

Far-UV spectroscopy of molecules for industrial and planetary applications

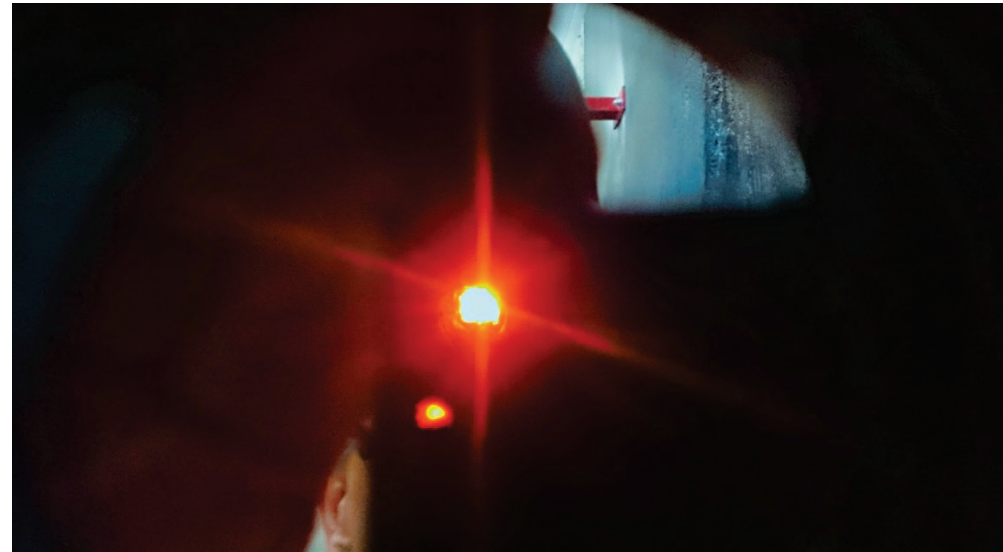
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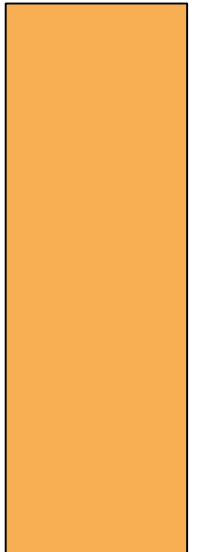
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Outline

- Re-born of oldies:
 - Rydberg-state spectroscopy
 - VUV as far-UV without vacuum: a practical approach
- Experimental facilities:
 - gas cells for wide-range of P/T's: 20-1500C/1-200bar
- Experiments on the Earth:
 - lab-measurements: far-UV cs database
 - field measurements: producer (gasification) and stack gases (combustion)
- Conclusions and Perspectives
 - let's do it together

ASTROBIOLOGY
Volume 16, Number 6, 2016
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DOI: 10.1089/ast.2015.1404

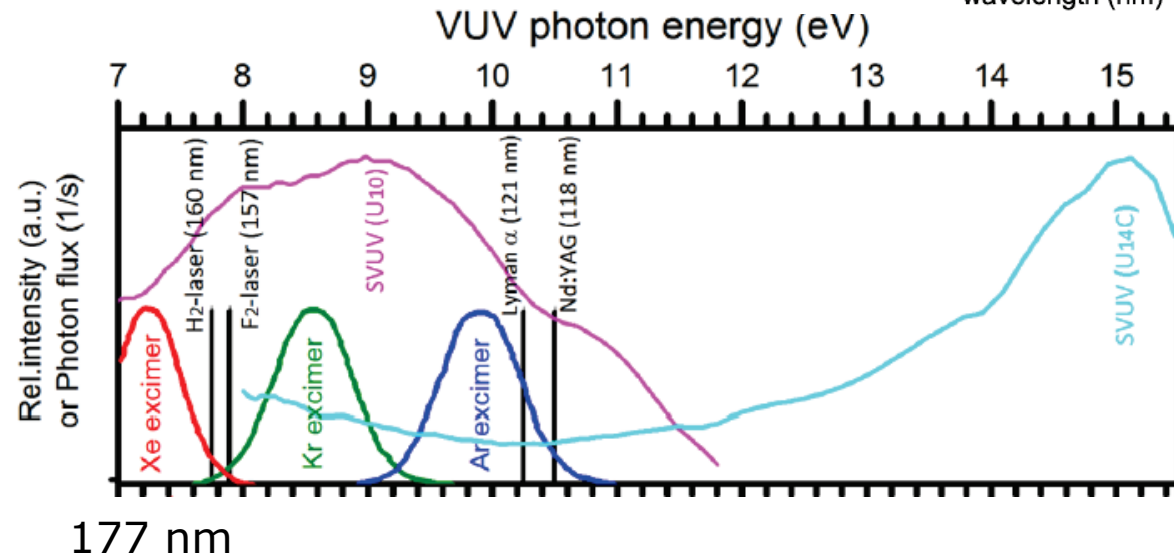
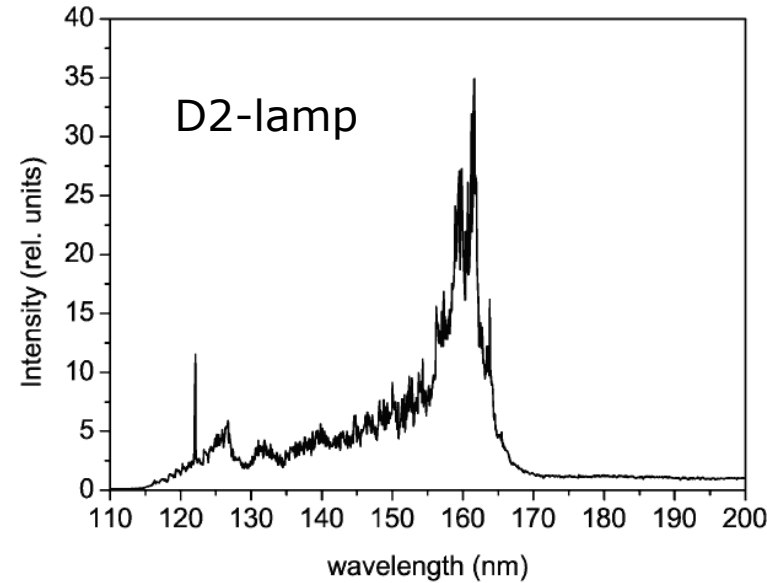
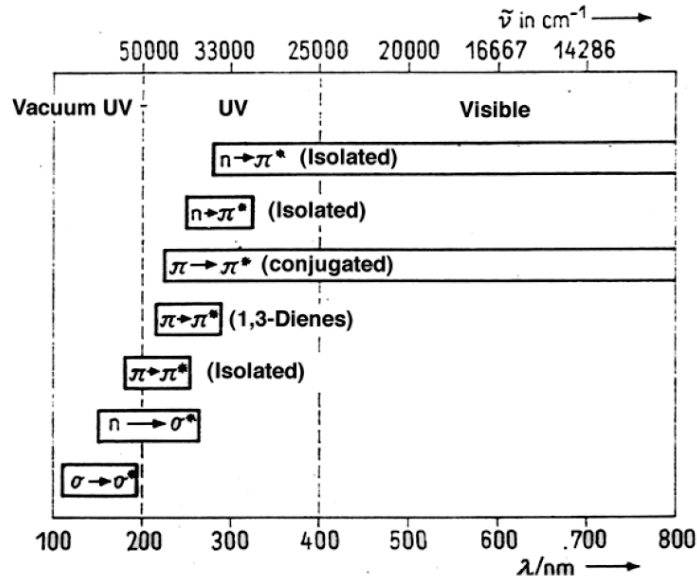
Toward a List of Molecules as Potential Biosignature
Gases for the Search for Life on Exoplanets
and Applications to Terrestrial Biochemistry

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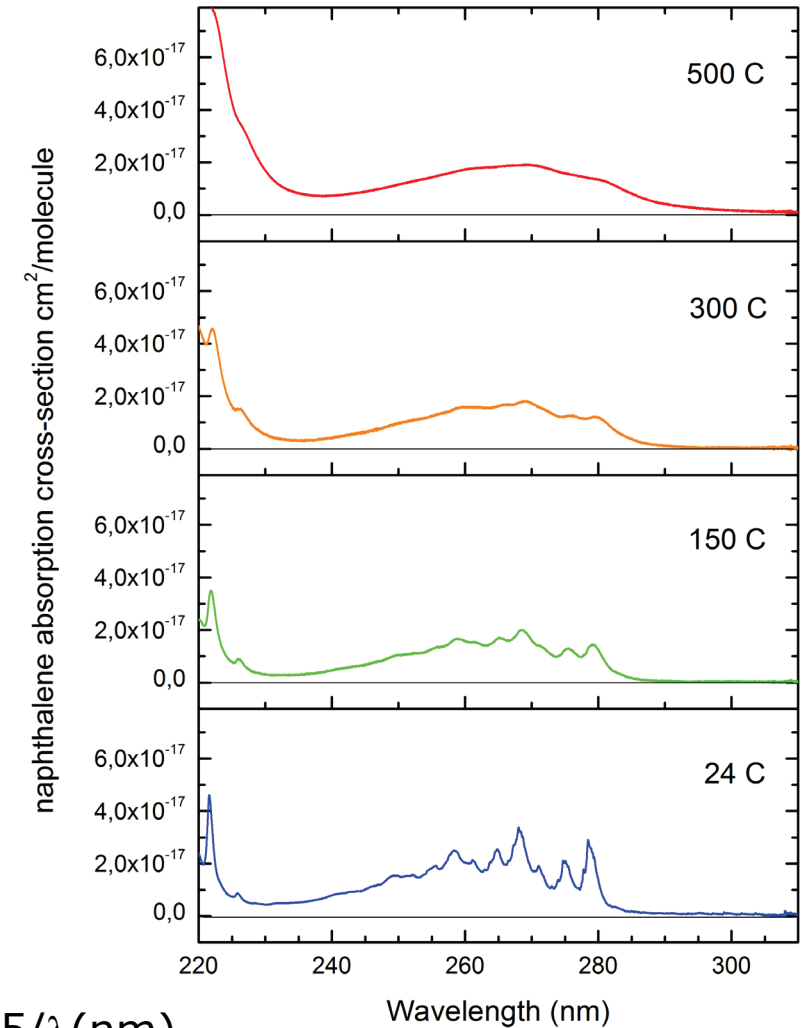
Re-born of oldies: VUV as far-UV

- Classical VUV definition: $\lambda < 200$ nm (when O₂ absorption matters)
4 main “-”:
 - forced use of HV-pump
 - light source availability (synchrotron the best)
 - spectrometer/optics performance drop at $\lambda < 110$ nm
 - windowless system design (i.e. coupled system)
- Far UV definition: $110 \text{ nm} < \lambda$ (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



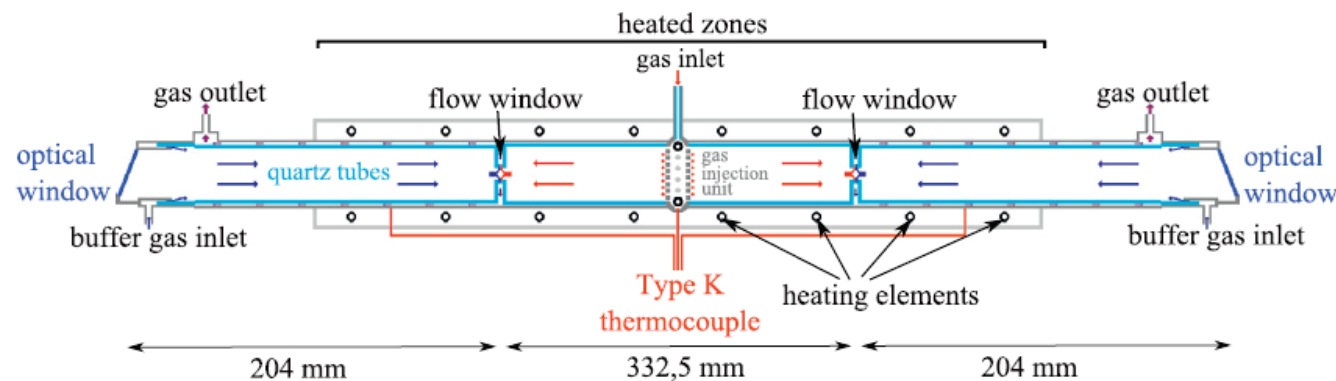
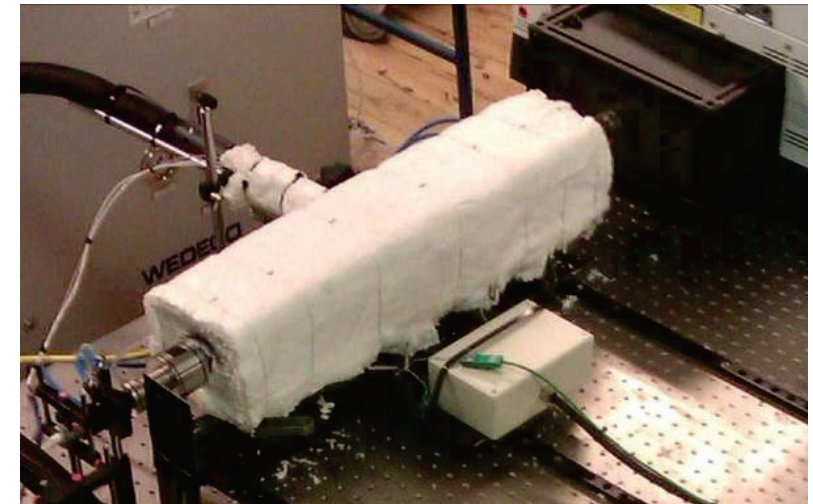
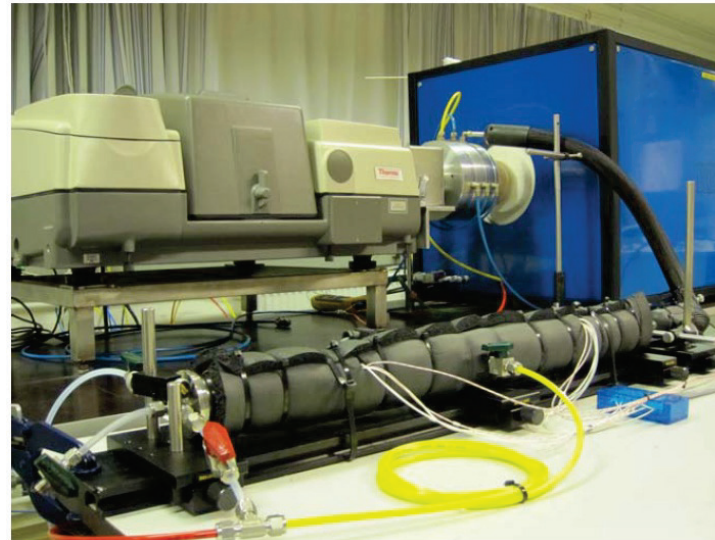
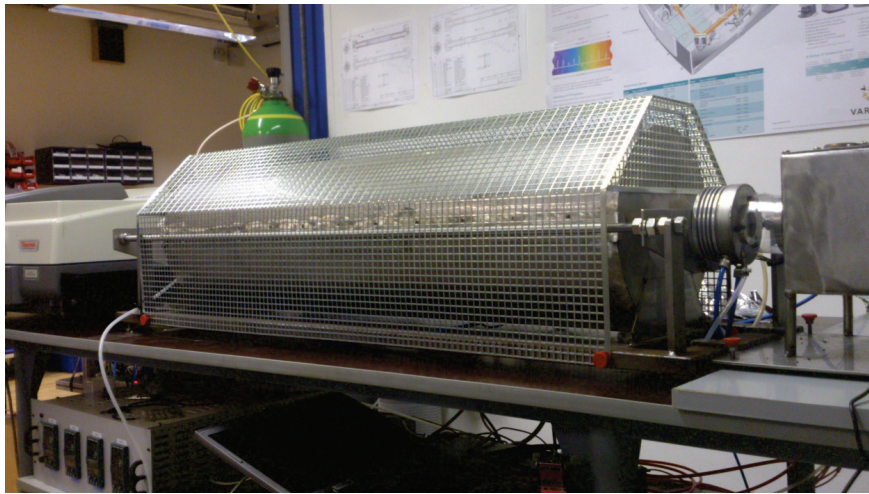
T-effects on spectra



$$E(\text{eV}) = 1239.85 / \lambda(\text{nm})$$

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

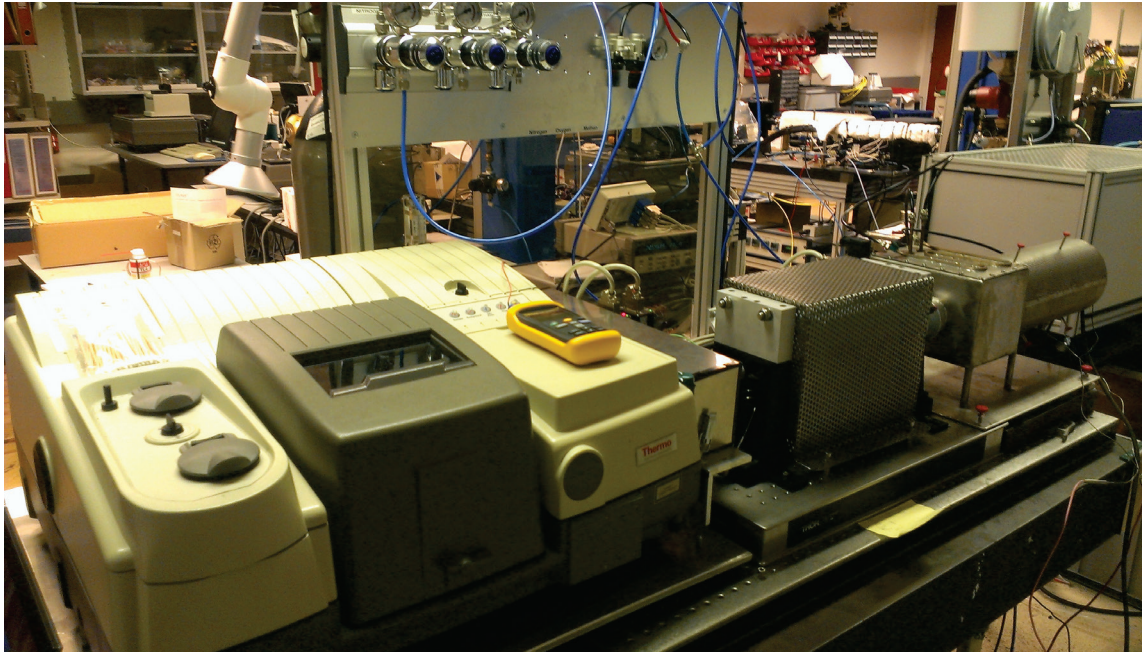


Replaceable outer windows:

- ❑ no reactive gas contact with windows
- ❑ far UV to μ w coverage

Experimental facilities: special case

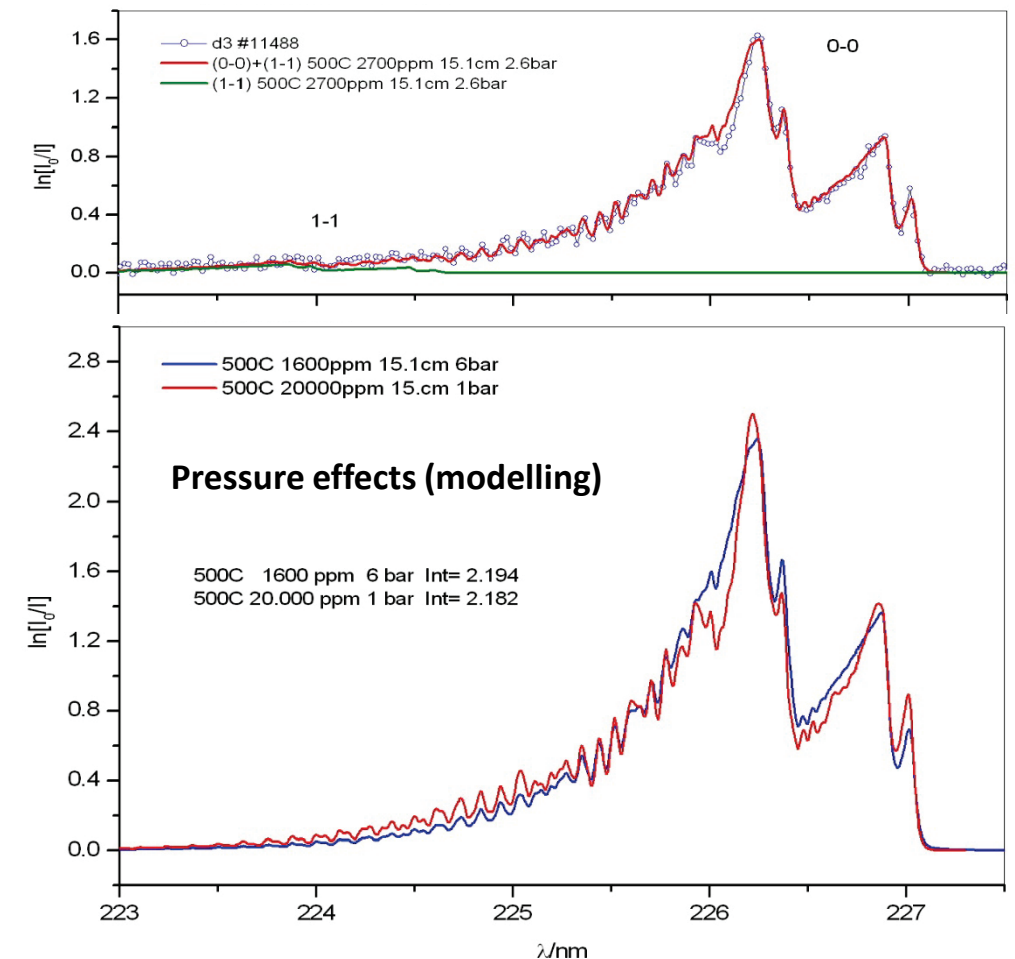
- high-pressure (up to 1000°C)/high pressure (up to 200 bar) flow gas cell



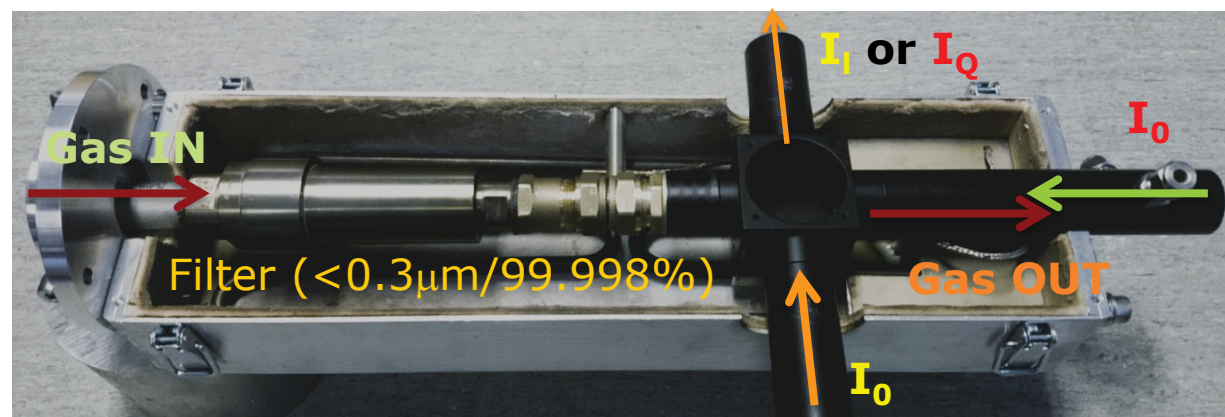
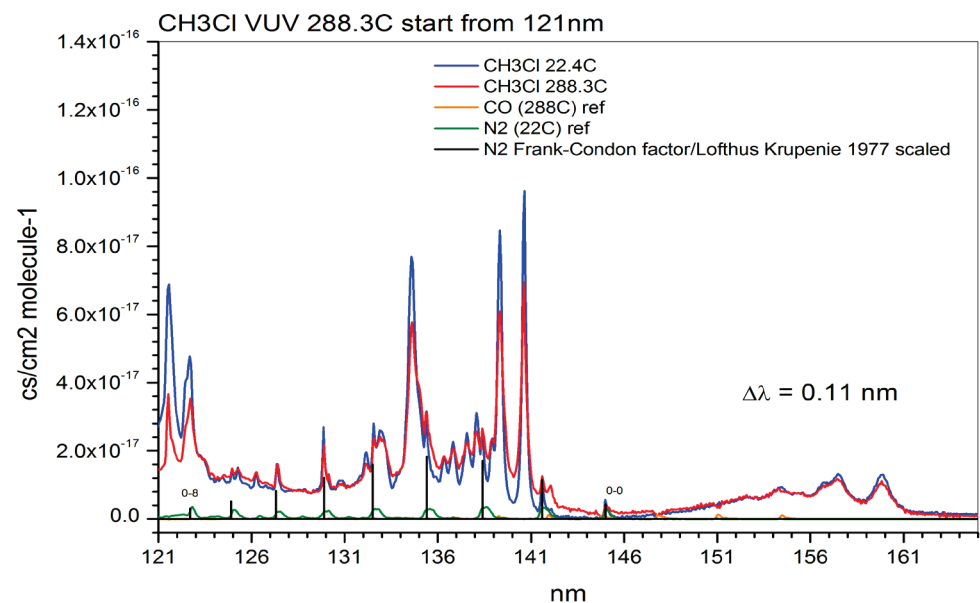
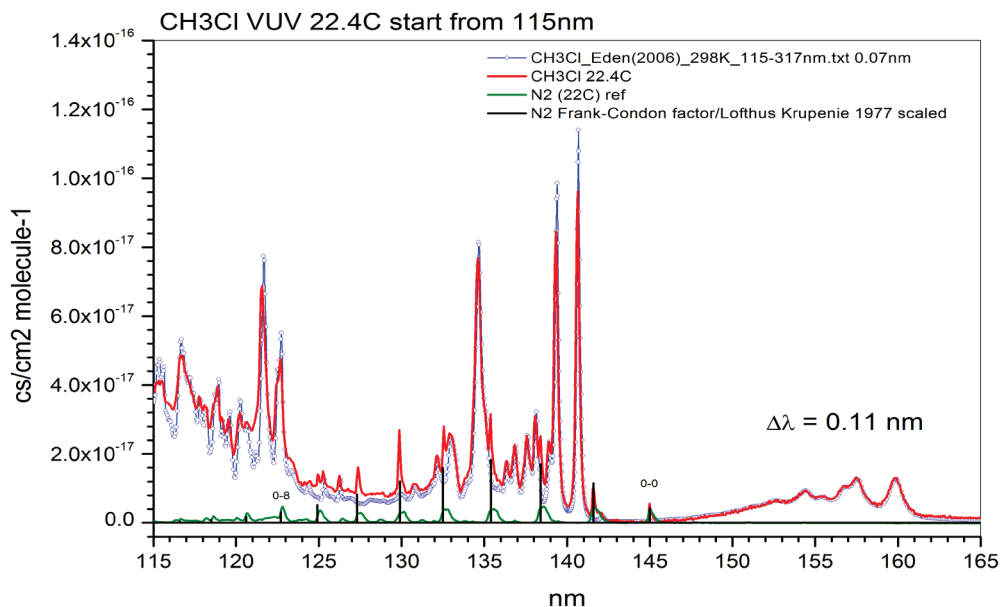
- sapphire windows:
- far UV to mid IR: CO₂, CO, O₂, NO, H₂O

UV NO band:

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



Far-UV spectroscopy of CH₃Cl and C₂H₄



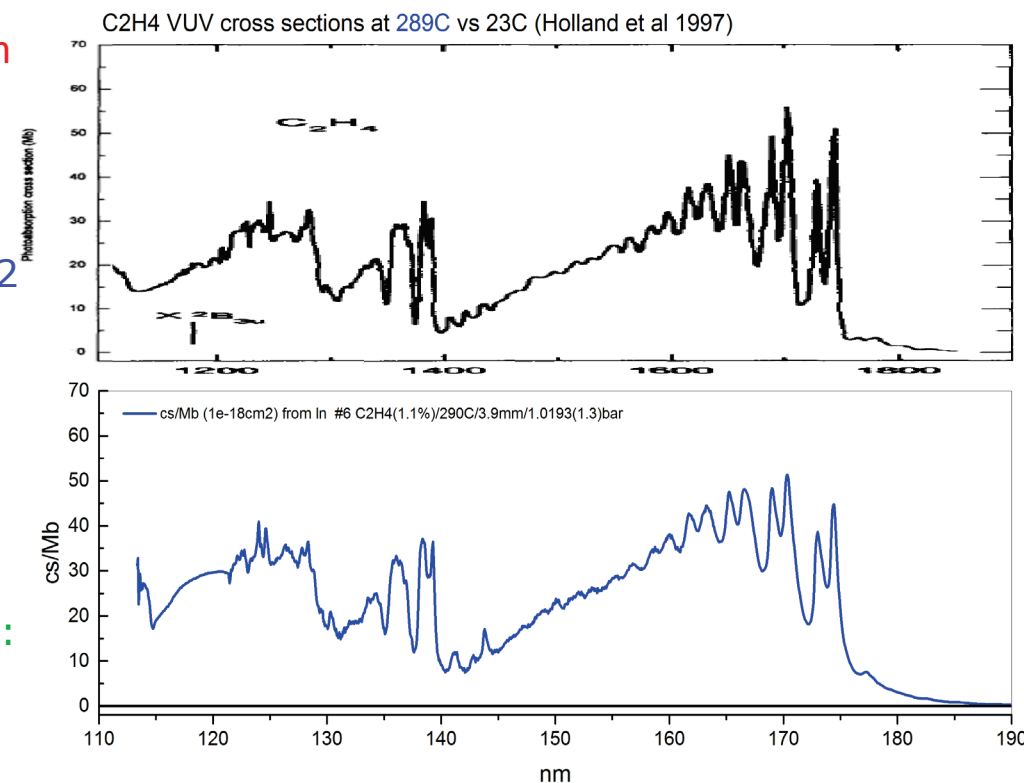
Measurements on 0.39 cm gas cell (up to 300C)

(λ -calibration with NH₃ spectrum)

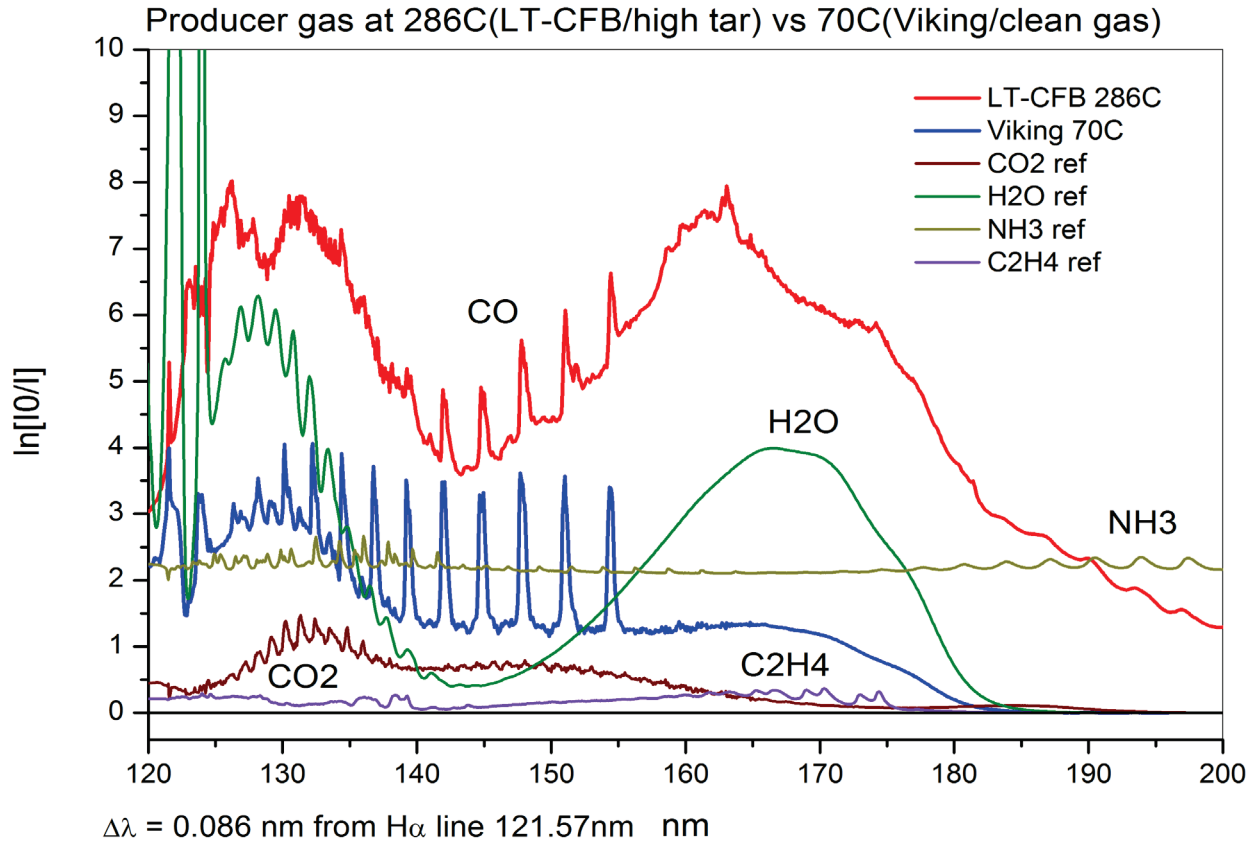
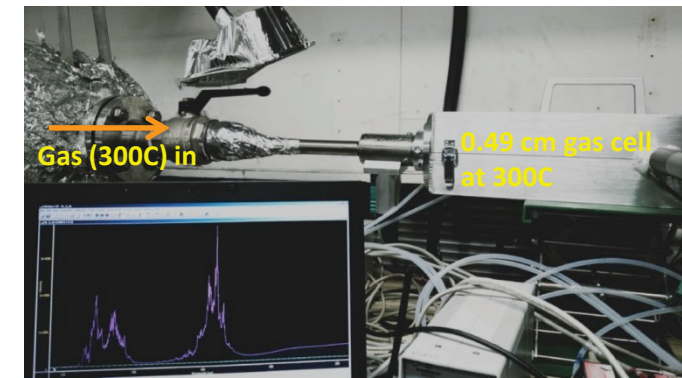
Lower end limited by MgF₂ cut off (temperature depended)

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

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

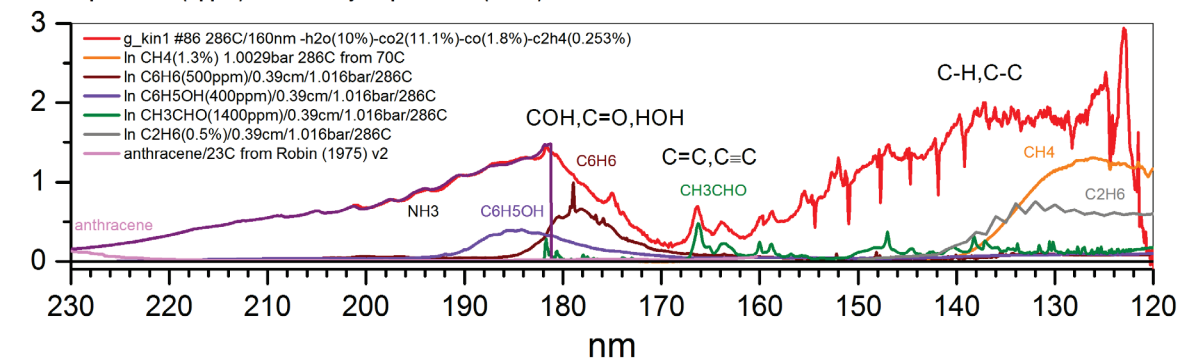
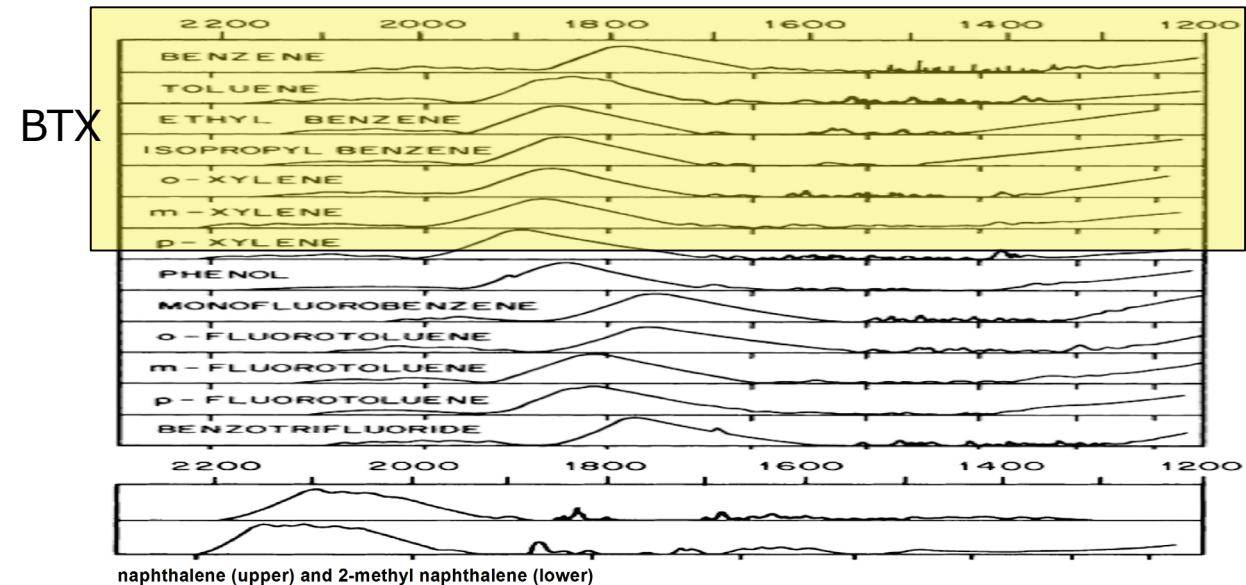


Field measurements: gasification



Tar (PAH) contribution to the total absorption:

- high:(most absorption(=concentration) due to BTX (170-190nm)
- medium: "light tar" (naphthalene+) (190-220nm)
- low: "heavy tar" (anthracene+) ($\lambda < 200 \text{ nm}$)

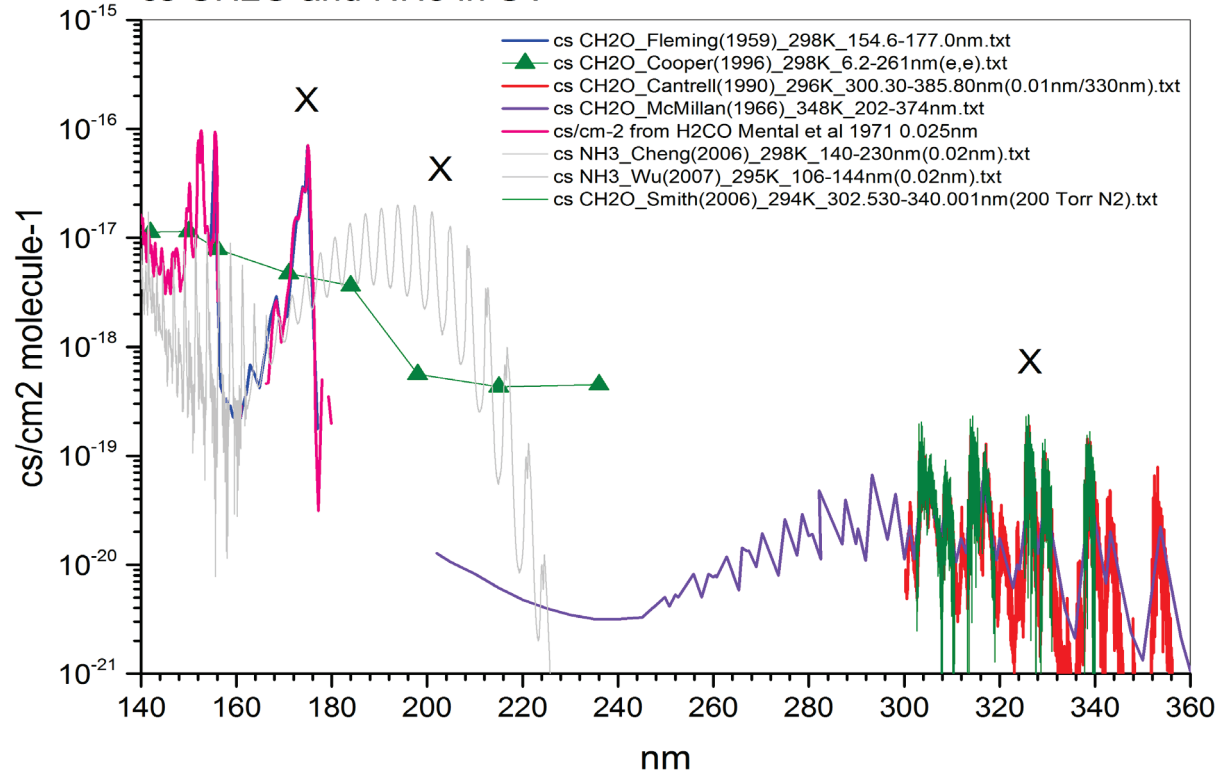


Typical residual spectrum after H₂O+CO₂+CO+C₂H₄ subtraction

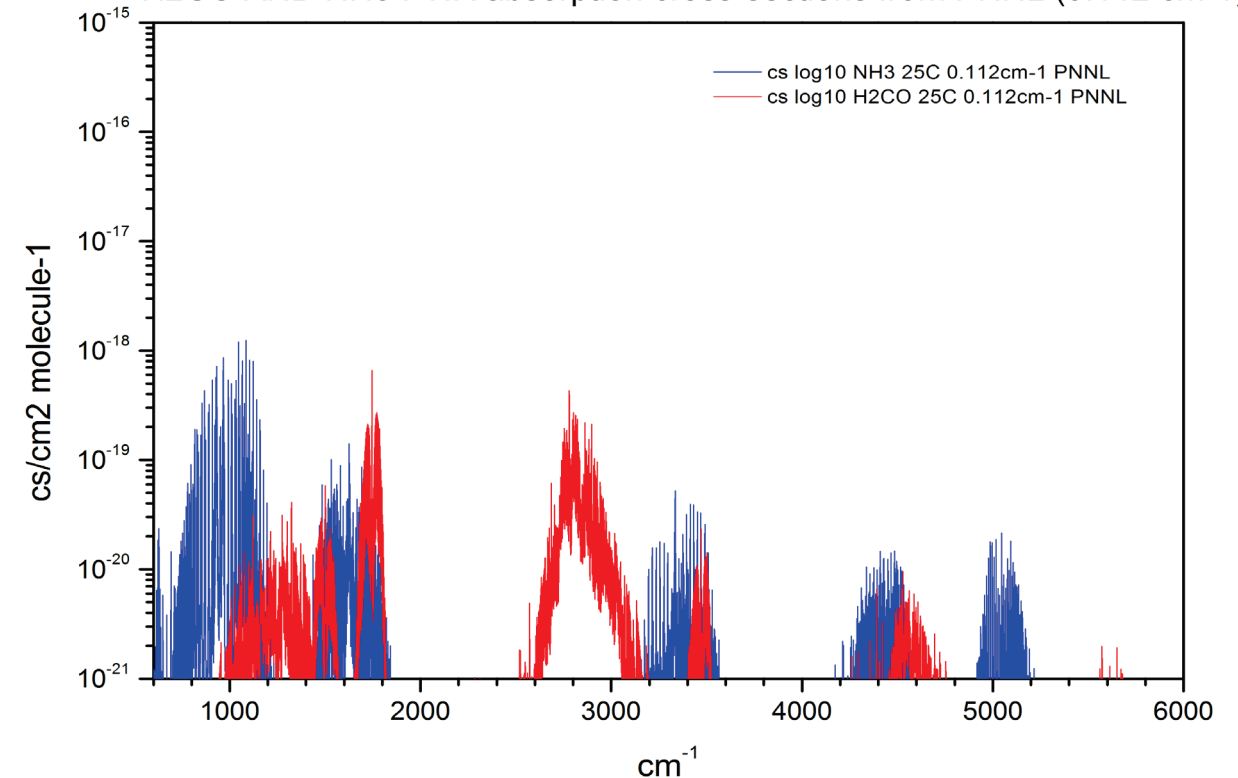
Far-UV spectroscopy of NH₃ and H₂CO

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

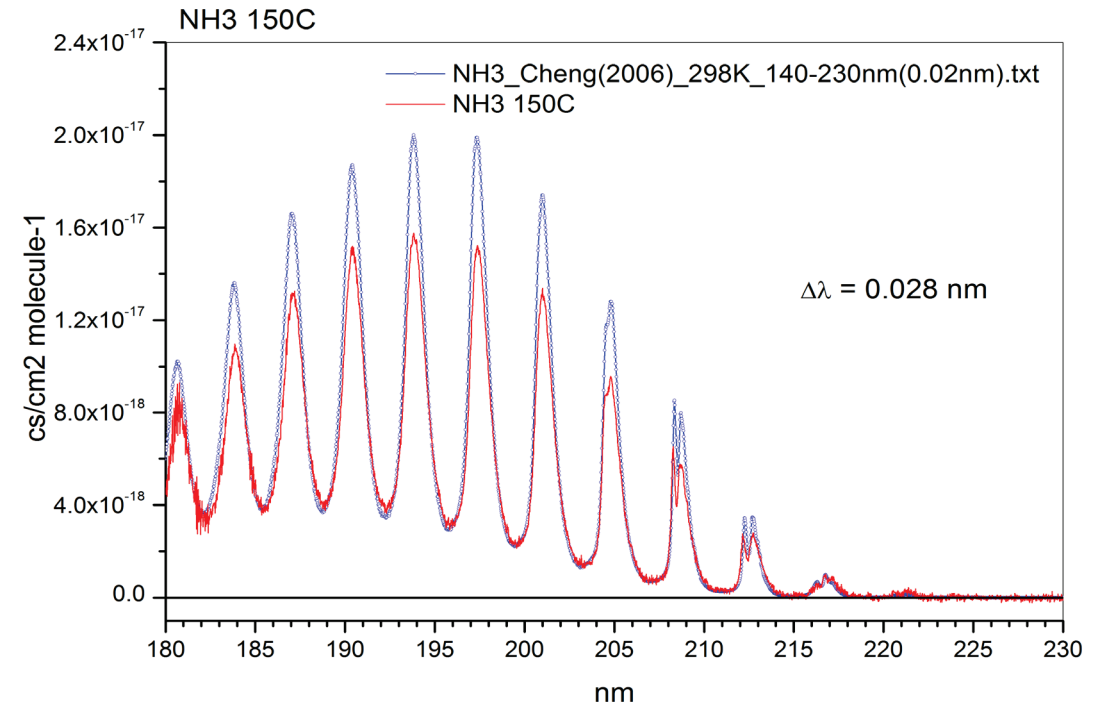
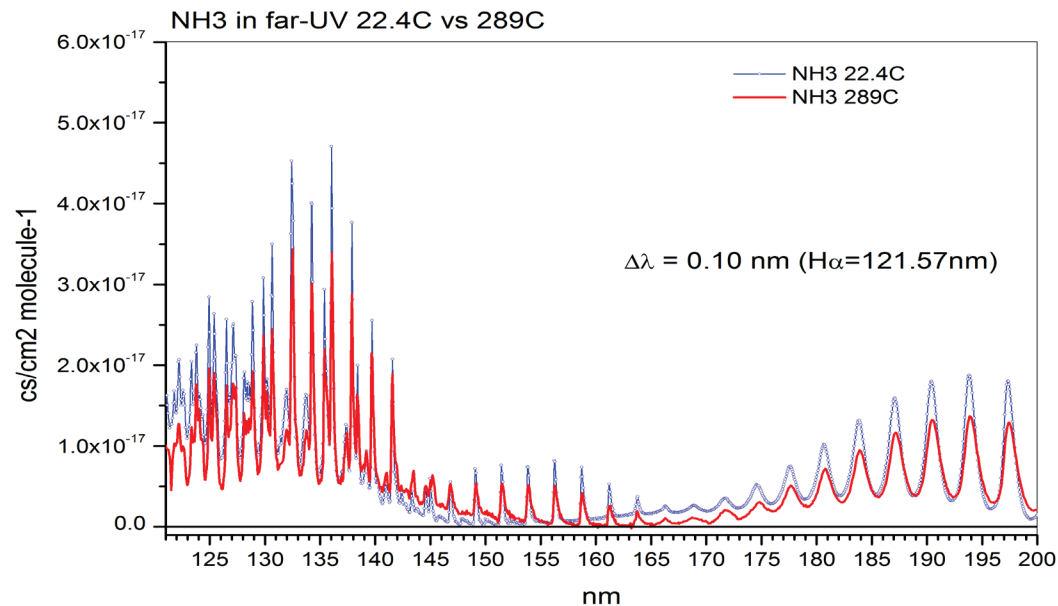
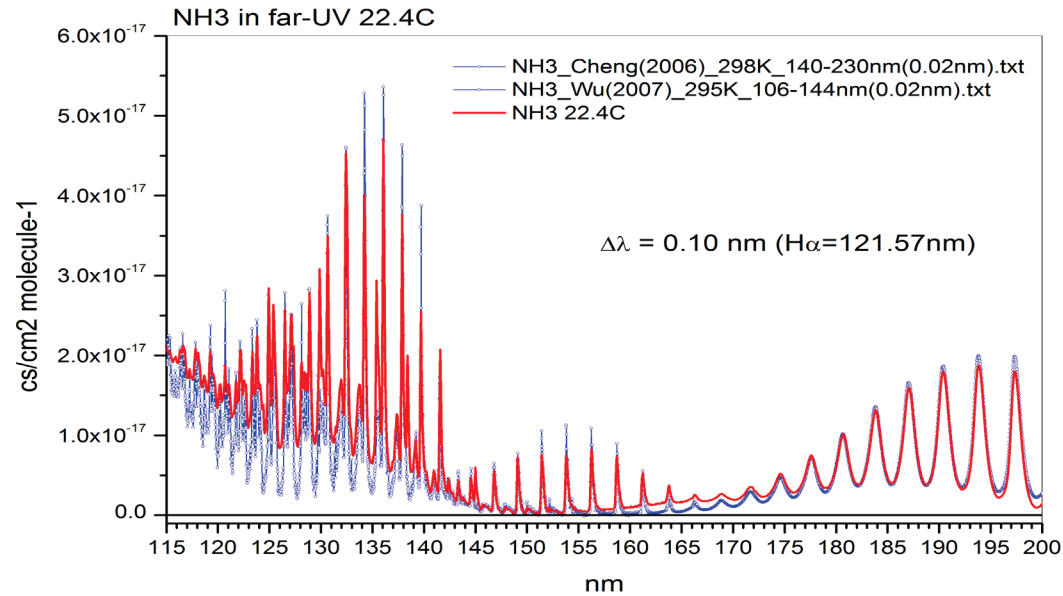
cs CH₂O and NH₃ in UV



H₂CO AND NH₃ FTIR absorption cross-sections from PNNL (0.112 cm⁻¹)



Far-UV spectroscopy of NH₃



- ❑ Difficult molecule to deal with
- ❑ Most reliable data: $180 < \lambda$

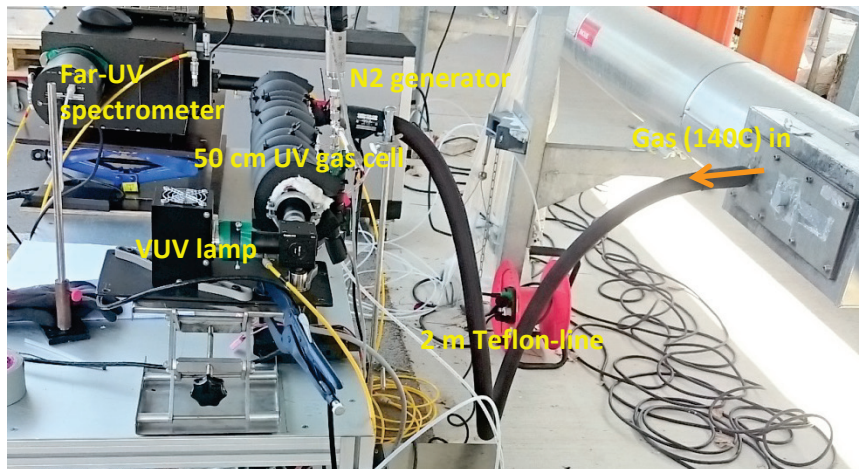
NH₃ spectra analysis:

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

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

IMPRESS 2: **Metrology for
Air Pollutant Emissions**

Field measurements: NH3 in stack gas

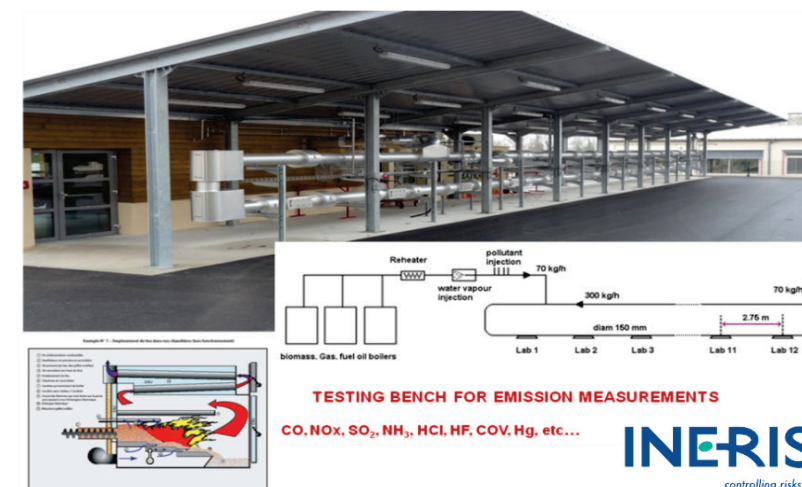


Combustion cases:

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

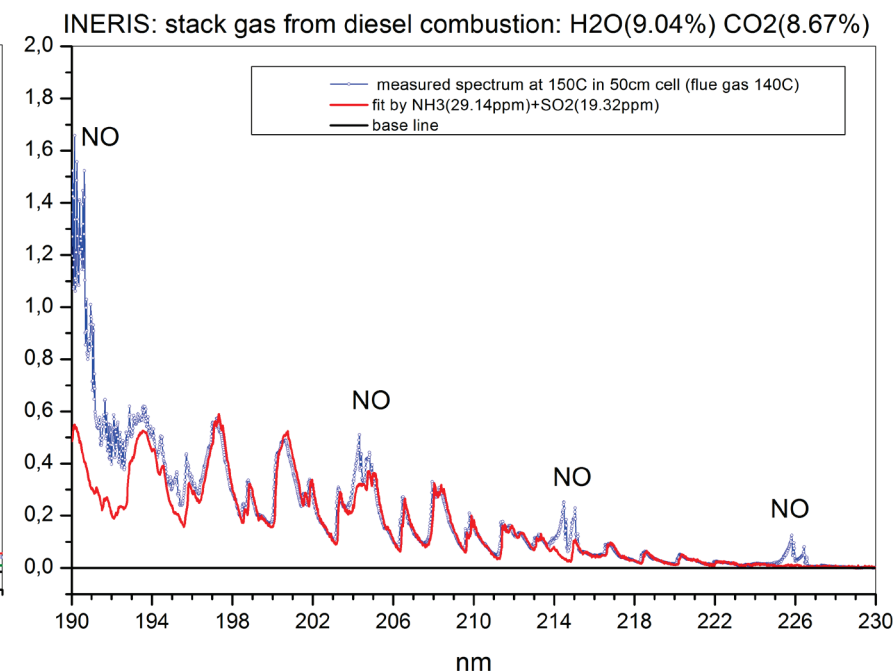
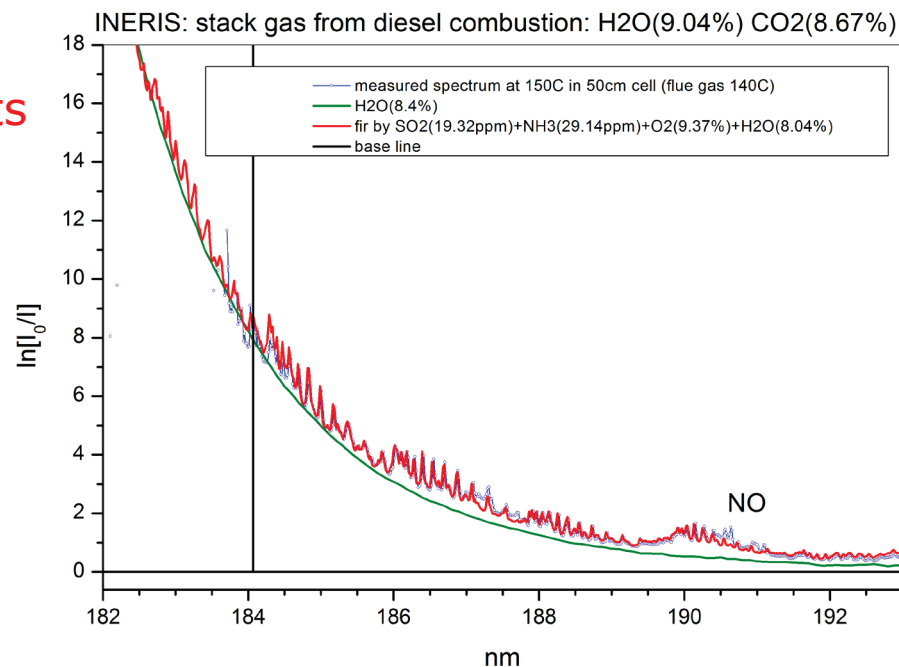
On-line measurements at 150C

- above stack gas temperature 130-140C

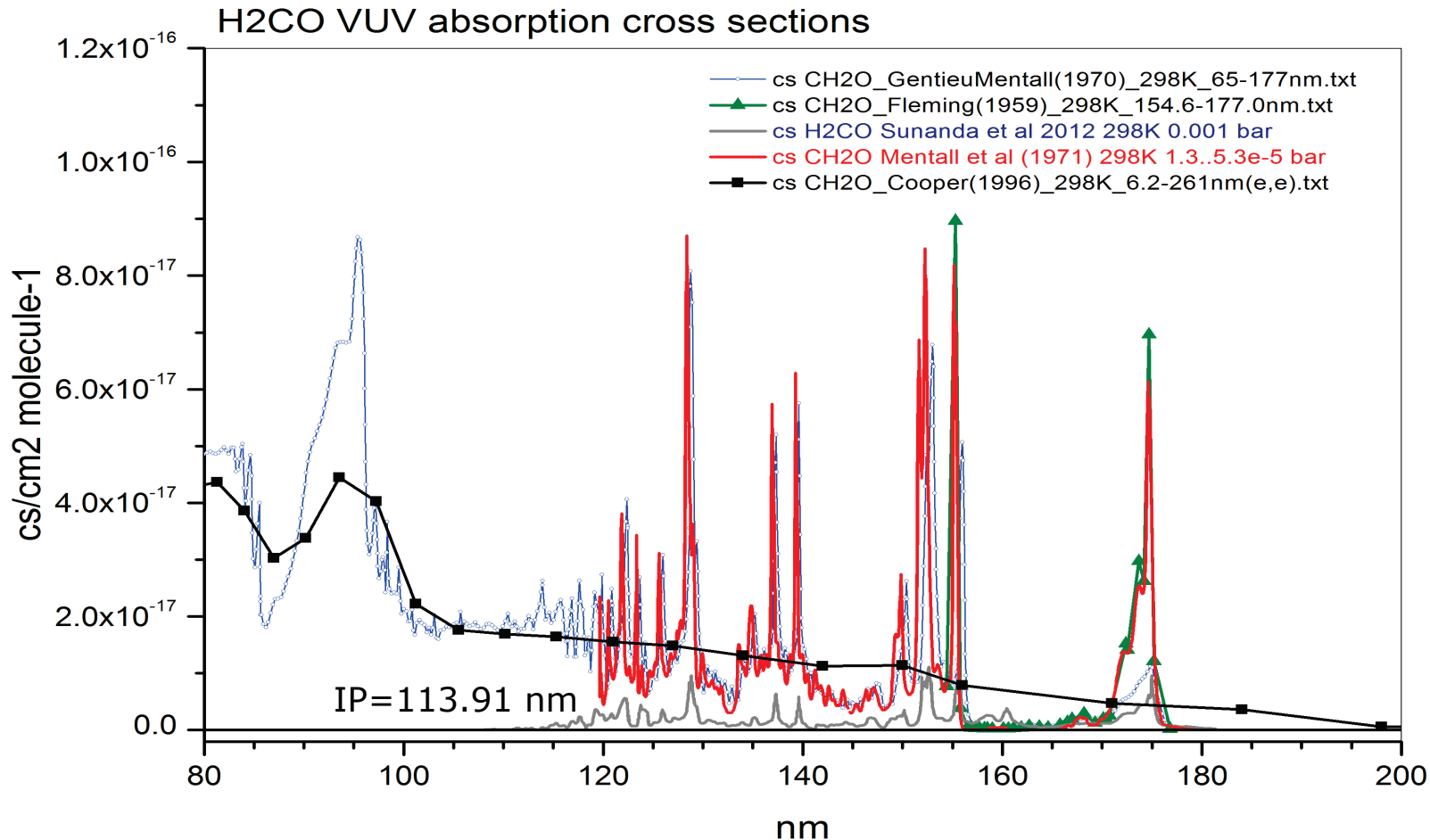


- ✓ In situ/on-line measurements
- ✓ Limited by H2O (50cm)
- ✓ Excellent sensitivity to NH3, SO2, O2, H2O, NO

IMPRESS 2: Metrology for Air Pollutant Emissions



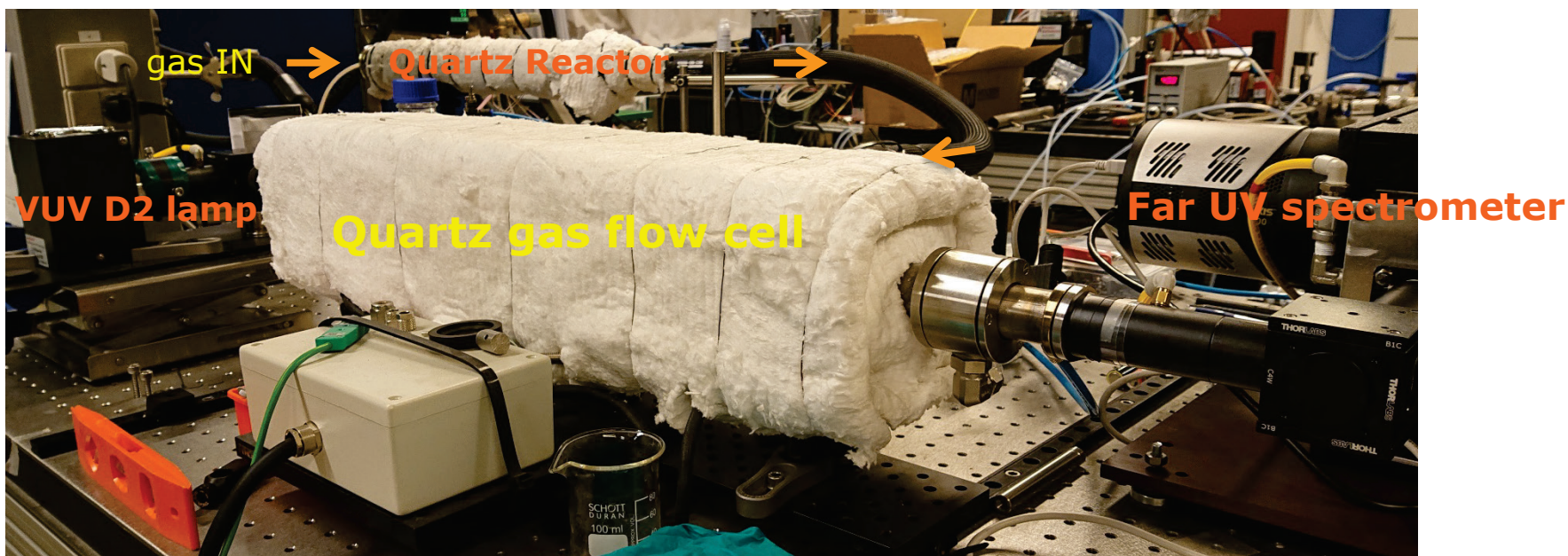
Far-UV spectroscopy of H₂CO



□ Very dispersed cs-data *)

□ Large variations in cs's at 175 nm

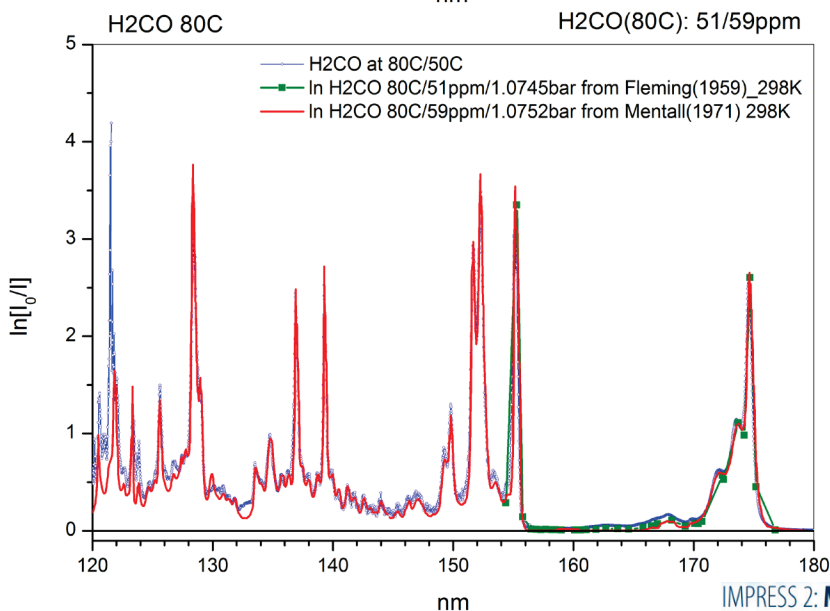
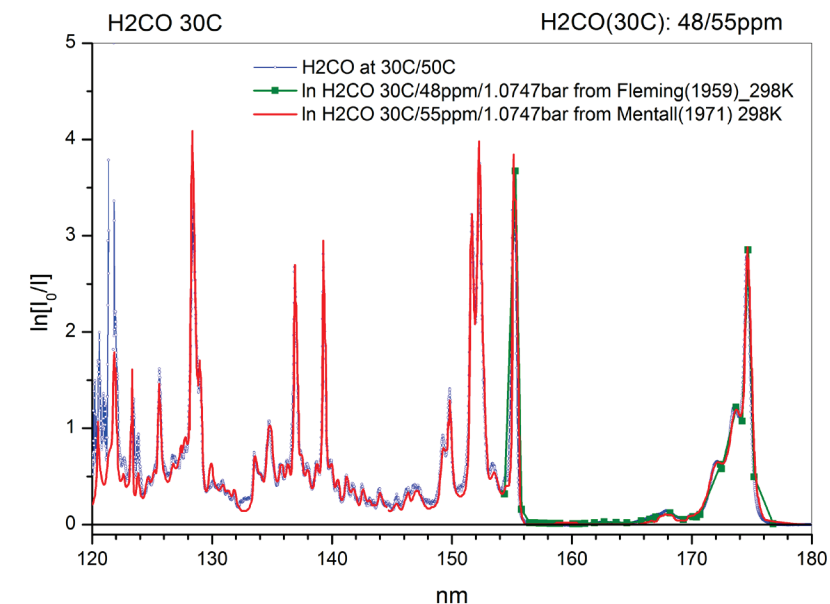
Far-UV spectroscopy of H₂CO: set up



- ❑ Used as a water solution
- ❑ Easy polymerized to paraformaldehyde at ambient conditions: special treatment needed
- ❑ Paraformaldehyde available (powder)
- ❑ Can be converted to formaldehyde if heated

- ❑ Heat paraformaldehyde powder in a dish in a carry gas flow over the dish (N₂, Ar)
- ❑ Heating to 50-70°C (in Reactor) can produce about 50-350 ppm of formaldehyde in the carry gas
- ❑ Need absolute calibration with use reference data or sampling

Far-UV spectroscopy of H₂CO



□ Heating to 50C gives 48/55 ppm (30C) or 51/59 ppm (80C)

□ Excitation to Rydberg triplet states (160 nm, Sunanda et al 2012)?

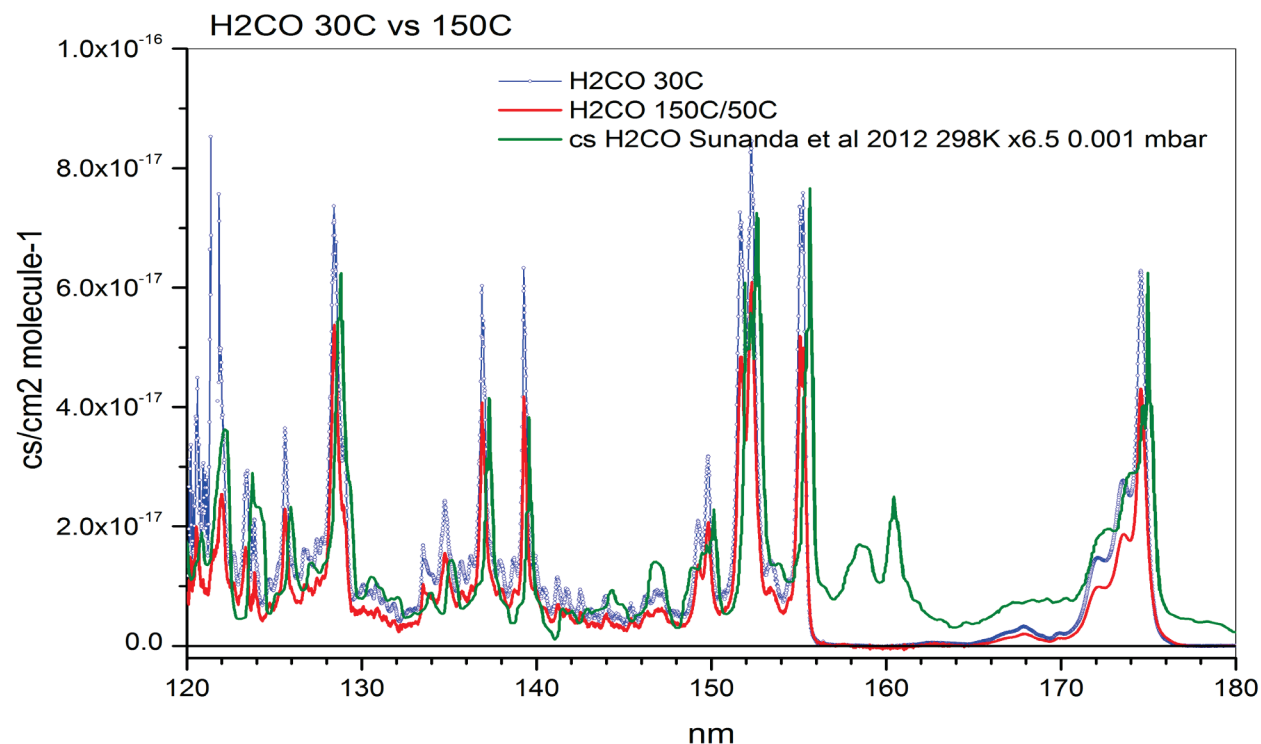
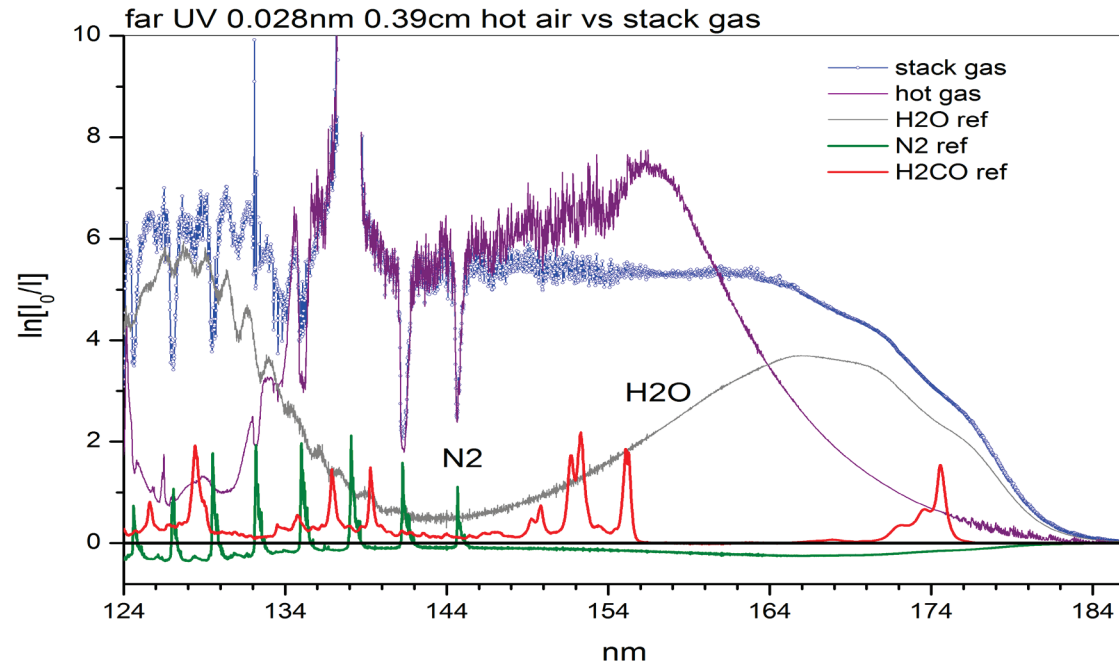


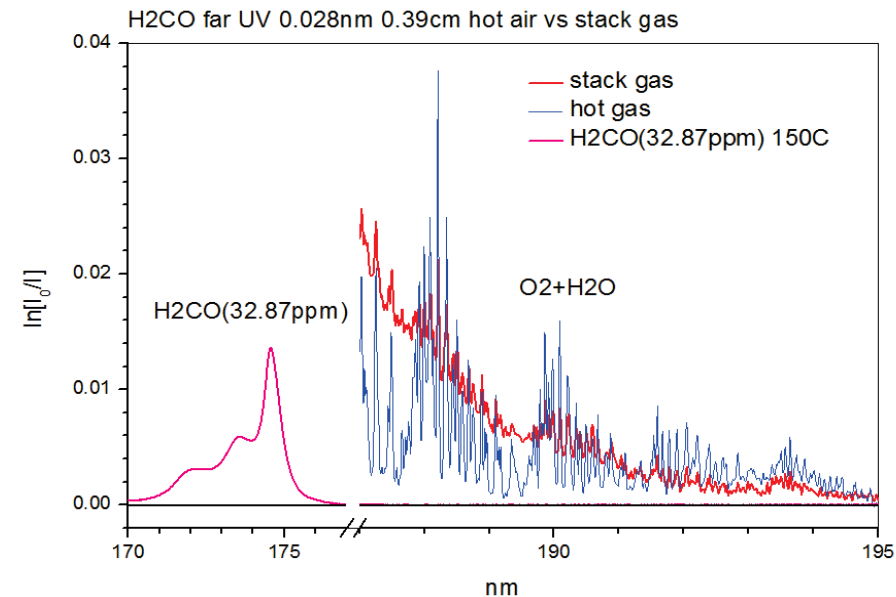
TABLE 5 Calculated Vertical Excitation Energies (in eV) for Rydberg and Valence Transitions, Oscillator Strengths and Charge Transfer Character in Triplet States of HCHO

No.	State	Transition	CIS		TDDFT		λ	Level of theory			Exptl. Present work
			6-311	apc2	6-311	apc2		CIS-MP2	MRD-CI	TDDFT	
5	³ A ₁	n – 3p _y	9.607	9.487	7.426	7.247	0.166	7.78	7.92	7.10	7.784
6	³ B ₂	n – 3p _z	9.306	9.192	7.448	7.209	0.246	7.75	7.93	7.07	7.728
7	³ A ₂	n – 3p _x	10.587	9.854	9.854	7.713	0.188	8.16	8.41	–	8.059

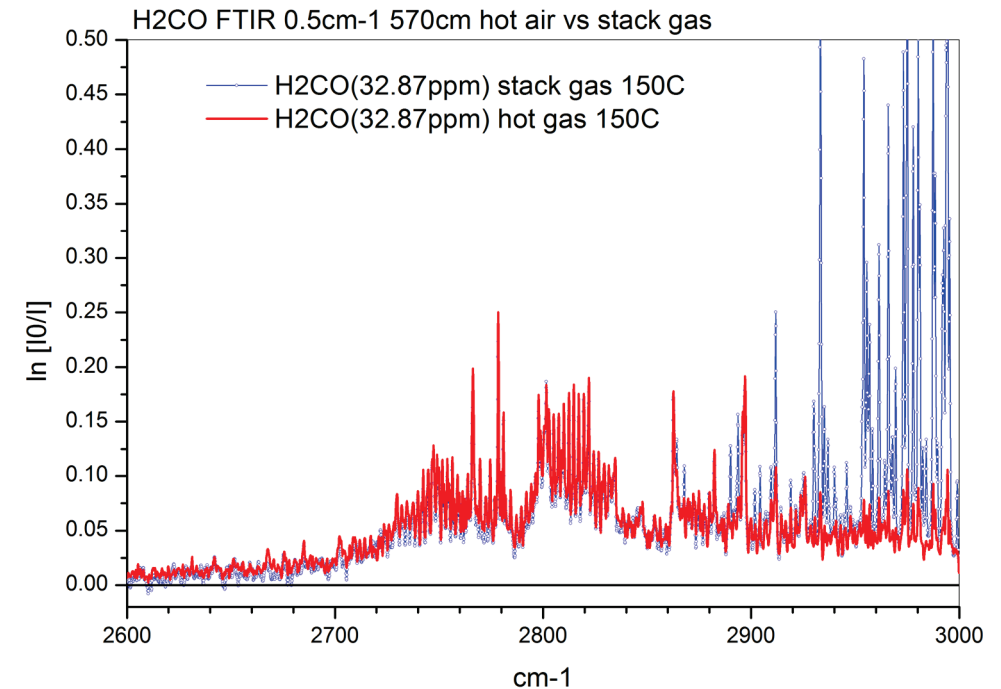
Field measurements: H₂CO in stack gas



- ❑ H₂CO(32.87ppm) measured in hot air but not in stack gas (natural gas combustion)
- ❑ N₂/O₂ measurements possible
- ❑ no need for high-resolution measurements



- ❑ Far UV H₂CO measurements is at least 100x more sensitive compare to IR
- ❑ H₂CO measurements in IR require much longer pathlengths



Conclusions and perspectives



- ✓ Far UV spectroscopy technique is power tool for various applications
- ✓ No need for HV pumps, just Ar or N₂ (bottles or generators)
- ✓ No needs for expensive light sources and measurement campaigns and travels
- ✓ Mobile and flexible system
- ✓ Can easily coupled to various high-pressure/high-temperature gas cells
- ✓ Low pressure/low-temperature extension possible
- ✓ 2x examples are shown (trace gas measurements)
- ✓ Opened for collaboration

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The Need for Laboratory Work to Aid in The Understanding of Exoplanetary Atmospheres

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chemistry. Specifically highlighted are needs for: (1) molecular opacity linelists with parameters for a diversity of broadening gases, (2) extended databases for collision-induced absorption and dimer opacities, (3) high spectral resolution opacity data for a variety of relevant molecular species, (4) laboratory studies of haze and condensate formation and optical properties, (5) significantly expanded databases of chemical reaction rates, and (6) measurements of gas photo-absorption cross sections at high temperatures. We hope that by meeting these needs, we can make the next two decades of exoplanet science as productive and insightful as the previous two decades.

Acknowledgments



- Energinet.dk: projects No. 2013-12027 and 2011-1-10622
- The work partly has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme

IMPRESS 2: **Metrology for
Air Pollutant Emissions**

Thank You

Questions? Comments?



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