Final report

1.1 Project details

Project title	**High-resolution spectroscopy of Cl-compounds in gasification**
Project identification (program abbrev. and file)	**2013-1-12027**
Name of the programme which has funded the project	**Forsk EL**
Project managing company/institution (name and address)	**DTU Chemical Engineering, Søltofts Plads 229, 2800 Kgs. Lyngby, Danmark**
Project partners	**University College London (UK)**
CVR (central business register)	**30060946**
Date for submission	**15-12-2017**

1.2 Short description of project objective and results

The main objective of the project is to develop the technique and establish data needed to measure and analyse the gas composition from gasifiers at high temperatures by high resolution spectroscopy with focus on Cl-compounds, e.g. using a high temperature gas cell or a direct optical measurements across the hot producer gas flow.

The technique consists from a base knowledge (reference spectra data sets easily expandable) and tools (far UV spectroscopy).The results obtained in the project can be used for developing a far UV analyzer targeting various species as various Cl-compounds, N_2, O_2, NH_3, HC, BTX and tar. Line lists for HCl, CH_4, CH_2O and CH_3Cl can be used for quantifying their respective concentrations in *in situ* optical infrared measurements in various hot harsh environments.

1.3 Executive summary

The project is about developing far UV *in situ* measurement technique which can be used on various types of gasification units and other oxygen lean systems for trace Cl-compounds monitoring and control. The technique consists from a base knowledge (reference spectra data sets easily expandable) and tools (far UV spectroscopy).

The results obtained in the project can be used for developing a far UV analyzer targeting various species as e.g. various Cl-compounds, N_2, O_2, NH_3, HC, BTX and tar. Line lists for HCl, CH_4, CH_2O and CH_3Cl developed by UCL in IR make a solid basis and can be used for quantifying their respective concentrations in *in situ* optical infrared measurements in various hot gas environments either by a broad-band FTIR spectroscopy or by tunable narrow-band laser systems.

1.4 Project objectives

The main original objectives in the project were:

- Development of *in situ* high-resolution FTIR measurement technique of Cl-compounds which can be used on various types of gasifiers;
- Development of high-temperature spectroscopic database of Cl-compounds those will be used in the accurate analysis of complex datasets obtained from measurements on gasification units.

Due to project execution it was decided to move into development of *in situ* far UV measurement technique instead of high-resolution FTIR one as in the first objective.

The project consists from 6 work packages (WP).

1.5   Project results and dissemination of results

Originally the project was about use a high-resolution IR (FTIR) spectroscopy for gas composition measurements on gasification units. Due to project execution and developments it was shown that other spectral range (far UV) has several advantages over the IR one. Therefore upon an agreement and permission from Energinet.dk some project activities in WP1, 2 and 5 have been extended to far UV spectral range. Relevant new experimental equipment was acquired keeping however the budget frames of the project. Here new activities, not described in the original project application are summarized.

New activities not previously described in the project

With the new equipment the work under WP's 1, 2 and 5 was extended to far UV (120-200 nm) spectral range. The equipment here is defined as a far UV spectrometer equipped with far UV CCD camera with a high output far UV light source.

The changes regarding the projects WP's are listed below. More detailed description can be found under relevant WP below.

WP1: Because two KCl gas cells suitable for UV measurements (200-400 nm) are established and proven at Lund University and Vattenfall R&D (Älvkarleby) it was intended to use one of them with minor modifications in the project. In this way there is no need to establish a new KCl gas cell, what was a goal for the WP1. With the new equipment the KCl measurements in the UV spectral range have been extended to far UV range. It should be noted that there is only one paper from 1967 about KCl measurements in the UV range and new (recently published) data from Lund University (T Leffler et al (2017). There are no far UV data for KCl at all. The work under WP1 was carried out in collaboration with Vattenfall R&D (Älvkarleby).

WP2: The work under this work package has been extended to far UV range. The existing hot flow gas cell at Vattenfall R&D (Älvkarleby) was used for KCl measurements in far UV. A new small gas cell mounted in the heated box and the heated 2 m probe has been designed and made. Reference measurements for selected molecules CH_3Cl, H_2O, CO_2, CH_4, C_2H_4 and NH_3 have been made in temperature range 23C-300C because existing reference data for the mentioned molecules in far UV are limited by low temperatures only (about 23C). Therefore reference measurements in far UV spectral range 1) support future publications under the project (dissemination) and at the same time 2) are used in analysis of the data obtained in in situ measurements at LT-CFB and Viking gasifiers (WP5).

WP5: Several in situ measurements in far UV spectral range on high-temperature gasifier Viking (two operation conditions) and low-temperature LT-CFB one (two operation conditions) have been made in June and November 2017, respectively.

WP1: Vapor generation system: KCl

Optical measurements with KCl are quite challengeable because KCl which is at normal conditions is in form solid crystals has to be brought into the gas phase by heating at 650-850C.

A gas cell suitable for ultraviolet (UV) KCl absorption measurements in 200-350 nm spectral range has been developed by Vattenfall Research and Development AB and Umeå University (Sweden) for several years ago. The cell has several advantages and disadvantages. Advantages are: it's the flow cell which can be operated at around ambient pressure, changeable, relatively cold outer windows and no contact of the KCl with windows because of left/right N_2-buffer zones in the cell. Disadvantages are: only Ø6 mm aperture size in the active measurement path, high operation temperature (850C) and not simple way for KCl concentration calibration.

Another low-pressure sealed in Ar (1mbar at 25C) KCl-cell has recently been developed by Tomas Leffler in frames of his industrial PhD project between Lund University and Vattenfall Research and Development AB (Sweden) about KCl UV absorption cross sections measurements. The cell which is also designed for KCl UV measurements in 200-350 nm spectral range has Ø30 mm aperture size, low operation temperature (from 650C), accurate KCl concentration calibration possibility, but low total pressure in the cell.

It was hold a meeting and several other discussions with Tomas Leffler about new (at Lund) and old (at Vattenfall, Älvkarleby) KCl cells design, operation and KCl calibration. It was confirmed that both cells can be available for the UV measurements upon an agreement.

Based on the results under the WP3, far-infrared (FIR) KCl absorption cross-sections at 650C and 850C have been calculated by UCL in 10-300cm^{-1} spectral range, Fig. 1 (left). In the same Figure UV absorption cross sections from Forsberg et al (2009) are shown for comparison.
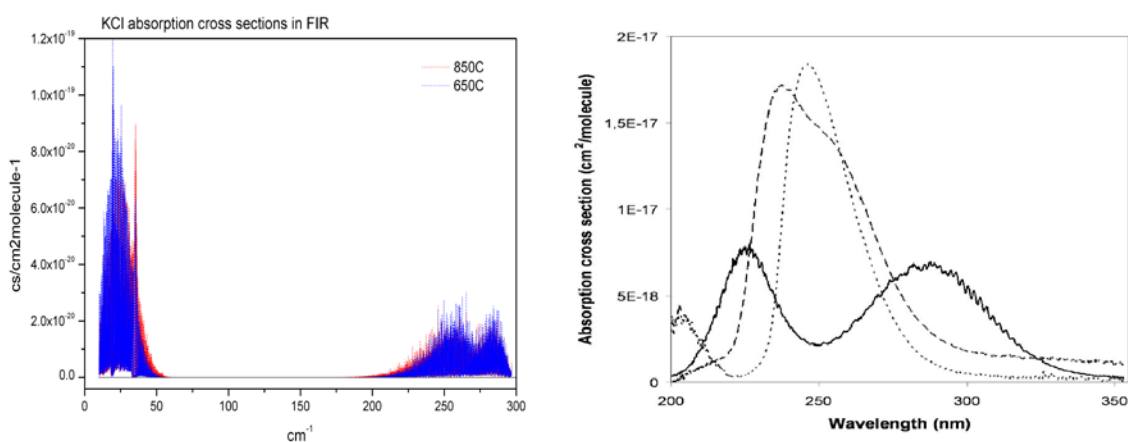
Figure 1: Calculated absorption cross sections for KCl in FIR (left) at 650C (blue) and 850C (red) and measured KCl UV absorption cross-sections at 860C (rigt, dotted line). SO$_2$ is presented by a solid line, NaCl by a dashed line. UV data are from Forsberg et al (2009).

One can see that the absorption cross-sections for KCl differ about 200 times at their maximum values in FIR and UV. It means that KCl absorbs light about 200 times more efficiently in UV compare to the FIR range.

The gas cell design at Lund can be modified to suit for FIR measurements. However UCL calculations (Fig.1) show that it will be impossible to perform FIR measurements with this cell because of extremely low KCl absorption in 20-300cm^{-1}.

Measurements on the gas cell at Älvkarleby seem to be on the edge of the FTIR spectrometer sensitivity with FIR detector in both 10-50cm^{-1} and 200-300cm^{-1} spectral ranges. Therefore an alternative way for KCl measurements has been investigated.

It is known that all molecules (e.g. H_2O, CO_2, CO, C_xH_y etc.) have very strong absorption in far UV spectral range (< 200 nm). This spectral range is commonly (outdated) called as a vacuum ultraviolet (VUV) meaning that O_2 will strongly block UV light below 185 nm and N_2 below 115 nm and therefore evacuation of the optical equipment is normally needed if one wants to work below 185 nm.

In 115-140 nm N_2 has a week absorption and therefore in 120-200 nm spectral range and in the absence of O_2 the measurements can successfully be performed if a relevant purge of the optical equipment is used (e.g. by N_2 (140-200 nm) or Ar (115-200 nm)). The spectral range 120-200 nm is called "far UV" and low limit (120 nm) is defined by MgF_2 transmittance cut off used as a window material for far UV D_2-lamps and other optical components like optical windows available from several vendors for affordable price. MgF_2 can moreover withstand a decent heating that has a benefit for in situ measurements with hot gases. Recently this concept have been implemented as a new combination of gas chromatography (GC) and far UV spectroscopy (115-200 nm) in a new commercial instrument VGA-110 offered by VUV Analytics[1].

Producer gas from a gasifier or natural gas are examples when O_2 concentration is zero. Therefore measurements in far UV have an advantage for in situ/on-line trace gas measurements over the UV or IR ones. Unfortunately information about absorption cross-sections in far UV range is normally limited by ambient temperature and therefore few reference measurements with gases of interest for the project in temperature range 23C-300C have been required. In case of natural gas applications far UV spectroscopy allows one to trace O_2 in the gas (if any) and therefore to control its quality and to avoid unwanted dilution of the gas. In case of the producer gas, far UV measurements give also information about water content in the gas, which is an important gas component in gasification process (e.g. in calculations of mass balances and heat value of the gas).

As it was demonstrated in the Energinet.dk project 2011-1-10622 "On-line trace gas measurement technique for gasification" measurements of tar/PAH compounds can be performed in situ and on-line in 200-350 nm spectral range. Because of tar/PAH strong UV absorption, in situ measurements require a very short absorption pathlength (typically 2-4 mm). In opposite, infrared measurements require about few meters absorption pathlengths in order to measure trace gases. Measurements at 2-4 mm pathlengths lead to a significant miniaturization of the measurement system.

Far UV absorption by tar/PAH compounds is also stronger compare to the UV one. However in 138-155 nm there is a spectral "window" where tar and water absorptions are low and therefore this spectral range can be used for e.g. CH_3Cl and HCl in situ/on line measurements.
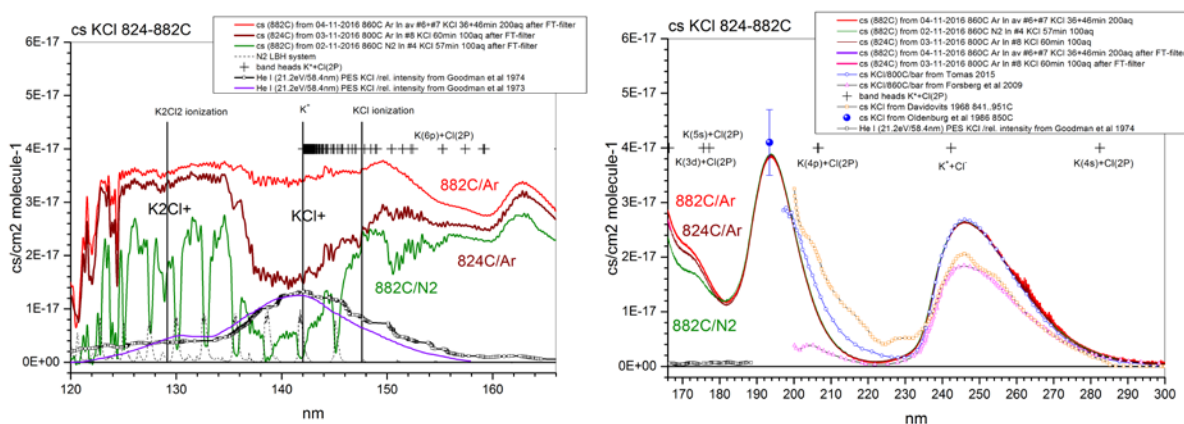
Figure 2: KCl absorption cross-sections measured in 120-300nm. Below 160 nm starts K_2Cl_2 dimer absorption and ionization of KCl and K_2Cl_2 dimer. Available data from the literature in 200-300 nm are shown for comparison. Part of KCl spectrum in 220-300 is used in Vattenfall's IACM monitor system (KCl in situ measurements in combustion).

[1] www.vuvanaytics.com

Far UV/UV KCl absorption measurements have been performed at Vattenfall R&D facilities in Älvkarleby. The outer quartz cell windows were replaced by MgF_2 ones. The measurements were done with use a new far UV spectrometer with special far UV coatings and X-UV CCD from Princeton Instruments (USA) and far UV D_2-lamp (HAMAMATSU). The results obtained are shown in Fig. 2 below (taken from KCl paper draft).

As one can from the Fig. 2 useful for KCl measurements spectral range is 160-300 nm. KCl absorption cross-sections are incentive to large temperature variations in 180-300 nm (Fig. 1 and T Leffler private communication).

## WP2: High resolution FTIR measurements in the lab on a gas cell (i.e. HCl, KCl, CH$_3$Cl, CH$_4$, H$_2$O and H$_2$CO)

High-resolution (0.09 cm^{-1} to 0.56 cm^{-1}) FTIR absorption measurements (HCl, CH_3Cl, CH_4) have been performed on a hot flow gas cell (HGC) suitable for work with corrosive gases for temperatures up to 500C. The obtained data were used in the WP3-4 for corresponding line lists validation and further development. The data also extend our own unique spectral data-base.

The spectra show clear temperature dependence. Few examples of CH_3Cl and HCl absorption cross-sections spectra at 25C and 500C are shown in Fig. 3 (left and right, respectively).
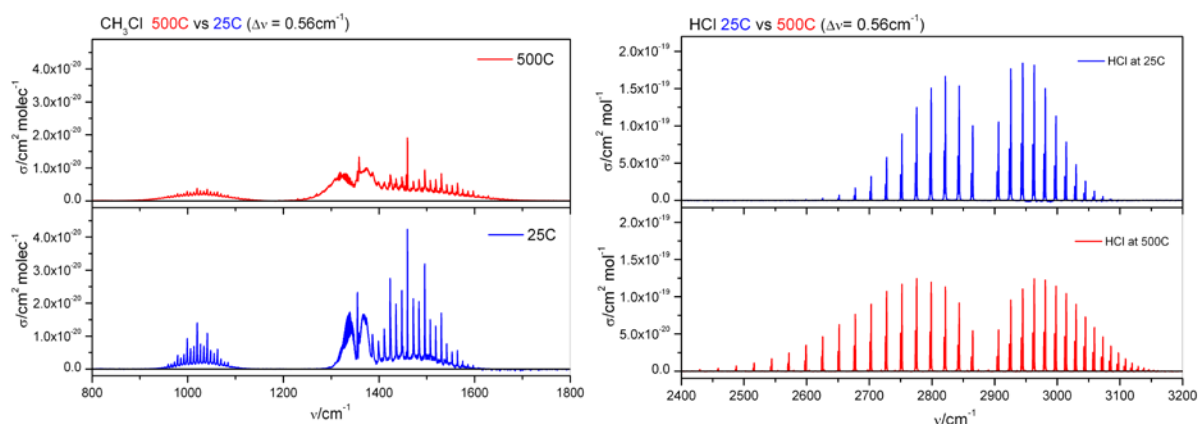
Figure 3: Absorption cross sections for CH_3Cl (left) and HCl (right) at 25C (blue) and 500C (red).

Spectra at 25C (0.09 cm^{-1}) have been compared with available (experimental data from the PNNL database[2] where a similar class FTIR spectrometer is used. It was found very good agreement between the obtained results and that from the database.
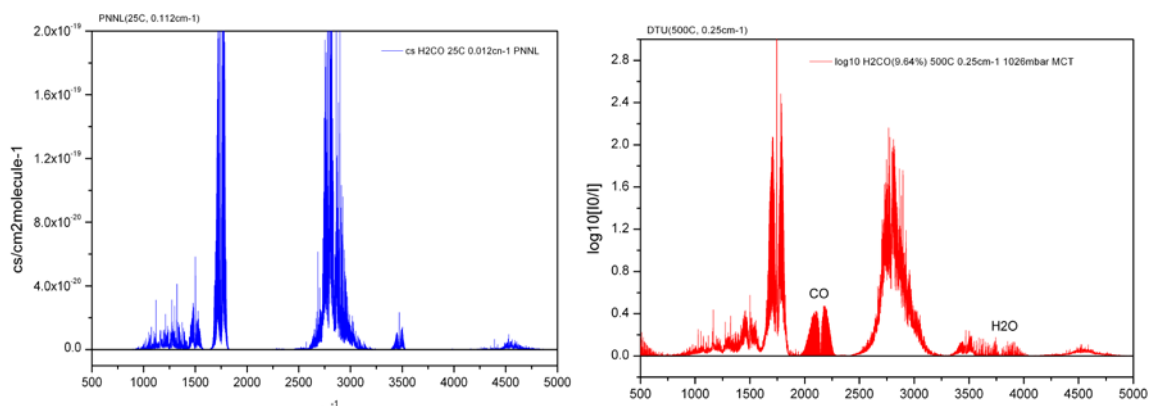
Figure 4: Absorption cross sections for H_2CO at 25C (blue, left, PNNL data) and H_2CO absorption spectrum at 500C (red, right).

[2] Pacific Northwest National Laboratory: https://secure2.pnl.gov/nsd/nsd.nsf/Welcome

Paraformaldehyde measurements were more complicated because its solid form at normal conditions. Paraformaldehyde (SIGMA-ALDRICH, CAS 30525-89-4, 95% purity) which is white-looking powder was evaporated in an elongated dish placed into Ø50 mm x 500 mm heated quartz tube at 190C. The tube was connected (through a Teflon tube at 200C) in series to the HGC. Preheated (170C) N_2 was flowing through the quartz tube over the dish taking H_2CO vapors and further down to the HGC.

At 190C there is decomposition of paraformaldehyde into formaldehyde known as H_2CO. This is an effective way to get H_2CO in the gas phase compare to PNNL's approach, but it's limited for measurements starting from 190C and up. The drawback is because the outlet of the cell is not heated all evaporated H_2CO will come back into its original (solid) form and cause blocking of the gas tubes in the gas cell outlet. Therefore all measurements have been performed for a limited measurement time. However the S/N ratio obtained in the spectra was very good. In Fig. 4 (red, right) measured H_2CO absorption spectrum is shown together with H_2CO cross-sections spectrum at 25C from PNNL database (blue, left).

The dish was weighted before and after the measurements. And knowing residence time of the dish in the heated quartz tube, gas flow and pressure, H_2CO concentration has been calculated. Here there are some uncertainties in calculations, but the results are quite consistent.

One can see that the spectra show clear temperature dependence. There are other by-products of H_2CO thermal decomposition: H_2O and CO marked in the Fig. 4.

Far UV measurements in the lab on a gas cell (CH_3Cl, CH_4, H_2O, CO_2 and NH_3)

Few reference measurements (spectral resolution 0.086 nm) in far UV spectral range have been performed at 23C, 70C and 289C on specially designed and made small flow gas cell. The temperatures have been selected according to producer gas temperatures which was ca. 60C (Viking) and ca. 375C (LT-CFB) in order to be above water/tar dew points and at the same time as low as possible to preserve significant spectral shape degradation of the selected gases which is a common effect when temperature increases.

The cell is mounted in the electrically heated box and has additional heating elements to keep the cell at constant temperature. The heated box is mounted on the 2 m long Ø25 mm heated probe made from Ti. Prior the cell there is a filter device to hold a glass thimble in order to remove any solid particle matter. The filter device and the cell are placed in the box. The probe, box, filter device and the cell can be heated up to 300C.
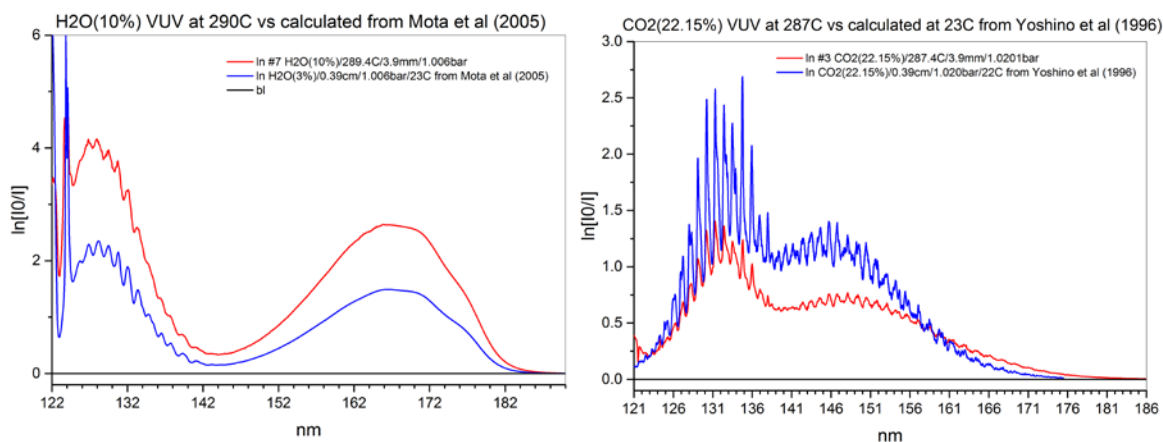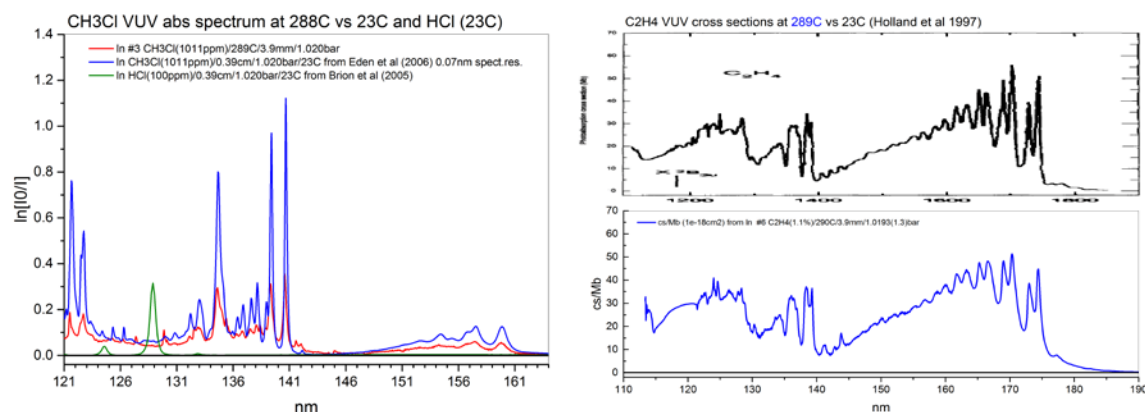

Figure 5: Left: measured H_2O absorption at 289C (red) and calculated from cs at 23C (blue). Right: the same for CO_2 at 23C (blue, calculated) and 289C (red. measured).

The light from D_2 far UV lamp is passing the cell perpendicular to the gas flow and focusing on opposite site into the far UV spectrometer with CCD camera. All optical paths, spectrometer and the lamp are purged by Ar. The optical pathlength in the (3.9 mm) is defined by two

Kalrez o-rings sealing two MgF$_2$ windows in the cell. The pressure is measured at the cell outlet.

Examples of measured far UV spectra of CH$_3$Cl, H$_2$O, CO$_2$ and C$_2$H$_4$ are shown Fig. 5 and 6 together with calculated ones from cross section (cs) data available in the literature.

All measured spectra are obtained for the first time in 23C-300C temperature range at about atmospheric pressure. Most far UV/VUV spectra available (typically with use a synchrotron radiation as a light source) correspond to about 23C and low pressure. One can see that CH$_3$Cl and C$_2$H$_4$ have characteristic "fingerprints" in far UV spectral range. The same is true also for NH$_3$.


Figure 6: Left: measured CH$_3$Cl absorption at 289C (red) and calculated at 23C from cs at 23C. Calculated HCl spectrum from cs at 23C (olive). Right: C$_2$H$_4$ cs spectrum at 23C (black) and 289C (blue).

WP3: Line list generation for HCl, KCl, CH$_4$ and H$_2$CO

In this WP the work under generation of the line lists for KCl, HCl, CH$_4$, H$_2$CO and NH$_3$ are presented. NH$_3$ is frequently another by-product in gasification process and therefore is of interest in connection to NOx emissions. The line lists cover IR and FIR (KCl) spectral ranges and are suitable for IR optical absorption measurements in hot gases.

KCl
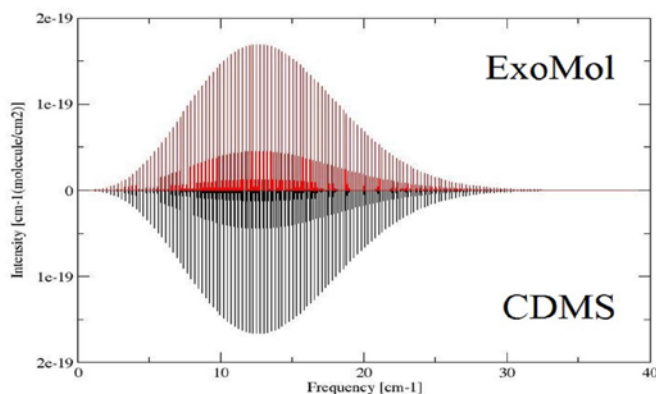
Figure 7: Absorption lines of ^{39}K^{35}Cl at 300K: this work vs CDMS.

The aim was to calculate the rotational-vibrational spectrum of KCl which is largely concentrated in the region 200 – 400 cm^{-1}. Initial calculations were based on fitting to available experimental data Ram et al. [1], for which there were suspect assignment issues, and Caris et al. [2]. New experimental data from Bernath and Frohman [3], and [2], were used in the final fit.

Rotational-vibrational line lists for four isotopologues of KCl ($^{39}K^{35}Cl$, $^{39}K^{37}Cl$, $^{41}K^{35}Cl$ and $^{41}K^{37}Cl$) in their ground electronic states have been calculated. These line lists are suitable for temperatures up to 3000 K.

A potential energy surface (PES) was characterised by fitting an ab initio PES to experimental frequencies [2] [3] using program DPOTFIT [4].

This refined PES and an ab initio Dipole Moment Surface (DMS) were used in program LEVEL [5] to calculate vibrational and rotational energy levels ($v_{max} = 120$, $J_{max} = 839$). Transition frequencies and Einstein coefficients were calculated for all transitions between these levels satisfying the dipole selection rule ΔJ = ± 1 (around 7 million per isotopologue).

Comparisons with rotational lines from the semi-empirical CDMS database [6] are presented in Fig. 7. As can be seen, the agreement is excellent for both frequency and intensity. In particular, predicted line intensities agree within 2 percent for the isotopomers considered in CDMS. This suggests that the calculated pure rotational intensities are accurate.

The calculated transition frequencies are in very good agreement with experiment, Table 1.
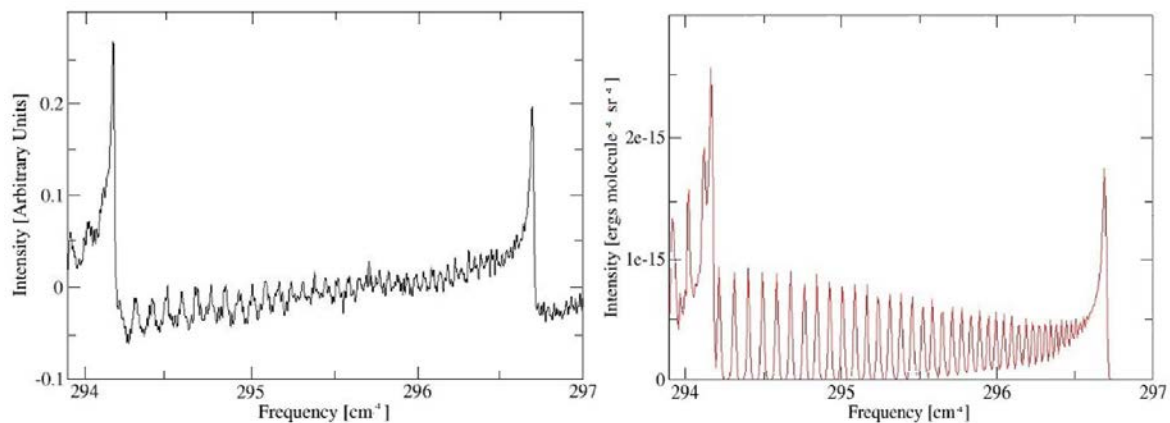
Figure 8: Emission spectra of KCl at 1273 K: Ram et al. [1] (left), this work (right).

Emission cross-sections for $^{39}K^{35}Cl$ were simulated using Gaussian line-shape profiles with half-width = 0.01 cm^{-1} as described by [7]. The resulting synthetic emission spectrum was compared to the experimental one [1], Fig. 8.

When making a comparison, one has to be aware of a number of experimental issues. The spectrum is very weak and the baseline, which has a large offset, was not properly adjusted to zero [3]. Given these considerations, the comparison must be regarded as satisfactory. Therefore better experimental data are required for further KCl line list improvement/validation.

Table 1: Comparison of theoretically predicted rotational-vibrational frequencies, in cm^{-1}, with some of the experimental frequencies used to characterise the PES [2,3].

v'	v''	J'	J''	Experiment	Calculated	E - C
1	0	130	129	296.4855	296.4861	-0.0006
2	1	117	116	293.4473	293.4451	0.0022
3	2	127	126	291.3902	291.3898	0.0004
4	3	117	116	288.4943	288.4984	-0.0041
5	4	129	128	286.5315	286.5312	0.0003
6	5	121	120	283.8156	283.8181	-0.0025

HCl

Line lists for $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$ have been provided by Li et al. [8, 9] and are available from HITRAN online [16].
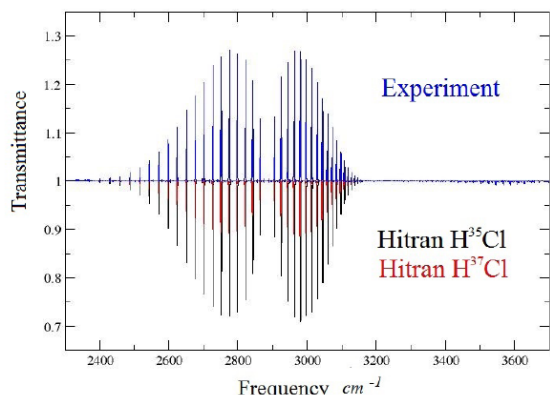

Figure 9: Transmission spectra of HCl at 500C: experiment vs HITRAN

The current HCl line lists [4, 5] are accurate in both frequency (within 0.01 cm^{-1}) and intensity (within 10%). This was demonstrated by the simulation of laboratory transmission spectra obtained in the WP2, Fig. 9.

The partition function, a direct sum over calculated energy levels, is at least 95% converged at 1500K ($\simeq$1226C). Therefore the line lists should be suitable for high temperatures applications up to at least 1500K. Therefore no further work is required on this molecule at present.
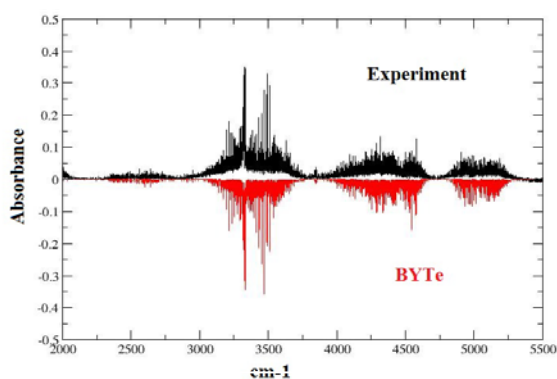
NH3

A line list for hot (up to 1500K) NH_3, BYTe, has been computed by Yurchenko et al [10]. 4961 highly accurate experimental energy levels (uncertainty ~10^{-4} cm^{-1}) for NH_3 have been determined by Al Derzi et al. [11] using the MARVEL algorithm [12, 13].
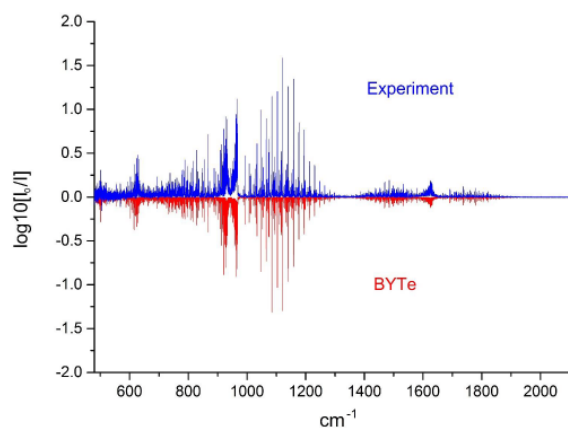
Figure 10: Absorbance spectra of NH_3 at 500C

High-resolution (0.09 cm^{-1}) absorption spectra of NH_3 in the regions 500 - 2100 cm^{-1} and 2100 - 5500 cm^{-1} at temperatures up to 1027C and approximately atmospheric pressure (1013 $\pm$ 20 mbar) were measured in the WP2. A comparison between the measurements and BYTe, Fig. 10 and 11 shows in general good agreement through there are some shifts in line position (up to 0.5 cm^{-1}) and BYTe has some difficulty reproducing experimental intensities. Work towards a new NH_3 line list is being carried out by the ExoMol group [14].

The region 500 - 2100 cm^{-1} has been analysed using BYTe and MARVEL. 1967 lines have been assigned, of which 851 are newly assigned to mainly hot bands involving vibrational states as high as $v_2 = 5$.

The intention was to perform a similar analysis for the measurements of NH_3 in the region 2100 - 5500 cm^{-1}.

Figure 11: Absorbance spectra of NH_3 at 1027C

CH4

A line list for hot (up to 1500K) CH_4, YT10to10, has been computed by Yurchenko et al. [15].

High resolution (0.09cm^{-1}) absorption spectra of CH_4 in the region 1000 - 3500 cm^{-1} at a temperature of 500C and approximately atmospheric pressure (1013 $\pm$ 10 mbar) were measured in WP2.
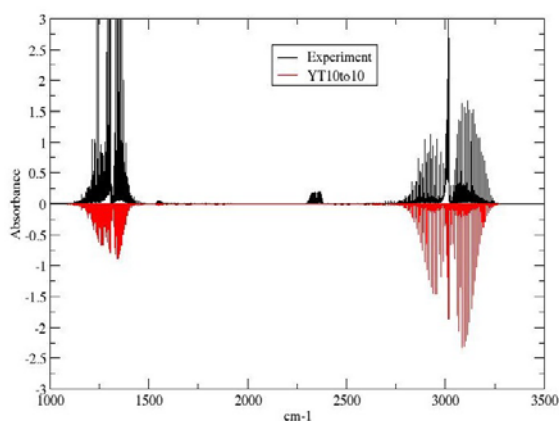
Figure 12: Absorbance spectra of CH_4 at 500C

A comparison between the measurements and YT10to10, Fig. 12 shows in general good agreement through there are some shifts in line position (up to 0.5 cm^{-1}) and YT10to10 has some difficulty reproducing experimental intensities of the higher band. Work towards an extended CH_4 line list is being carried out by the ExoMol group [14].

Due to the highly congested nature of the spectrum only a couple of hundred lines could be assigned by hand. Lines assigned to the lower band, v_3, are also present in HITRAN [16], lines assigned to the higher band, v_4, have been previously observed by high temperature study [17].

More measurements of the CH_4 spectrum in the regions > 12,000 cm^{-1} (for extending the theoretical line list) and < 1500 cm^{-1} (for making new assignments) could provide avenues for future work.

A new highly accurate ab initio potential energy surface (PES) of CH_4 was generated using a combination of high levels of theories. This PES is now being used to describe absorption of CH_4 in near-IR.

A new method to describe the continuum (super-lines) of the methane absorption has been presented and used to generate absorption cross sections for methane for a large range of temperatures.

H_2CO

A computed line list for formaldehyde, H_2CO, applicable to temperatures up to T=1500 K is have been published in [3]. The resulting line list, referred to as AYTY, contains 10.3 million rotational-vibrational states and around 10 billion transition frequencies. Each transition includes associated Einstein-*A* coefficients and absolute transition intensities, for wavenumbers below 10 000 cm−1 and rotational excitations up to J=70.

Room temperature spectra are compared with laboratory measurements and data currently available in the HITRAN data base. These spectra show excellent agreement with experimental spectra and highlight the gaps and limitations of the HITRAN data. The full line list is available from the CDS data base as well as at www.exomol.com.

WP4: Line list generation for CH_3Cl
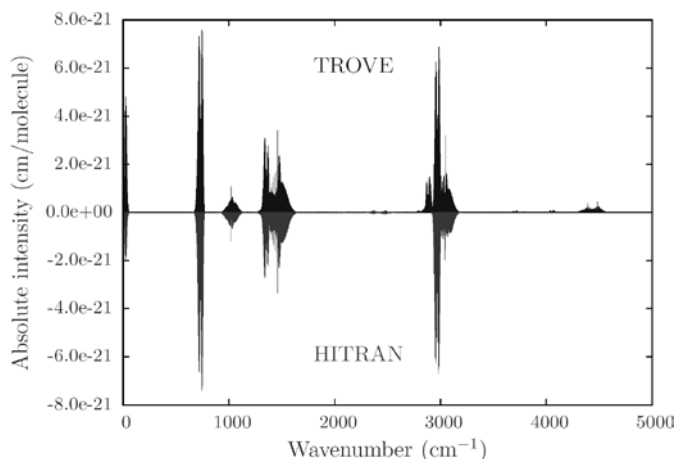
Figure 13: Comparison between TROVE calculations and HITRAN database.

Calculations of the vibrational energies for the two main isotopologues of methyl chloride were reported in Ref. [18]. There was excellent agreement with previous experimental results and confirmed the computational process employed for the potential energy surface (PES) is correct. To ensure accurate and converged results, a new numerical procedure to construct the rovibrational Hamiltonian [19] was implemented in the computer program TROVE [20]. These recent developments guarantee that any future rotation-vibration

line list calculations are computationally tractable.

The dipole moment surface (DMS) of CH_3Cl has undergone extensive testing. There is again good agreement with previous experimental studies, as well as with several major spectroscopic databases such as HITRAN and PNNL. Intensity simulations using the ab initio PES and DMS involved transitions up to J=82 with a frequency range of 0 to 5000 cm^{-1}. As shown in Fig. 13, TROVE calculations highlight a missing band in the HITRAN database around 2900 cm^{-1}. The intensities of pure rotational transitions appear too strong but we are looking at the experimental datasets to confirm this. Extending the DMS analysis, new CH_3Cl experimental measurements (WP2) performed at a range of temperatures was used to validate the DMS and line intensities.

A new global ab initio dipole moment of CH_3Cl was computed using a high level of theory (CCSD(T)/aug-cc-pVQZ(+d for Cl)). A new machine learning algorithm was developed and applied to generate an accurate potential energy surface of CH_3Cl. A production of the hot line list for two isotopologues of CH_3Cl based on these surfaces is now under way (expected by the end of 2017).

References to WP3-4

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WP5: Measurements on 6MW demonstration plant

Originally in situ measurements of Cl-components in the producer gas have planned to be performed at 6 MW demonstration plant (Pyroneer Project, DONG Energy). Because the plant was closed by DONG after about one year since the project started, all in situ measurements have been performed on LT-CFB and Viking gasifiers located at DTU Risø Campus. It should be noted that Pyroneer gasifier (6MW) was built with use the principle as the LT-CFB (100 kW) one.

Measurements at Viking gasifier (high-temperature gasification process)

The measurements on Viking gasifier have been performed in June 2017 in two operation modes: "normal" (with air) and "CO_2/O_2" (CO_2 substitutes N_2 in the air) with wood chips as a fuel. The producer gas was taken through a heated to 70C Teflon line after cyclone filter where gas temperature was held just above water dew point. The Teflon line was directly connected to the heated box kept also at 70C. The Viking gasifier was claimed to produce very clean (tar/particle matter free) gas.

Typical far UV absorption spectra measured in both operation modes are shown in Fig 14 below.
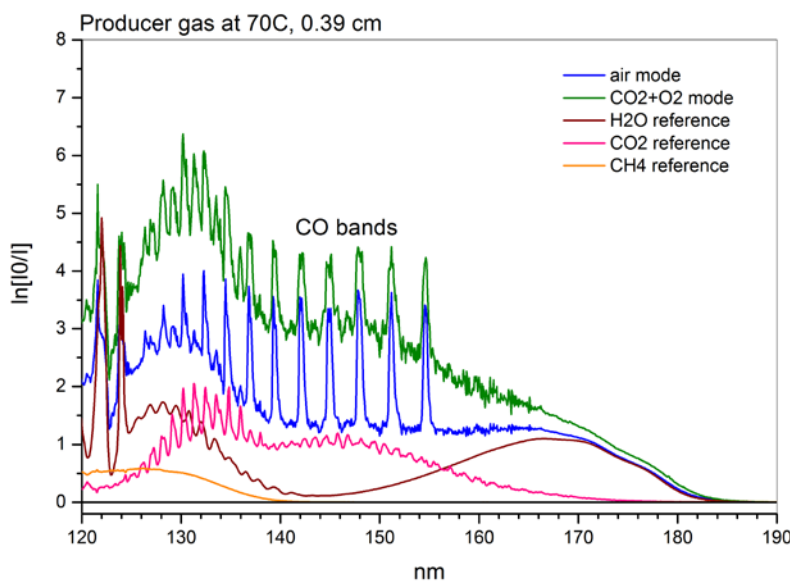
Figure 14: Far UV absorption spectra measured in "air" mode (blue) and "CO_2/O_2" mode (olive). Few reference spectra are also shown.

The spectra show a moderate absorbance with manly clearly-seen characteristic absorption features which simplify spectra analysis. Detailed analysis of measured spectra confirms that the producer gas is quite clean although some minor (trace) gas components are always present in the gas, Table 1.

Table 1: Typical gas composition measured in producer gas of Viking gasifier in two operation modes.

Viking	Air ***	O2-CO2 1st run ***	O2-CO2 2nd run***
CH4	0.433%	0.866%	1.028%
CO2	12.2%	31.08%	24.42%
H2O	2.74%	2.82%	2.8%
O2	0.354%	0.885%	0.955%
CO	8%	14%	14%
N2	77%	0%**	0%**
NH3	33ppm	0ppm**	0ppm**
C6H6	0ppm**	22ppm	22ppm
CH3CHO*	0pmm**	100ppm	100ppm
OCS, CH3Cl, HCl	0ppm**	0ppm**	0ppm**

*) Aldehydes in CH3CHO equivalent

**) below detection limit

***) shown concentration numbers are calculated ones from the spectra measured over 10 min measurement time

Measurements at LT-CFB gasifier (low-temperature gasification process)

The measurements on LT-CFB gasifier were made in November 2017. The gasifier was running on straw. In "normal" operation the measurements have been performed on few days to investigate possible variations in gas composition. The measurements have also been performed when the LT-CFB was running on fine-grinded straw, lower operation temperature and therefore higher tar content in the producer gas, "high-tar" mode.

Few examples of measured far UV spectra are shown in Fig. 15. One can see that the spectra show much stronger absorbance than that measured on the Viking gasifier. The overall structure of the spectra is considerably more complex compare to the Viking's spectra. Therefore in order to understand "what is what" in the steady-state spectra dynamical measurements have also been done. Dynamical measurements started with counter Ar flow through the cell towards the probe tip. Then the flow was stopped and producer gas was allowed to flow through the probe to the cell (there is an overpressure in the gasifier) and then out. The time-dependent were measured every ca. 6 ms.

Typical results are shown in the Fig. 15, right. One can see the spectra have more clear structure where major and minor gas components can much easily identified. This approach is similar to controlled dilution with e.g. Ar method or further reduction absorption pathlength.
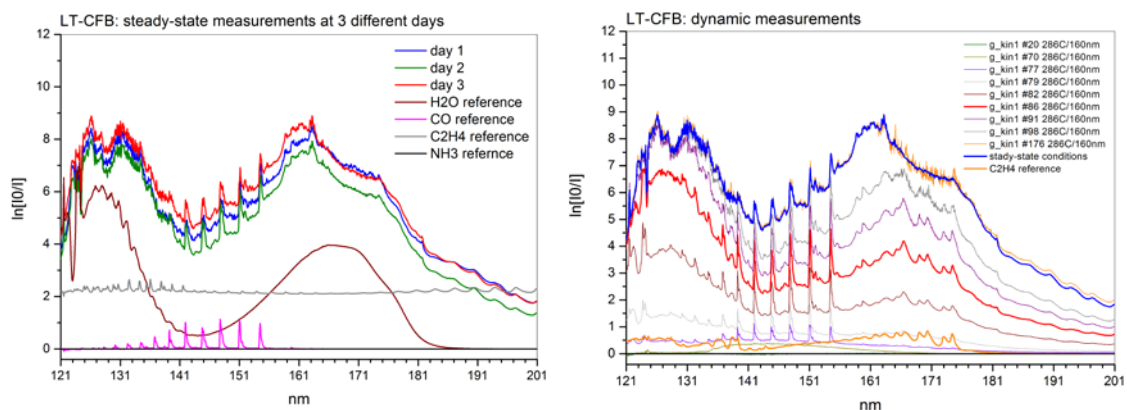
Figure 15: Far UV steady-state spectra measured over few days (left, measured time ca. 4 min) and time depended spectra (time step ca. 6 ms) when gas was allowed to flow through

the probe/cell (right). Dynamic spectra converge to steady-state spectrum (blue). Some reference spectra are also given. Red (#86) spectrum was used for further analysis shown in Fig. 16.

A differential time-dependent spectrum #86 from the Fig. 15 is shown in Fig. 16 after subtraction of H_2O, CO_2, CO and C_2H_4 absorptions. One can see that the spectrum has more clear structure.
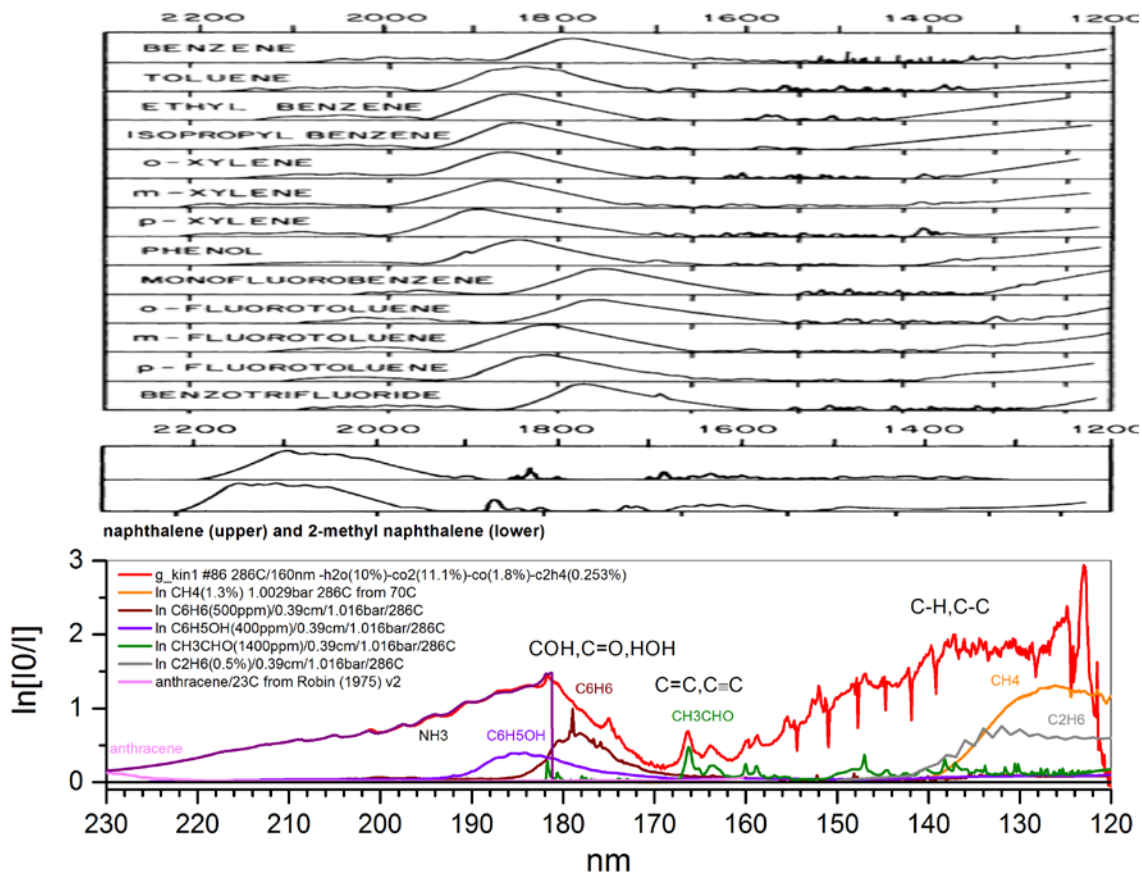

Figure 16: Lower: Far UV #86 time-depended (dynamic) spectrum (ca. 6 ms measured time, before reaching steady-state absorption level) after subtraction of H_2O, CO_2, CO and C_2H_4 absorptions. Few other reference spectra are shown. Upper: Reference spectra of BTX-family (light PAH's). Middle: Reference spectra of two representative of tar-family (naphthalene and 2-methyl naphthalene).

The Fig. 16 shows that PAH/tar components have very small contribution to the total absorption in 120-170 nm spectral range where CH_3Cl and HCl absorptions lye. This confirms the original idea to use far UV spectroscopy for CH_3Cl and HCl measurements.

The 120-170 nm spectral range is dominated by absorption of saturated hydrocarbons (HC) in 120-150 nm, unsaturated (double/triple C-C bond and C=O) in 150-170nm. Spectral range between 170-190 nm is "occupied" by absorption of BTX-family compounds those have low dew points and therefore tend to survive further gas cleaning (e.g. cooling of the gas to remove tar). Spectral range between 190 and 230 nm (and further longer) corresponds to double benzene-ring and higher aromatics (naphthalene, anthracene etc.).

Because heavy PAH's (tar) have about the same absorption cross sections as BTX-family, Fig. 17, their contribution into total absorption signal in 170-230 nm will be proportional their concentrations. This can be used for their in situ measurements (absolute or relative) by simple weighting of the 195-230 nm and 170-200 nm areas under the absorption spectrum in the Fig. 16. Spectral resolution of the spectrometer does not play any role for this approach and use an ordinary N_2 for purge of the optics would be enough. Ability much less expensive far UV small spectrometers (e.g. OCEAN deep UV, down to 160 nm) opens possi-

bility for a new in situ tar/BTX sensor development when a complex tar/BTX sampling can be avoided. This is a subject for a possible patent application.
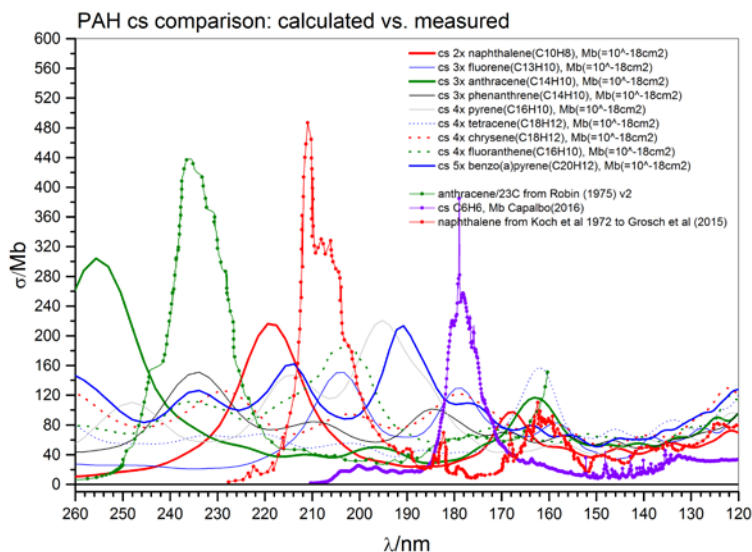
Figure 17: Far UV theoretically calculated absorption cross-sections for various PAH's in Mb (1Mb=1e-18 cm^2) (lines, Malloci et al (2004)) and measured ones for anthracene (relative), naphthalene and benzene (BTX-family) (points). There is a wavelength shift for calculated and measured cross sections for anthracene (olive line/points) and naphthalene (red line/points).

In Fig. 18 typical far UV steady-state absorption spectra for two LT-CFB operation modes are shown together with their simple residuals.
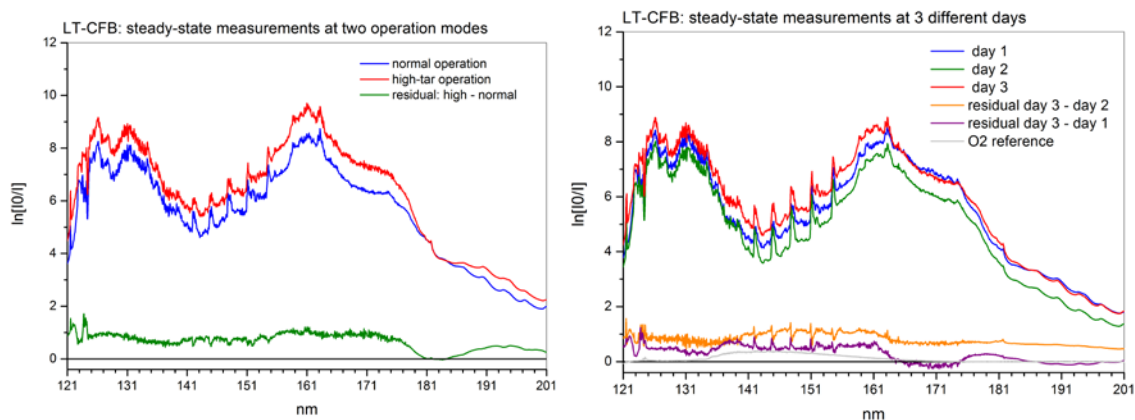
Figure 18: Left: far UV steady-state spectra in "normal" and "high-tar" operation mode. Their difference is shown by olive line. Right: far UV steady-state spectra measured at different days at "normal" operation. Differences are shown by orange and purple lines. O$_2$ reference is given by a grey line.

One can see that "high-tar" operation mode gives more BTX/tar (absorption from 190 nm) and more NH$_3$. In 120-190 nm additional tar absorption gives a base-line like "shift" that is because nearly flat absorption structures for tar/BTX in 120-170 nm. Residuals for "normal" operation mode at three different days show either no change in 170-200 nm or a constant-like offset in the base line with some minor O$_2$ changes in the gas.

Detailed analysis of e.g. spectra in the Fig. 15 show no HCl and CH$_3$Cl(120ppm) in the gas. This however should be confirmed by GC-MS analysis of the gas samples that is still under the work. However this CH$_3$Cl concentration is in that range (120-200 ppm) previously measured on this gasifier with straw as a fuel. Absence of HCl is in agreement with first year FTIR in situ measurements across 640 cm pathlength in 360C producer gas.

1.6 Utilization of project results

The results obtained in the project can be used for in situ trace gas measurement analyzer which can be built targeting various species: Cl-compounds, NH_3, HC, BTX and tar. At certain conditions O_2 and N_2 measurements are also possible.

We will consider a potential patent application for BTX/tar in situ analyzer.

The project partly supported a PhD student at UCL (Emma Burton) who was involved in NH_3/HCl/KCl line list database development and validation. The PhD student has spent about two weeks at DTU Chemical Engineering where she participated in NH_3 far IR measurements in the lab and in discussion of the experimental results and their comparison with calculations. She has got insights about use of applied high-resolution IR spectroscopy and made a presentation about her work at a seminar.

NH_3/HCl/KCl/CH_4 line list are available for free download from the EXOMOL-web site (www.exomol.com) and partly implemented in the HITRAN database (www.hitran.org). Both databases are an essential tool in the modeling of molecular absorbance/transmittance properties at moderate and high temperatures.

The CH_4/NH_3 results have been published in the Journal of Quantitative Spectroscopy and Radiative Transfer and parts have been presented orally and in poster form at two conferences:

- A. Fateev (2015) *Spectroscopy in high-temperature industrial process on Earth.* Oral presentation at the conference: Spectroscopy of Exoplanets (Windsor, UK), July 2015.

- E. J. Barton, S. N. Yurchenko, J. Tennyson, S. Clausen and A. Fateev (2015), *"Modelling High Resolution Absorption Spectra with ExoMol Line Lists: NH3 and CH4",* Poster at The 24th Colloquium on High Resolution Molecular Spectroscopy, 2015 August 24-28; Dijon, France.

Initial CH_3Cl results have been published in The Journal of Chemical Physics. The CH_3Cl results have been presented in a poster form at two international conferences:

- A. Owens, S. N. Yurchenko, A. Yachmenev, J. Tennyson, W. Thiel (2015), *Pushing the ab initio limit for methyl chloride: Vibrational energies at the complete vibrational basis set limit.* Poster presented at the conference: Anharmonicity in medium-sized molecules and clusters (Madrid, Spain), April 2015.

- A. Owens, S. N. Yurchenko, A. Yachmenev, J. Tennyson, W. Thiel (2015), *Towards a hot line list for methyl chloride.* Poster presented at the conference: Spectroscopy of Exoplanets (Windsor, UK), July 2015.

- Owens, S. N. Yurchenko, A. Yachmenev, J. Tennyson, and W. Thiel "A global ab initio dipole moment surface for methyl chloride", J. Quant. Spectrosc. Radiat. Transf. 184, 100 (2016)

- Owens, S. N. Yurchenko, A. Yachmenev, J. Tennyson, and W. Thiel "A highly accurate ab initio potential energy surface for methane", J. Chem. Phys. 145, 104305 (2016).

- P. O. Dral, A. Owens, S. N. Yurchenko, and W. Thiel "Structure-based sampling and self-correcting machine learning for accurate calculations of potential energy surfaces and vibrational levels" J. Chem. Phys. 146, 244108 (2017)

1.7 Project conclusion and perspective

It has successfully been demonstrated that far UV spectroscopy is a highly valuable tool in *in situ* analysis of trace gases in gasification and other applications where any conventional gas sampling is problematical.

The results obtained in the project can be used for developing a far UV analyzer targeting various species as e.g. various Cl-compounds, N_2, O_2, NH_3, HC, BTX and tar.

Line lists for HCl, CH_4, CH_2O and CH_3Cl developed by UCL in IR make a solid basis and can be used for quantifying their respective concentrations in *in situ* optical infrared measurements in various hot gas environments either by a broad-band FTIR spectroscopy or by tunable narrow-band laser systems.

Annex
Relevant links

Web sites with line lists for high/low temperatures and databases:

EXOMOL web site: www.exomol.com

HITRAN web site: http://www.hitran.org/

HITEMP, high-temperature extension of HITRAN: http://www.hitran.org/hitemp/

Pacific Northwest National Laboratory (PNNL):
https://secure2.pnl.gov/nsd/nsd.nsf/Welcome