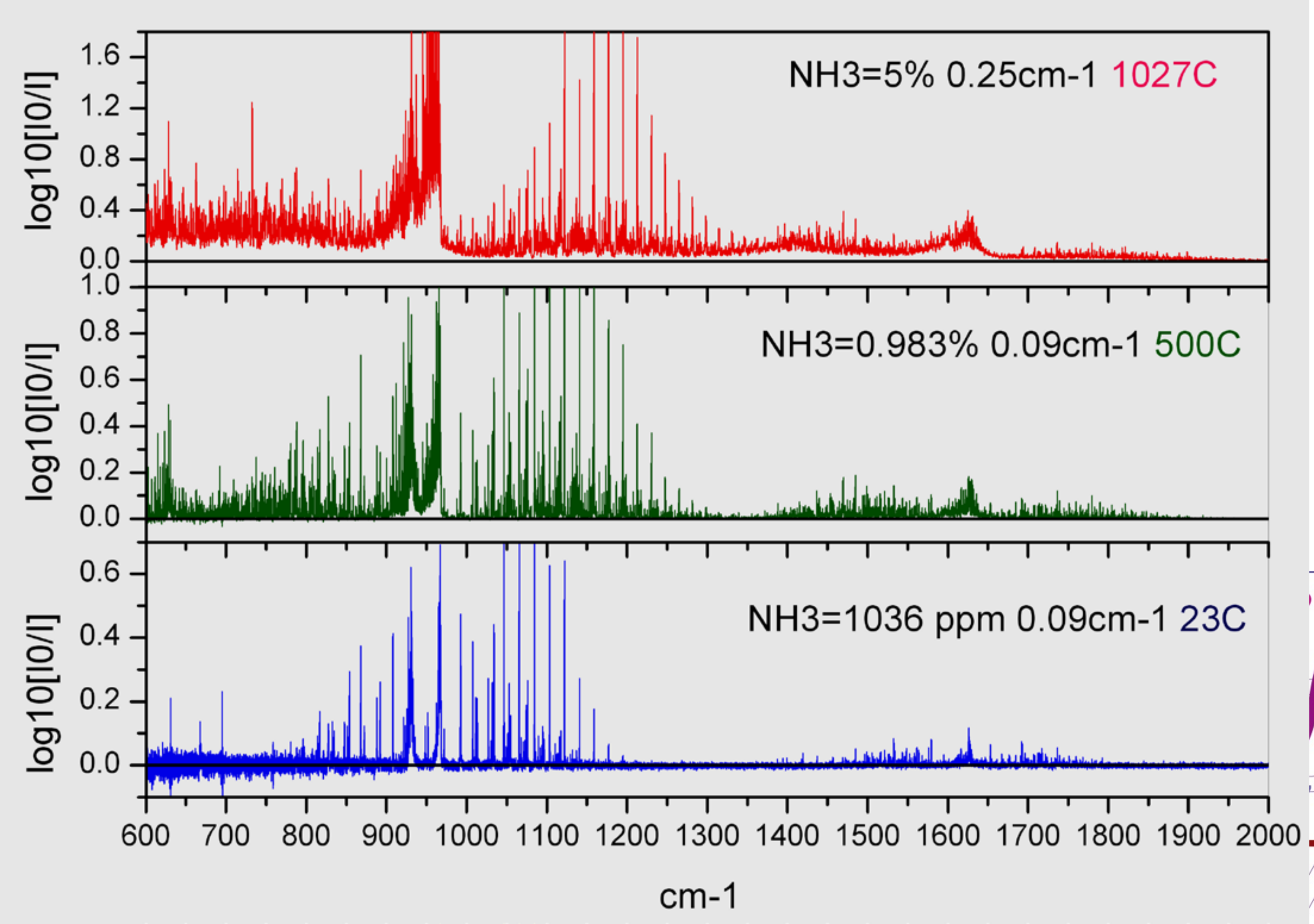
- 3-zones flow gas cell for corrosive gases;
- No internal windows;
- Stable uniform T-profile (±1.8C);
- Tmax= 525C
- L=33.25 cm
- P=1 bar
- suitable for UV-FIR optical measurements
- more details: H. Grosch et al. JQSRT 130 (2013) 392–399

- FTIR Spectrometer (Agilent 660), 0.09 cm-1
- an IR light source (up to 1500C)

- UV spectrometer (Acton 250i/CCD), 0.019 nm
- a highly stable D2-lamp



NH3 FTIR absorption spectra: changes with T



Lab (Home work) | NH3 spectroscopy: line assignments, new results

Table 1: Lines assigned to previously observed bands

	Lines Assigned This Work				Previously measured			
Band	J_{max}	K_{max}	Frequency Range cm^{-1}	Number of Lines	J_{max}	K_{max}	Number of Lines	Reference
v_4	17	17	1290 - 1868	277	15	15	1663	Cottaz 2000
v_2	20	20	634 - 1333	385	23	20	177	Yu 2010
$v_2+v_4-v_2$	12	12	1412 - 1818	83	10		384	Cottaz 2001
$2v_2$	16	15	1407 - 1870	43	15	15	403	Cottaz 2000
$2v_2-v_2$	18	18	607 - 1236	180	10	10	32	Singh 1988
$3v_2-v_2$	12	12	1104 - 1652	18	10		132	Cottaz 2001

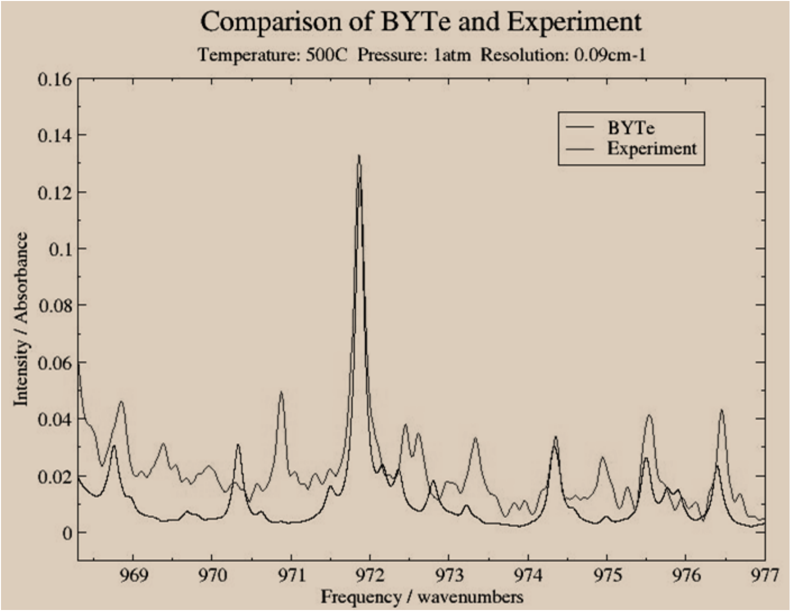
500C
1 bar
0.09cm-1

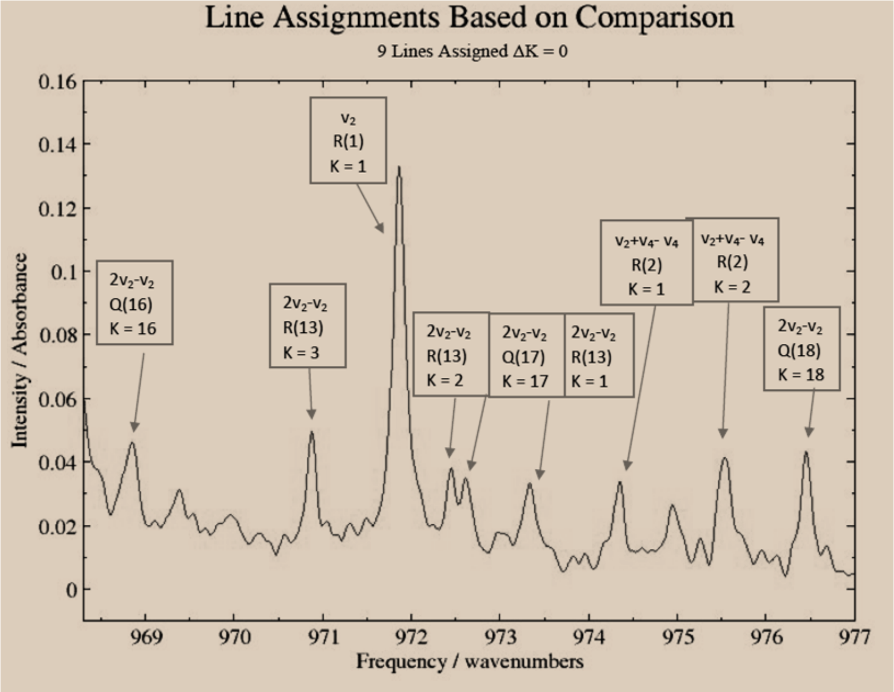
Table 2: Lines assigned to previously unobserved bands* with 10 or more lines assigned in this work.

	Lines Assigned This Work			
Band	J_{max}	K_{max}	Frequency Range cm^{-1}	Number of Lines
v_4-v_2	11	11	622 - 1013	20
$2v_4-v_4$	9	5	1430 - 1792	10
$2v_4^2-v_4$	8	5	1420 - 1805	10
$v_2+v_4-v_4$	13	13	680 - 1270	77
$3v_2-2v_2$	14	12	628 - 1455	31
$3v_2-3v_2$	12	9	628 - 743	12

Have not found measurements in published works.

NH3 spectroscopy: line assignments, an example



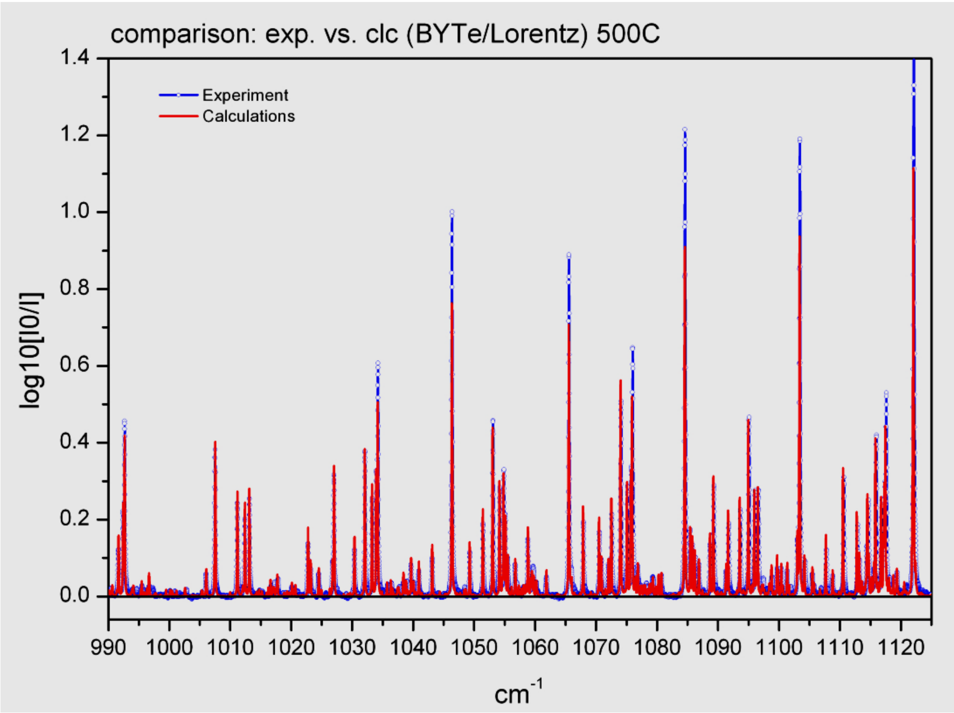


List of Assigned Lines

BYTe Frequency	Experimental Frequency	Obs - Calc	Upper Quantum Numbers*	Lower Quantum Numbers*
968.761998	968.825639	0.063641	- 0 2 0 0 0 0 16 16	+ 0 1 0 0 0 0 16 16
970.332898	970.874628	0.54173	- 0 2 0 0 0 0 14 3	+ 0 1 0 0 0 0 13 3
971.871137	971.868991	-0.002146	- 0 1 0 0 0 0 2 1	+ 0 0 0 0 0 0 1 1
972.159794	972.456569	0.296775	+ 0 2 0 0 0 0 14 2	- 0 1 0 0 0 0 13 2
972.363167	972.60723	0.244063	+ 0 2 0 0 0 0 17 17	- 0 1 0 0 0 0 17 17
972.801729	973.330403	0.528674	- 0 2 0 0 0 0 14 1	+ 0 1 0 0 0 0 13 1
974.317864	974.354898	0.037034	- 0 1 0 1 0 1 3 1	+ 0 0 0 1 0 1 2 1
975.511534	975.530054	0.01852	+ 0 1 0 1 0 1 3 2	- 0 0 0 1 0 1 2 2
976.392929	976.449086	0.056157	- 0 2 0 0 0 0 18 18	+ 0 1 0 0 0 0 18 18

*Parity v_1 v_2 v_3 v_4 l_3 l_4 J K

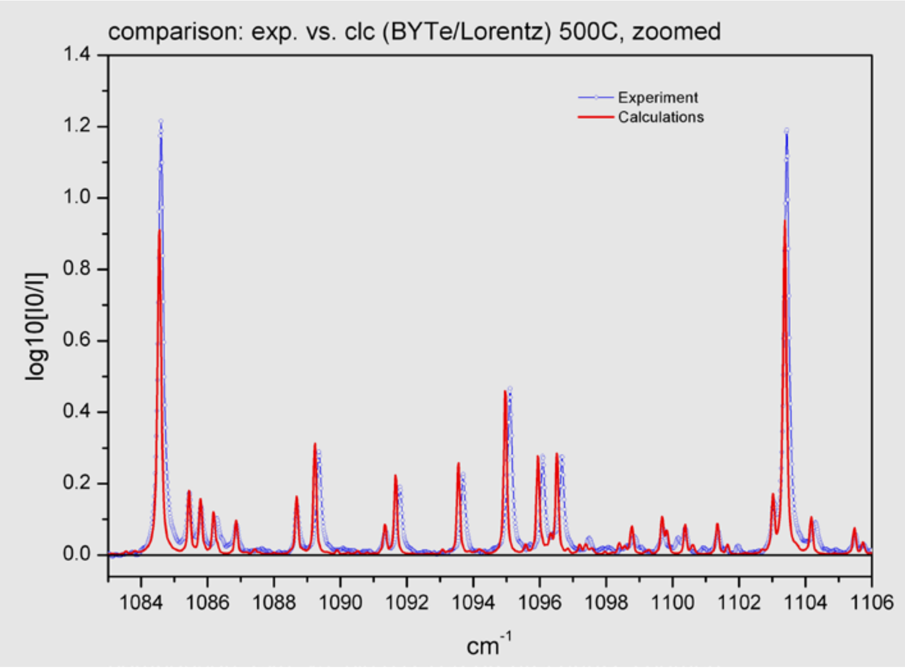
NH3: experiment (0.09cm-1) vs calculations (BYTe)



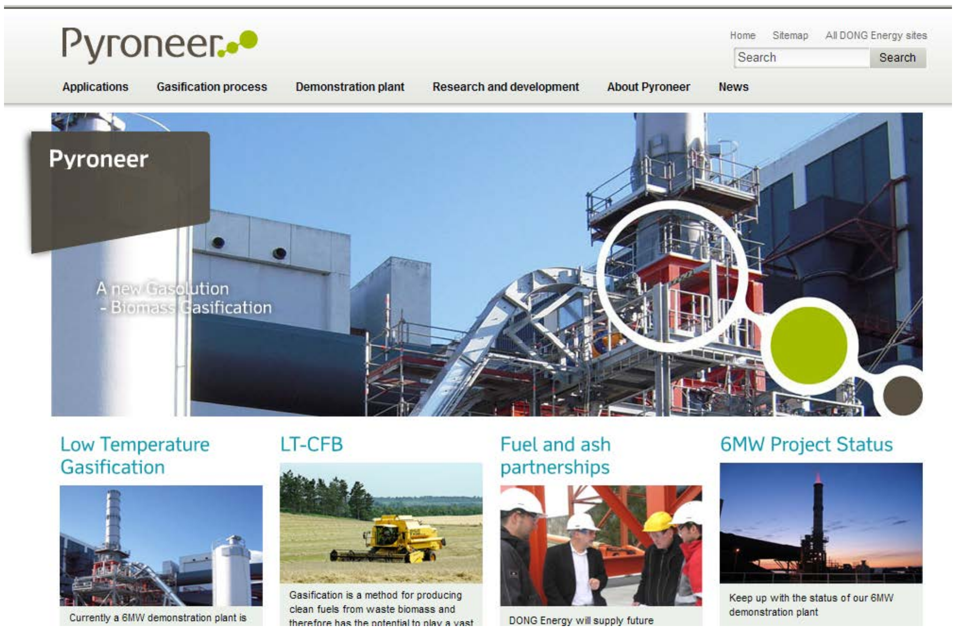
Can we use BYTe at 500C for practical apps?

- in general a good agreement
- some difficulties with strong line intensities
- some frequency shifts in line positions

More work to do at even higher T (>500C)



In Situ measurements on Pyroneer (6MW) gasifier



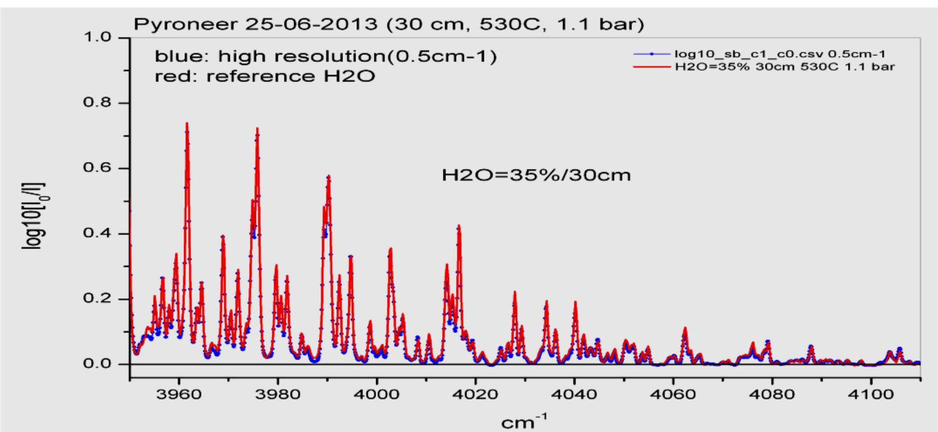
- Very complex producer gas composition ($CO2$, $H2O$, CO, $H2$, HC, PAH, tars) + particles
- Producer gas is feeded into an industrial burner of a power plant

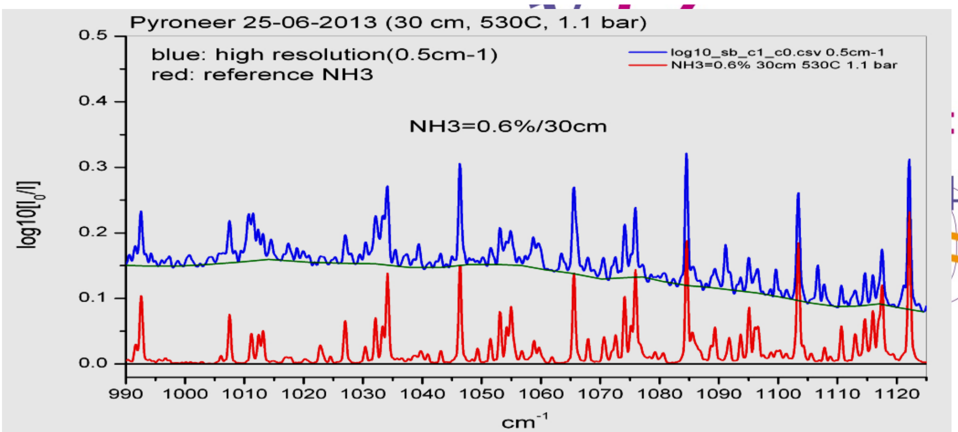
Why to do it? (examples):

- H2O (related to mass balance)
- NH3 (related to NOx formation)

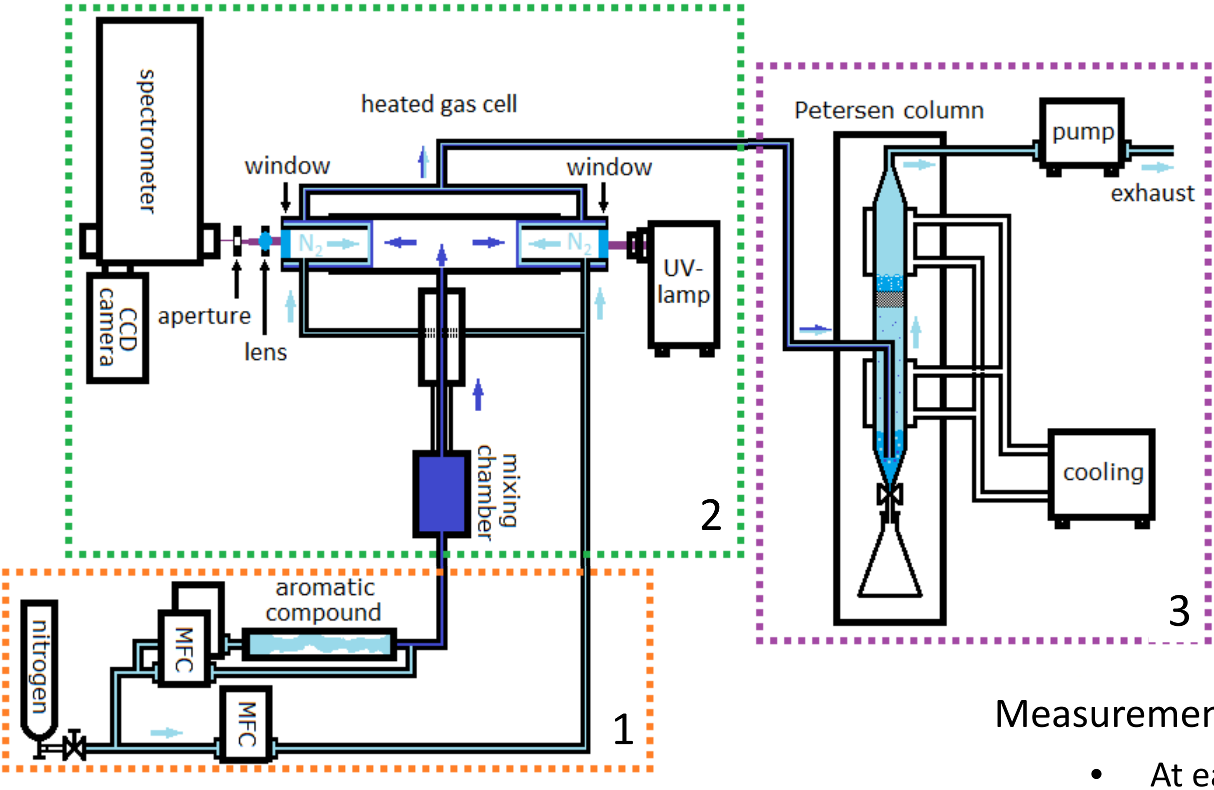
How?: In Situ IR abs measurements: <u>no gas extraction</u>

- Tough: out of the building on a platform (safety) with limited space (practical issues);
- Tgas about 530C;
- optical measurements over 30 cm;
- very strong any (UV-IR) light attenuation.





Phenol UV absorption cross-sections: experimental set up



1. Gas mixing unit
   - N_2 (industrial standard)
   - molten aromatic crystals in tube

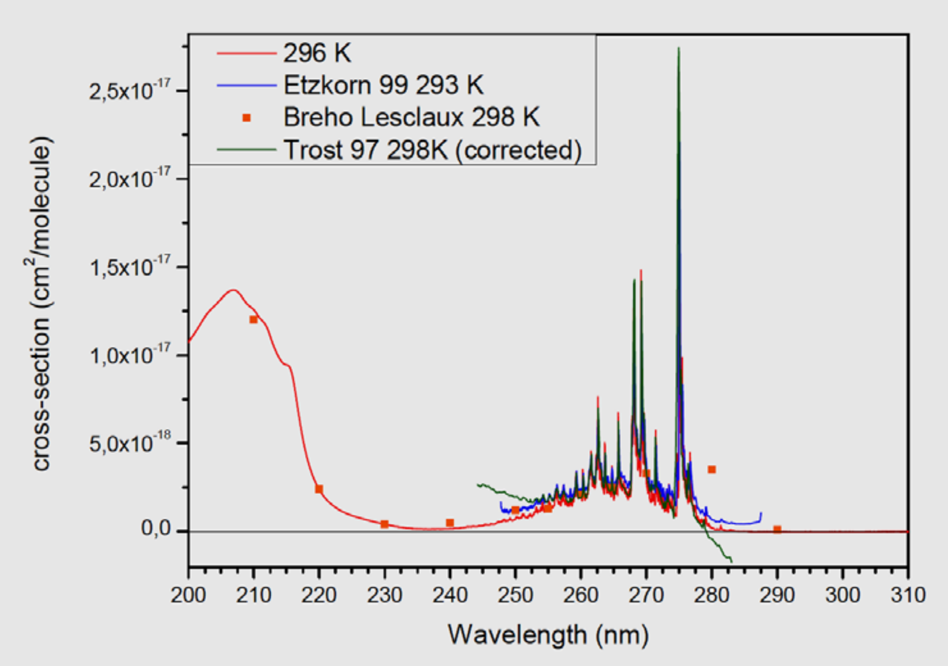
   ⇒ concentration unknown
   - admixture of N_2 for different concentration
2. Gas cell and optics
3. Petersen column
   - sampling in acetone
   - Sampling time 30 min
   - analysis with GC/MS

Measurements strategy:

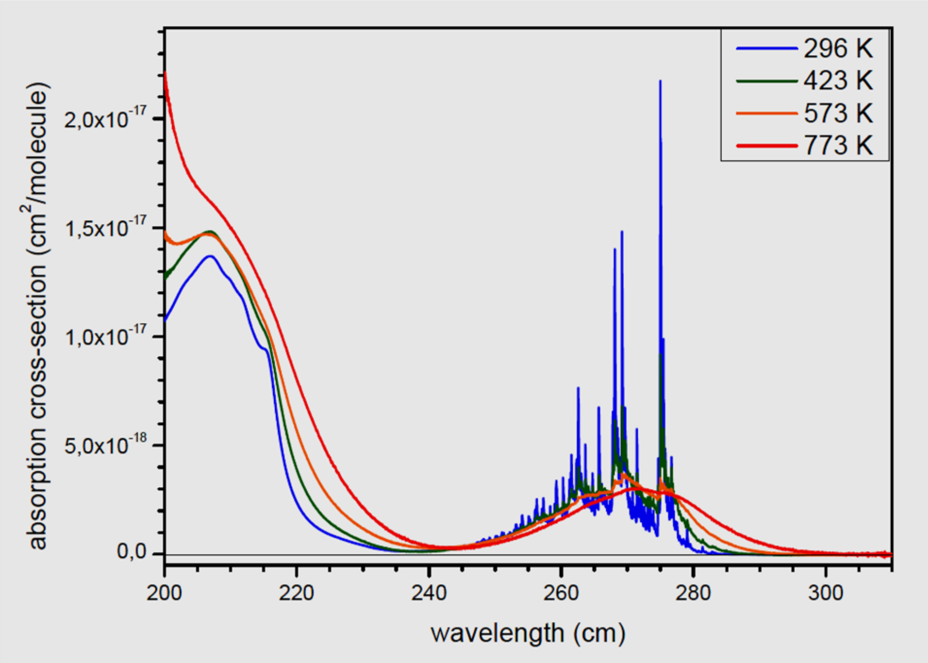
- At each T two phenol concentrations
- At each concentration two sample
- During each sampling three UV spectra and three double concentration determination

- Not too many reference data available even at low T (about 23C)
- An excellent agreement with published data at low T
- Significant changes in the fine structure of the cross-section spectra with T

Low-temperature abs cross-sections: comparison

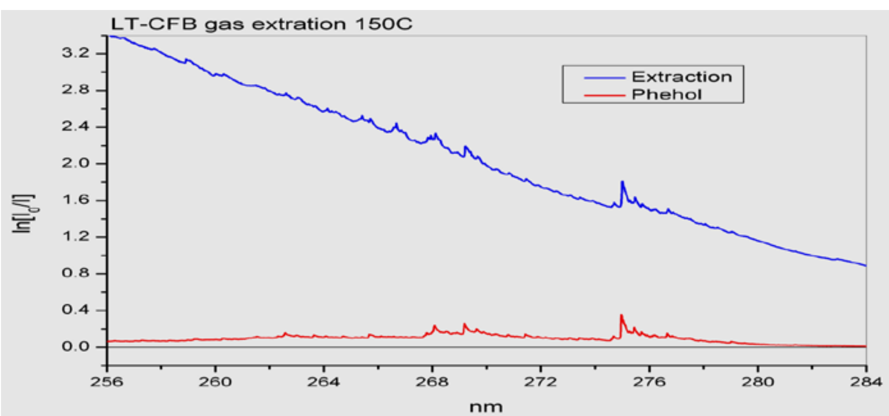


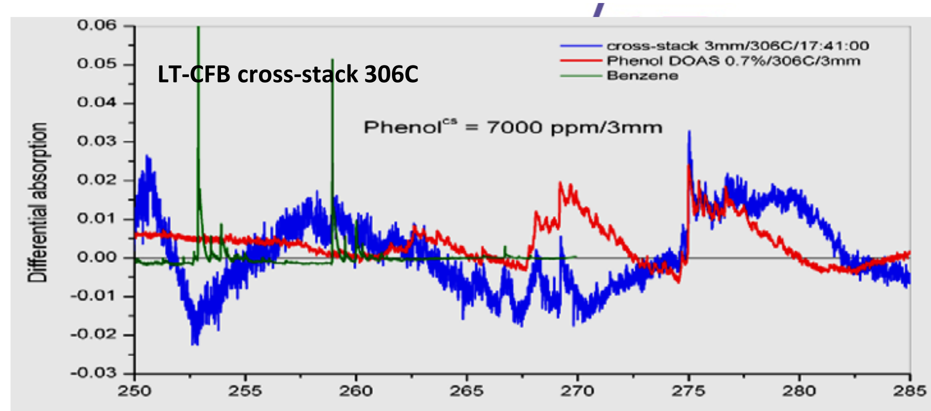
Abs cross-sections: from 23C to 500C



In Situ measurements on LT-CFB (100kW) gasifier

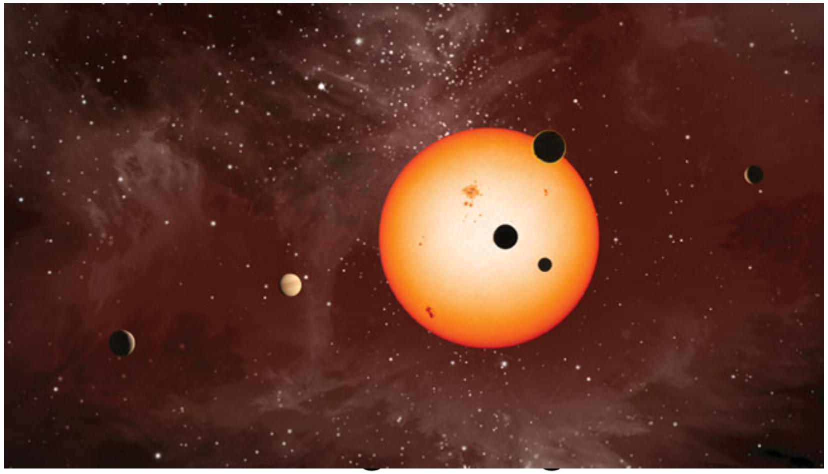
- Focus on trace gases in low- and high-temperature gasification processes;
- Producer gas issues:
  - corrosion (boilers)
  - reduced gas quality (fuel cells, gas grids)
- Phenol – major trace gas from PAH's in the producer gas (LT-CFB process);
- Tgas = 300-500C; In Situ UV abs measurements over 3 mm;
- Phenol measurements by various techniques:
  - GC/MS (Petersen column (30 min) 215 ppm (±5%)
  - Gas extraction, 150 C: 407 ppm (±5%) (3 min)
  - In Situ, 306 C (DOAS approach): 7700 ppm (±10%) (3 min)





How other planets meets the Earth

- Far away planets on a global scale (e.g. exoplanets, stars) and current Earth's problems on a local scale (energy, emissions , taxes)
- Spectroscopy of hot planets and high-temperature processes: the same gases/temperatures of interest;
- DTU's projects about optical measurements in combustion (SO_2, SO_3, NH_3, etc), gasification (trace gases, Cl- compounds) and waste utilization in collaboration with industry (DONG Energy, Vattenfall and Babcock &Wilcox Vølund)
- UCL's and DTU's common PhD/postdocs projects: SO_3/SO_2 and Cl-compounds (KCl, HCl, CH_3Cl, CH_4, H_2CO)



Conclusions

In general

- You can find a lot inspirations for the work on the Earth
- Different research areas can have the same origin
- Scientists can make industry guys happy

In particular:

- o Excellent experimental tools are available for (VUV) UV-FIR optical measurements
- o Temperature range can be also negative (e.g. gases at low T)
- o New data/lines for NH_3 BYTe extension and development
- o New data for phenol
- o Try always In Situ and avoid any Ex Situ (extraction) measurements

Acknowledgements

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- To UCL (Prof. Jonathan Tennyson's group)