Final Publishable JRP Summary for JRP ENV06 EUMETRISPEC
Spectral Reference Data for Atmospheric Monitoring

Overview

This project developed the first European infrastructure for metrologically controlled measurements to derive highly accurate spectral reference data. Improved spectral reference data are needed to determine concentrations of pollutants or greenhouse gases in the atmosphere more accurately, both for remote and in-situ sensing. Ultimately, the project's results will contribute to improve the international efforts to track and model the progress of climate change, and to developing the government policies needed to mitigate future climate effects.

Need for the project

Spectroscopy is a technique used in environmental and climate science to determine concentrations of pollutants and greenhouse gases in our atmosphere. Different molecules absorb and emit different wavelengths of electromagnetic radiation, called a spectral signature. The results of spectroscopic analyses are compared against reference data that describe these spectral signatures, allowing the molecules to be identified. More accurate reference data ensures more accurate analysis, which leads to more effective modelling. Ultimately, the higher the quality of the reference data, the more effectively European and global governments can monitor and mitigate atmospheric pollution and climate change.

With the large number of existing and planned global atmospheric monitoring networks and satellites dedicated to environmental monitoring, there is a global need for a long-term infrastructure to provide high-quality spectral reference data. Yet, despite considerable advances being made in the last decade in spectroscopic methods, the availability of high-accuracy reference data traceable to measurement standards is limited. There can be large deviations in the spectral data created by different research groups because multiple measurement methods are used, and there are no standardised procedures for establishing traceability and uncertainty. Additionally, environmental conditions such as temperature and pressure affect the properties of molecules, altering their spectral signature. Reference data are needed that have been produced under controlled conditions, to provide spectral signatures of molecules under the range of conditions experienced at different altitudes and temperatures in the atmosphere.

Scientific and technical objectives

The goal of the project was to develop a European measurement infrastructure for producing traceable spectral reference data for atmospheric monitoring. Three inter-related objectives were established to achieve this goal:

1. To set-up, test and validate a Central spectroscopic Facility (CF) for making traceable spectroscopic measurements under well controlled conditions.
2. To develop metrological procedures for spectral data determination and data handling.
3. To generate samples of high accuracy spectral line data and related metrological uncertainties for key greenhouse gases, including carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_20), water vapour (H_2O) suitable to demonstrate the CF capabilities and for reference gases like hydrogen chloride (HCl) or hydrogen bromide (HBr) used to test field FT-spectrometer performance.

Report Status: PU Public

EMRP
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Results

1. To set-up, test and validate a Central spectroscopic Facility (CF) for making traceable spectroscopic measurements under controlled conditions. A highly versatile Central spectroscopic Facility (CF) was established, characterised and validated at PTB, including the necessary gas handling hardware, FT-IR control software, as well as metrological measurement and spectral data evaluation software to derive spectral data. The CF is based on an ultra-high resolution, visible to mid-infrared Fourier transform (VIS to MIR FT-IR) spectrometer. The absorption cells and metrological control infrastructure developed, provide highly stable and accurate measurement conditions, but still allow precise variation of gas pressure and temperature over the atmospheric range. Several Satellite facilities (SFs) were also developed or adapted at partner institutes - France (CNAM and LNE), DFM (Denmark), VTT-MIKES (Finland) and VSL (the Netherlands) - using high-resolution laser-based spectrometers to validate CF results and provide traceability. The SFs at MIKES, DFM and VSL were operational by the end of the project, and those at LNE/CNAM soon after.

2. To develop metrological measurement procedures for spectral measurements and data handling. Standardised procedures are needed to generate high-quality data, and to ensure that data from different sources/techniques can be analysed and compared within defined uncertainties. Data evaluation and analysis procedures were successfully developed for spectroscopic measurements at the CF and the SFs. Technical procedures on general requirements for line parameter measurements were developed, agreed and adopted by each partner institute. Specific procedures were defined and documented to enhance the comparability of data from the most common spectroscopic techniques. For this, the consortium developed and optimised the procedures and documentation through practical use during the work carried out in objectives 1 and 3. The procedures are available on the EUMETRISPEC website. The most recent procedures, which are molecule-specific and spectrometer technique specific, were disseminated via publications on the spectral data derived from the CF and the SFs.

3. To generate samples of metrological line data and related uncertainties for key greenhouse gases
Large sets of metrological pressure-dependent spectra were recorded at the CF and SFs for numerous greenhouse gases (incl. N_2O, CO_2, CO, CH_4) and HCl, the TCCON reference molecule. Novel, highly stable absorption cells specifically designed for the CF also enabled the recording of gas spectra over a pressure/temperature range of -70 °C to 70 °C / 0.01 to 1200 mbar, which allowed to study the effects of variable atmospheric temperature and pressure on the gas spectra. The data were generated using the CF and SFs created in objective 1, and in accordance with the measurement and traceability protocols developed in objective 2. Metrological line data, including line strength, pressure broadening, pressure line position shifts as well as absolute positions were derived from the measured spectra. Multiple evaluation runs of line data with different line shape models are still ongoing due to the large amount of data. One exemplary data set derived from the CF is a new, complete, high-accuracy line data set comprising all spectral N_2O parameters needed for atmospheric remote sensing (strength, broadening, shift, and positions). This set is uniquely coherent as it originates for the first time from a single spectroscopic setup. It includes the first high-resolution, self-broadening measurements for N_2O (previously this data was based on interpolation not measurement). The new N_2O-results are for the majority of spectral parameters and lines in good agreement with the HITRAN database, but they are now available with up to 80x improved uncertainties. Strong systematic deviations were found for certain regions of the N2O band particular for pressure induced line shifts and self-broadening of low J lines. The project generated a set of new or improved accuracy HCl self-broadening, self-shift and line strength data which is used for referencing of TCCON/NDACC instruments and for remote sensing purposes. Further data sets on spectral line positions and data retrievals were also achieved for CH_4 and N_2O at MIKES and CNAM/LNE, for CO_2 at DFM and H_2O at PTB using laser-based instruments. Results were broadly disseminated accompanied by meta-data, traceability statements, and measures of uncertainty. Data sets have been submitted to the HITRAN and GEISA databases – online, open-access databases of atmospheric spectral data – to important focus points of the atmospheric and the spectral sciences communities, and to peer reviewed journals. Social network like *Linkedin* were used to trigger the communities for cooperation.

Actual and potential impact

Dissemination of results

To promote the uptake of the project's results, outputs were shared broadly with end-user communities, including spectral data community, climate and environmental researchers, industrial process control communities, and international standards organisations. In 2012 a stakeholder workshop in Germany brought the environmental monitoring, spectral data and metrology community together to explain measurement science perspectives and to describe the aims of the project. The workshop was attended by representatives from 31 institutions from 12 different nations. A second stakeholder workshop was then held in 2014 to update the community on the project's results. The 53 participants represented 28 institutions from 12 countries in Europe, Russia and the US, ensuring a broad awareness and uptake of results by the stakeholder community. A more immediate and wide spread dissemination was realized via publication in peer reviewed journals like JQSRT, J Mol Spec, Appl. Opt. or by active participation in conferences. 17 papers were published in international journals (listed in the next section), and a large number of presentations were given at conferences and workshops. Web based activities further enhanced the dissemination via a dedicated project website and by active distribution via *ResearchGate*, *LinkedIn*, or *GoogleScholar*. Individual high impact members were also directly contacted, to ensure immediate use and evaluation of the project spectral data (e.g. members of TCCON data evaluation group, and other members of the spectral sciences community).
To further enhance the dissemination of the results it is planned to also offer metrological raw spectra from the CF incl. meta data to allow comparisons of data evaluation procedures from the different communities, to further develop and support comparability between communities and to foster cooperation with the spectral data community by coordinated data retrievals.

Early impact

Crucially, the project's data have been submitted to the global HITRAN and GEISA databases – the most widely used open-access spectral databases – to allow a wide range of users to access the project's results. A sub data set has been passed-on, for example, to the Total Carbon Column Observing Network (TCCON), a global network of 23 ground-based spectrometers that monitor atmospheric greenhouse gasses: TCCON is a key user of the HITRAN database, and is currently testing the new spectral data set. The project's contribution of highly accurate and traceable spectral data will reduce TCCON's reliance on the practice of side-by-side validation and calibration, which is difficult to achieve and expensive to perform. This high-quality reference data provided to TCCON will enhance the data the network provides to its users, such as climate modellers. Other users of the project's reference data include the Atomic, Molecular, Optical and Positron Physics group at the University College London, UCL, UK, or the combustions diagnostics group (RSM) at the Technical University of Darmstadt, TUDa, Germany. UCL is currently modelling spectral lines for environmental, climate and planetary research and uses the project's spectral results as an independent and experimental corroboration of their theoretical quantum-chemical models, providing validation and weight to their own and related environmental and climate research. TUDa, on the other hand is using e.g. the HCl and H_2O data set, to further develop absolute laser spectrometric in-situ analysers to better monitor e.g. pollutant formation or temperature in oxyfuel coal combustion in a large integrated research cluster called SFB129.

Potential future impact

The project will enable users of spectral reference data to derive increasingly accurate and traceable spectroscopic results, with higher-resolution modelling. Reducing uncertainties in environmental and climate analyses, as well as in industrial spectrometric applications, will aid effective monitoring and prediction of climate change, allowing European and global governments to mitigate and adapt. Furthermore, industrial process monitoring will also be advanced by the development of absolute species monitors using high accuracy spectral data. Finally, metrological quality spectral data will also serve metrological key services like the development and dissemination of gas standards. High accuracy spectral data are a prerequisite to foster the development of spectroscopy-based optical gas standards, which serve as absolute analytical transfer standards in cases where high adsorptivity or reactivity of the target gas, prohibits or hinders the development of classical reference gas mixtures due to a lack of chemical stability.

List of publications

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