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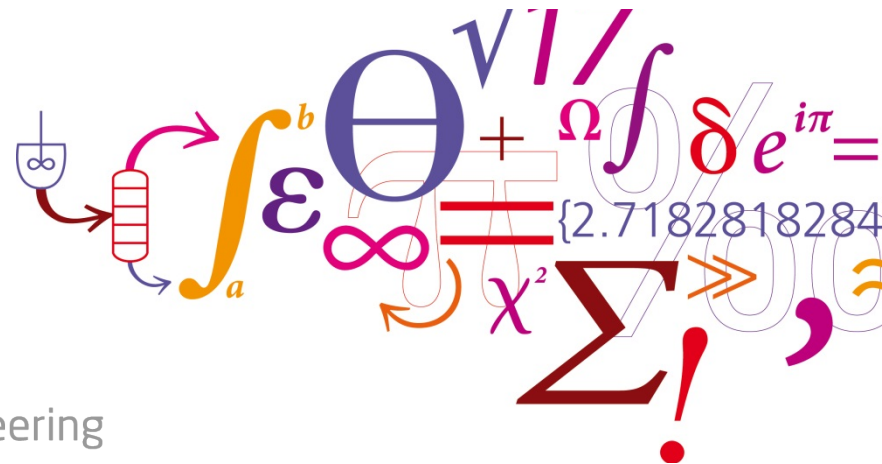
Spectroscopy for Industrial Applications: High-Temperature Processes

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Emma J Barton, Sergei N Yurchenko, Jonathan Tennyson (Department of Physics and Astronomy, UCL, UK)

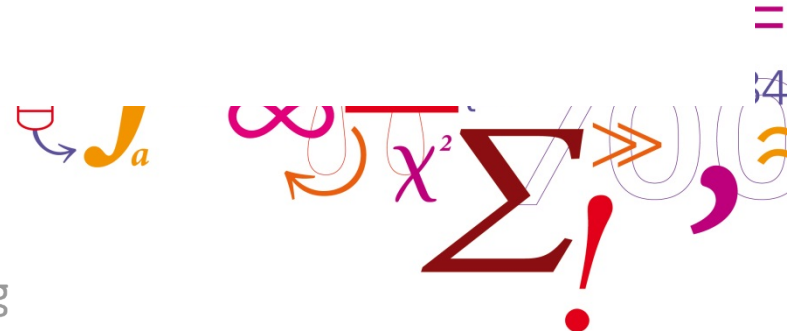
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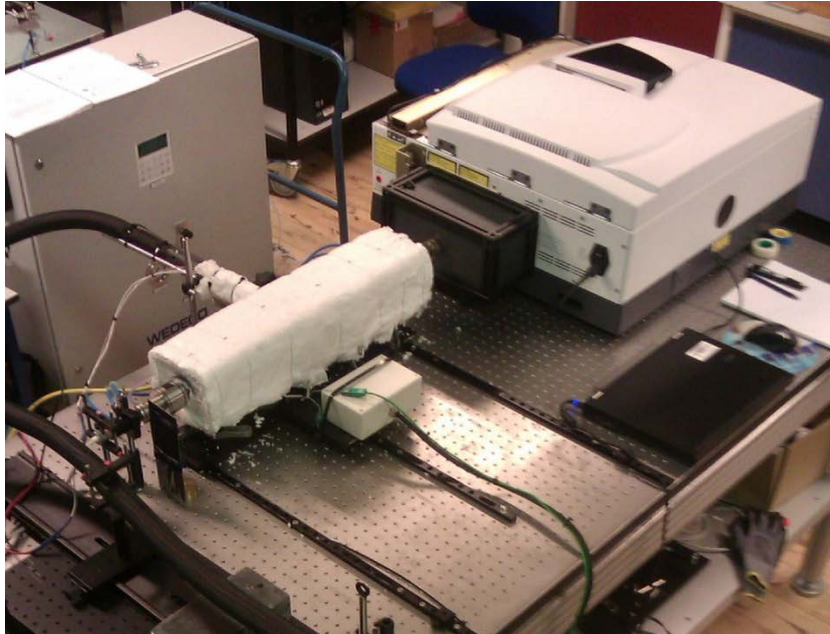


Outline

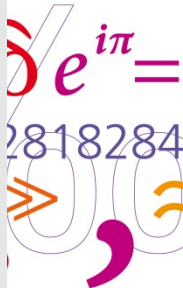
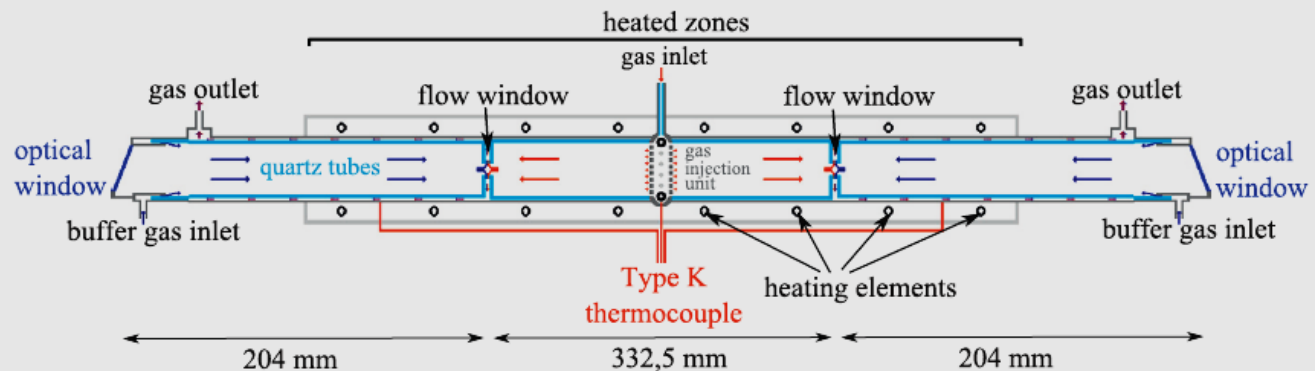
- Hot flow gas cell and FTIR/UV optical set up
- A road to In Situ measurements:
 - NH₃ spectroscopy at high-temperatures: band assignment and spectra modelling
 - NH₃/H₂O field measurements at a pilot scale 6MW gasifier
 - Phenol –major trace gas from PAH's in low temperature gasification
 - Temperature-dependent 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 ($\pm 1.8\text{C}$);
- $T_{\text{max}} = 525\text{C}$
- $L = 33.25\text{ cm}$
- $P = 1\text{ bar}$
- 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



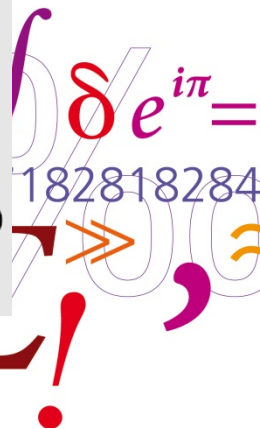
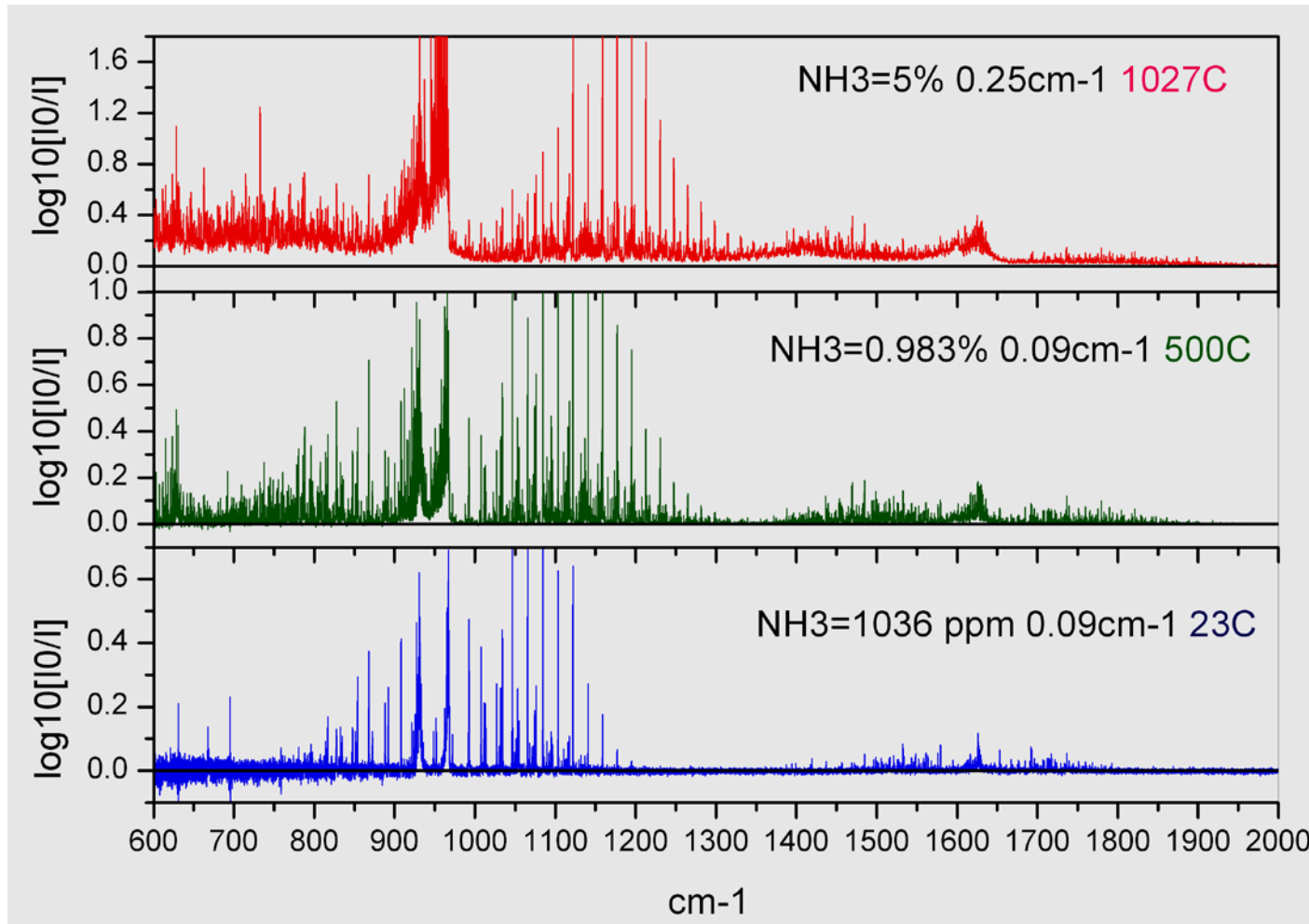


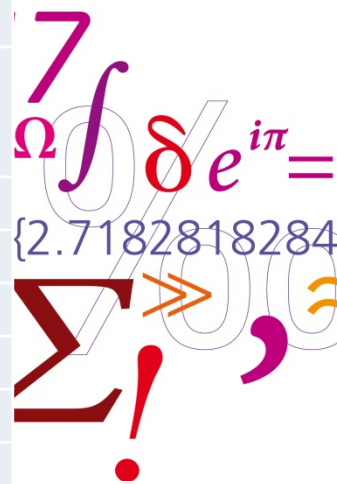
Table 1: Lines assigned to previously observed bands

Band	Lines Assigned This Work				Previously measured			
	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

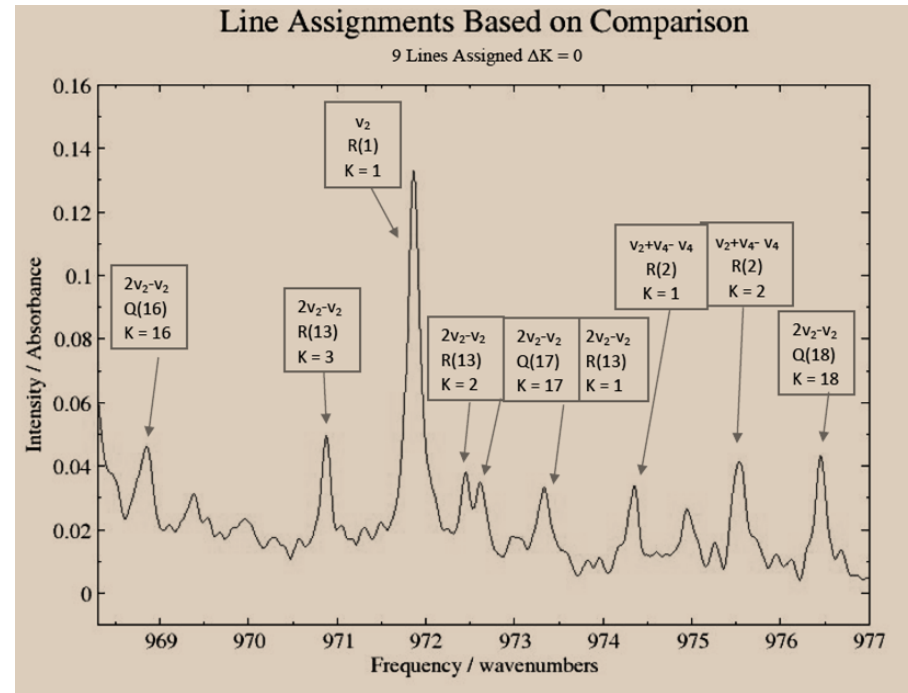
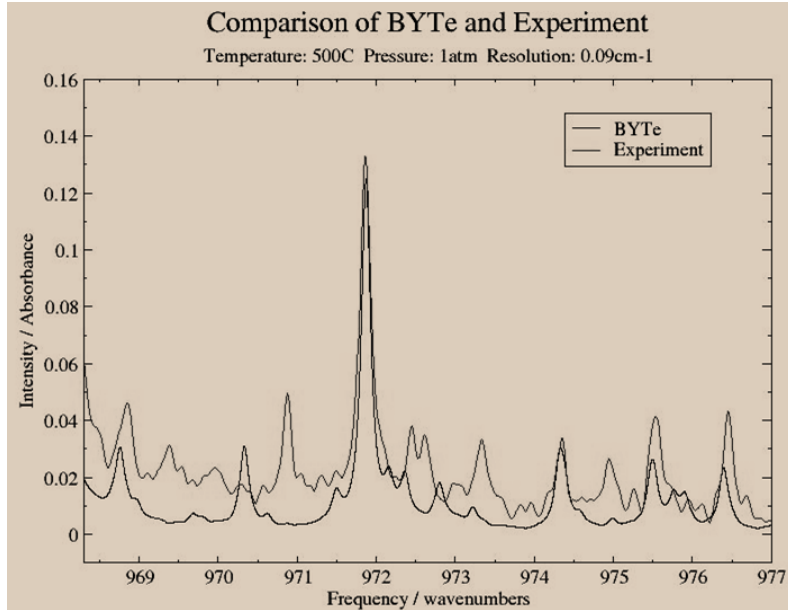
500C
1 bar
0.09cm⁻¹

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

Band	Lines Assigned This Work			
	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



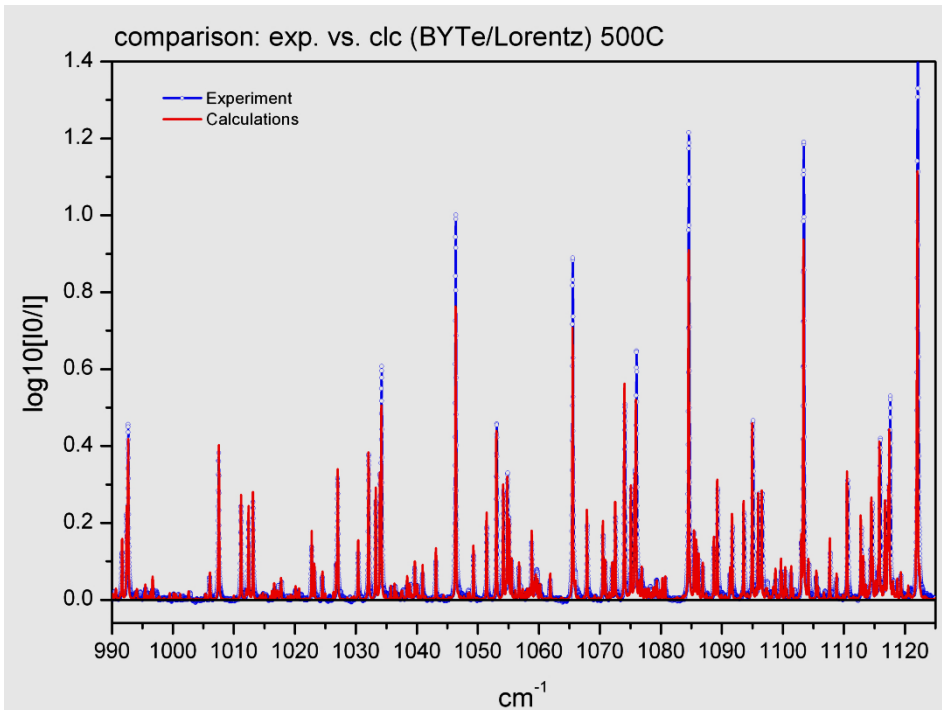
*Have not found measurements in published works.



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 16 16	+ 0 1 0 0 0 16 16
970.332898	970.874628	0.54173	- 0 2 0 0 0 14 3	+ 0 1 0 0 0 13 3
971.871137	971.868991	-0.002146	- 0 1 0 0 0 2 1	+ 0 0 0 0 0 1 1
972.159794	972.456569	0.296775	+ 0 2 0 0 0 14 2	- 0 1 0 0 0 13 2
972.363167	972.60723	0.244063	+ 0 2 0 0 0 17 17	- 0 1 0 0 0 17 17
972.801729	973.330403	0.528674	- 0 2 0 0 0 14 1	+ 0 1 0 0 0 13 1
974.317864	974.354898	0.037034	- 0 1 0 1 0 13 1	+ 0 0 0 1 0 12 1
975.511534	975.530054	0.01852	+ 0 1 0 1 0 13 2	- 0 0 0 1 0 12 2
976.392929	976.449086	0.056157	- 0 2 0 0 0 18 18	+ 0 1 0 0 0 18 18

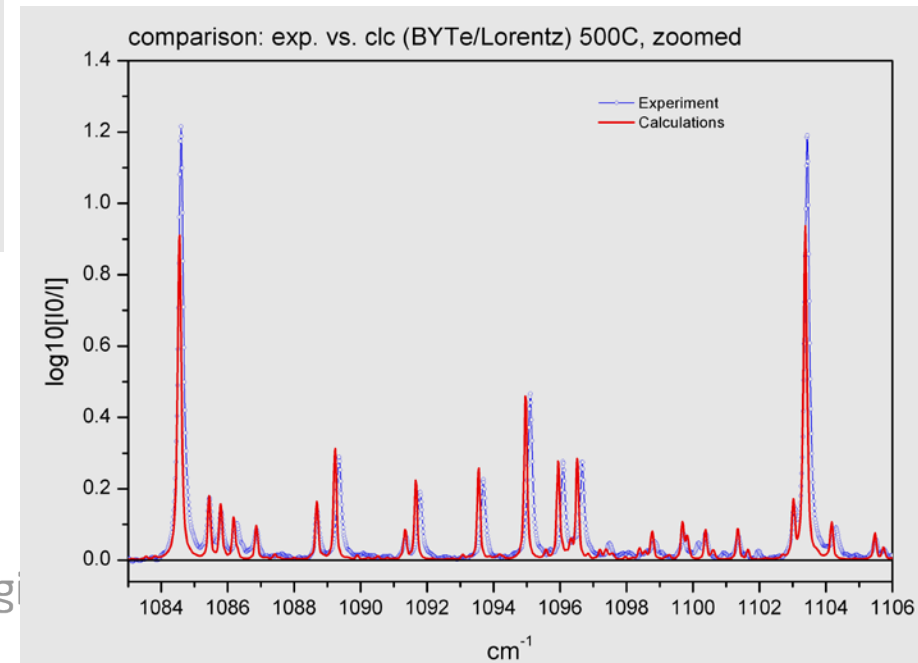
*Parity $v_1 v_2 v_3 v_4 l_3 l_4 J K$



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)



Pyroneer

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Low Temperature Gasification



LT-CFB



Fuel and ash partnerships



6MW Project Status



- 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

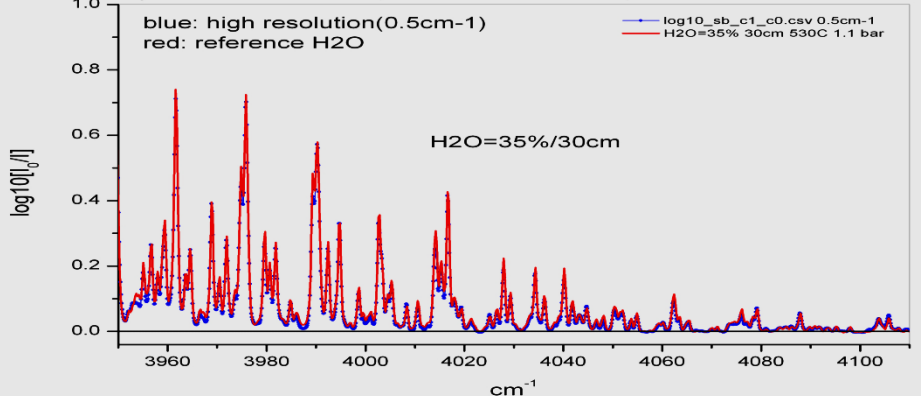
Why to do it? (examples):

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

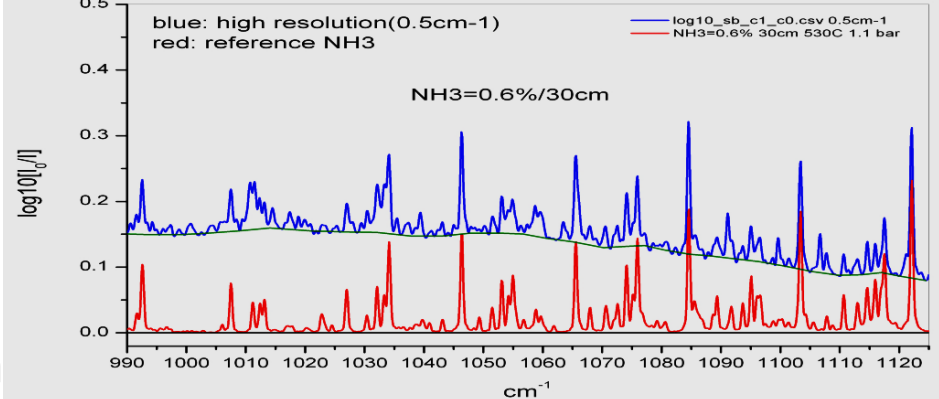
How?: In Situ IR abs measurements: no gas extraction

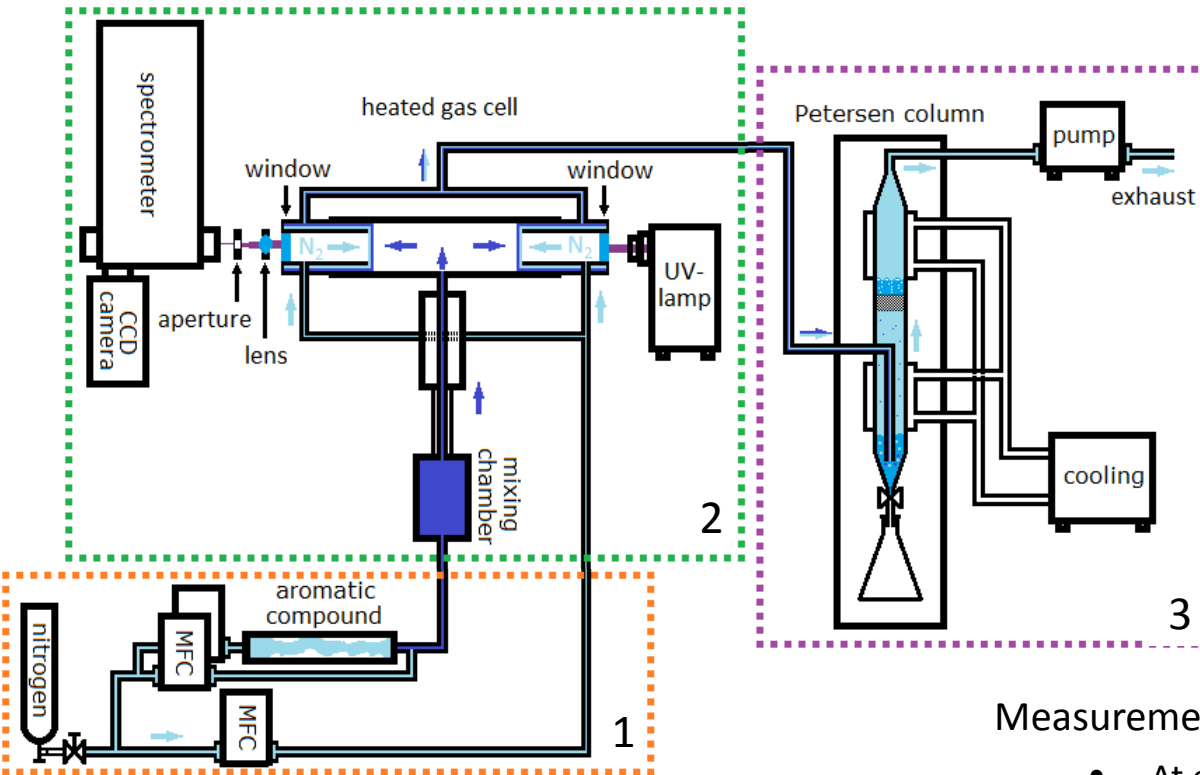
- Tough: out of the building on a platform (safety) with limited space (practical issues);
- T_{gas} about 530C;
- optical measurements over 30 cm;
- very strong any (UV-IR) light attenuation.

Pyroneer 25-06-2013 (30 cm, 530C, 1.1 bar)



Pyroneer 25-06-2013 (30 cm, 530C, 1.1 bar)





1. Gas mixing unit

- N₂ (industrial standard)
- molten aromatic crystals in tube
- ⇒ concentration unknown
- admixture of N₂ for different concentration

2. Gas cell and optics

3. Petersen column

- sampling in acetone
- Sampling time 30 min
- analysis with GC/MS

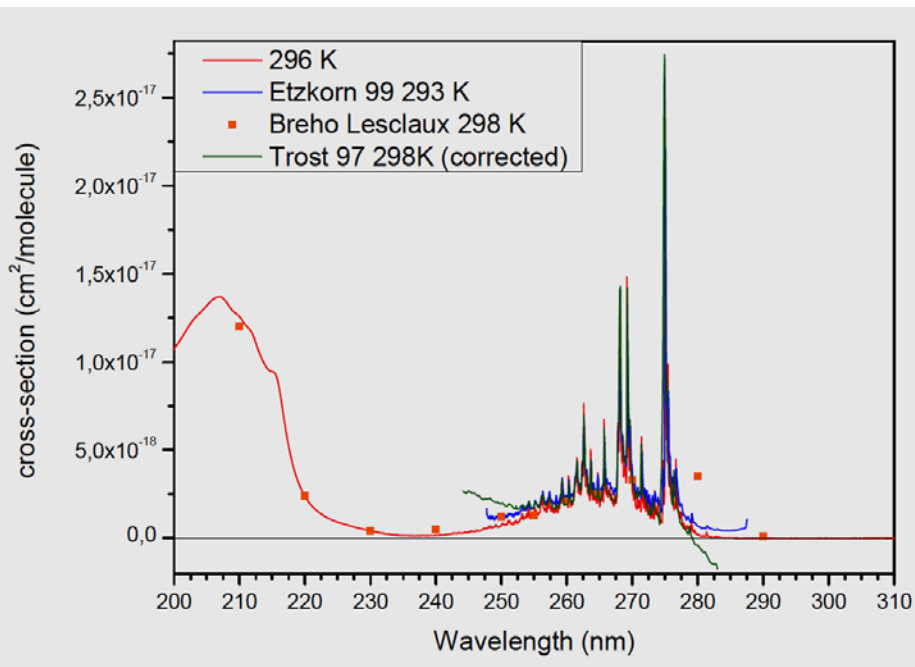
Measurements strategy:

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

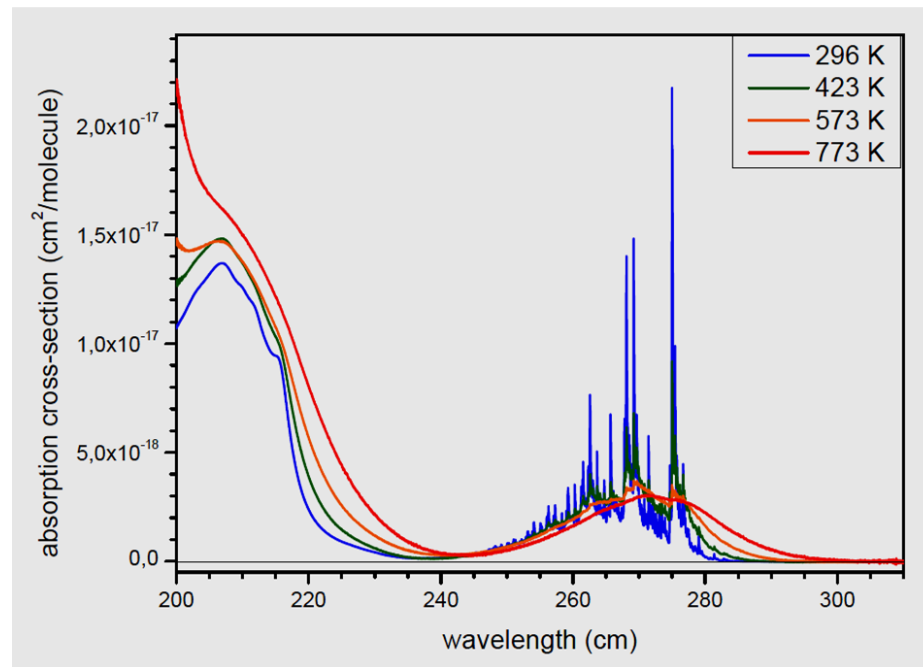


- Not too many reference data available even at low T (about 23C)
- An excellent agreement with published data at low T
- Significant changes in the fine structure of the cross-section spectra with T

Low-temperature abs cross-sections: comparison



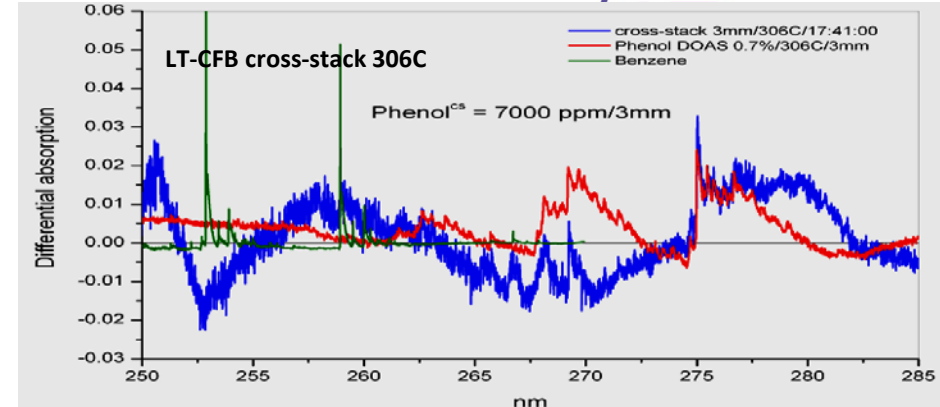
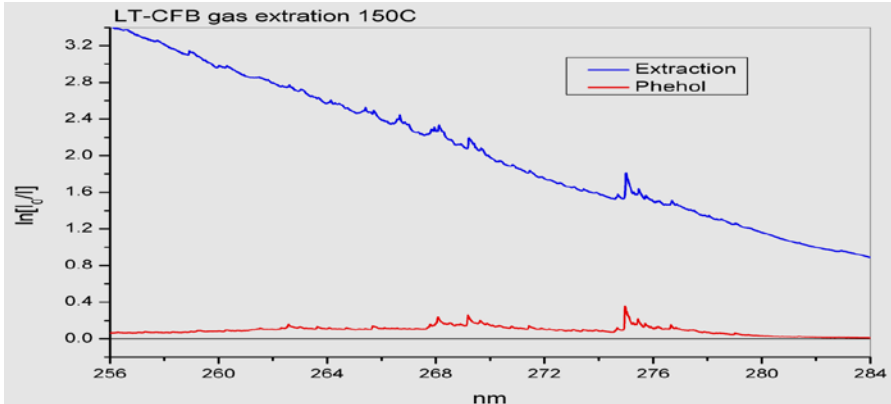
Abs cross-sections: from 23C to 500C



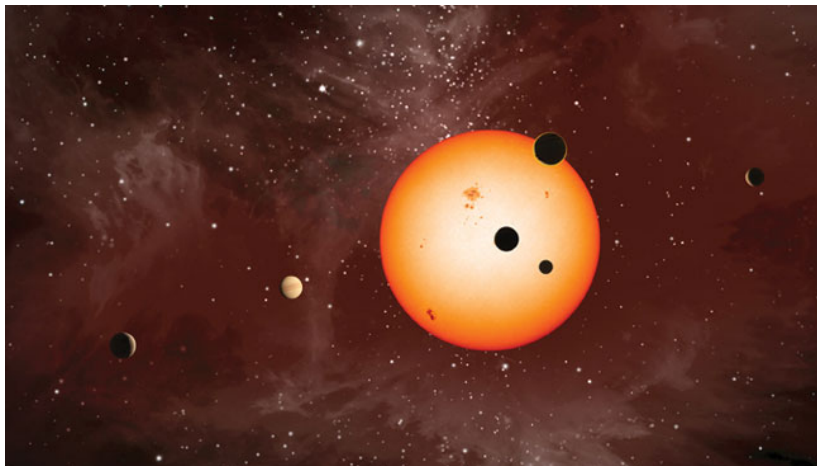
In Situ measurements on LT-CFB (100kW) gasifier



- 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);
- $T_{gas} = 300-500C$; In Situ UV abs measurements over 3 mm;
- Phenol measurements by various techniques:
 - GC/MS (Petersen column (30 min) 215 ppm ($\pm 5\%$))
 - Gas extraction, 150 C: 407 ppm ($\pm 5\%$) (3 min)
 - In Situ, 306 C (DOAS approach): 7700 ppm ($\pm 10\%$) (3 min)



- 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 (SO₂, SO₃, NH₃, 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: SO₃/SO₂ and Cl-compounds (KCl, HCl, CH₃Cl, CH₄, H₂CO)



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:

- Excellent experimental tools are available for (VUV) UV-FIR optical measurements
- Temperature range can be also negative (e.g. gases at low T)
- New data/lines for NH₃ BYTe extension and development
- New data for phenol
- Try always In Situ and avoid any Ex Situ (extraction) measurements



- To Energinet.dk: projects No. 2013-12027, 2011-1-10622, 2010-1-10422
- To MST.dk
- To DONG Energy and Vattenfall
- To UCL (Prof. Jonathan Tennyson's group)

