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Sulfur trioxide measurement technique for SCR units

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Foreword

The report describes the work performed under MST funded project "Sulfur trioxide measurement technique for SCR units" and partly under Energinet.dk funded project 2010-1-10442 "Sulfur trioxide measurement technique for energy systems".

The purpose of the project is the development of SO_3 *in situ* measurement technique which will be suitable for industrial applications where SO_2/SO_3 emissions occur as e.g. SCR units of power plants, large ship engines running on heavy S-fuel and etc.

The project consists of five work packages (WP) reflecting the objectives described in the project application. Activities and results under WP's 1 to 5 are reported:

- WP1 SO_3 reactor and its matching to high temperature flow gas cell;
- WP2 Matching of the SO_3 reactor to HGC and their optimization for FTIR absorption measurements;
- WP3 FTIR high resolution measurements on HGC;
- WP4 Measurements on industrial facilities;
- WP5 Data analysis and reporting.

Conclusion and Summary

The project has been very challengeable because of highly reactive SO_3 nature and conducted during several years to most fully fulfil projects goals and objectives. During the project the work under the five work packages (WP) has been performed.

In the first two WP's (WP1+2) on-place SO_3 generation system based on temperature-dependent SO_2+O_3 reaction has been established and proven in operation. Ozone has been produced with a commercial ozone-generator.

In the WP3 the SO_2/SO_3 infrared absorption measurements have been performed on various gas cells from 150C and up to 500C. Several corrosion problems related to H_2SO_4/SO_3 have been experienced. The new quartz hot flow gas cell has been developed and validated. The on-place SO_3 generation system and the new quartz hot flow gas cell is a unique system suitable for work with extremely reactive gases like SO_3.

Then the new high-resolution absorption measurements for CO_2, H_2O, NH_3, SO_2 and SO_3 have been performed for several temperatures of interest (300-500C) related to practical applications. Apparent experimental absorption cross-sections for SO_2/SO_3 for various temperatures between 25C and 500C have been generated. The cross-sections have been used in the analysis of the results from two measurement campaigns under WP4.

We have changed the WP4 from "Measurements on CHEC 30kW unit exhaust" to "Measurements on industrial facilities" because opened possibilities to perform IR absorption/emission cross-stack measurements on an industrial scale facilities. The measurements have been performed in collaboration with Vattenfall (OxPP facility, Germany) and DONG Energy (AVV1 block, Denmark).

The data analysis has been performed under the WP5.

The results obtained under the project show that SO_3 IR absorption measurements require careful gas handling and measurements itself. Any water traces have to be removed from the system to prevent sulfuric acid formation. It is much more beneficial to produce SO_3 on-place rather to use a pre-ordered one because the later one requires extra handling. A gas cell for SO_3 measurements should be a "flow-windows" concept in order to avoid possible reaction of the SO_3 on windows surfaces. A distance between SO_3 production and the gas cell should be minimized in respect to residence time in the suppling tubes. Mostly chemical inert materials like Teflon and quartz should be used in order to minimize SO_3 side reactions.

Spectral resolution of 0.25-1 cm^{-1} is sufficient for SO_3 FTIR absorption measurements up to 500C. Choice of resolution depends on which SO_3/SO_2 bands are going to be used in the data analysis. SO_3 in general has higher IR absorption cross-sections than SO_2. However in most practical applications the SO_3 concentration is significantly low compare to the SO_2 one. The most absorption-strong SO_3 band lies at about 1386 cm^{-1} where water and SO_2 have also absorption features. This overlap between various H_2O lines and closed spaced SO_2 band make SO_3 measurements quite challengeable. Another SO_3 band at about 2438 cm^{-1} is more attractive because large SO_2/SO_3 bands separation and no interference with H_2O. There is still an interference with a weak CO_2 band which can however be handled. The drawback of use SO_3 band at 2438 cm^{-1} is because this band about 66 times weaker than the one at 1386 cm^{-1}.

It has been shown at a long absorption pathlength for SO_3 *in situ* measurements when a few ppm SO_3 detection level at 300-500C is required.

The SO_3 cross-sections measurements have been done at only few temperatures. To quantify amount of SO_3 in a hot flue gas at any gas temperature SO_2/SO_3 spectral lines databases are needed. Activities under this topic have been done under an Energinet.dk funded project in cooperation with University College London (UK). In December 2015 the work has been finalized for both SO_2/SO_3. The SO_2 database has been validated with the measurements available and it can now be used for SO_2 spectra calculations at temperatures up to 1700C. The SO_3 database can only be used up to 500C because very high complexity of calculations and should be used with a constant scaling factor in order to fit the existing measurements.

Two kinds of *in situ* measurements on two industrial facilities have been performed: optical absorption and optical emission measurements.

Optical absorption measurements have been performed at normal-S and high-S coal burner operations across 4 m flue hot gas at OxPP facility in Germany. The measurements have been supplied by gas temperature and gas-composition mapping measurements across the gas flow.

The analysis shows that there is no difference between *in situ* cross-stack measurements in the high- and low-S combustion cases. It may indicate that SO_3 concentration in the flue gas was the same. This is quite interesting because of large SO_2 concentration difference in two cases. Modelling of the measured *in situ* spectrum with use of reference data for H_2O and SO_2 shows that the experimental spectrum can well be described by the synthetic one as H_2O+SO_2 in the spectral range of SO_3 absorption. This may indicate that SO_3 concentration in the flue gas is very low, i.e. below detection limit (which is a few ppm). This may be true considering that the facility has only one burner and quite a long distance between the flame end and the measurement location that can in overall cause a capture of SO_3 on colder ash particles (compare to the gas temperature) those concentration is higher in high-S case.

Optical emission measurements have been performed at normal-S coal operation across the 14.16 m flue hot gas at AVV1 Block (Avedøre Power Satation). The measurements have been supplied by gas temperature and gas-composition measurements from AVV1 control system. It was not possible to perform optical absorption measurements because very strong light attenuation by particles and/or ports misalignment during boiler operation.

Two SO_3 bands can potentially be used for SO_3 concentration calculations: 1386 cm^{-1} and 2438 cm^{-1}. Assuming a uniform temperature profile, an absorptivity spectrum of the gas can be calculated from its emission spectrum. The measured absorptivity spectrum can well be modelled by the $CO_2(11\%)+H_2O(9\%)+SO_2(370ppm)$ composite spectrum. Adding of $SO_3(50ppm)$ changes clearly calculated absorptivity in 1360-1420 cm^{-1} where the strongest 1386 cm^{-1} is located. This spectral range can be used for SO_3 concentration calculations if SO_3 concentration is “high enough”. A “high enough” concentration is defined by uniformity of temperature/gas concentration/particles profiles, gas/particle temperature ratio, detector’s S/N ratio and measurement time. In opposite changes in 2400-2480 cm^{-1} range where 2438 cm^{-1} band is located are small. Those changes are below the noise level in the absorptivity spectrum. Estimated SO_3 detection limit from emission measurements was about 15 ppm.

In the spectral 2400-2480 cm^{-1} range a InSb detector can be used instead of the MCT (broad band) one used. An InSb detector has typically 10 to 15 times higher sensitivity compare to the MCT one. Use of the InSb will further increase S/N ratio in the spectrum for the same measurement time.

Despite of low SO_3 absorption strength at 2438 cm^{-1} the use of 2400-2480 cm^{-1} spectral range has few advantages: it is free from H_2O absorptivity bands and (in post combustion) there is only interference between CO_2 and SO_3/SO_2. The later simplify significantly the data analysis. The drawback of the measurements in 2400-2480 cm^{-1} is a very high S/N ratio about 3333 required for SO_3 measurements on 5 ppm level.

Moving to more hotter (500-600C) flue gas region (e.g. in downstream of super heaters) will increase the gas/particle emission signal falling into the FTIR spectrometer and improve gas/particle temperature ratio, and at the same time it will keep temperature-dependent SO_3/SO_2 absorption cross-sections variations on a moderate level that is important for low SO_3-level measurements.

SO_3 *in situ* measurement technique consists from a base knowledge (SO_3/SO_2 absorption cross section databases) and tools (high-resolution FTIR spectroscopy). Acquired under the project SO_3/SO_2 apparent absorption cross sections together with SO_3/SO_2 spectral databases developed by UCL make a solid basis and can be used for quantifying SO_3/SO_2 concentrations in *in situ* optical infrared measurements either by a broad-band FTIR spectroscopy or tuneable narrow-range laser systems. A FTIR spectrometer with sensitive InSb/MCT detectors in a combination with a powerful IR light source can be used for in situ SO_3/SO_2 concentration measurements either in optical absorption or emission mode. Detection limit of this kind of the system is about 5-15 ppm depending on the measurement conditions. Further system improvement seems to be possible by moving measurement emission strategy towards use of hotter gases (300-500C) and an InSb/MCT(narrow band) detectors for power-plants applications. In case of large ship engines running on heavy S-fuel an absorption strategy with a MCT(narrow band) detector can be used.

Konklusion og sammenfatning

Pålidelige målinger af SO_3 er vigtigt i industrielle processer og forbrændingsanlæg, men meget vanskelig med eksisterende målemetoder og udstyr. Projektet ligger op til en direkte optisk måling af SO_3 på anlæggene uden gasudtag. Projektet har forsøgsmæssigt været en udfordring pga. SO_3 er en særdeles reaktiv gas og det er gennemført over flere år mht. at opfylde mål og indhold. Projektet er opdelt i 5 arbejdspakker.

I arbejdspakke 1 og 2 blev et system til generering af SO_3 etableret baseret på en temperaturafhængig SO_2+O_3 reaktion med brug af en kommerciel ozongenerator.

Infrarøde absorptionsmålinger på SO_2/SO_3 blev udført i arbejdspakke 3 med flere forskellige gasceller i temperaturområdet fra 150°C til 500°C. Flere korrosionsproblemer relateret til H_2SO_4/SO_3 blev konstateret i dette arbejde og en ny højtemperatur flow-gascelle i kvarts blev udviklet og valideret. Den nye kvarts gascelle er sammen med SO_3 genereringssystemet en unik facilitet til udmåling af ekstremt reaktive gasser som SO_3. Efter etablering af facilitet blev infrarøde absorptionsmålinger med høj opløsning gennemført for CO_2, H_2O, NH_3, SO_2, SO_3 i temperaturområdet 300-500°C, dvs. under betingelser relevant i praktiske applikationer. Eksperimentelle absorptions målinger (cross-sections) for SO_2/SO_3 er udført systematisk i temperaturområdet fra 25°C til 500°C og måleresultater er senere anvendt som reference data i analyse af målinger foretaget i 2 målekampagner under arbejdspakke 4.

Måleprogram i arbejdspakke 4 var oprindelig planlagt på en 30kW forsøgsfacilitet på DTU Kemiteknik, men undervejs i projektet opstod mulighed for i stedet at udføre målekampagner på to industrielle anlæg i samarbejde med hhv. Vattenfall (Oxy-fuel facilitet i Spremberg, Tyskland) og DONG Energy (Avedøreværket, Danmark). Analyse af data fra målekampagner er udført under arbejdspakke 5.

Resultater opnået i projektet viser at SO_3 IR absorptionsmålinger kræver omhyggelig gashåndtering og kompetencer mht. målingerne. Selv meget små spormængder af vand må således fjernes for at undgå dannelse af svovlsyre. Det er en fordel at generere SO_3 på stedet fremfor at indkøbe gassen og dermed undgå en ekstra håndtering. Gascellen for SO_3 måling skal være med ”flow-vinduer” koncept for at undgå reaktion af SO_3 med gascellens vinduer. Afstanden mellem gascellen og enhed for SO_3 produktion skal holdes kortest mulig for at reducere opholdstiden i varmeslanger og dermed reaktioner med overflader. Kemisk inerte materialer som teflon og kvarts skal anvendes for at reducere SO_3 reaktion med overflader.

En spektralopløsning på 0.25 cm^{-1} er tilstrækkeligt for SO_3 i FTIR absorptionsmålinger ved temperaturer op til 500°C. Valg af spektralopløsning afhænger af hvilke SO_3/SO_2 bånd i spektre der vælges i gasanalysen. SO_3 har generelt en større IR absorption end SO_2, men i de fleste praktiske anvendelser er SO_3 koncentrationer betydelig lavere end SO_2. Det kraftigste absorptionsbånd for SO_3 ligger ved 1386 cm^{-1} hvor vand og SO_2 også har absorption. Dette overlap af gaslinjer i dette samme spektralområde gør SO_3 målinger ved lave koncentrationer til en udfordring. SO_3 andet bånd ved 2438 cm^{-1} er mere attraktivt fordi der ikke er interferens med vand og bånd for SO_2 og SO_3 ligger adskilt, dog er der interferenser med et svagt CO_2 bånd som dog kan håndteres. Ulempen ved at bruge 2438 cm^{-1} båndet for SO_3 er at det er ca. 66 gange svagere end båndet ved 1386 cm^{-1}. Det er vist at en lang absorptionsvejlængde er nødvendig for in-situ måling af SO_3 i ppm området ved temperatur på 300-500°C.

SO_3 absorptionsmålinger (cross-section) er kun udført ved få udvalgte temperaturer. For at kvantisere mængden af SO3 i en varm røggas ved en vilkårlig temperatur vil det være ønskeligt at bruge en database over SO_3 spektrallinjer. Aktiviteter på dette punkt er udført under en kontrakt med energinet.dk i samarbejde med University College London (England). Dette arbejde blev afsluttet i december 2015 for både SO_2 og SO_3. SO_2 databasen er valideret med tilgængelige målinger og kan nu anvendes til beregning og modellering af SO_2's spektrum for temperaturer op til 1700°C. SO_3 databasen kan kun anvendes op til 500°C pga. den meget store kompleksitet i beregningerne af spektra og skal bruges med en konstant skaleringsfaktor for at stemme overens med målinger.

Der er i projektet udført to type af in-situ målinger på to forskellige anlæg, dvs. dels en optisk absorptionsmåling hvor lys sendes på tværs af gaskanal og dels en emissionsmåling hvor gassernes egen termiske udstråling måles uden brug af en lyskilde.

Absorptionsmålingerne er udført på Vattenfall's OxPP facilitet i Tyskland med en fuldskal brænder fyret med kul som brændsel ved normal og høj svovl indhold. Der blev anvendt en direkte optisk måling med DTU FTIR måleudstyr over en 4 m lang målestrækning igennem den varme røggas. Målingerne blev suppleret med målinger af gastemperatur og gaskoncentrationer langs målestrækningen.

Analyse af målingerne viser at der ikke er forskel mellem de optiske in-situ målinger på tværs af anlæg med fyring af kul med normal og højt svovlindhold. Dette indikerer at SO3 koncentrationen i røggassen er ens uanset brændsels svovlindhold, hvilket ikke var ventet. Dette er interessant pga. den store forskel i SO_2 koncentration i de to tilfælde. Modellering af de målte spektre med brug af reference data for vand og SO_2 viser at det målte in-situ spektrum kan beskrives godt med et syntetisk beregnet spektrum i spektralområdet hvor SO_3 har absorption. Dette indikerer at SO_3 koncentrationen i røggassen er meget lav, dvs. under detektionsgrænsen af det anvendte måleudstyr der er få ppm. Dette understøttes af at der var langt mellem flamme og målested, dvs. SO_3 reagerer med askepartikler.

Optiske FTIR emissionsmålinger er udført på Avedøreværket ved fyring med kul med normal svovlindhold. Målestrækning i den varme røggas var 14.16 m. Målingerne blev suppleret med målinger fra værket kontrol og reguleringssystem. Det var ikke muligt at udføre absorptionsmålinger pga. en meget kraftig dæmpning af lyset (askepartikler) og problemer med at sende lyset på tværs af de to måleporte (forskydning af porte og vanskelighed med at rette lyset op under drift af anlægget).

To SO_3 absorptionsbånd kan potentielt anvendes til bestemmelse af SO_3 koncentrationen i målingerne udført på Avedøreværket, dvs. bånd ved ved 1386 cm^{-1} og 2438 cm^{-1}. Det er muligt, at beregne absorptionsspektrum ud fra det målte emissionsspektrum når det antages at røggastemperaturen er konstant over den 14.16 m lange målestrækning. I det tilfælde kan absorptionsspektrum for den varme røggas modelleres fint med en gassammensætning på CO_2 (11%)+H_2O (9%) + SO_2 (370 ppm). Ved at addere 50 ppm SO_3 i det modellerede spektrum ses en tydelig absorption in området 1360-1420 cm^{-1} og med størst absorption ved 1386 cm^{-1}. Dette spektralområde kan bruges for måling af SO_3 koncentrationen når koncentrationen er tilstrækkelig høj. Detektionsgrænsen er afhængig af faktorer som temperaturjævnhed over målestrækningen, koncentration af partikler i målestrækning, målesystemet signal-støjforhold og måletiden. En anden mulighed er bestemmelse af SO_3 koncentrationen ud fra bånd ved 2438 cm^{-1} i området 2400-2480 cm^{-1}, men ændring i signal er meget lille og under detektionsgrænsen i de målte spektre. Det estimeres at detektionsgrænsen er omkring 15 ppm ud fra de målte FTIR emissionsmålinger.

En mere følsom detektor (InSb) kan anvendes i spektralområdet 2400-2480 cm^{-1} fremfor den anvendte detektor i målingerne (MCT bredbånd). En InSb detektor har typisk 10-15 gange bedre signal-støjforhold (SNR) end den anvendte MCT-detektor og vil dermed tilsvarende forbedre detektionsgrænsen. På trods af lav SO_3 absorptionsstyrke for bånd ved 2438 cm^{-1} er der flere fordele, f.eks. fri for interferens fra vand og kun en mindre påvirkning fra CO2's bånd. Sidstnævnte simplificerer dataanalysen betydeligt. En ulempe er at måling ved 2400-2480 cm^{-1} kræver et godt signal-støjforhold på omkring 3333 for at kunne måle en SO_3 koncentration på 5 ppm niveau.

Det vil være en fordel at anvende FTIR emissionspektroskopi i områder med højere røggastemperatur end anvendt i projektet, dvs. til et temperaturniveau på 500-600°C hvor den termiske udstråling er kraftigere. Dette vil desuden give en mindre følsomhed mht. temperaturvariation over målestrækningen, hvilket er vigtigt ved lave SO_3 koncentrationsmålinger. SO_3 in-situ måleteknikken består af dels en grundviden om gasserne absorptionsegenskaber (SO_3/SO_2 absorption cross-sections) og et værktøj (højopløst FTIR spektroskopi). I projektet er absorptionsegenskaberne for SO_3 og SO_2 udmålt i ny gascelle på DTU. Dette giver et solid grundlag for måling SO_3 og SO_2 koncentration i optiske in-situ målinger ved brug af en spektral database for gasserne. Databasen for SO_3 og SO_2 er udviklet i et sideløbende projekt mellem UCL og DTU. I projektet er der anvendt et bredbånd FTIR spektrometer, men følsomheden kan dels øges ved at bruge en anden detektor og en mere kraftig IR-lyskilde eller ved brug af et tunbart laser system. Detektionsgrænsen for denne type måleudstyr ligger på 5-15 ppm afhængig af måleforhold. En forbedring af den nedre målegrænse ser ud til at kunne opnås ved at måle i et område hvor røggassen er varmere (300-500°C) og med en smalbåndet MCT eller InSb detektor for kraftværksmålinger. For en større skibsmotor som kører med svovlholdig brændsel vil en FTIR absorptionsmåling med en smalbåndet MCT detektor være tilstrækkelig.

1. Introduction

Combustion of fossil fuels causes emission of, for example, NO_x and SO_x those in addition to CO_2 are the major of environmental concern. The most effective way to reduce NO_x is with selective catalytic reduction (SCR) which combines the flue gas with certain amount of ammonia over catalyst that speed NO_x reduction into nitrogen and water.

A major SCR concern is the release of unreacted ammonia (ammonia "slip") which can cause large problems than the NO_x itself. In, for example, biomass co-firing SO_x in the flue gas contains mainly from sulfur dioxide (SO_2) with small (a few ppm) amount of sulfur trioxide (SO_3). Over catalyst some additional oxidation of SO_2 to SO_3 is also taking place. SO_3 in the presence of ammonia forms ammonium sulfate and ammonium bisulfate salts those deposits on catalyst, air heater baskets, heat recovery steam generators and other downstream equipment. Resultant ammonium bisulfate and sulfate particle diameters are on the order of a few microns and thereby contribute to PM_{10} emissions finally fouling the micropore structure of the catalyst and limiting catalyst reactivity.

Modern energy market demands to run at lower boiler loads leads to lower catalyst operation temperatures (< 370°C) and therefore make favorable conditions for formation of ammonium salts. From the other end it is not longer allowed to turn off ammonia injection even at lower loads. Therefore ammonium injection system must be better controlled in order to follow variations in NO_x and SO_2/SO_3 concentrations. DONG Energy is developing a feedback control system for ammonia injection and SO_3 concentration values obtained with a SO_3 monitor will be used in that system.

On line SO_3 measurements by, for example, commercial condensation probe has a long response time and are not stable at lower flue gas temperatures typical for lower load operation when gas stream consists from H_2SO_4 vapor or mixture H_2SO_4 liquid aerosols and H_2SO_4 vapor. Commercially available SO_3 monitors based on extractive techniques can yield biased results due to reactive nature of SO_3. Additional problems can arise from further oxidation of SO_2 in the sampling line and long response time of the whole system. In general extractive techniques require adherence to proper procedures and have been shown to have a significant degree of variability from tester to tester leading to testing inaccuracies (in *Continuous Measurement Technologies for SO_3 and H_2SO_4 in Coal-Fired Power Plants*, EPRI, Palo Alto, CA: 2004. 1009812).

Therefore development of SO_3 *in situ* measurement technique with fast response time suitable for modern industrial applications is highly of interest.

The purpose of the project is the development of SO_3 *in situ* measurement technique which will be suitable for industrial applications where SO_2/SO_3 emissions occur as e.g. SCR units of power plants, large ship engines running on heavy S-fuel and etc.

2. Method

The project is as a research project and consists from 5 work packages (WP). Ideologically the project is built from two major parts: “lab-based” and “on-site” work parts. The lab-based part comprises from So_3 on-place generation and SO_3 FTIR absorption measurements at well-controlled conditions on a flow gas cell in the lab. The “on-site” work consists from *in situ* measurements on two industrial facilities: OxPP facility in Germany (Vattenfall) and AVV1 block Avedøre Power Plant (DONG Energy). The knowledge accumulated under “lab-based” activities has been used in the in situ measurements on two industrial facilities.

An overall structural perspective about project actions can be described with a flow-down diagram and an overall content of all WP is given after:

SO_3 on place generation (WP1+2)
↓
SO_3 FTIR flow gas cell measurements (WP3)
↓
On-site measurements (WP4)
↓
Data analysis (WP5)

WP1 SO_3 reactor and its matching to high temperature flow gas cell
The SO_3 is extremely reactive substance which is possible to buy from some gas suppliers. If it should be used for reference (calibration) optical measurements it should first be underdone through multiple freeze-thaw cycles at LN_2 temperature to remove air and SO_2. The measurements itself on a commercial gas cells are tricky because SO_3 reacts immediately with window material and gives extra “window” features in the absorption spectra those are difficult to remove in further data analysis. The residuals still observable in composite spectrum as “derivative” shaped features. Therefore it was decided to generate SO_3 on place (i.e. in so-called SO_3-reactor), just before the flow gas cell and therefore to minimize any possible SO3 degradation channels. Two different (water-free) methods of SO_3 generation have been tested:

- SO_2 oxidation to SO_3 by ozone. Ozone is produced with an ozone generator operated on pure oxygen;
- SO_2 oxidation in O_2 over Pt catalyst at high temperatures;

SO_2 oxidation by O_3 was chosen as a best method of SO_3 generation for the project.

WP2 Matching of the SO_3 reactor to HGC and their optimization for FTIR absorption measurements;
SO_3 reactor has been matched to several hot gas cells set ups (HGC) and several SO_3/SO_2 measurements have been carried out. It was experienced several operation problems with the existing gas cells. Therefore a new quartz-based flow gas cell has been developed and made for SO_3 infrared absorption measurements.

WP3 FTIR high resolution measurements on HGC;
The FTIR (reference) absorption measurements have been performed with two high-resolution FTIR spectrometers op till 500C. Measurements for following gases of interest were made: NH_3, H_2O, SO_2 and SO_3. For the first three gases measurements were compared with calculations based on known databases for IR spectral calculations: HITRAN, HITEMP and BYTe and it was shown that new high-temperature databases for SO_2/SO_3 are needed. The SO_2/SO_3 temperature-dependent apparent cross sections database has been created based on the measurements on the quartz HGC at few temperatures of interest assuming that all consumed SO_2 gave a rise for SO_3. Databases are needed for complex *in situ* data analysis accumulated under the WP4.

WP4 Measurements on industrial facilities;
In situ measurements on two industrial facilities: OxPP facility in Germany (Vattenfall) and AVV1 block Avedøre Power Plant (DONG Energy) have been done. Reference absorption spectra gases of interest studied in WP3 have been used in the data analysis.

WP5 Data analysis, conclusions and reporting
Analysis of data obtained in WP4 has been performed. Conclusions and perspectives of the developed SO_3 detection technique for industrial applications are made.

3. SO3 reactor

Because sulfur trioxide (SO_3) is a highly reactive specie it is necessarily to produce it "in situ" before infrared (IR) absorption measurements. SO_3 can be produced either by reaction of sulfur dioxide (SO_2) with ozone (O_3) in the gas phase or by SO_2 reaction with oxygen (O_2) over a catalyst. Therefore two types of SO_3 production devices (reactors) have been developed and made.

- **SO_2 + O_3 reactor**
  The reactor is shown in Fig. 1. The reactor is a laminar flow tubular-like reactor which consists from two sections each made from quartz. Heaters wrapped around sections allow one to uniformly heat the gas up to 200°C. Ozone produced from oxygen by Risø DTU's ozone generator (O_3 maximum output 6% (vol.) at ca. 1 kW_e) is injected at point 1 (and, if necessarily, 2) in the reactor where it is mixed with N_2/SO_2 flow, Fig. 1. First experimental results with SO_2 + O_3 reactor are reported in the report.

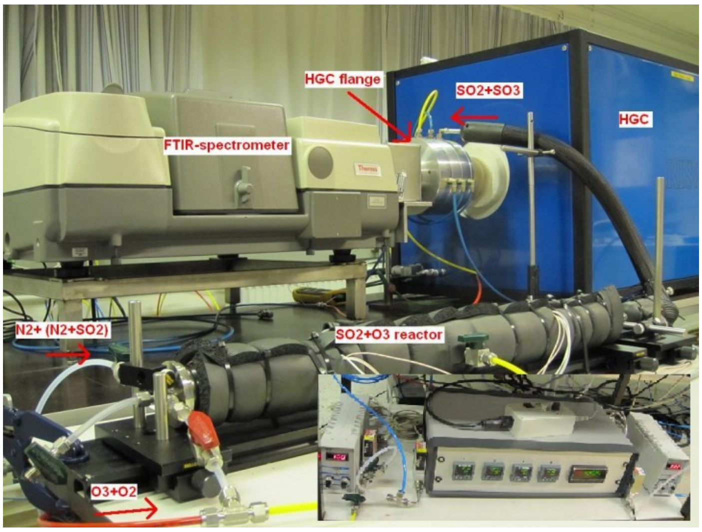

FIGURE 1: LAMINAR FLOW REACTOR USED FOR SO_3 PRODUCTION IN SO_2 + O_3 REACTION AT TEMPERATURES UP TO 200°C. INSERT: MASS FLOW CONTROLLERS AND TEMPERATURE CONTROL BOX FOR THE REACTOR.

- **SO_2/Pt reactor**
  Second type of reactor designed for SO_3 production is based on SO_2 reaction with O_2 at elevated temperatures (400-500°C) over a catalyst surface. Pt catalyst (Pt-gauze) has been chosen because it high surface reactivity. The catalyst is placed in the quartz tube and the later is placed in the high-temperature own, Fig. 2. Experiments with this type of SO_3 reactor is planned for November 2010.

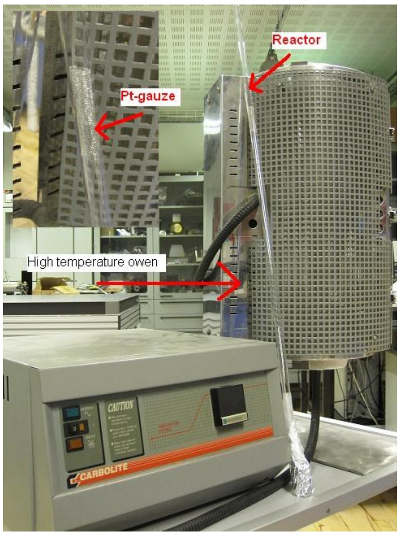

FIGURE 2: REACTOR FOR CATALYTIC SO_3 PRODUCTION IN SO_2 OXIDATION OVER PT CATALYST. INSERT: A PIECE OF PT-GAUZE.

Chemistry in SO_2 +O_3 system can be described by several reactions:

$SO_2 + O_3 \rightarrow SO_3$ (1)
$O_3\ (+ M) \rightarrow O_2 + O\ (+ M)$ (2)
$SO_2 + O\ (+ M) \rightarrow SO_3\ (+ M)$
$O + O_2\ (+ M) \rightarrow O_3\ (+ M)$
$O + O\ (+ M) \rightarrow O_2\ (+ M)$
$SO_3 + H_2O \rightarrow H_2SO_4$ (3)
$SO_3\ (+ M) \rightarrow SO_2 + O\ (+ M)$ (4)
SO_3 + surface → products
H_2SO_4 + surface → products (5)
…

Most of reactions are temperature dependent. Consider simplified reaction scheme with only reactions (1) and (2) and assume SO_2 >> O_3 time behavior of O_3 and SO_3 concentrations at various temperatures can straightly be calculated, Fig. 3. Rate constants from NIST Chemical Kinetics Database are used.

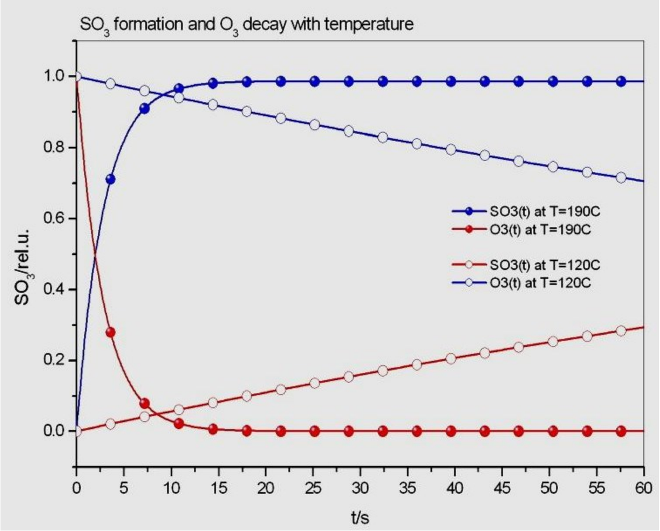

FIGURE 3: CALCULATED SO_3 FORMATION AND O_3 DECAY AT 120°C (OPEN CIRCLES) AND 190°C (SOLID CIRCLES) ACCORDING TO SIMPLIFIED REACTION SCHEME: (1) + (2). TIME SCALE CORRESPONDS TO TYPICAL RESIDENCE TIME IN THE SO_2 + O_3 REACTOR.

It is clearly seen that higher temperatures are favourable for efficient SO_2 conversion to SO_3 at typical residence time (60 s) in the reactor.

4. Matching of SO3 reactor

Because of high reactivity of SO_3 the SO_2 + O_3 reactor has first been coupled to DTU's gas sampling system in order to evaluate the method of SO_3 production and get practical experience with SO_3 handling and measurements, Fig. 4.

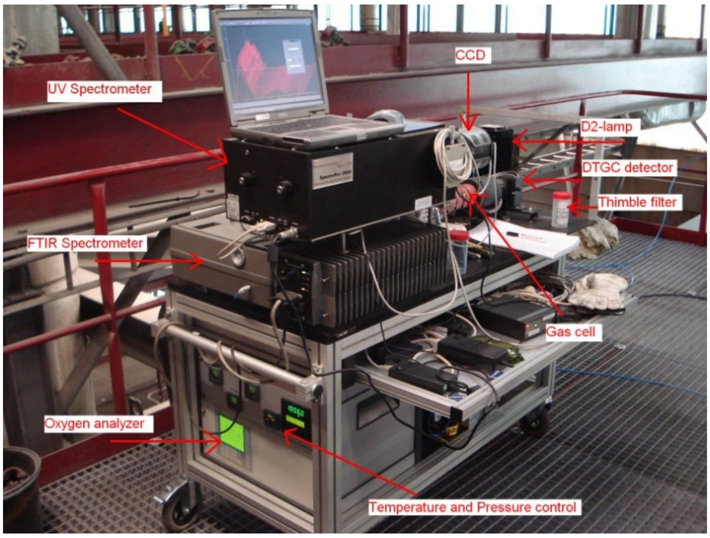

FIGURE 4: A GENERAL VIEW OF THE MOVABLE GAS SAMPLING SYSTEM DESIGNED FOR ON-SITE MEASUREMENTS.

The gas analysis system is designed for sampling of gases and particles from hot flue gas flows or flames. Simultaneous UV/IR absorption measurements (by UV and FTIR spectroscopy) of reactive species (e.g. NO, SO_2, CO, HCN and etc.) are performed in two 50 cm length gas cells connected in parallel and oxygen content in the gas is measured by an oxygen analyzer. The cells can uniformly be heated up to 150°C. The system has been successfully used in many measurement campaigns at power plants in Denmark and Germany.

Two cases of SO_3 absorption measurements have been considered:

Case 1: Reactor was connected to the gas sampling system with *unheated* (at 23°C) Teflon line. Temperature in the reactor was set to 200°C whereas the temperature in the gas cells was kept at 50°C.

Case 2: Reactor was connected to the gas sampling system with *heated* (at 150°C) Teflon line. Temperature in the reactor was set to 200°C and temperature in the gas cells was kept at 150°C.

Typical SO_3 absorption spectrum at 50°C (after subtraction of SO_2 reference spectrum) is shown in Fig.'s 5 and 6 (Case 1).

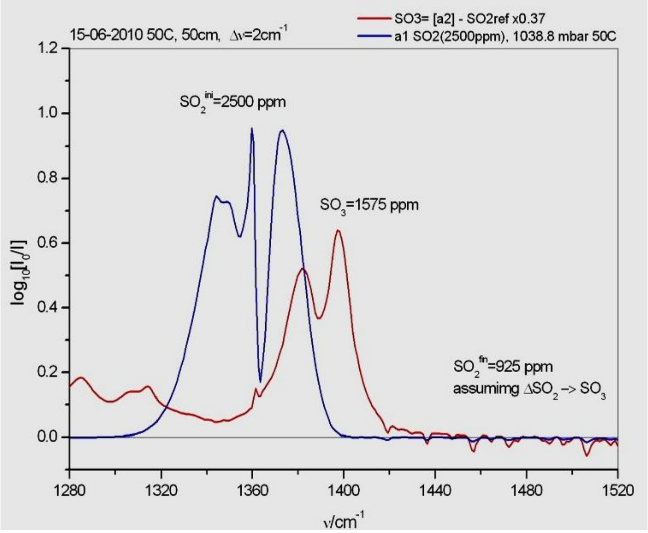

FIGURE 5: MEASURED SO_3 ABSORPTION SPECTRUM (RED) AT 1400 CM^{-1} AFTER SUBTRACTION OF SCALED SO_2(2500 PPM) REFERENCE SPECTRUM (BLUE). MAXIMUM CONVERSION OF SO_2 TO SO_3 IS 63%, SEE TEXT FOR DETAILS. SPECTRAL RESOLUTION: 2 CM^{-1}. MEASUREMENT TIME 50 S. DTGS DETECTOR. CASE 1.

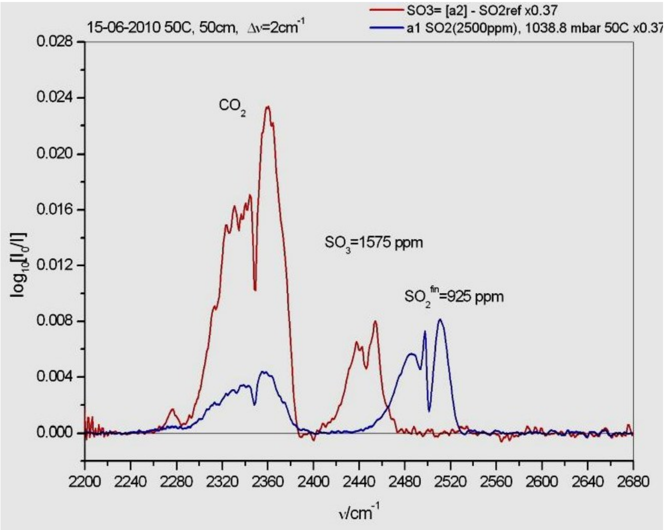

FIGURE 6: SO_3 ABSORPTION SPECTRUM (RED) AT 2440 CM^{-1} AFTER SUBTRACTION OF SCALED SO_2(2500 PPM) REFERENCE SPECTRUM (BLUE). MAXIMUM CONVERSION OF SO_2 TO SO_3 IS 63%, SEE TEXT FOR DETAILS. SPECTRAL RESOLUTION: 2 CM^{-1}. MEASUREMENT TIME 50 S. DTGS DETECTOR. CASE 1.

Spectral shift between SO_2 and SO_3 absorption bands at higher wavenumbers is larger compare to that at lower ones. Moreover in most of practical cases spectral range between 2400-2560 cm^{-1} remains free from absorption by other species which gives an advantage in SO_3 absorption measurements at 2440 cm^{-1}. However absorption in this second SO_3 band is about 84 times weaker compare to that in the first absorption band (1400 cm^{-1}). Despite small shift between SO_2 and SO_3 bands in 1320-1440 cm^{-1} and interference with water accurate SO_3 measurements are still possible because water has well-defined (and predictable) sharp absorption features those can be eliminated by modern software tools from high-resolution experimental spectra.

An overview of the whole (SO_3 + products) absorption spectrum is shown in Fig. 7.

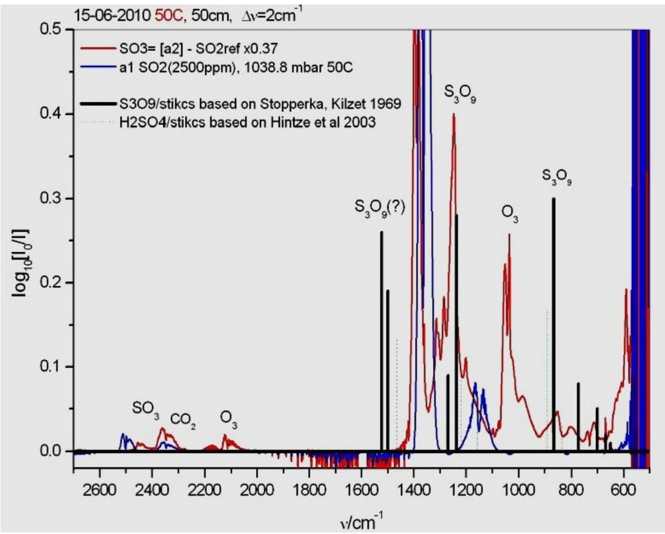

FIGURE 7: SO_3 + PRODUCTS ABSORPTION SPECTRUM (RED) AFTER SUBTRACTION OF SCALED SO_2(2500 PPM) REFERENCE SPECTRUM (BLUE). SEVERAL ABSORPTION BANDS ARE MARKED. POSITION OF ABSORPTION BANDS OF SO_3-TRIMER (S_3O_9) AND H_2SO_4 ARE MARKED BY BLACK AND OLIVE DOT STICK LINES, RESPECTIVELY. SPECTRAL RESOLUTION: 2 CM^{-1}. CASE 1.

As it is seen in Fig. 7 several additional absorption features can be attributed to SO_3-trimer (S_3O_9) and (minor) sulfuric acid H_2SO_4 absorption. In gaseous state pure SO_3 is in an equilibrium mixture of monomeric SO_3 and trimeric S_3O_9 [1]. Favorable conditions for trimer formation are lower temperatures and high pressures. Intensity of S_3O_9 absorption bands decrease rapidly with temperature rise [2]. Only weak S_3O_9 absorption was observed at temperatures above 70°C [2]. Measurements performed in Case 2 have also confirmed disappearance of S_3O_9 absorption bands.

It was noted that after measurements a liquid condensate with small particles appeared inside of Teflon *unheated* line. General chemical analyses show that the liquid is strongly acid ($pH < 1$). The liquid seems to be sulfuric acid (H_2SO_4) because even in presence trace level of water high molecular weight poly-sulfuric acids exist [1]. Particles found are difficult to characterize and they can be formed due to attack of SO_3 on Teflon or some extension of sulfur chemistry SO_2 + SO_3. Therefore SO_2 conversion can be higher than 63% (Case 1).

In Case 2 measurements SO_3 absorption spectrum shows a little broader structure due to higher temperature level, Fig. 8. It has been noted about significant rise in time absorption in 1230-1320 cm^{-1} range which is attributed to chemical reactions with window material (KBr).

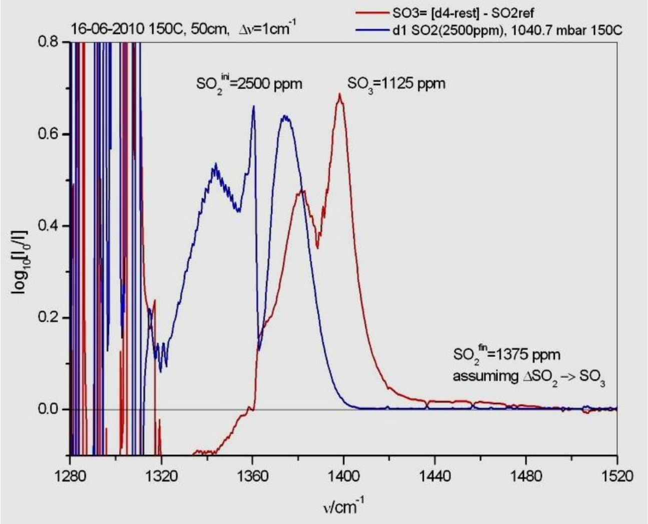

FIGURE 8: MEASURED SO_3 ABSORPTION SPECTRUM (RED) AT 1400 CM^{-1} AFTER SUBTRACTION OF SO_2(2500 PPM) REFERENCE SPECTRUM (BLUE). MAXIMUM CONVERSION OF SO_2 TO SO_3 IS 55%, SEE TEXT FOR DETAILS. SPECTRAL RESOLUTION: 1 CM^{-1}. CASE 2.

An overview of the whole SO_3 absorption spectrum at 150°C is shown in Fig. 9. In the same figure H_2SO_4 spectrum at the same temperature taken from [3] is shown. Clear fingerprints from H_2SO_4 in 800-900 cm^{-1} are seen. Because SO_3(1000 ppm) dew point is about 150°C (Fig. 12) significant part of it is converted to H_2SO_4. The later reacts with KBr and forms potassium sulfate salt (K_2SO_4). At the end of Case 2 measurements it was found that KBr-windows in IR gas cell where strongly attacked by H_2SO_4/SO_3.

Reactions of alkali-halogen compounds with H_2SO_4/SO_3 are used in industry, e.g. in ChlorOut technique developed by Vattenfall AB in order to remove KCl (and NO_x) in vicinity of superheaters [4]. An aqueous solution of ammonium sulfate, $(NH_4)_2SO_4$, is sprayed into to hot turbulent zone prior superheaters aiming at sulfation of corrosive gaseous alkali chlorides in the flue gas. Ammonium sulfate decomposes into NH_3 and SO_3. Alkali chlorides are converted into less harmful sulfates in reactions with H_2SO_4/SO_3. Ammonia reacts with NO_x and forms eventually nitrogen and water as in selective non-catalytic NO_x reduction process.

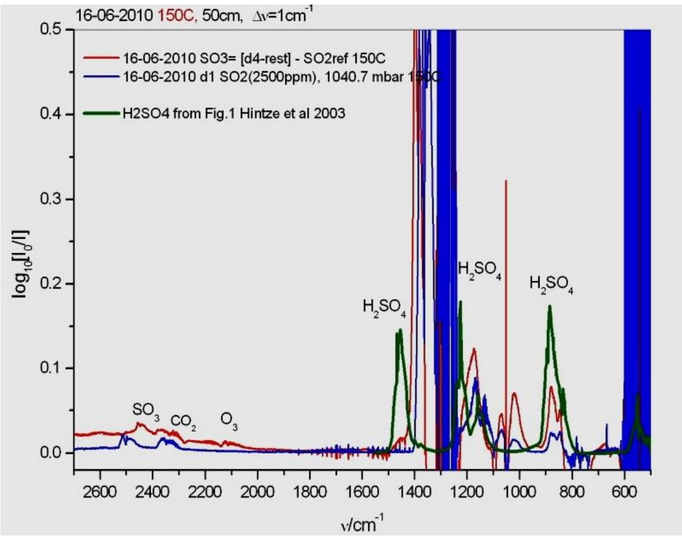

FIGURE 9: MEASURED SO_3 + PRODUCTS ABSORPTION SPECTRUM (RED) AFTER SUBTRACTION OF SO_2(2500 PPM) REFERENCE SPECTRUM (BLUE). H_2SO_4 ABSORPTION SPECTRUM AT 150°C FROM [3] IS SHOWN BY OLIVE LINE. SPECTRAL RESOLUTION: 1 CM^{-1}. CASE 2.

Results of the first measurements with gas extraction system give hints about matching of the reactor to the existing HGC. Because SO_3 formation and O_3 decomposition reactions are temperature dependent the temperature in the reactor has to be set to 190°C in order to maximize SO_3 yield and minimize the amount of un-reacted O_3 leaving of the reactor and undesirable reactions of SO_3 with sealing material (Viton, T_{max} = 200°C). The reactor has to be connected through a heated Teflon line (200°C) to the HGC. Risø DTU's hot flow gas cell (HGC) is made on principle of three zones windowless gas cell [5]. The central "hot" zone (53.3 cm in length) is designed for absorption-emission measurements of gases of interest and kept at highly uniform temperature. Two other "cold" zones from both sides of the central one are purge by IR inactive gas (e.g. N_2). The HGC allows one to avoid any contact of highly reactive gas with window material that is a general problem in optical measurements.

Nicolet 5700 FTIR high-resolution spectrometer with nominal spectral resolution of 0.125 cm^{-1} operated with a MCT detector and external infrared light source (black body (BB), 800°C) was aligned and tested for infrared absorption measurements, Fig. 10. The choice of IR detector was defined by high sensitivity of MCT detector compare to DTGS one at 1400 cm^{-1}. An InSb detector has typically cut off about 1780 cm^{-1} and cannot be used for measurements of SO_3 absorption band at 1400 cm^{-1}. However InSb detector has about 30 times higher sensitivity at 2440 cm^{-1} compare to MCT one and it is free from non-linear behavior typical for MCT detectors. Therefore in the project the InSb detector available for Nicolet 5700 spectrometer will also be used.

The IR light beam, after passing through HGC, is restricted by variable Aperture 1 in order to minimize possible surface effects in the HGC with following pass through Jacquinot stop (J-stop, Aperture 2) system mounted on the outer part of FTIR Nicolet 5700 spectrometer operated in the external light source mode. The Aperture 1 is variable from 10 to 20 mm whereas the Aperture 2 is normally set to 1.4 mm. The blackbody, buffer volumes between the BB – HGC, HGC – J-stop and FTIR spectrometer are purged by dry, CO_2-free air. The gas flow (e.g. N_2, N_2+H_2O or N_2+CO_2) through the HGC maintained at highly uniform and stable temperatures up to 1500°C.

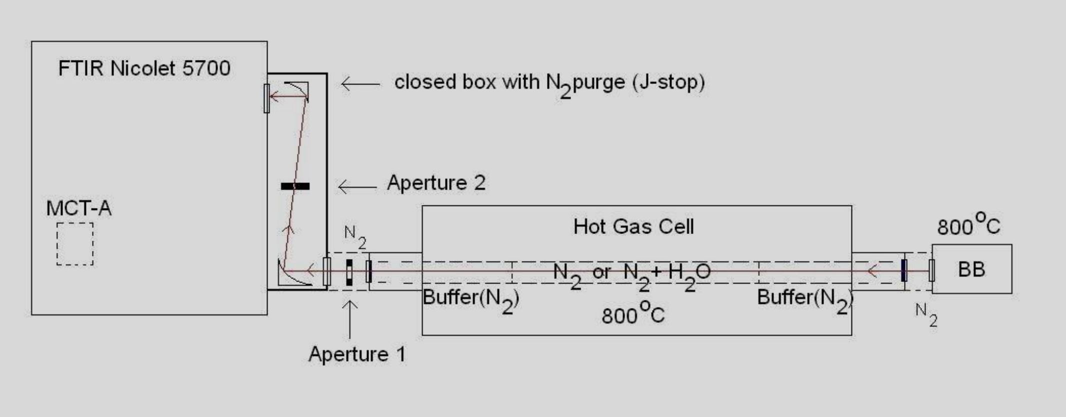

FIGURE 10: THE EXPERIMENTAL SET UP. A REPRESENTATIVE IR RAY EMITTED BY BB AND PASSING THROUGH THE HGC AND J-STOP IS SHOWN BY THE RED LINE. ALL PARTS HAVE BEEN ALIGNED IN HORIZONTAL AND VERTICAL PLANES BEFORE MEASUREMENTS.

Performance of the optical set up has been check first with InSb detector at various temperatures in the HGC and CO/CO_2/H_2O concentrations. Transmission spectra of CO/CO_2 have been measured and compared with available databases (HITRAN/HITEMP) at temperatures of interest. Very good agreement between measurements and calculations has been found.

Then the same measurements in the HGC have been repeated with MCT detector. Non-linear behavior of MCT detector has observed even at low signal value on the MCT detector, Fig. 11.

The transmission spectrum of H_2O in the Fig. 11 was calculated as

$$T_{H_2O^{800^oC}} = \frac{E_{H_2O^{800^oC}+BB^{800^oC}} - E_{H_2O^{800^oC}}}{E_{N_2^{800^oC}+BB^{800^oC}} - E_{N_2^{800^oC}}}, \qquad (1)$$

where

- $E_{N_2^{800^oC}+BB^{800^oC}}$ is the net emission spectrum from HGC at 800°C filled by N_2 and black body at 800°C;
- $E_{N_2^{800^oC}}$ is the emission spectrum from HGC at 800°C filled by N_2 only (when the black body emission was blocked);
- $E_{H_2O^{800^oC}+BB^{800^oC}}$ is the net emission spectrum from HGC at 800°C filled by N_2+H_2O(1%) and black body at 800°C;
- $E_{H_2O^{800^oC}}$ is the emission spectrum from HGC at 800°C filled by N_2+H_2O(1%) only (when the black body emission was blocked);

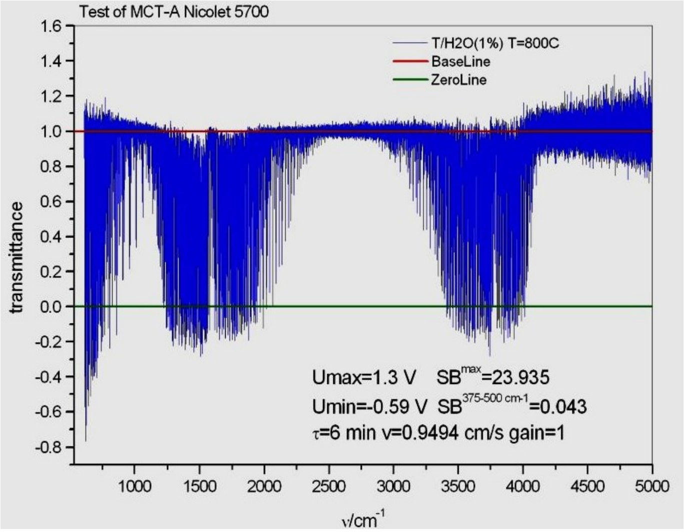

FIGURE 11: A TRANSMISSION SPECTRUM OF H_2O(1%) MEASURED AT THE "RIGHT" (ACCORDING TO THE *NICOLET FTIR USER'S GUIDE, P.63*) UMIN AND UMAX VALUES. THE SECOND APERTURE WAS SET TO 1.4 MM. SPECTRAL RESOLUTION: 0.125 CM^{-1}.

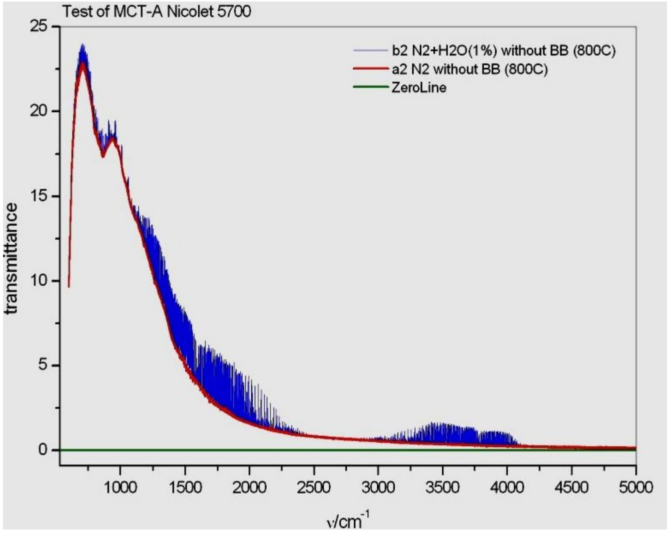

FIGURE 12: EMISSION SPECTRUM OF H_2O(1%) (BLUE) AND THERMAL RADIATION FROM THE HGC AT 800°C (RED) USED IN CALCULATION OF THE TRANSMITTANCE SPECTRUM IN FIG. 11. SPECTRAL RESOLUTION: 0.125 CM^{-1}.

Measurements with a reference gas cell filled by CO_2(10%) and CH_4(100%) in the internal compartment of Nicolet shown nearly linear behavior of MCT response at the same signal level. Therefore it was concluded that "non-linear" MCT response for the set up in Fig. 10 may be due to back reflections from Nicolet beam splitter towards external windows of HGC and then back to the spectrometer (double modulated signal). This signal indeed is relatively week but seen by the MCT detector because it high sensitivity.

Negative transmittance signal in Fig. 11 is due to negative value in numerator of Eq. 1 which may appear because changes in the emission signal from strong H_2O emission bands due to double modulated signal, Fig. 12. This effect is very pronounced at high temperatures and high species concentrations under of interest. At temperatures below 500°C and SO_3 concentrations a few hundreds ppm, SO_3 emission is negligible. Moreover against bright background from BB (800°C) SO_3 bands will appear in absorption.

5. FTIR high resolution measurements on HGC

First measurements were made at 200°C and 400°C in the HGC. Temperature in the SO_2+O_3 reactor was set to 190°C. The reactor was connected through a heated Teflon line (200°C) to the HGC. Gas flows were set as follow: N_2= 1 l_n min^{-1}, O_2= 1 l_n min^{-1}) and N_2/SO_2(5000ppm)= 0.1..0.4 l_n min^{-1}. N_2 and O_2 gases of either “technical” (N_2/O_2 > 99.9%) or “laboratory” (N_2 > 99.998%, O_2 > 99.999%) quality were used. Pressure in the HGC was about one atmosphere.

An example of SO_3 low-resolution absorption spectrum (2 cm^{-1}) in vicinity of 1400 cm^{-1} at 200°C and 400°C band is shown in Fig. 13. It should be noted that although the temperature in the HGC was 200°C (or 400°C) the temperature of the HGC flange where heated Teflon line connected was only 49°C (or 61°C). In general flange temperature is significantly lower than the temperature of the “hot” zone HGC. This is due to the design of the HGC.

At 200°C absorption by H_2SO_4 is also appearing in the range 1420-1500 cm^{-1}, Fig. 13.

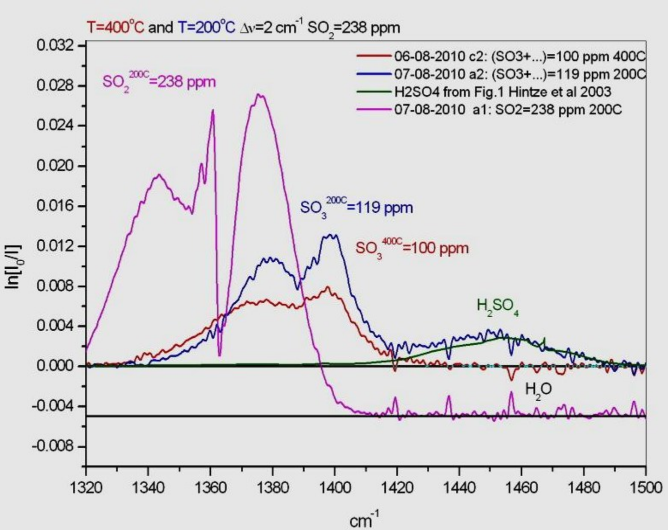

FIGURE 13: SO_3 ABSORPTION SPECTRUM AT 1400 CM^{-1} MEASURED IN HGC AT 200°C (BLUE) AND 400°C (RED). SO_3 CONCENTRATIONS CALCULATED BASED ON THE ASSUMPTION: $\Delta SO_2=SO_3$. PORTIONS OF SO_2 (200°C HGC, MAGENTA, ARTIFICIALLY SHIFTED) AND H_2SO_4 (150°C [3], OLIVE) ABSORPTION SPECTRA ARE ALSO SHOWN FOR COMPARISON. SPECTRAL RESOLUTION: 2 CM^{-1}. MCT DETECTOR. MEASUREMENT TIME 16 MIN.

It is because of presence (minor) water vapors in the system. One can also see “negative” absorption by water (sharp deeps) because water from N_2/SO_2 gas mixture is consumed in the reaction (3). Portions of SO_2(238 ppm, 200°C) absorption spectrum and H_2SO_4 [3] are also shown in the Fig. 13 for comparison. At 400°C SO_3 absorption band becomes broader due to population of higher J-rotational states. H_2SO_4 absorption disappears because thermal decomposition of the acid in the HGC back into SO_3/H_2O and to some extent, $SO_2/O_2/H_2O$.

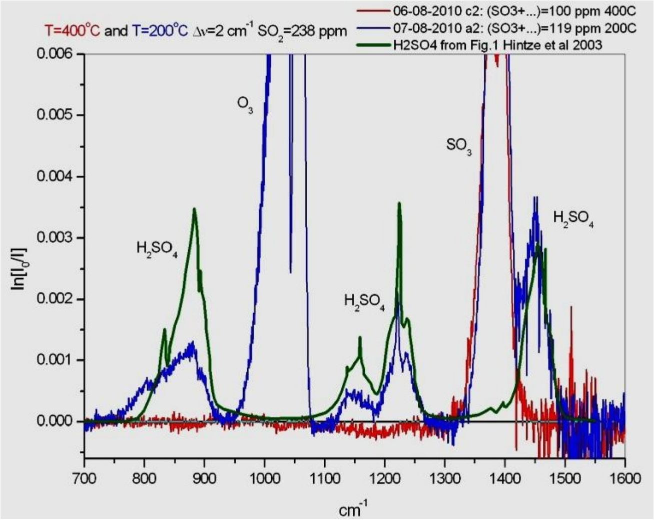

FIGURE 14: FULL SO_3 + PRODUCTS ABSORPTION SPECTRUM MEASURED IN HGC AT 200ºC (BLUE) AND 400ºC (RED). H_2SO_4 (150ºC [3], OLIVE) ABSORPTION SPECTRUM IS SHOWN FOR COMPARISON. SPECTRAL RESOLUTION: 2 CM^{-1}. MCT DETECTOR. MEASUREMENT TIME 16 MIN.

Full SO_3 + products absorption spectrum is shown in Fig. 14 together with H_2SO_4 reference spectrum taken from [3]. Although the ratio between absorption intensities in different H_2SO_4 bands is not the same as in [3] all bands have characteristic structure allowing its easy identification.

High-resolution SO_2(833 ppm) absorption spectrum (0.125 cm^{-1}) at 1360 cm^{-1} and 200ºC is shown in Fig. 15 together with low-resolution one (2 cm^{-1}). Improvement in spectral resolution gives at least two advantages: 1) Intensity of single absorption lines in quasi-discrete spectrum (e.g. H_2O or SO_2) is increased. 2) Because fine structure in the spectra species of interest is unique for each component and placed at well-defined wavelengths follow analysis of complex overlapped spectra can be done by modern mathematical tools.

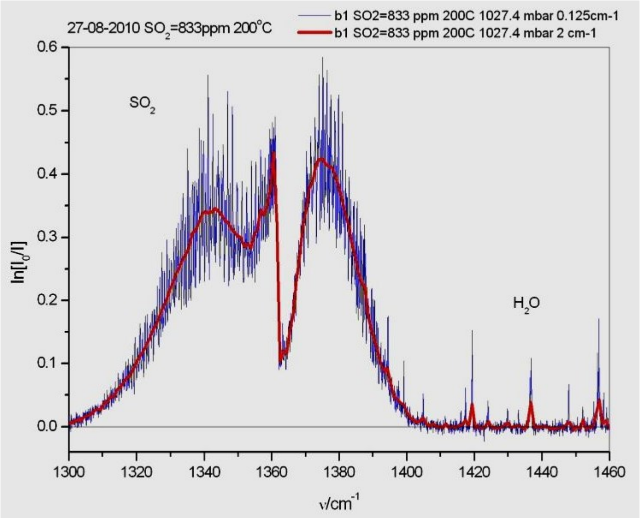

FIGURE 15: SO_2(833 PPM) HIGH RESOLUTION (0.125 CM^{-1}, BLUE) AND LOW RESOLUTION (2 CM^{-1}, RED) ABSORPTION SPECTRA (1360 CM^{-1}) MEASURED IN HGC AT 200ºC. MCT DETECTOR.

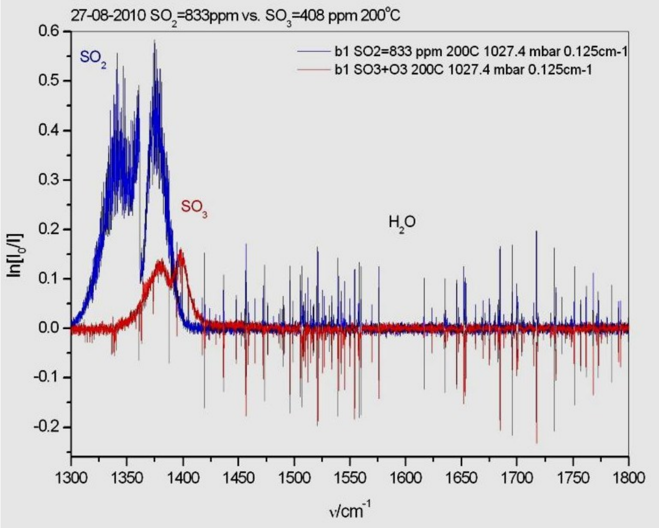

FIGURE 16: SO_2(833 PPM, BLUE) AND SO_3(408 PPM, RED) HIGH RESOLUTION (0.125 CM^{-1}) ABSORPTION SPECTRA (1360 CM^{-1}) MEASURED IN HGC AT 200°C. NOTE: ALL WATER FROM N_2+SO_2 IS CONVERTED TO H_2SO_4. SO_3 CONCENTRATIONS CALCULATED BASED ON THE ASSUMPTION: $\Delta SO_2=SO_3$. MCT DETECTOR. MEASUREMENT TIME ABOUT 14 MIN.

In Fig. 16 high-resolution SO_2 and SO_3 absorption spectra at 200°C are shown. Because of high concentration of SO_2 absorption by H_2SO_4 is hard to see. As in the Fig. 13 negative H_2O absorption in the SO_3 spectrum corresponds to consumption of water from N_2/SO_2 gas mixture and N_2 and O_2 gases. In opposite to SO_2 spectrum with characteristic sharp structure the SO_3 one looks as a continua-like feature.

Low temperature of the HGC flange causes condensation of sulfuric acid vapors because its high dew point values. In Fig. 17 calculated H_2SO_4 dew points at two values of water concentrations (H_2O= 0.05% and H_2O= 0.001%) are shown in the range of SO_3 concentrations used. The water content was assumed based on N_2/O_2 gas quality used and assuming that one half of the rest gas composition is water. For "technical quality" nitrogen an oxygen and SO_3 concentrations 100..400 ppm dew point of H_2SO_4 is about 120-140°C, Fig. 17. That is in agreement with experimental results discussed above and observation of significant corrosion in the connector (made from brass) matching heated Teflon line and the HGC flange. The situation may be improved if better quality (more expensive) gases will be used (e.g. N_2(4.8) and O_2(5.0)). However even in this case acid dew point will be still significantly higher than the temperature of HGC flange. Therefore existing HGC has to be modified or a new one has to be built in order to perform reliable SO_3 measurements.

Reaction (3) is reversible and the products and reactants will both be present to some extent. Equilibrium constant for reaction (3) is expressed as

$$K = \frac{p_{H_2SO_4}}{p_{SO_3} p_{H_2O}} , \qquad (2)$$

where p_i is partial pressure (or concentration) of components.

The equilibrium constant depends on the temperature and the Gibbs free energy of the reaction (3), $\Delta_r G^0 = \Delta_r G^0(T)$:

$$RT \ln K = -\Delta_r G^0 , \qquad (3)$$

and

$$\Delta_r G^0 = \Delta_f G^0(T)^{products} - \Delta_f G^0(T)^{reactants} \qquad (4)$$

where $\Delta_f G^0$ is Gibbs energy of formation, R is universal gas constant and T is the absolute temperature. The NIST-JANAF tables [7] give values of $\Delta_f G^0$ for temperatures from 0 to 6000K.

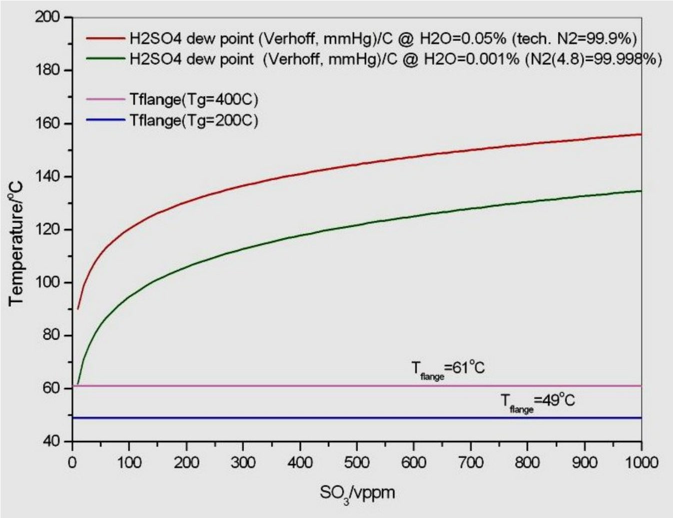

FIGURE 17: CALCULATED SULFURIC ACID DEW POINTS AT VARIOUS SO_3 CONCENTRATIONS AND H_2O=0.05% (RED) AND H_2O=0.001% (BLUE) BASED ON [6]. TEMPERATURES OF THE HGC FLANGE AT 200°C (BLUE) AND 400°C (MAGENTA) OF HGC ARE SHOWN BY HORIZONTAL STRAIGHT LINES.

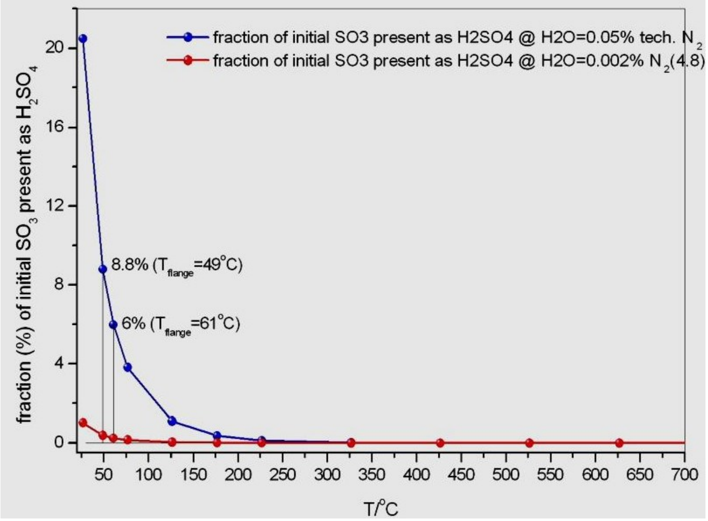

FIGURE 18: FRACTION (IN VOL %) OF INITIAL SO_3 PRESENT AS H_2SO_4 CALCULATED AT H_2O=0.001% (RED) AND H_2O=0.05% (BLUE) BASED ON NIST-JANAF THERMOCHEMICAL TABLES [7]. FRACTIONS OF SO_3 AT 49°C AND 61°C FLANGE TEMPERATURES ARE 8.8% AND 6%, RESPECTIVELY.

Use of Eq's (2-4) allows us to calculate ratio Q of H_2SO_4 to SO_3 for any given temperature and water concentration. The fraction F of initial SO_3 present as H_2SO_4 can be calculated as

$$F = 100\frac{Q}{Q+1} \qquad (5)$$

Figure 18 shows variations of F with temperature at two water concentrations as in the Fig. 17. At HGC flange temperatures 49°C and 61°C one can expect 8.8% and 6% conversion of SO_3 to H_2SO_4 with use of "technical" N_2 and O_2. Better quality gases give very low F values (< 0.4%).

Thermochemical consideration of the process does not show how fast SO_3 conversion to acid might be but rate constant does. Rate constant for (homogeneous) reaction (3) reported by NIST Chemical Kinetics Database is 1.2x10^{-15} cm^3 s^{-1} at 298K. However more resent gas-phase studies yielded a second-order dependence of this rate with respect to water vapor pressure [8], i.e. the reaction (3) is indeed:

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \qquad (3')$$

Theoretical consideration suggests that different reactions paths involving two or three water molecules are taken in the process of forming sulfate aerosols [10].

Taking into account temperature dependence rate constant for the reaction (3'), first order rate coefficients (k_I) for the SO_3 losses can be calculated, Fig. 19. As one can see temperature significantly reduces k_I or by other words effective reaction time ($\tau = (k_I)^{-1}$) increases. Therefore if the temperature of the HGC flange would be higher than 150°C no acid formation in the gas phase would be happened because residence time in the SO_2 + O_3 reactor and HGC. Thus for example at 200°C effective reaction time is more than 5 minutes compare to about 1 min residence time in the system.

Temperature has also influence on stability of sulphur trioxide formed in the reaction (1). In the work [10] has been reported that SO_3 decomposition back to SO_2 starts at 350°C. Decomposition of SO_3 is in fact reversible process of its formation in reaction

$$SO_2 + 0.5O_2 \rightarrow SO_3 \qquad (6)$$

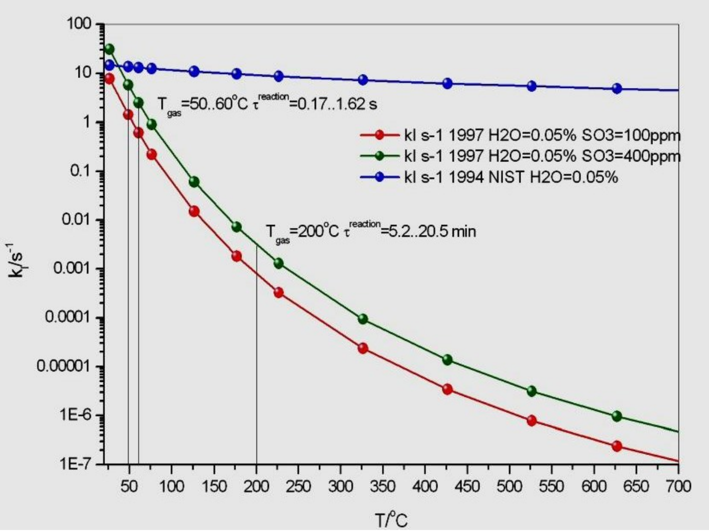

FIGURE 19: FIRST ORDER RATE COEFFICIENTS FOR THE SO_3 LOSSES BY GAS-PHASE REACTIONS (3') (OLIVE, RED) AND (3) (BLUE) CALCULATED AT H_2O=0.05 VOL % AND VARIOUS SO_3 CONCENTRATIONS. RATE CONSTANTS ARE TAKEN FROM [8] AND NIST, RESPECTIVELY.

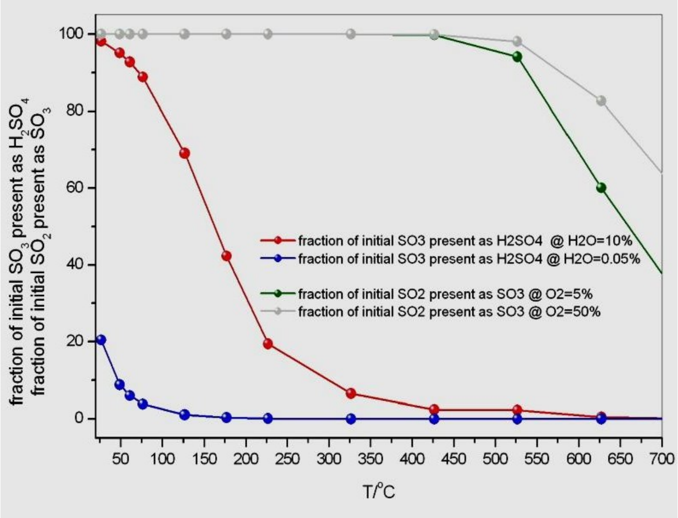

FIGURE 20: FRACTIONS (IN VOL %) OF INITIAL SO_3 PRESENT AS H_2SO_4 AND SO_2 AS SO_3 CALCULATED AT VARIOUS H_2O AND O_2 CONCENTRATIONS RELATED TO THE LAB MEASUREMENTS (BLUE AND GREY) AND TYPICAL HOT FLUE GAS COMPOSITION (RED AND OLIVE). CALCULATIONS BASED ON NIST-JANAF THERMOCHEMICAL TABLES [7] AND WORK [12].

The reaction is exothermic, reversible and shows a decrease in molar volume on the right-hand side. i.e. in the direction of SO_3 formation [1]. Thermodynamical calculations as fraction of SO_2 as SO_3 through Eq's 3-5 are shown in Fig. 20 for two water concentrations assumed in lab measurements and typical for hot flue gas composition. In the same figure fraction of SO_3 present as H_2SO_4 is also shown for the same water concentrations. One can see only at temperatures higher than 500°C there is a contribution to SO_3 formation through the reaction (6) in addition to the main reaction (1). According to NIST Chemical Kinetics Database reverse reaction (6) has extremely very low k_I values (< $1x10^{-5}$ s^{-1}) in the temperature range 20-1100°C. Therefore SO_3 decomposition reported in [10] can be only attributed to a heterophase process. Because internal surface of the HGC is high grade alumina (99.995%) all heterophase process including SO_3/H_2SO_4 will give a minor influence on equilibrium SO3 concentration.

SO_3/H_2SO_4 interaction with HGC material

As it has been described in the previous section low temperature on the HGC flange can cause a corrosion problem. Indeed observations made after SO_3 measurements confirm that. In the Fig. 21 one of two ends of the HGC is shown. One can see a lot of black deposit from both – inlet and outlet ends of the HGC, which is composed from a solid and amorphous-like stuff. In the figure rests from O-rings those were also affected is seen.

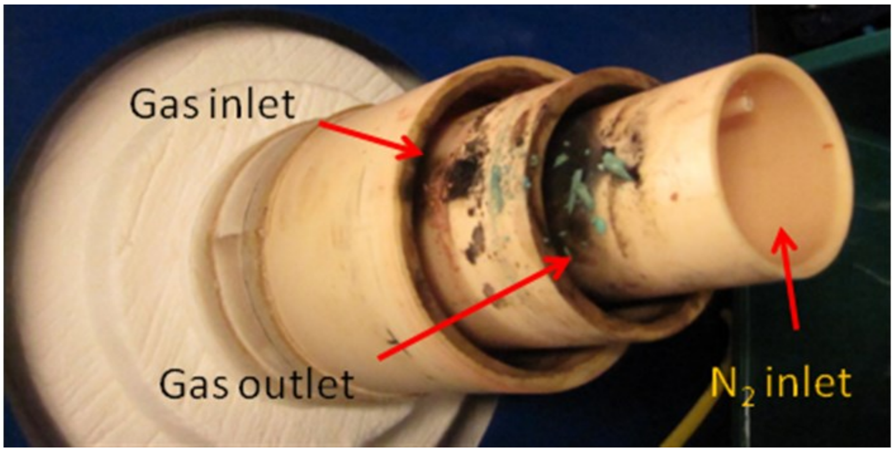

FIGURE 21: ONE OF TWO GAS INLET/OUTLET ENDS OF THE HGC WITH DISMOUNTED FLANGE AFTER SO_3 MEASUREMENTS. ARROWS SHOW CONCENTRIC AREAS WHERE GASES ARE ENTERING INTO THE HGC.

Flanges of the HGS have been also affected by reactive species. Parts of one of the dismounted flanges are shown in Fig. 22. Parts build the flange like a sandwich. One can see no corrosion on the part from N_2 side. In opposite parts corresponding to gas inlet and outlet sides are affected. All black stuff can easily be removed by water that supports its acid-based nature. The black color is due products of SO_3/H_2SO_4 reactions with material of o-rings. Cleaned from the deposit parts show appearance of the permanent changes of Al surface those can be removed by fine polishing.

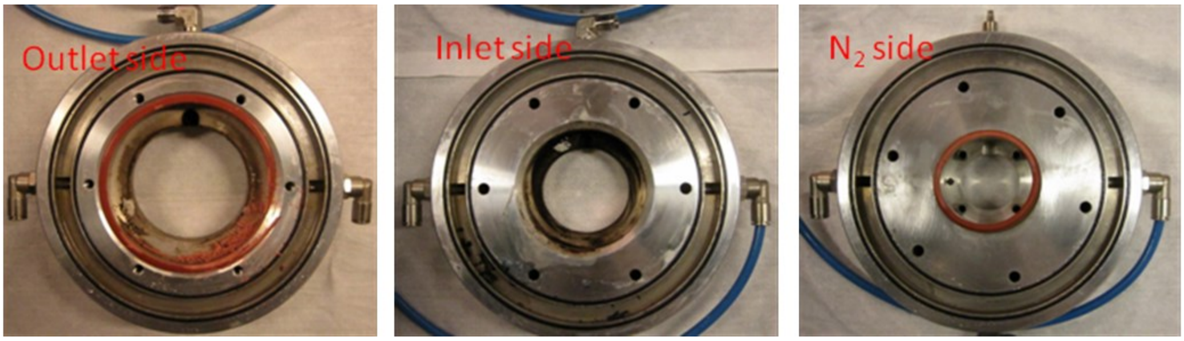

FIGURE 22: DISMOUNTED HGC FLANGE. PARTS OF THE FLANGE CORRESPONDING TO GAS OUTLET, INLET AND N_2 INLET SIDES ARE SHOWN FROM LEFT TO RIGHT.

Corrosion observed on the HGC flanges and calculations clearly indicate that the temperature on the HGC is the major problem for reliable SO_3/H_2SO_4 measurements. Moreover use of the nHGC designed for high temperature operation and not designed for work with highly corrosive gases is highly inefficient from both running costs and quality of the data is obtained. Therefore a new hot gas cell suitable for work with highly reactive gases has been design and made [12].

FTIR high-resolution SO_3 measurements on nHGC [12]

At the start of November 2011 SO_3 IR absorption and extraction measurements (by controlled condensation method) in collaboration with Chalmers University (Sweden) have been done on nHGC. The idea for these measurements was to calibrate SO3 IR measurements by a well-known SO_3/H_2SO_4 gas extraction technique which is used as a routine tool on industrial scale.

The nHGC and new FTIR high-resolution spectrometer (Cary 660, Agilent) are shown in Fig. 23 below (in the middle and top right corner, respectively).

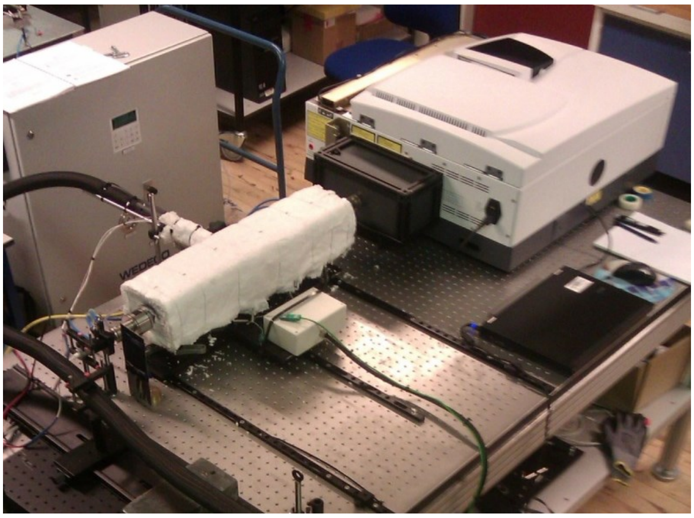

FIGURE 23: OPTICAL SET UP INCLUDING NHGC AND FTIR SPECTROMETER.

Reaction of SO_2 with O3 has been used for SO_3 generation in SO_3 flow reactor. SO_3 was mixed after the SO_3-reactor with water vapours (1% in total flow) before injecting into the nHGC. Temperature in the nHGC was set to 473°C and 200°C in the SO3-rector and the line which connected the SO_3-reactor and HGC in order to 1) be well above dew point of H2SO4 (160°C at SO3=370 ppm), 2) avoid formation SO_3 from un-reacted SO_2 in the HGC and 3) avoid any H_2SO_4 formation from reaction of SO_3 with H_2O in the nHGC. Gas flows has been chosen in order significantly reduce residence time between SO_3-reactor and the nHGC (0.26 s) compare to effective reaction time SO_3(370 ppm)+H_2O(1%) of 16.2 s at 200°C.

SO_3 extraction measurements have been performed from the middle of the nHGC. Controlled condensation method used is based on British Standard BS 1756: Part 4 (L Gustavsson och G Nyquist *Värmeforsks Mäthandbok*, Utgåva 3 (2005) Kap. 5.6.3, p. 96, ISSN 1653-1248). Samples have been analysed by ion chromotography. Results obtained are very consistent: 1) at SO_2=629 ppm initial concentration measured SO_3 concentration was 244 ppm and 2) at SO_2=313 ppm initial concentration measured SO3 concentration was 123 ppm. As one can see SO_2 to SO_3 conversion is 39%. IR absorption measurements have been shown 60% conversion of SO_2 in SO_2+O_3 reaction. Therefore it was conclude that even in such advanced system (SO_3-reactor + nHGC) there are some losses of SO_3(or H_2SO_4) probably due to heterophase reactions.

There is still a concern that some (minor amount) H2SO_4 aerosols have not been captured by the extraction system. Therefore use of other suitable SO_3 gas extraction technique is of interest for comparison with measurements done. In general SO_3 sampling is very difficult and there is simply no “best ever” method available. Extractive techniques require adherence to proper procedures and have been shown to have a significant degree of variability from tester to tester leading to testing inaccuracies (in *Continuous Measurement Technologies for SO_3 and H_2SO_4 in Coal-Fired Power Plants*, EPRI, Palo Alto, CA: 2004. 1009812). Therefore possible alternatives for SO_3 IR spectra calibration have been explored.

IR absorption spectra can theoretically be calculated from the first principles (*ab initio* calculations). Because SO_2 and SO_3 IR absorption bands are in strong overlap, analysis of SO2 absorption features is essential in proper SO_2 concentration calculations. To our knowledge there are no databases available for SO_3/SO_2 spectra calculations at temperatures of interest (500-800K). Therefore a Supplementary Project application about SO_3/SO_2 databases generation in collaboration with UCL has been made and submitted to Energinet.dk. The project has been supported by Energinet.dk and the work has been started by UCL from April 1st 2012 and finalized in December 2015.

Agilent FTIR spectrometer (nominal resolution 0.09 cm^{-1}) with linearized high-sensitivity MCT detector has been purchased at the end of 2011 year and used in followed $SO_3/SO_2/H_2O/NH_3/CO_2$ high-resolution IR absorption measurements. Two examples of SO_2/SO_3 high-resolution FTIR absorption spectra at 300C and 500C are shown in Fig. 24 below.

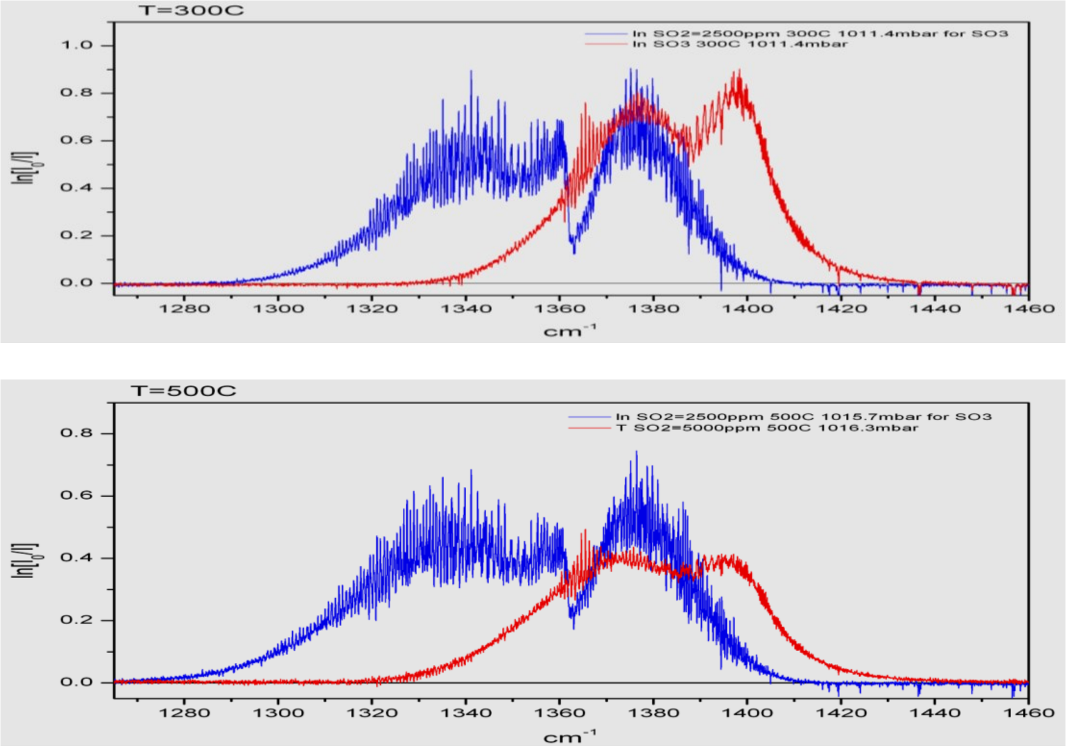

FIGURE 24: SO_2/SO_3 HIGH-RESOLUTION ABSORPTION SPECTRA AT 300C (UPPER PANEL) AND 500C(LOWER PANEL).

According to Agilent linearized MCT detector technology delivers substantial advantages for quantitative measurements. It extends the linear range of the detector versus energy flux relationship by about a factor of ten above the range that can be obtained with a standard MCT detector, while still maintaining high photometric accuracy. The result is a wider concentration range when performing quantitative measurements. This is very important in quantitative measurements reference spectra of gases relevant to the project (e.g. SO_3, SO_2, NH_3, H_2O and etc).

Measurements under WP4 require a powerful IR light source. The source has been developed and made. The source has a large aperture (about 5 cm) and operates at 1500C. The source has successfully been used in *in situ* FTIR measurements along 5.5 m pipe on 100kW LT-CFB gasifier at Risø Campus under Energinet.dk project 2011-1-10622 “On-line trace gas measurement technique for gasification”. The powerful IR light source is shown in Fig. 25 below.

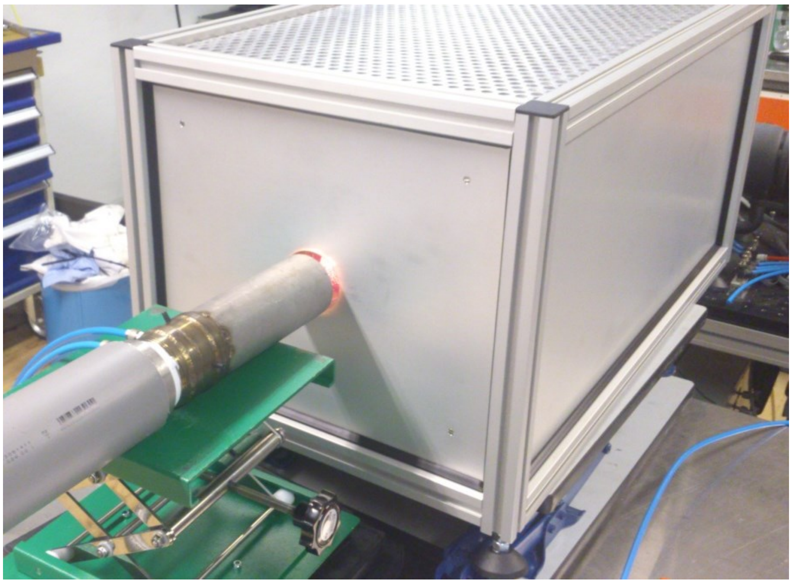

FIGURE 25: IR LIGHT SOURCE WITH OPERATION TEMPERATURE 1500C AND APERTURE Ø50 MM.

IR absorption measurements with $NH_3/SO_2/SO_3$ have been performed at 25C, 300C, 400C and 500C in 450-6000 cm^{-1} spectral range with DTGS and MCT detectors and at various spectral resolutions. Several pre-mixed gas mixtures N2+NH3(1000 ppm, 1%) and N_2+SO_2(5000ppm) have been used. Additional dilution has been performed with use BRONKHORST high-end mass flow controllers. Reaction of SO_2 with O_3 has been used for SO_3 generation. O_3 has been produced by a commercial ozone generator.

Measurements at 25°C have been compared with available data from PNNL database (http://www.pnl.gov/ or http://nwir.pnl.gov) which contains a lot experimental reference data of compounds mostly measured up to 50C with similar class FTIR spectrometer (Bruker). It was found very good agreement between our measurements and that performed at PNNL for SO_2/NH_3. There are however some discrepancies in SO_3 measurements that is not a big surprise because of extremely high reactivity of SO_3. It should be noted that in the measurements at PNNL a gas is always in the contact with the windows of the gas cell where IR absorption measurements are performed.

In two Fig's 26-27 below SO_2 and SO_3 IR absorption cross sections measured in HGC at 25C (blue) and 300C (red) are shown. The spectral resolution 0.56 cm^{-1} has been used.

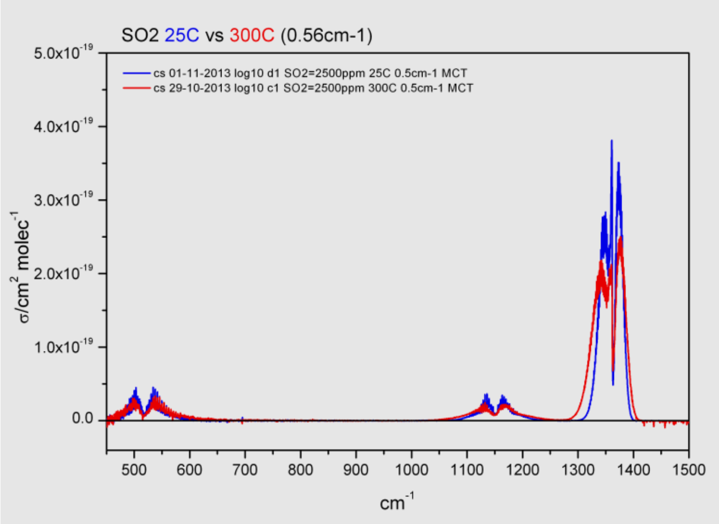

FIGURE 26: SO_2 ABSORPTION CROSS-SECTIONS MEASURED AT 25C AND 300C.

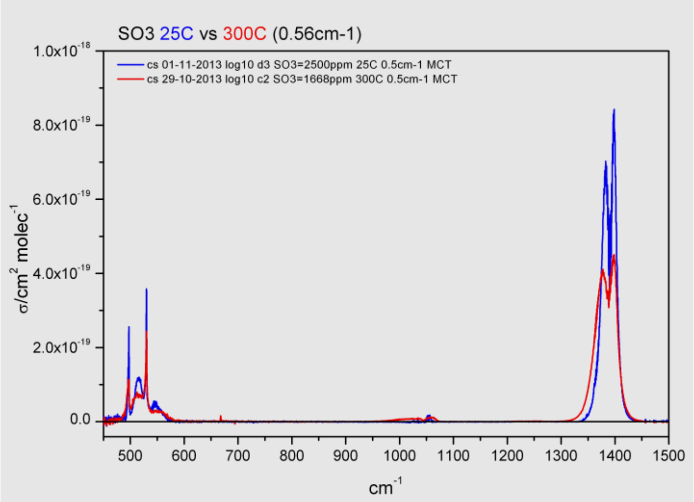

FIGURE 27: SO_3 ABSORPTION CROSS-SECTIONS MEASURED AT 25C AND 300C.

The structure in the SO_3 spectrum around 1050 cm^{-1} is due to traces of O_3 in the system. One can see that temperature has significant impact on the shape and the value absorption cross section spectra.

The choice of the spectral resolution is based on

- SO_2 and SO_3 spectra have a continua-like structure. This is even more pronounced at high temperatures because diminishing of the fine structure with the temperature. Fig. 28 below shows a part of SO_3 IR absorption cross section spectra at 400C measured in nHGC at 0.56 cm^{-1} and 0.1 cm^{-1} spectral resolution. One can see that the high-resolution spectrum (red) is noisy because lower S/N ratio and shows few fine details between 1360-1410 cm^{-1} compare to that measured at low-resolution (blue). Therefore better spectral resolution, say 0.1 cm-1 compare to 0.56 cm^{-1} used will give us not so much extra useful information.

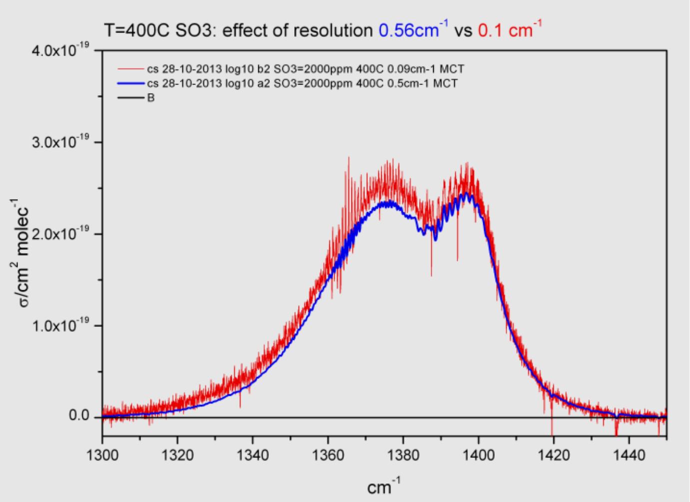

FIGURE 28: SO_3 ABSORPTION CROSS-SECTIONS MEASURED AT 400C AT 01.CM^{-1} AND 0.56CM^{-1} SPECTRAL RESOLUTIONS.

- measurements at higher spectral resolution (e.g. 0.1 cm-1) will in general require much longer measurement time because low S/N ratio;

- measurements on Pyroneer gasifier (Energinet.dk project 2011-1-10622) have shown that 0.56 cm-1 spectral resolution is sufficient for measurements of trace gases (e.g. NH_3). In Fig. 29 below a IR absorption spectrum (0.56cm^{-1}) measured at Pyroneer gasifier (blue) is shown in comparison with NH_3 reference spectrum measured in HGC (red).

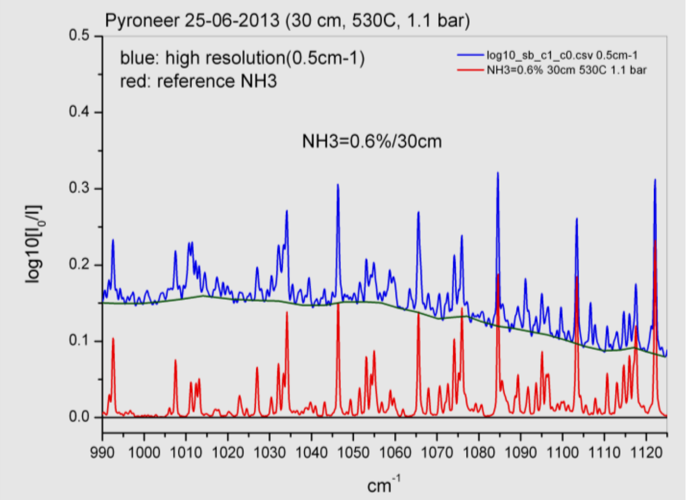

FIGURE 29: A PART OF HIGH-RESOLUTION ABSORPTION SPECTRUM MEASURED AT PYRONEER GASIFIER (BLUE) AND NH_3 REFERENCE SPECTRUM (RED).

Several high-resolution FTIR absorption measurements (0.25cm^{-1}) have been performed on the HGC in order to build a reference spectra set gases relevant to in situ SO_3 cross-stack measurements described in WP4. Those measurements included H_2O, CO_2 and SO_2. Because the cell has a finite absorption pathlength (53.3 cm), concentrations gases of interest have been set to match cross-stack conditions (4 m) of the measurements at OxPP facility. The measurements have been performed at 500C in the cell.

6. Measurements on industrial facilities

OxPP facilty
In May 2014 2 days cross-stack (4 m) emission/transmittance measurements have been performed in collaboration with Vattenfall on 30 MW thermal pilot plant (OxPP facility) at Schwarze Pumpe in Germany. The facility has only one industrial burner facing downwards in 4 m x 4 m boiler house with several access ports placed at different boiler levels.

The major reasons to do those measurements were 1) OxPP facility is industrial scale facility compare to research-type 30 kW unit at DTU Chemical Engineering and 2) it has been found in the WP3 that SO3 IR absorption measurements in ppm concentration level will require longer absorption pathlengths (few meters) those are difficult to implement on a small 30 kW unit.

The measurements were performed before SCR unit (Second draft, Level 10), where typical gas temperature was about 500C. On the first day a high-S coal has been used (2.4 wt%). On the second day low-S coal (lignite dust) has been used (0.8 wt%). In both days the burner was operated at 80% of a full load in order to have 1) high flame temperature which favor SO3 formation and 2) long time stable operation (which was pre-defined by availability of high-S coal reserves).

The main focus was placed on SO2/SO3 measurements at high spectral resolution (0.25cm^{-1}). In addition to that mapping of the gas temperature and the major gas composition (NO, SO2, CO2 and H2O) profiles were performed. Gas temperature measurements were performed with a calibrated thermocouple, whereas gas composition was measured with DTU's special gas extraction system. SO2/CO2/H2O concentrations calculated from cross-stack measurements and gas extraction ones were found to be the same.

AVV1 Block
In February 2016 2 days cross-stack (14.16 m) emission measurements have been performed in collaboration with DONG Energy on AVV1 Block (Avedøre Power Station). The measurement location was chosen based on available access ports before SCR unit. In both days the block was operated at between 60-100% of the full load which was a subject of weather/electricity marked situation. The main focus was placed on SO_2/SO_3 measurements at high/low spectral resolutions (0.25cm^{-1}/1cm^{-1}).

7. Data analysis

OxPP facilty

The basic gas composition was (typically) found as follow (% = concentration in volume %, wet):

High S-coal: CO2=12.7%, O2= 4.6%, H2O=6.2-8.6%, **SO2=0.176%**.

Low S-coal: CO2=13.6%, O2= 4.1%, H2O=7.8-8.8%, **SO2=0.0482%.**

In addition to that Vattenfall has performed elemental analysis of the fuel and boiler/fly ashes for both days of the measurement campaign. It was found a difference about two times in SO_3 content in both fly/boiler ashes in high- and low-S containing fuel operation (i.e. ashes from the high-S fuel contains more SO_3 than that from the low-S fuel). Fly ash in the high-S combustion has been found to be white-coloured and in low-S one – grey coloured that is probably due to significantly higher Al_2O_3 content in the in the fly ash in the high-S combustion than in the low-S case. The temperature profiles have been found to be quite uniform, as one can see in Fig.30 below.

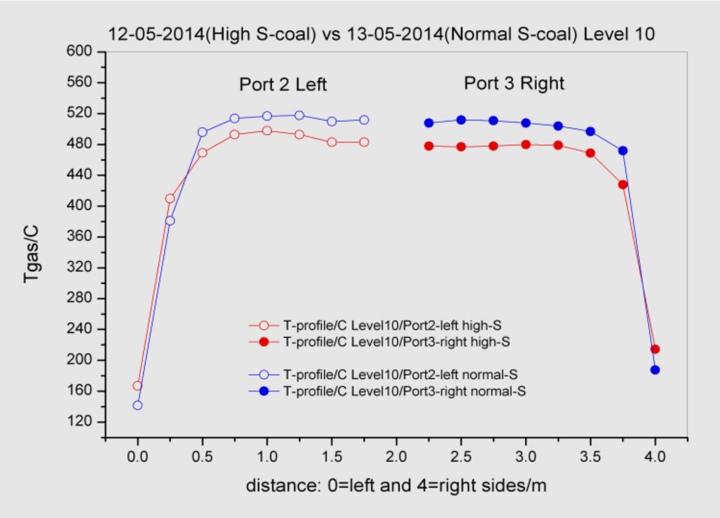

FIGURE 30: GAS TEMPERATURE PROFILES MEASURED IN A HOT FLUE GAS AT OXPP FACILITY (LEVEL 10, BEFORE SCR) AT NORMAL S-COAL (BLUE) AND HIGH S-COAL (RED) OPERATIONS.

A difference in the temperature profiles about 25C can be attributed to different particle concentrations (and consequently different radiative heat transfer) in the high- and low-S cases (assuming that other parameters are the same).

The analysis shows that there is no difference between in situ cross-stack measurements in the high- and low-S combustion cases. It may indicate that SO_3 concentration in the flue gas was the same. This is quite interesting because of large SO_2 concentration difference in two cases. Modelling of the measured *in situ* spectrum with use of reference data for H_2O and SO_2 obtained in the WP3 shows that the experimental spectrum can well be described by the synthetic one as H_2O+SO_2 in the spectral range of SO_3 absorption. This may indicate that SO_3 concentration in the flue gas is very low, i.e. below detection limit (which is a few ppm). This may be true considering that the facility has only one burner and quite a long distance between the flame end and the measurement location that can in overall cause a capture of SO_3 on colder ash particles (compare to the gas temperature) those concentration is higher in high-S case.

AVV1 Block

During service stop at AVV1 in summer 2015 it was checked access ports alignment and their visibility across 14.16 m distance. However during both measurements days in February 2016 the visibility from port-to-port (checked with a LED powerful hand lamp and human eyes) was very lower, especially in the first day of the measurements. Attempts “to see” an IR light from a light source at 1500C visually and with a FTIR spectrometer (MCT detector) were unsuccessful. This can be explained by ports miss-alignment during block operation and/or heavy particle load in the hot flue gas. Typical gas temperature during the measurements, measured by process control equipment further downstream close to SCR unit entrance, was about 320C.
Therefore only emission measurements have been performed. An example of emission spectrum is shown in Fig. 31 below.

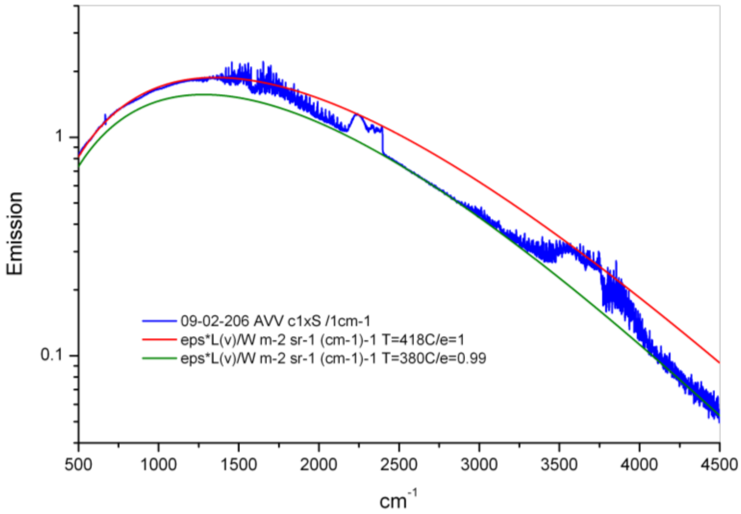

FIGURE 31: AN EMISSION SPECTRUM (W M^{-2} SR^{-1}) MEASURED AT 1 CM-1 SPECTRAL RESOLUTION (BLUE). THE RED LINE SHOWS A PLANCK’S CURVE (BLACK BODY) FIT TO CO_2 BANDS AND THE OLIVE LINE SHOWS GREY BODY FIT TO GAS EMISSION FREE SPECTRAL RANGES.

The blue line in the Fig. 31 shows measured IR emission spectrum with 1cm^{-1} spectral resolution after calibration with a black body-like source at 366C. The red and olive lines show a fit to CO_2 emission bands at 2240 cm^{-1} and 3626 cm^{-1} which give an effective (brightness) gas temperature (418C) and an effective particle (brightness) temperature (380C), respectively.

Calculated absorptivity spectrum from the emission spectrum is shown in Fig’s 32-33 below. The spectrum is shown in 1320-1460 cm^{-1} and 2390-2560 cm^{-1} spectral ranges where two SO_3 absorption bands are located. The measured absorptivity spectrum has been modelled by $CO_2/H_2O/SO_2/SO_3$ reference spectra measured at the same spectral resolution. Because of the small port dimensions it was not possible to do mapping of the gas flow by a gas extraction probe. Therefore CO_2 and H_2O initial concentrations have been chosen based on data available from AVV1 measurement equipment placed close to the stack and have later been adjusted during modelling assuming a constant temperature profile across the two measurement ports. Obtained CO_2 and H_2O concentrations (9% and 11%) are typical for post combustion region in a coal combustion process. The SO_2 concentration, 370 ppm, was calculated from the modelling as well and its value is agrees with a typical SO_2 concentration one can expect for coal combustion.

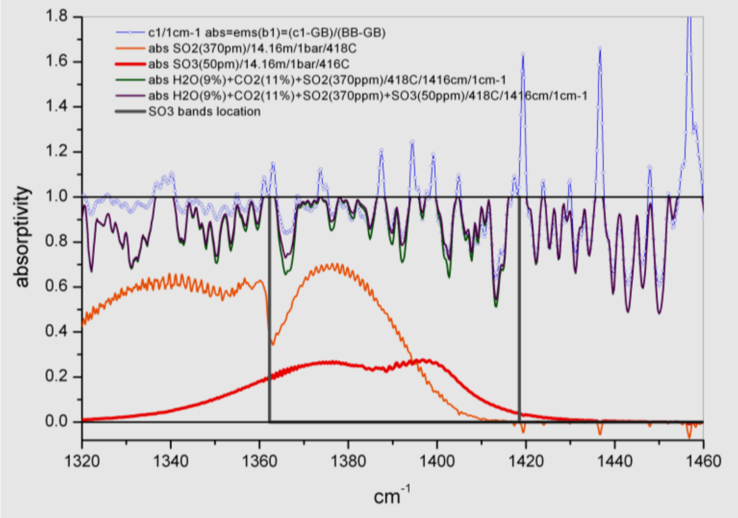

FIGURE 32: A PART OF ABSORPTIVITY SPECTRUM (OPEN BLUE CIRCLES) CALCULATED FROM THE EMISSION SPECTRUM IN THE FIG. 31 AND ITS MODEL BY CO_2(11%)+H_2O(9%)+SO_2(370PPM) SPECTRA AT 418C AND 14.16M ABSORPTION PATHLENGTH (PURPLE). THE OLIVE LINE SHOWS EFFECT OF SO_3(50PPM) ABSORPTION BAND ON THE MODELLED SPECTRUM. CORRESPONDING SO_2(370PPM) AND SO_3(50PPM) ABSORPTIVITY SPECTRA ARE SHOWN BY ORANGE AND RED LINES, RESPECTIVELY. A PART OF SO_2/SO_3 SPECTRA USEFUL FOR SO_3 CONCENTRATION CALCULATIONS IS SHOWN BY A GREY BOX.

As one can see from the Fig. 32 there is very strong absorption by H_2O vapours in 1320-1450 cm-1 spectral range (optically thick gas layer, absorptivity is 1). However there are regions where absorptivity is about 0.8. In 1360-1460 cm^{-1} there is in general a good agreement between the modelling and measurements (blue circles and purple line). Adding for example of SO_3(50ppm) changes clearly absorptivity (olive line) in 1360-1420 cm^{-1}. Therefore this spectral range can be used for SO_3 concentration calculations if SO_3 concentration is "high enough". As can see SO_3/SO_2 absorption bands (red/orange) are very strong. A "high enough" concentration for this case is defined by uniformity of temperature/gas concentration/particles profiles, gas/particle temperature ratio, detector's S/N ratio and measurement time. For the spectrum in the Fig. 31 the measurement time was about 15 min and SO_3 detection limit can be estimated as 15 ppm.

1

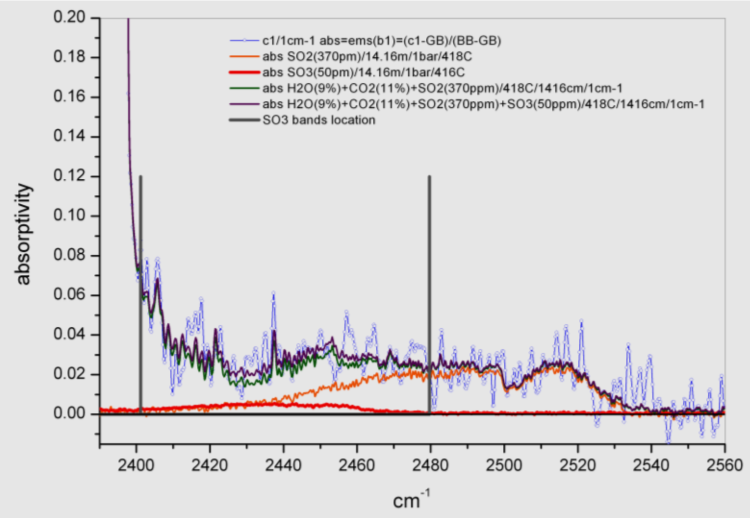

FIGURE 33: THE SAME AS IN THE FIG. 32 BUT IN 2390-2560 CM^{-1} SPECTRAL RANGE.

The other SO_3 band at 2438 cm^{-1} can also be used for concentration calculations. However it has about 66 times less absorption strength compare to that at 1386 cm^{-1}, Fig. 33. In addition to that the absorptivity in 2400-2560 cm^{-1} is noise-limited for measurements in questions. One can see that the measured spectrum can well be modelled by the same CO_2(11%)+H_2O(9%)+SO_2(370ppm) composite spectrum (purple). Adding of SO_3(50ppm), olive line, changes a little absorptivity in 2400-2480 cm^{-1}. Those changes are however below the noise level in the absorptivity spectrum.

In the spectral 2400-2480 cm^{-1} range a InSb detector can be used instead of the MCT (broad band) one used. An InSb detector has typically 10 to 15 times higher sensitivity compare to the MCT one. Use of the InSb will further increase S/N ratio in the spectrum for the same measurement time. Unfortunately due to some technical issues the existing InSb detector was not able to use in the measurements.

The 2400-2480 cm^{-1} spectral range is also promising for SO_3/SO_2 measurements (despite of low SO_3 absorption strength) because it is free from H_2O absorptivity bands and (in post combustion) there is only interference between CO_2 and SO_3/SO_2. The later simplify significantly the data analysis. The drawback of the measurements in 2400-2480 cm^{-1} is a very high S/N ratio about 3333 required for SO_3 measurements on 5 ppm level.

Moving to more hotter (500-600C) flue gas region (e.g. in downstream of super heaters) will increase the gas/particle emission signal falling into the FTIR spectrometer and improve gas/particle temperature ratio, and at the same time it will keep temperature-dependent SO_3/SO_2 absorption cross-sections variations on a moderate level that is important for low SO_3-level measurements.

References

References

[1] *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. **23**, John-Wiley & Sons, Inc.

[2] K Stopperka and F Kilz (1969) *Z. anorg. allg. Chem.* **370**, pp. 59-66.

[3] PE Hintze, HG Kjaergaard, V Vaida and JB Burkholder (2003) *J.Phys.Chem. A*, **107** pp. 1112-1118.

[4] M Broström, H Kassman, A Helgesson, M Berg, Ch Andersson, R Backman and A Nordin (2007) *Fuel Proc. Techn.* **88**, pp.1171-1177.

[5] A Fateev and S Clausen (2009) *Int. J. Thermophys.* **30**, pp. 265-75.

[6] FH Verhoff and JT Banchero (1974) *Chem. Eng. Prog.* **70**(8), pp. 71-72

[7] MW Chase Jr(Ed) (1998) *NIST-JANAF Thermochemical Tables, 4th Ed.* American Institute of Physics, *Phys. Chem. Ref. Data Monograph* **9**,
and
OV Dorofeeva, VS Iorish, VP Novikov and DB Neumann (2003) *J. Phys. Chem. Ref. Data* **32**, pp. 879-901.

[8] JT Jayne, U Pöschl, Y-M Chen, LT Molina, DR Worsnop, CE Kolb and MJ Molina (1997) *J. Phys. Chem. A* **101**, pp.10000-10011.

[9] T Loerting and KR Liedl (2000) *Proc. Natl. Acad. Sci. USA* **97**, pp. 8874-8878

[10] T Fukuchi and H Nikomiya (2006) *IEEJ Trans. Fund. Mater.* **126**, pp. 977-982

[11] WH Evans and DD Wagman (1952) *J. Res. Nat. Bur. Stand.* **49**, pp. 141-148.

[12] H Grosch, A Fateev, KL Nielsen and S Clausen, (2013), *J Quant. Spect. Radiat. Transfer* **130**, pp. 392-399

Appendix 1: Spectroscopy for industrial applications: high-temperature process (oral presentation at 13th Biennial HITRAN Conference 23-25 June 2014, Boston USA)

HITRAN/ASA-2014

Spectroscopy for Industrial Applications: High-Temperature Processes

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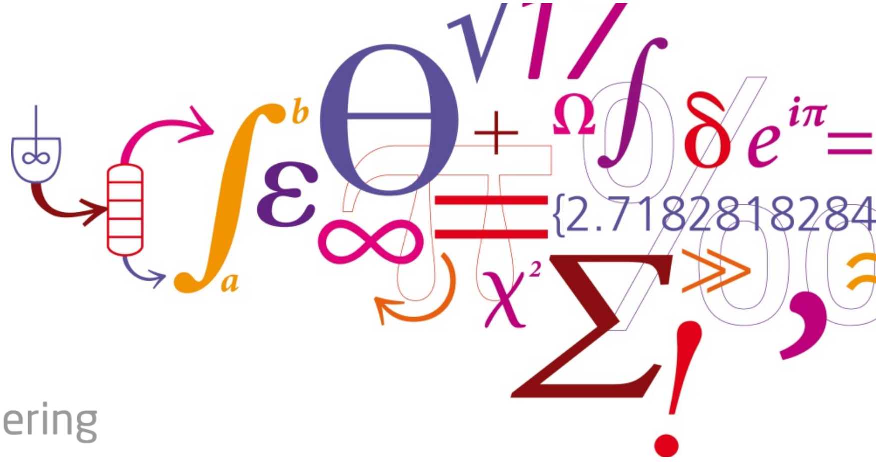


DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Outline

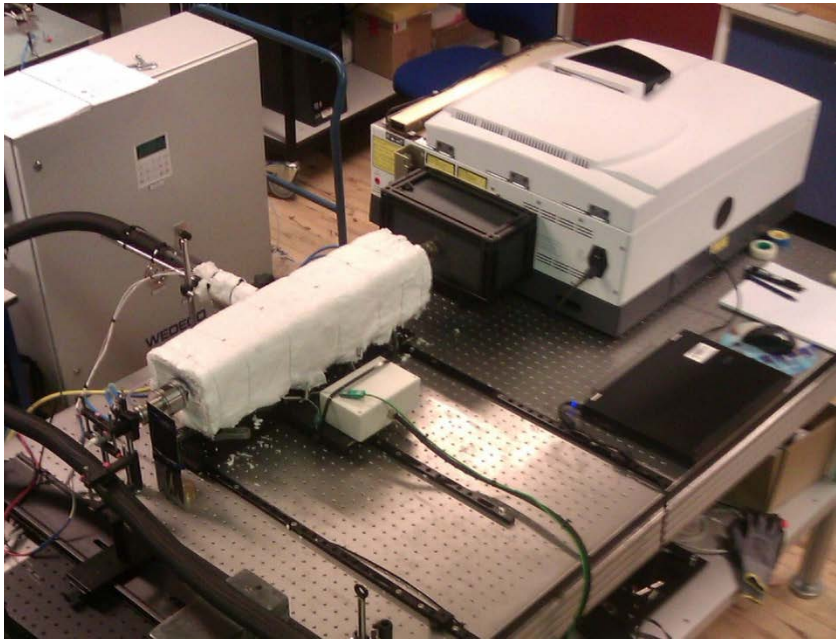
- Hot flow gas cell and FTIR/UV optical set up
- A road to In Situ measurements:
    - NH3 spectroscopy at high-temperatures: band assignment and spectra modelling
    - NH3/H2O field measurements at a pilot scale 6MW gasifier

    - 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

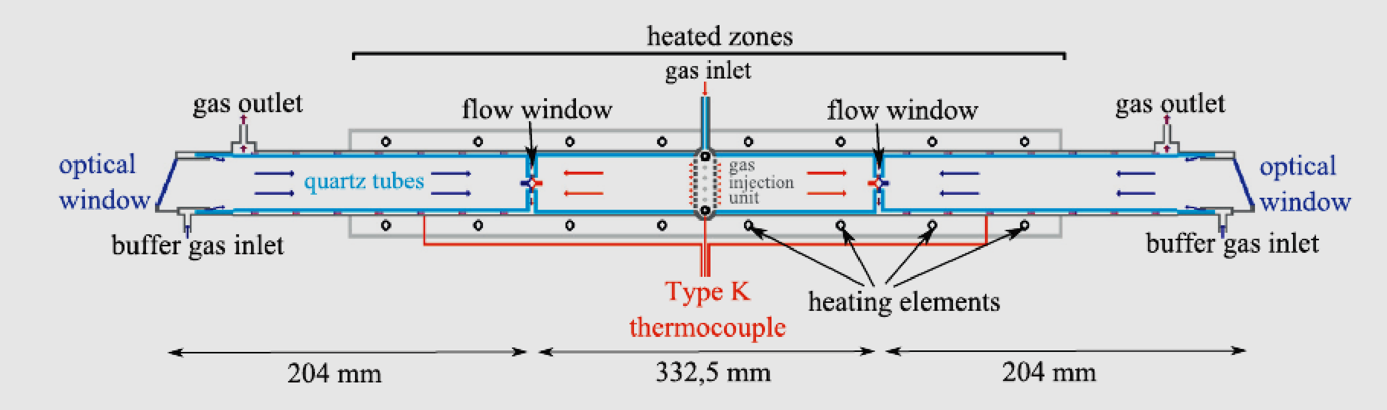
NH3/Phenol: experimental set up



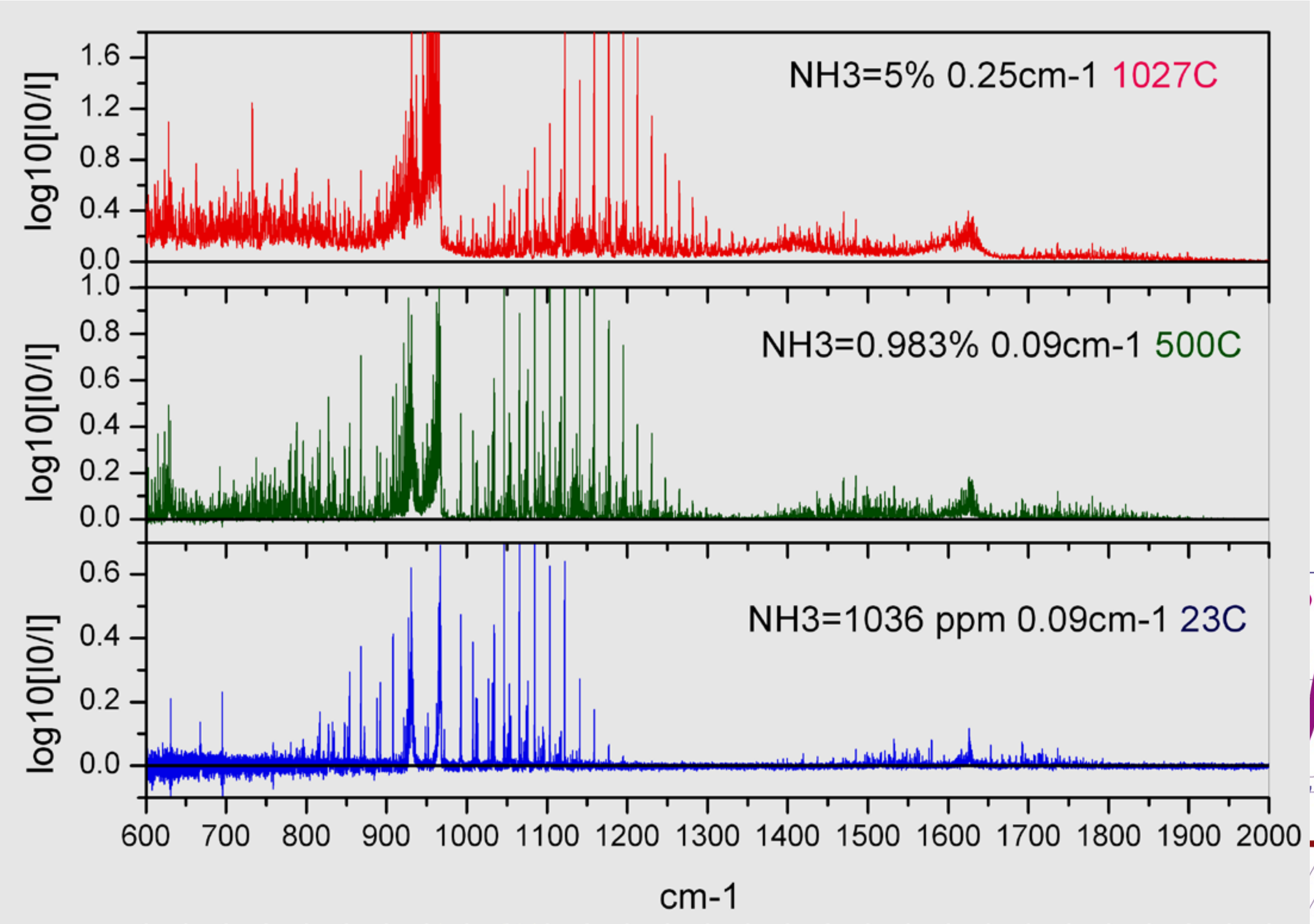
- 3-zones flow gas cell for corrosive gases;
- No internal windows;
- Stable uniform T-profile (±1.8C);
- Tmax= 525C
- L=33.25 cm
- P=1 bar
- suitable for UV-FIR optical measurements
- more details: H. Grosch et al. JQSRT 130 (2013) 392–399

- 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



NH3 spectroscopy: line assignments, new results

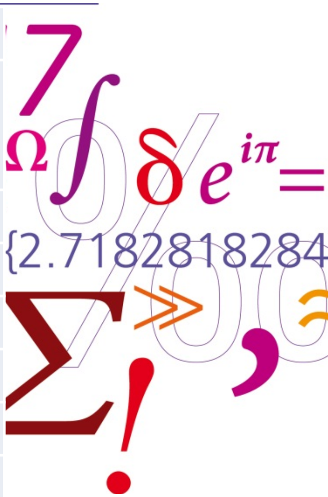
Table 1: Lines assigned to previously observed bands

	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

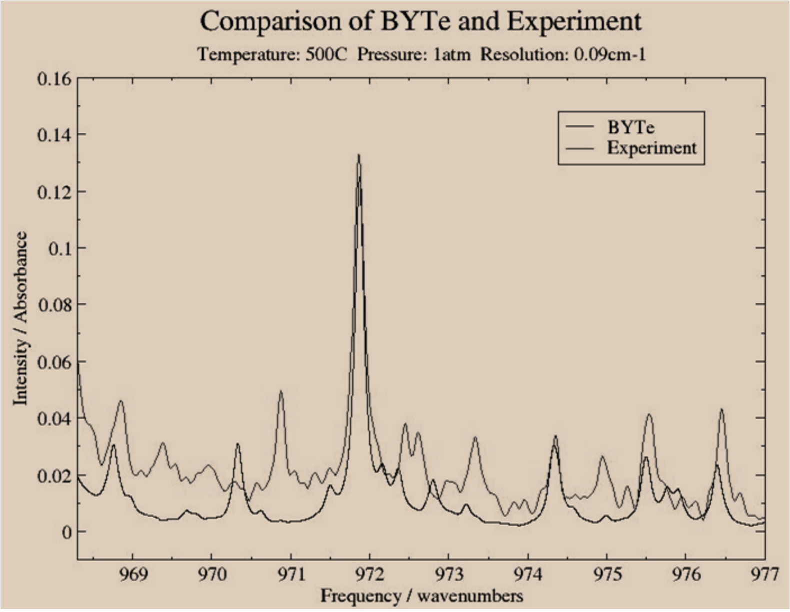
Table 2: Lines assigned to previously unobserved bands* with 10 or more lines assigned in this work.

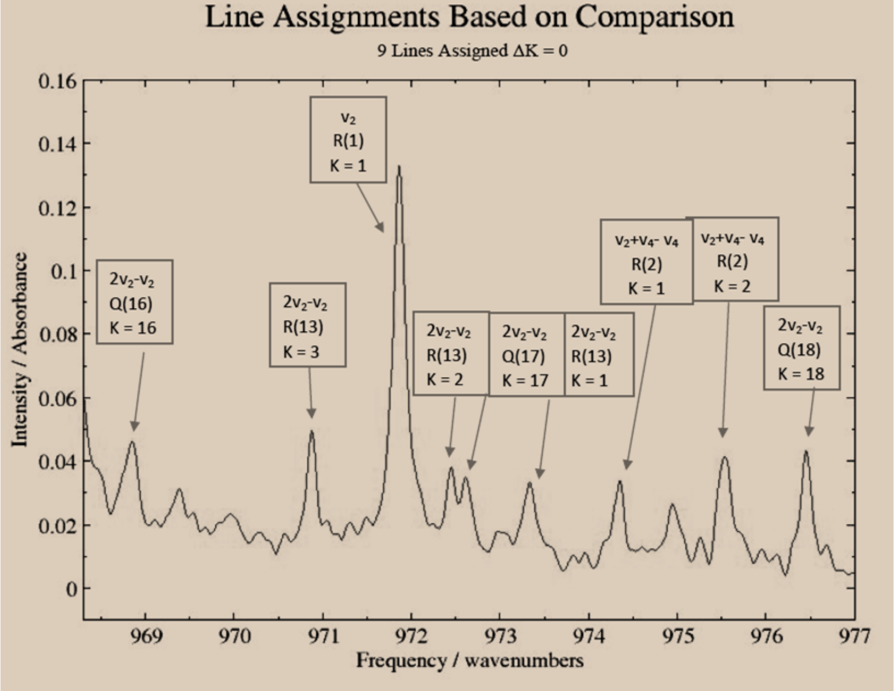
	Lines Assigned This Work			
Band	J_{max}	K_{max}	Frequency Range cm^{-1}	Number of Lines
v_4-v_2	11	11	622 - 1013	20
$2v_4-v_4$	9	5	1430 - 1792	10
$2v_4^2-v_4$	8	5	1420 - 1805	10
$v_2+v_4-v_4$	13	13	680 - 1270	77
$3v_2-2v_2$	14	12	628 - 1455	31
$3v_2-3v_2$	12	9	628 - 743	12



*Have not found measurements in published works.

NH3 spectroscopy: line assignments, an example



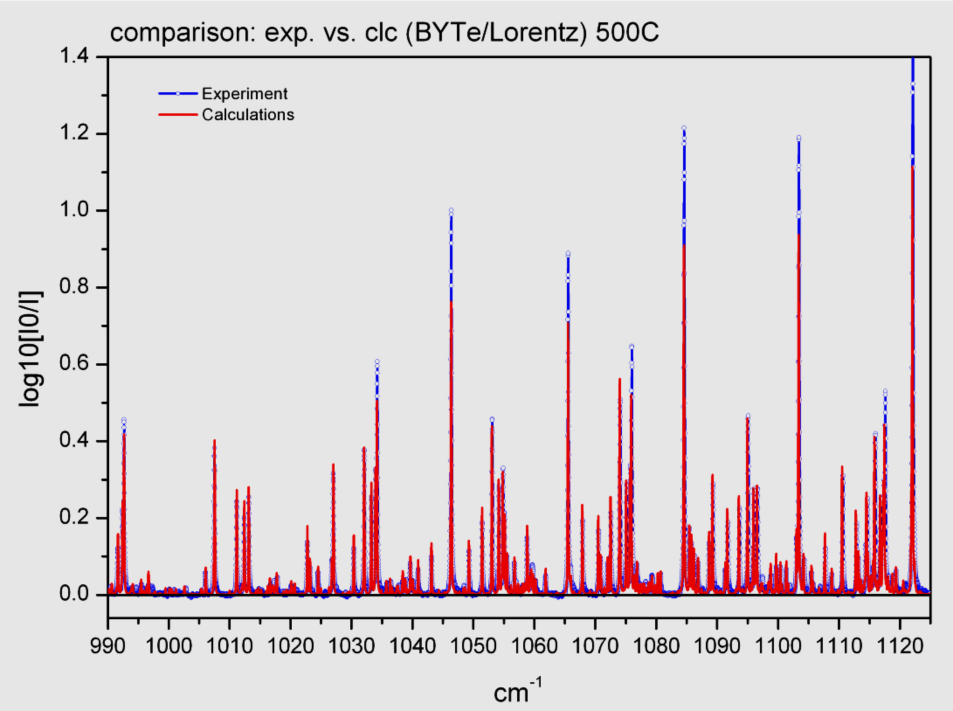


List of Assigned Lines

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

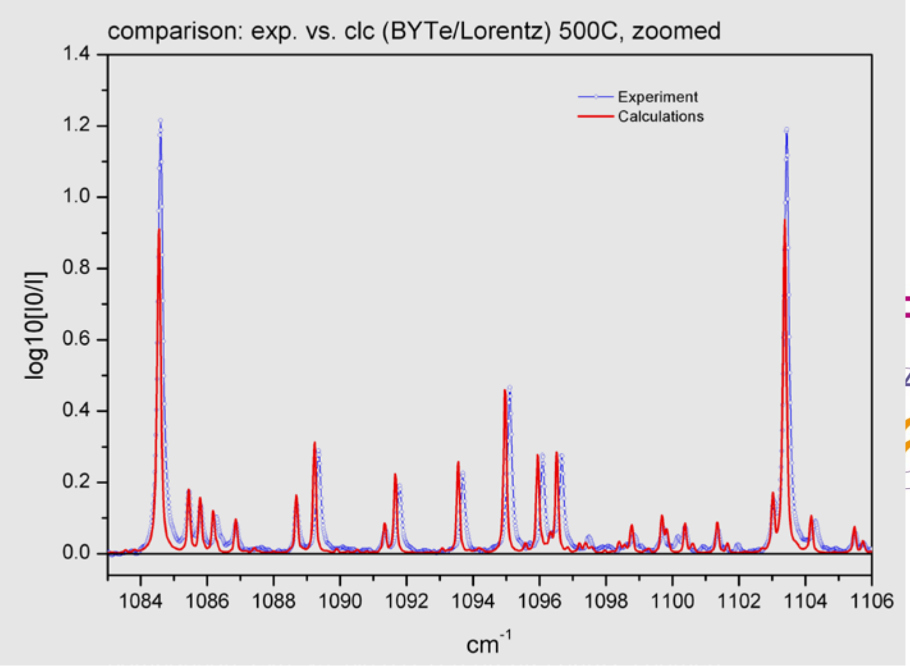
NH3: experiment (0.09cm-1) vs calculations (BYTe)



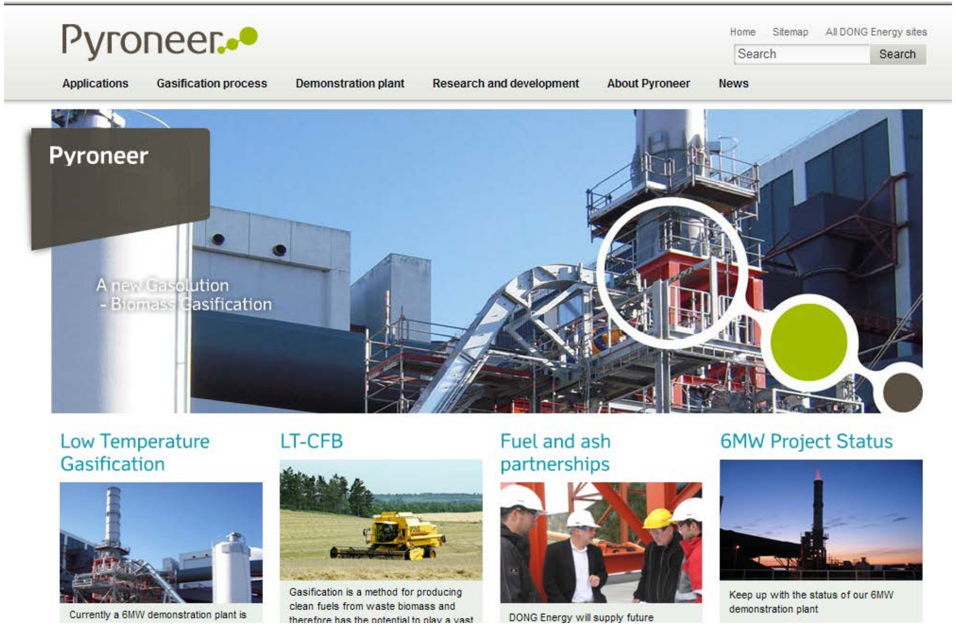
Can we use BYTe at 500C for practical apps?

- 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



Pyroneer

A new Gasolution
- Biomass Gasification

Low Temperature Gasification

Currently a 6MW demonstration plant is

LT-CFB

Gasification is a method for producing clean fuels from waste biomass and therefore has the potential to play a vast

Fuel and ash partnerships

DONG Energy will supply future

6MW Project Status

Keep up with the status of our 6MW demonstration plant

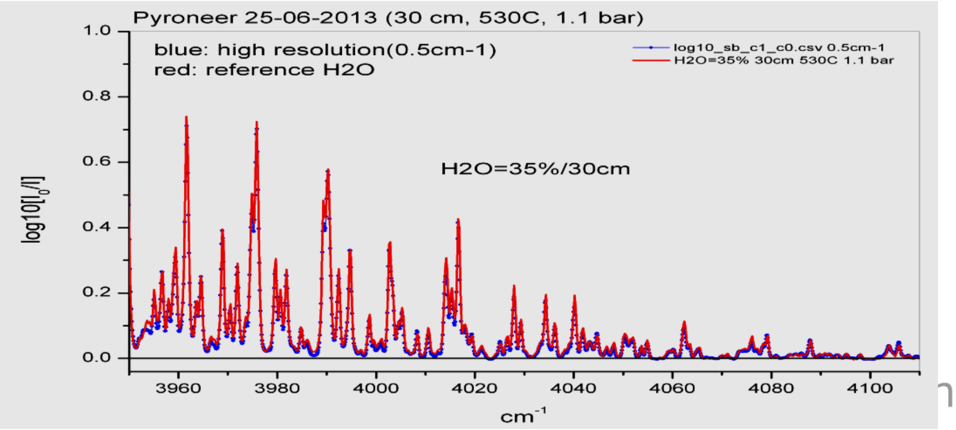
- Very complex producer gas composition (CO2, H2O, CO, H2, HC, PAH, tars) + particles
- Producer gas is feeded into an industrial burner of a power plant

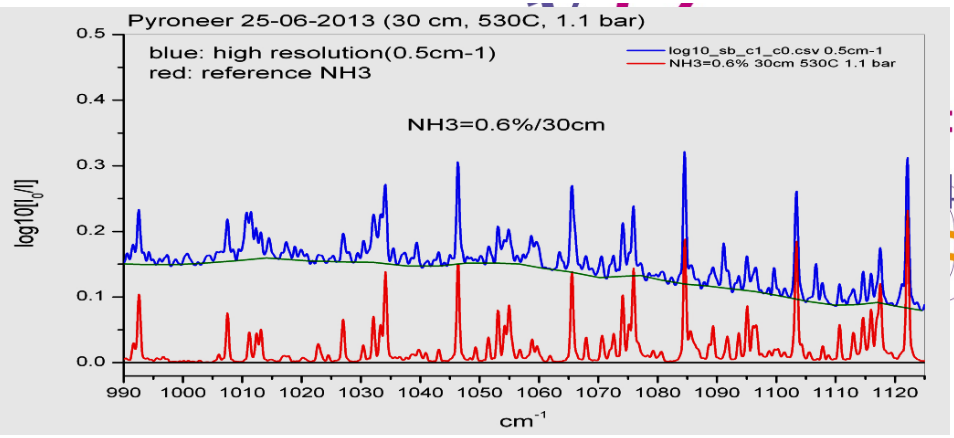
Why to do it? (examples):

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

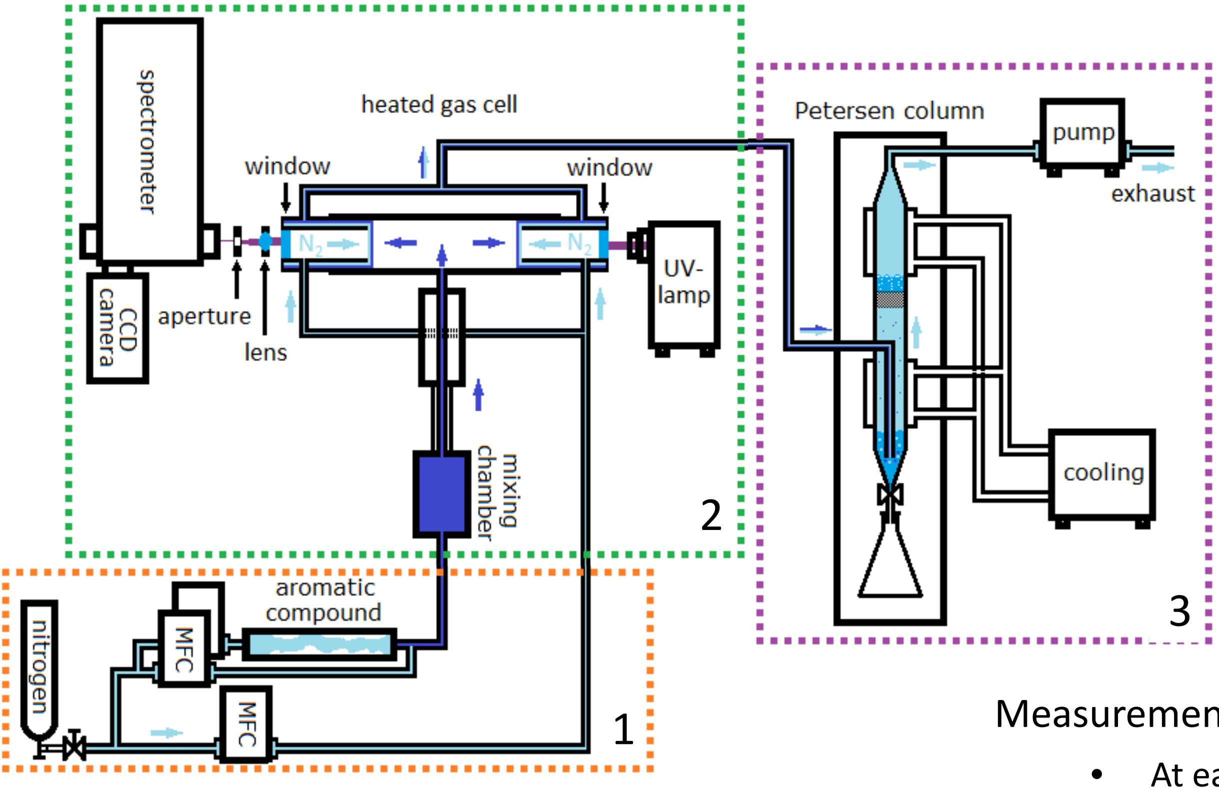
How?: In Situ IR abs measurements: <u>no gas extraction</u>

- 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

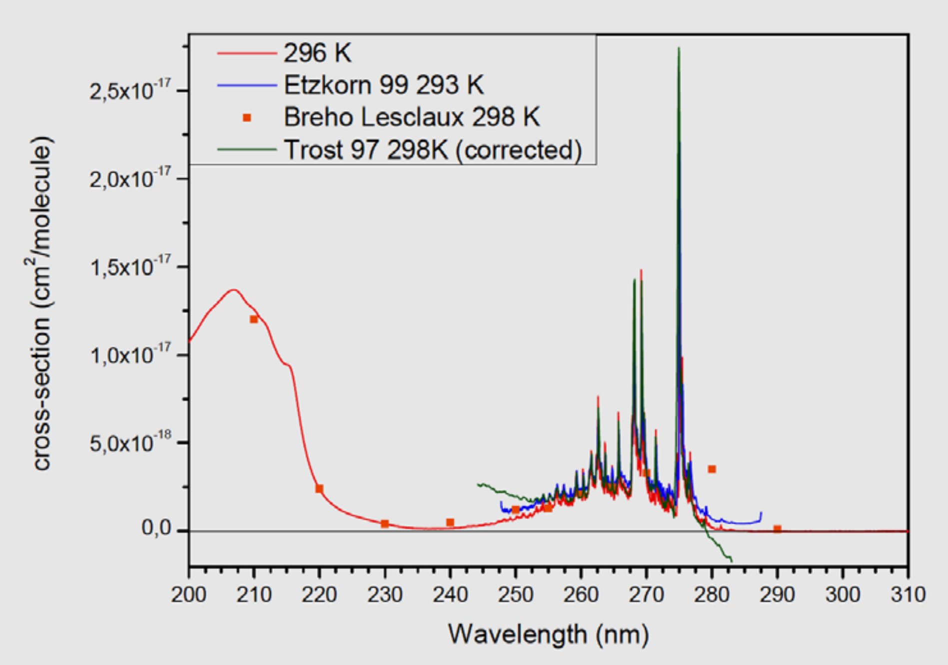
Measurements strategy:

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

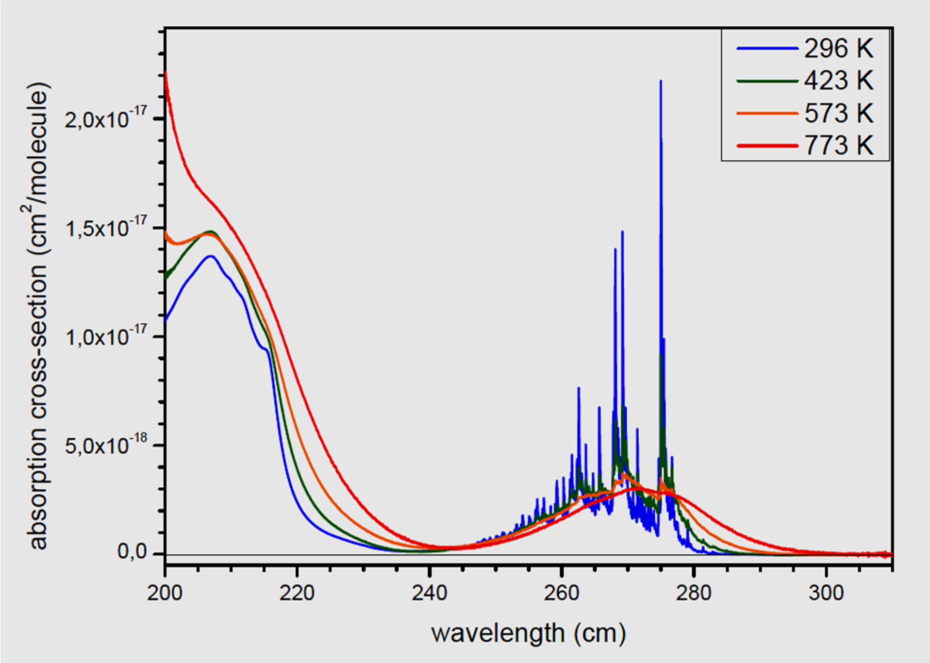
Phenol UV absorption cross-sections: temperature effects

- 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

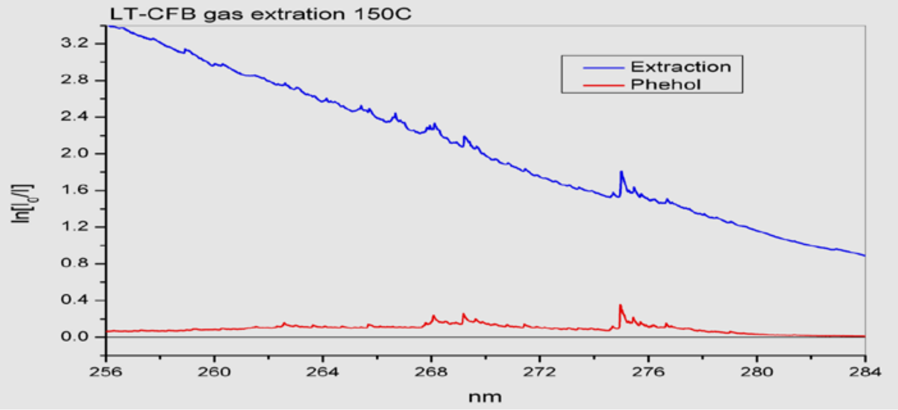


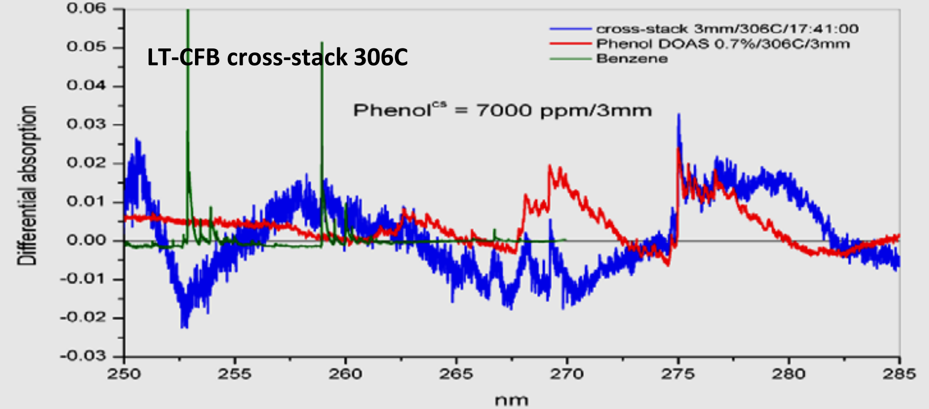
Abs cross-sections: from 23C to 500C



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)





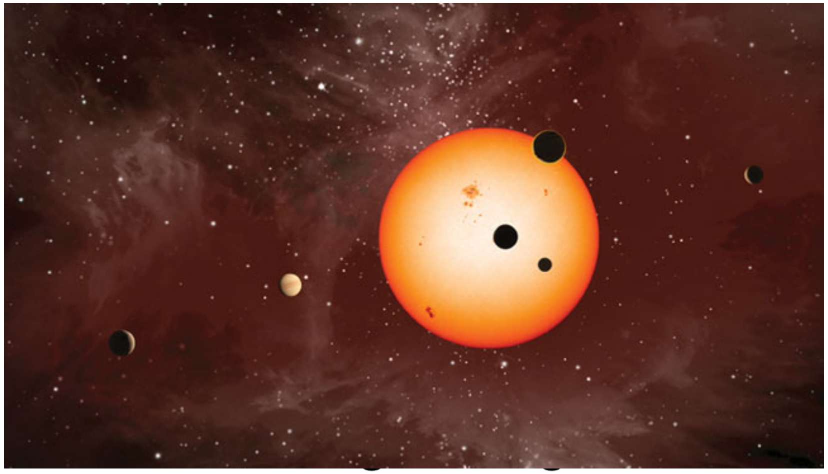
How other planets meets the Earth

- 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 (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

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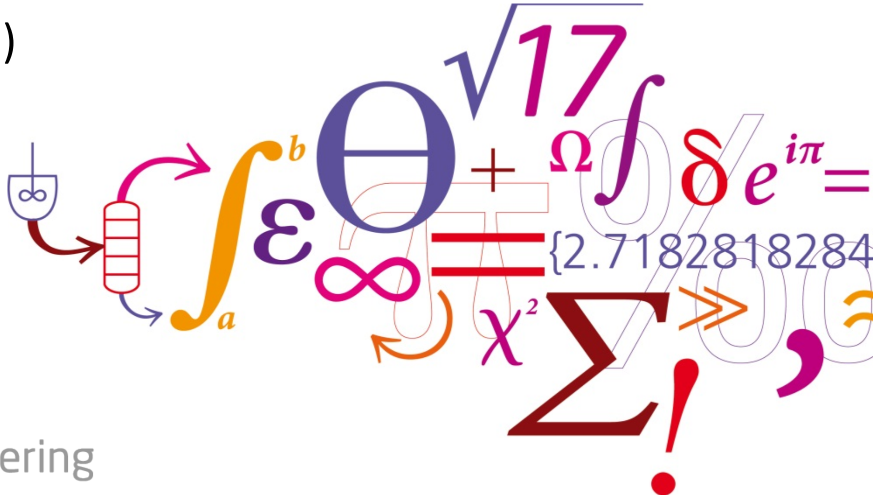
- To DONG Energy and Vattenfall
- To UCL (Prof. Jonathan Tennyson's group)



Sulfur trioxide measurement technique for SCR units
Combustion of fossil fuels causes emission of, for example, NOx and SOx those in addition to CO2 are the major of environmental concern. The most effective way to reduce NOx is with selective catalytic reduction (SCR) which combines the flue gas with certain amount of ammonia over catalyst that speed NOx reduction into nitrogen and water.

A major SCR concern is the release of unreacted ammonia (ammonia “slip”) which can cause large problems than the NOx itself. In, for example, biomass co-firing SOx in the flue gas contains mainly from sulfur dioxide (SO2) with small (a few ppm) amount of sulfur trioxide (SO3). Over catalyst some additional oxidation of SO2 to SO3 is also taking place. SO3 in the presence of ammonia forms ammonium sulfate and ammonium bisulfate salts those deposits on catalyst, air heater baskets, heat recovery steam generators and other downstream equipment. Resultant ammonium bisulfate and sulfate particle diameters are on the order of a few microns and thereby contribute to PM10 emissions finally fouling the micropore structure of the catalyst and limiting catalyst reactivity.

Development of SO3 in situ measurement technique with fast response time suitable for modern industrial applications is highly of interest.

The purpose of the project is the development of SO3 in situ measurement technique which will be suitable for industrial applications where SO2/SO3 emissions occur as e.g. SCR units of power plants, large ship engines running on heavy S-fuel and etc.

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