

Final report

1.1 Project details

Project title	Sulfur trioxide on-line measurement technique for energy systems
Project identification (program abbrev. and file)	2010-1-10442
Name of the programme which has funded the project	Forsk EL
Project managing company/institution (name and address)	DTU Chemical Engineering, Søtofts Plads 229, 2800 Kgs. Lyngby, Danmark
Project partners	University College London (UK)
CVR (central business register)	30060946
Date for submission	09-09-2016

1.2 Short description of project objective and results

The main objective of the project is a development of SO₃ *in situ* IR measurement technique which will be suitable for various industrial applications on energy systems as e.g. SCR units of power plants. The technique consists from a base knowledge (SO₃/SO₂ absorption cross section and line lists databases) and tools (high-resolution FTIR spectroscopy). Results obtained in the project can be used for developing a SO₃/SO₂ analyzer which can be built with use of various approaches: emission or absorbance measurements with broad/narrow-band light sources as e.g. FTIR spectrometers or tunable lasers.

1.3 Executive summary

The project is about developing SO₃ *in situ* measurement technique which can be used on energy system platforms for SO₃/SO₂ monitoring, control and potentially in feed-back control systems for SO₂/SO₃/NH₃ emissions/corrosion reduction. The SO₃ *in situ* measurement technique consists from a base knowledge (SO₃/SO₂ absorption cross section and line-lists databases) and tools (high-resolution FTIR spectroscopy). Acquired under the project SO₃/SO₂ apparent absorption cross sections together with SO₃/SO₂ spectroscopic line list databases developed by UCL make a solid basis and can be used for quantifying SO₃/SO₂ concentrations in *in situ* optical infrared measurements either by a broad-band FTIR spectroscopy or by tunable narrow-band laser systems. The results obtained in the project can be used for developing a SO₃/SO₂ measurement analyzer which can be built with use of various approaches: emission or absorbance measurements with broad/narrow-band light sources as e.g. FTIR spectrometers or tunable lasers.

1.4 Project objectives

The project originally started by as a pure experimental research project at Risø DTU (later as DTU Chemical Engineering) and was later extended with theoretical research part in

frames of a supplementary project, merged with the main one. The main project consists from 5 work packages (WP). The supplementary project consists from 5 WPs as well.

The main original objectives in the main project were:

- to develop a SO₃ reactor for SO₃ production free from water vapors based on reaction of SO₂ with ozone and/or over a catalyst surface (with oxygen). The SO₃ yield should be optimized through the adjustment of the experimental conditions and balance calculations.
- to match the SO₃ reactor to the existing hot flow gas cell (HGC) without any SO₃ losses. Apart of that special precaution for introducing of other gases of interest as NH₃, H₂O, SO₂ and H₂SO₄ into the HGC will be made.
- to build a high-resolution high-temperature apparent absorption cross section database gases of interest: SO₃, NH₃, H₂O, SO₂ and H₂SO₄ suitable for *in situ* industrial applications. Absorption measurements in the HGC will be done by a Risø DTU's high performance FTIR spectrometer (nominal resolution 0.125 cm⁻¹) equipped with a sensitive MCT detector and powerful light source.
- to develop an IR probe for *in situ* SO₃/NH₃ measurements in vicinity of a SCR unit of a power plant. Full scale SO₃ *in situ* measurements will be performed at a power plant operated on multi-fuel loads at typical operation conditions in collaboration with DONG Energy.

During the project SO₃ generation from SO₂+O₃ and (SO₂+O₂)/Pt reactions has been tested and it has been shown that both ways of SO₃ generation can be used. The choice was however made in favor of the SO₂+O₃ reaction. First measurements with SO₃/SO₂ on the existing gas cells are shown various problems as H₂SO₄ formation and corrosion. Therefore it was decided to develop and made a new flow gas cell which will be best suitable for measurements with corrosive gases.

The SO₃/SO₂ measurements have been repeated on the new flow gas cell and it was shown a good time reproducibility of the measurements with this complex system as SO₂+SO₃+O₂+O₃+N₂, even when the cell was used for measurements with other corrosive gases. It was shown that spectral resolution (0.25 cm⁻¹) can be used for SO₃/SO₂ measurements at high temperatures without sacrificing quality of the results.

SO₃ extraction measurements and a detailed review of other SO₃ extraction measurements available are shown that it will be impossible to quantify the amount of SO₃ converted from SO₂. Therefore a supplementary project has been established where SO₃/SO₂ spectroscopic databases were developed in collaboration with University College London (UCL). The databases were theoretically developed with use of ab initio calculations on a power computer grid available at UCL and Oxford University.

SO₃ measurements on the gas cell, UCL calculations as well modeling of the SO₃/SO₂/H₂O spectra have shown that a long pathlength about 4 m for *in situ* SO₃ measurements on few-ppm level is required and this is usually the case for many industrial applications. Therefore two large scale measurement campaigns: one in Germany (Vattefall) and one in Denmark (DONG Energy) were done.

Despite on the large difference in the S-content in the coals used in the measurements in Germany no difference between SO₃ *in situ* cross-stack absorption measurements have been found for both cases. The very low SO₃ concentrations in both cases (below 2 ppm at 500C) indicate that SO₃ generated during coal combustion at high temperatures has been quickly and almost completely reacted by some reactive components in the fly ash before the flue gas is cooled down.

Measurements in Denmark were done across 14.16 m distance that is about 4 times longer as it was available in Germany. This location was chosen from two possibilities taking into account logistic and additional costs associated with establishing of the measurements. It was found that the light from a high temperature light source was totally attenuated by strong particle absorption, when the unit was in operation. Therefore only IR emission measurements were done. Few spectral windows for SO₃/SO₂ measurements were identified and it

was shown that IR emission approach is promising and it requires some technical improvements in the measurement system. Relatively high SO₃ detection limit (15 ppm at 400C) for the system is caused not optimal measurement system position (existing access ports with narrow field of view (FOV) angle) and not best detector choice (because a technical issue).

The project had couple times prolongations (under however the same budget frame) to cover possibilities SO₃/SO₂ in situ measurements (subject of agreement and access availability with the third party).

1.5 Project results and dissemination of results

The main purpose of the experimental part of the project was a development of SO₃ *in situ* IR measurement technique which will be suitable for industrial applications on SCR units of power plants.

In the first two WP's on-place two SO₃ generation systems were made and proven in operation: 1) SO₃ generation in temperature-dependent SO₂+O₃ reaction and 2) SO₃ generation in SO₂ oxidation over a Pt catalyst at relevant temperatures. Ozone was produced with a commercial ozone-generator. Both systems have shown that SO₂/O₃ and SO₂/O₂/Pt concepts are working and can be used for SO₃ generation. However the first system has been chosen because possibilities to operate at higher gas flowrates than the second one.

In the third WP the SO₂/SO₃ infrared absorption measurements have been performed on various gas cells from 150C and up to 500C. Several corrosion problems related to H₂SO₄/SO₃ have been experienced.

The results obtained under this WP show that SO₃ 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 SO₃ on-place rather to use a pre-ordered one because the later one requires extra handling. A gas cell for SO₃ measurements should be with a "flow-windows" concept in order to avoid possible reaction of the SO₃ on windows surfaces. A distance between SO₃ production and the gas cell should be minimized in respect to residence time in the supplying tubes. Mostly chemical inert materials like Teflon and quartz should be used in order to minimize SO₃ side reactions.

As an outcome the first SO₃ measurements experience, the new quartz hot flow gas cell (qHGC) has been developed, made and validated. The new qHGC design allowed us to minimize SO₃ side reactions. On-place SO₃ generation system and the new qHGC is a unique system suitable for work with extremely reactive gases like SO₃.

With the new system, high-resolution absorption measurements for CO₂, H₂O, NH₃, H₂SO₄, SO₂ and SO₃ have been performed for several temperatures of interest (25-500C) related to practical applications and intercomparison with SO₃/SO₂ data (25C) available with known experimental high-resolution IR database (PNNL). It was found that H₂SO₄ starts to decompose into SO₃ and H₂O at T>150C. To quantify H₂SO₄ concentration in the gas either in the lab measurements or in situ ones in a flue gas a H₂SO₄ cross-section database is required. The database can theoretically be generated as it was done for SO₃/SO₂.

Apparent experimental absorption cross-sections for SO₂/SO₃ for various temperatures between 25C and 500C have been generated assuming that all SO₂ consumed in the SO₂+O₃ reaction was used to generate SO₃.

It was shown that spectral resolution of 0.25 cm⁻¹ is sufficient for SO₃ FTIR absorption measurements up to 500C. Choice of resolution depends on which SO₃/SO₂ bands are going to be used in the data analysis. SO₃ in general has higher IR absorption cross-sections than SO₂. However in most practical applications the SO₃ concentration is significantly low compare to the SO₂ one. The most absorption-strong SO₃ band lies at about 1386 cm⁻¹ where water and SO₂ have also absorption features. This overlap between various H₂O lines and closed spaced

SO₂ band make SO₃ measurements quite challengeable. Another SO₃ band at about 2438 cm⁻¹ is more attractive because larger SO₂/SO₃ bands separation and no interference with H₂O. There is still an interference with a weak CO₂ band which can however be handled. The drawback of use SO₃ band at 2438 cm⁻¹ is because this band about 66 times weaker than the one at 1386 cm⁻¹. It has also been shown that a long absorption pathlength for SO₃ *in situ* measurements when a few ppm SO₃ detection level at 300-500C is required.

In order to verify that all consumed SO₂ was used to generate the SO₃, SO₃ extraction measurements by controlled condensation method on the qHGC together with Chalmers University (Sweden) were performed. It was shown that the SO₃ concentration in the cell was 39% of initial SO₂ concentration, whereas SO₂ consumption was 60%. Therefore it was concluded that some heterophase losses of SO₃/H₂SO₄ appeared. It was also some concern that some (minor amount) H₂SO₄ aerosols have not been captured by the extraction system. Therefore possibilities to use other suitable SO₃ gas extraction techniques for comparison with measurements done were investigated. It has been found that in general SO₃ 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. Therefore possible alternatives for SO₃ IR spectra calibration have been explored.

IR absorption spectra can theoretically be calculated from the first principles (*ab initio* calculations). Because SO₂ and SO₃ IR absorption bands are in strong overlap, analysis of SO₂ absorption features is essential in proper SO₃ concentration calculations. Her other problem has been faced: there are no databases available for SO₃/SO₂ spectra calculations at temperatures of interest (500-800K). Therefore the project has been extended towards a development of SO₃/SO₂ high-temperature spectroscopic databases (so-called line list databases) under a supplementary project. The databases are an essential tool in the analysis of complex datasets obtained from measurements on an industrial scale. The project extension was possible due to an extra support from Energinet.dk and University College London (UK). A PhD student funded under Impact Studentship from UCL and Energinet.dk was hired by UCL for SO₃/SO₂ line-list database development.

The purpose of the supplementary project was to create SO₃/SO₂ high-temperature spectroscopic databases which will be used in SO₃/SO₂ concentration calculations from the data sets obtained through *in situ* measurements.

The UCL supported the PhD project with scientific staff manpower and extended computer resources available at UCL and Oxford University (UK) under EU-funded EXOMOL project (www.exomol.com). SO₃ and SO₂ calculations are also of interest for astrophysical community involved in exoplanet atmosphere research. Exoplanet atmospheres are typically hot (500-1000K) and minor gas components those can be found in a hot flue gas on the Earth (e.g. SO₃, SO₂, NH₃, HCN etc.) can also be found in exoplanet atmospheres.

SO₃/SO₂ calculations were performed with advanced software packages developed at UCL and with UCL's collaborators. Both line lists are computed using *ab initio* computational methods to calculate rovibrational energy levels and dipole moment transition intensities, and are augmented by experimental data, where possible, in order to achieve spectroscopic accuracy.

Here a short summary about five WPs of the supplementary project is given. More details can be found in the cited references below and the PhD thesis "Variationally Computed Line Lists for SO₂ and SO₃" by Daniel Underwood. The thesis has successfully been defended at UCL in May 2016.

SO₂

The production of the hot SO₂ line list (*ExoAmes*) [1] was carried out via collaboration with Huang *et al* as a continuation of their previous room temperature calculation [2]. Rovibrational energies and transition moments have been computed using the DVR3D triatomic code [3]. This procedure incorporates the potential energy and dipole moment surfaces (PES and

DMS) computed by Huang *et al* via electronic structure calculations. Initial test computations showed that the published PES had minor defects which lead to inaccurate rovibrational results, and required some collaborative investigation in order to make corrections.

A revised PES was then used to start calculations on a hot line list. This required various alterations to the core DVR3D code in order to optimize computations for the larger size of the problem. For example, the routine for calculating transition dipole moments between energy states was altered to harness the large memory capabilities of our available hardware, to speed up computations.

The *ExoAmes* line list is constructed to ensure coverage for all transitions between 0-8000 cm^{-1} and to simulate spectra up to temperatures of 1500K (and approximately for temperatures above this). This required the computation of all rovibrational energies up to 15000 cm^{-1} and $J \leq 165$.

To ensure sufficient quality for the line-list, spectral simulations of line positions and temperature dependent intensities are compared to

- i) the Ames 296K line list REF;
- ii) experimental data from HITRAN;
- iii) experimental absorption cross section data at high temperature obtained in the WP3 of the main project.

All comparisons yield good results; the agreement with (i) is good, with a standard deviation of 0.043 cm^{-1} in matched line positions, with a corresponding agreement to within 2% for absolute intensities.

Agreement with (ii) is also very good, with an overall root mean square error of 0.016 cm^{-1} in line positions, and within 80%-90% for absolute intensities.

Comparisons with (iii) at 573.15K (300C) and 773.15K (500C) shows good semi-quantitative agreement, with 2% and 6% difference, respectively, in integrated intensities across the ν_1 and ν_3 fundamental bands. Further details may be found in [1] and the main thesis.

The final SO_2 line list consists of 1.3 billion transitions between 3 255 954 energy levels.

SO_3

A preliminary, room temperature line list for SO_3 (UYT) was calculated using the TROVE program [4], in conjunction with a purely *ab initio* PES and DMS, computed by S. Yurchenko [5]. This line list covers all transitions between 0-4000 cm^{-1} , including rovibrational energies up for $J \leq 85$. The purpose of this precursor computation was to enable a relatively fast approach to enable comparisons of line positions and intensities to available experimental data. Such comparisons showed that the theoretically computed line positions for a number of important bands could not accurately simulate their experimental counterparts; e.g. an rms deviation of 0.77 cm^{-1} for ν_2 , 4.07 cm^{-1} for ν_3 . This reflects the requirement to spectroscopically refine the PES with experimental data.

In order to refine the PES the rovibrational results were compared to available experimentally derived energy level data obtained by Maki *et al* [6]. A total of 119 energy levels for $J \leq 5$ were chosen from this experimental set and used in a minimization scheme to reduce the rms differences between a number of rovibrational band positions. For example, the rms differences for the ν_2 , 4.07 cm^{-1} for ν_3 bands are improved to 0.05 cm^{-1} and 0.09 cm^{-1} respectively, and the overall rms comparison is improved from 3.23 cm^{-1} to 1.35 cm^{-1} .

The refined PES is subsequently employed in the calculation of the complete, hot line list (UYT2). Due to the size of the problem the extension from the room temperature line list is much more difficult compared to SO_2 . In order to attempt high temperature coverage, we aimed for the computation of rovibrational energies for $J \leq 130$ and $E \leq 10\,000\, \text{cm}^{-1}$. This required the harnessing of advanced CPU, GPU and RAM facilities in order to calculate the

vast amount of rovibrational energy states, and the subsequent transition moments between them.

Preliminary comparisons with experimental cross section data at various temperatures show that the *ab initio* DMS is slightly defective when used to simulate intensity data. Absolute intensity values are required to make a thorough comparison/analysis of computed intensities, and these have been unavailable for SO₃ during the project; for the preliminary line-list only comparisons of relative intensities was possible. However, the comparisons with experimental cross section data show that calculated intensities differ only by a (mostly) constant scaling factor, across a number of temperatures, and is not band dependent. Based on this, the Einstein A-coefficients have been multiplied by this factor in order to reproduce the experimental cross section data, with good agreement.

The line list is suitable for modelling SO₃ spectra up to 773.15K (500C), and is roughly 90% complete up to this temperature. It consists of 21 billion transitions between 18 million energy levels, between 0-5000 cm⁻¹ [7].

References

- [1] D. S. Underwood, J. Tennyson, S.N. Yurchenko, X. Huang, D.W. Schwenke, T.J. Lee, S. Clausen, A. Fateev, ExoMol molecular line lists XIV: The rotationvibration spectrum of hot SO₂, *MNRAS*, 459(4), 3890–3899, 2016;
- [2] X. Huang, D. W. Schwenke, and T. J. Lee. Highly accurate potential energy surface, dipole moment surface, rovibrational energy levels, and infrared linelist for ³²S¹⁶O₂ up to 8000 cm⁻¹. *J. Chem. Phys.*, 140:114311, 2014;
- [3] J. Tennyson, P. Barletta, R. E. A. Kelly, L. Lodi, J. J. Munro, and B. C. Silva. DVR3D: a program suite for the calculation of rotation vibration spectra of triatomic molecules. *Comput. Phys. Commun.*, 163:85–116, 2004;
- [4] S. N. Yurchenko, W. Thiel, and P. Jensen. Theoretical ROVibrational energies (TROVE): A robust numerical approach to the calculation of rovibrational energies for polyatomic molecules. *J. Mol. Spec.*, 245:126–140, 2007;
- [5] D. S. Underwood, J. Tennyson, S. N. Yurchenko, An *ab initio* variationally computed line list for SO₃, *Phys. Chem. Chem. Phys.*, **15**, 10118–10125, 2013;
- [6] A. Maki, T. A. Blake, L. S. Sams, N. Vulpanovici, J. Barber, E. T. H. Chrysostom, T. Masiello, J. W. Nibler, and A. Weber. Highresolution infrared spectra of the ν_2 , ν_3 , ν_4 , and $2\nu_3$ bands of ³²S¹⁶O₃. *J. Mol. Spectrosc.*, 210:240–249, 2001;
- [7] D. S. Underwood, J. Tennyson, S.N. Yurchenko, A. F. AlRefaie, S. Clausen, A. Fateev, ExoMol molecular line lists XVII: The rotationvibration spectrum of hot SO₃, *MNRAS (accepted)*, 2016.

Under the Wp4 two kinds of *in situ* measurements on two industrial facilities have been performed: optical absorption and optical emission measurements.

OxPP facility

In May 2014 2 days cross-stack (4 m) emission/transmittance measurements have been performed in collaboration with Vattenfall on 30MW thermal pilot plant (OxPP facility) in 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 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 SO_3 formation and 2) long time stable operation (which was pre-defined by availability of high-S coal reserves).

The main focus was placed on SO_2/SO_3 measurements at high spectral resolution (0.25cm^{-1}). In addition to that mapping of the gas temperature and the major gas composition (NO , SO_2 , CO_2 and H_2O) profiles were performed. Gas temperature measurements were performed with a calibrated thermocouple, whereas gas composition was measured with DTU's special gas extraction system. $\text{SO}_2/\text{CO}_2/\text{H}_2\text{O}$ concentrations calculated from cross-stack measurements and gas extraction ones were found to be the same. The temperature profiles have been found to be quite uniform.

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

High S-coal: $\text{CO}_2=12.7\%$, $\text{O}_2= 4.6\%$, $\text{H}_2\text{O}=6.2-8.6\%$, **$\text{SO}_2=0.176\%$** .
Low S-coal: $\text{CO}_2=13.6\%$, $\text{O}_2= 4.1\%$, $\text{H}_2\text{O}=7.8-8.8\%$, **$\text{SO}_2=0.0482\%$** .

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.

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).

Despite on the large difference in the S-content in the coals, no difference between SO_3 in situ cross-stack measurements have been found for both cases. The SO_3 concentration was calculated to be < 2 ppm at the measurement location (4 m, $T_{\text{gas}} \sim 500\text{C}$).

According to the SO_3 formation mechanism during coal combustion, it is expected that the formation of SO_3 would be more pronounced during the combustion of the high-S coal. The very low SO_3 concentrations (i.e. below detection limit of the system) in both cases indicate that SO_3 generated during coal combustion at high temperatures has been quickly and almost completely reacted by some reactive components in the fly ash before the flue gas is cooled down to 500C. The possible reactive components include metal oxides (such as CaO and MgO), or gaseous alkali species (such as KCl or NaCl). Since both coals contain high calcium and magnesium content, it is more likely that the oxides of these species are responsible for the observed low SO_3 concentrations. In terms of the facility operation this can be considered as a positive observation.

AVV1 Block

The measurements have been performed cross-stack the flue gas before SCR unit. 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 IR emission measurements have been performed.

The measurements have been performed at various spectral resolutions from 0.25 cm^{-1} to 1 cm^{-1} . Although thermal radiation from the gas seems to be as a quite uniform grey body continuum as one can expect, it has been found that there are many $\text{H}_2\text{O}/\text{CO}_2$ emission bands in $1250\text{-}4500\text{ cm}^{-1}$ spectral range on the top of a grey body continuum. 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. Because the bulk gas temperature expected to be relatively uniform across the boiler cross section this small (but quite well measured) temperature difference is because colder surroundings (walls) and particles having a little lower temperature than the gas. This observation has been confirmed by more measurements at different days.

An absorptivity spectrum calculated from an emission spectrum in $1320\text{-}1460\text{ cm}^{-1}$ and $2390\text{-}2560\text{ cm}^{-1}$ spectral ranges, where two SO_3 absorption bands are located, can be used SO_3 concentration calculations. The measured absorptivity spectrum has been modelled by $\text{CO}_2/\text{H}_2\text{O}/\text{SO}_2/\text{SO}_3$ 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% , respectively) 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 agrees with a typical SO_2 concentration one can expect for coal combustion.

In $1320\text{-}1450\text{ cm}^{-1}$ spectral range (optically thick gas layer, absorptivity is 1) absorption is mainly dominated by H_2O vapors. However there are regions where absorptivity is about 0.8. In $1360\text{-}1460\text{ cm}^{-1}$ there is in general a good agreement between modelling and measurements. It has been shown that adding for example of e.g. $\text{SO}_3(50\text{ ppm})$ changes absorptivity in $1360\text{-}1420\text{ cm}^{-1}$. Therefore this spectral range can be used for SO_3 concentration calculations if SO_3 concentration is "high enough". A "high enough" concentration for 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 performed the measurement time was about 15 min and SO_3 detection limit can be estimated as 15 ppm. It should be noted that existing access ports have been used in the measurements. The port configuration (length/diameter) was optimal for cross-stack measurements but unfortunately not optimal for emission measurements.

The other SO_3 band at 2438 cm^{-1} can also be used for concentration calculations. However the band has about 66 times less absorption strength compare to that at 1386 cm^{-1} . In addition to that the absorptivity in $2400\text{-}2560\text{ cm}^{-1}$ is noise-limited for measurements in questions. It has been shown that the measured spectrum can well be modelled by the same $\text{CO}_2(11\%)+\text{H}_2\text{O}(9\%)+\text{SO}_2(370\text{ppm})$ composite spectrum and adding of $\text{SO}_3(50\text{ppm})$ changed a little absorptivity in $2400\text{-}2480\text{ cm}^{-1}$. These changes are however below the noise level in the absorptivity spectrum.

In the spectral $2400\text{-}2480\text{ cm}^{-1}$ 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 it was not possible to use the existing InSb detector in the measurements.

The $2400\text{-}2480\text{ cm}^{-1}$ 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 $2400\text{-}2480\text{ cm}^{-1}$ is a 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 SO₃/SO₂ absorption cross-sections variations on a moderate level that is important for low SO₃-level measurements.

Under the main and supplementary projects the work under all WPs has been done and all project objectives have been realized. The SO₃ *in situ* measurement technique developed under the project consists from a base knowledge (SO₃/SO₂ absorption cross section and line lists databases) and tools (high-resolution FTIR spectroscopy). Acquired under the project SO₃/SO₂ apparent absorption cross sections together with SO₃/SO₂ spectroscopic databases developed by UCL make a solid basis and can be used for quantifying SO₃/SO₂ concentrations in *in situ* optical infrared measurements either by a broad-band FTIR spectroscopy or tunable narrow-band 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* SO₃/SO₂ concentration measurements either in optical absorption (cross-stack, active, narrow FOV) or emission mode (passive, wide FOV) depending on the scale of application. Detection limit of this kind of the system at the moment 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.

The results of the project have been disseminated in several publications in peer-reviewed journals and conferences (as oral or poster presentations). These include a cross-collaboration between various teams in Denmark (DTU), Great Britain (UCL) and USA (NASA):

Papers:

- D. S. Underwood, J. Tennyson, S. N. Yurchenko, An ab initio variationally computed line list for SO₃, *Phys. Chem. Chem. Phys.*, **15**, 10118 - 10125, 2013;
- D. S. Underwood, J. Tennyson, S. N. Yurchenko, P. Jensen, Rotational spectrum of SO₃ and theoretical evidence for the formation of sixfold rotational energy level clusters in its vibrational ground state, *J. Chem. Phys.*, **24**, 244316, 2014;
- D. S. Underwood, J. Tennyson, S.N. Yurchenko, X. Huang, D.W. Schwenke, T.J. Lee, S. Clausen, A. Fateev, ExoMol molecular line lists - XIV: The rotation-vibration spectrum of hot SO₂, *MNRAS*, **459(4)**, 3890 - 3899, 2016;
- D. S. Underwood, J. Tennyson, S.N. Yurchenko, A. F. Al-Refai, S. Clausen, A. Fateev, ExoMol molecular line lists - XVII: The rotation-vibration spectrum of hot SO₃, *MNRAS (accepted)*, 2016.

Posters

- PRAHA2012 (September 4-8, 2012, Prague);
- High Resolution Molecular Spectroscopy 2013 (August 25-30, 2013, Budapest);
- Spectroscopy of Exoplanets Conference (July 24-25, 2015, Windsor).

Oral presentations:

- The 22nd UCL Astrophysics Colloquium: *Opacities in Cool Stars and Exoplanets*, Cumberland Lodge, Windsor Great Park, UK, July 2-5, 2012;
- International Symposium on Molecular Spectroscopy (June 16-20, 2014, Urbana-Champagne);
- 13th Biennial HITRAN Conference, 23-15 June 2014, Boston, USA

- Spectroscopy of Exoplanets, Cumberland Lodge, Great Park, Windsor, 2015 July 24-26, UK;

1.6 Utilization of project results

The results obtained in the project can be used for developing a SO₃/SO₂ measurement analyzer which can be built with use of various approaches: emission or transmittance measurements with broad- narrow-band light sources as e.g. FTIR spectrometers or tunable lasers. To our knowledge SIEMENS AG (Germany) has had interests about development of a SO₃ tunable laser measurement system where developed SO₃/SO₂ line-list databases could be used.

There are no plans to take out patents from DTU's side. However there is a possibility to build an IR emission-based system where SO₃/SO₂ measurements will be a part of functionality of the system. The system itself can be patented.

The project partly supported a PhD student at UCL (Daniel Underwood) who was involved in SO₃/SO₂ line list database development. The PhD student has spent about two weeks at DTU Chemical Engineering where he participated in SO₃/SO₂ measurements in the lab and in discussion of the experimental results and their comparison with calculations. He has got insights about use of applied high-resolution IR spectroscopy and made a presentation about his work at a seminar.

The generated SO₃/SO₂ databases are available for free download from the EXOMOL-web site (www.exomol.com) and partly implemented in the HITRAN database (www.hitran.org). Both databases are an essential tool in the modeling of molecular absorbance/transmittance properties at moderate and high temperatures.

1.7 Project conclusion and perspective

The results obtained under the project show that SO₃ 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 SO₃ on-place rather to use a pre-ordered one because the later one requires extra handling. A gas cell for SO₃ measurements should be a "flow-windows" concept in order to avoid possible reaction of the SO₃ on windows surfaces. A distance between SO₃ 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 SO₃ side reactions.

Spectral resolution of 0.25 cm⁻¹ is sufficient for SO₃ FTIR absorption measurements up to 500C. Choice of resolution depends on which SO₃/SO₂ bands are going to be used in the data analysis. Two SO₃ bands can potentially be used for SO₃ concentration calculations: 1386 cm⁻¹ and 2438 cm⁻¹. It has been shown at a long absorption pathlength for SO₃ *in situ* measurements when a few ppm SO₃ detection level at 300-500C is required.

To quantify amount of SO₃ in a hot flue gas at any gas temperature SO₂/SO₃ spectral lines databases are needed. The work under database development has been finalized for both SO₂/SO₃. The SO₂ database has been validated with the measurements available and it can now be used for SO₂ spectra calculations at temperatures up to 1700C. The SO₃ 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.

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.

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 SO₃/SO₂ absorption cross-sections variations on a moderate level that is important for low SO₃-level measurements.

SO₃ *in situ* measurement technique consists from a base knowledge (SO₃/SO₂ absorption cross section and line lists databases) and tools (high-resolution FTIR spectroscopy). Acquired under the project SO₃/SO₂ apparent absorption cross sections together with SO₃/SO₂ spectral databases developed by UCL make a solid basis and can be used for quantifying SO₃/SO₂ 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* SO₃/SO₂ 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.

Annex

SO₃/SO₂ main papers:

ExoMol molecular line lists – XVII. The rotation–vibration spectrum of hot SO₃

<http://mnras.oxfordjournals.org/content/462/4/4300.abstract>

ExoMol molecular line lists – XIV. The rotation–vibration spectrum of hot SO₂

<http://mnras.oxfordjournals.org/content/459/4/3890.abstract>

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

EXOMOL web site: www.exomol.com

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

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

Pacific Northwest National Laboratory (PNNL):

<https://secure2.pnl.gov/nsd/nsd.nsf/Welcome>