EMPIR Call 2020 – Fundamental, Industry and Normative

Selected Research Topic number: **SRT-f17**
Version: 1.0

Title: Metrology for broadband - ro-vibrational spectroscopic gas thermometry

Abstract

Accurate gas temperature measurements are critical in modern science. Spectroscopic thermometry is particularly advantageous for numerous applications but often hampered by the uncertainties in molecular spectral parameters and their adoption to variable temperatures. Recent advances in quantum mechanical calculations in combination with metrological comb/FT-based spectrometric techniques offer novel routes towards highly accurate spectral parameters. Combined expertise in quantum-chemistry, spectroscopy and thermometry will enable the development of novel broadband ro-vibrational spectroscopic gas thermometry (RVSGT), to impact numerous applications such as environmental science, industrial process control and combustion research.

Keywords

Spectroscopic thermometry, primary temperature standard, molecular line parameter, quantum mechanical calculation, Fourier transform spectroscopy, comb-based FTS, comb-assisted cavity ring-down spectroscopy

Background to the Metrological Challenges

Spectroscopic temperature method works on the simple principle that the occupation probability of the initial state of a ro-vibrational molecular transition is temperature dependent. Variation in transition strength can be used to reveal thermodynamic temperature of gases. In contrast to platinum resistance thermometers (PRTs), spectroscopic methods are more rugged, stable under harsh conditions and more responsive for low density gases. Nevertheless, accurate spectroscopic methods have stringent requirements on the accuracy of the input spectral line parameters. New quantum mechanical models have been designed for CO_2 molecule to reach a targeted accuracy better than 0.3 % for the absolute line intensity. Such high accuracy calculations will be further applied to other bands of CO_2, as well as other important molecules in a broader temperature range, e.g. for H_2O, because it has the most prominent greenhouse effect in the atmosphere, followed by CO_2. Moreover, calculation is not affected by random experimental noise and therefore has much better relative accuracy (approximately 0.03 %) for line intensity. This high relative accuracy could potentially be exploited by multi-line broadband methodology to further improve accuracy of spectroscopic thermometry.

Recent developments in spectroscopic measurement techniques allow for dramatically more accurate determination of line shape parameters: comb-assisted cavity ring-down spectroscopy (CA-CRDS) significantly improves the resolution and brings the highest signal-to-noise ratio (SNR > 10^5) whereas comb-based Fourier transform spectroscopy FTS allows for fast broadband measurements with high SNR. Both methods provide accurate frequency axis and no influence of instrumental line shape functions. Precise modelling of spectra measured with such high SNR requires line shape models beyond the Voigt profile, which typically leads to a systematic error of over 0.4 % in line intensity. By adopting the IUPAC recommended Hartmann-Tran profile, the line-shape related error for line intensity could probably be reduced to a negligible level. This would be compatible to the present accuracy target of 0.1 % for line intensity.

The current state of the art accuracies for experimental line intensities are typically 1-3 %. The intensity accuracy of strong CO_2 bands to 0.3-0.5 % has been improved by using FTS. Single-line measurements of spectral shapes with the CA-CRDS technique, could provide spectra with high SNR (> 10^5), free from instrumental function.

Finally, the definition of air temperature is currently missing. Accurate thermodynamic temperature realised by non-contact methods in comparison to contact thermometry are crucial to pinpoint all the effects and parameters influencing the measurement process. Non-contact methods based on different physical principles (e.g. Doppler broadening thermometry (DBT), acoustic gas thermometry (AGT), refractive index gas thermometry (RIGT)) could improve the uncertainty evaluation.

Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on metrology research necessary to support primary spectroscopic thermometry.

The specific objectives are

1. To perform high accuracy quantum mechanical calculations on essential line parameters (line intensities and its rotational and vibrational dependence) of selected ro-vibrational bands of candidate “sensor” molecules (minimally for CO_2 and H_2O molecules) at least for temperatures of 300 ±200 K.
2. To perform high accuracy measurements of molecular transitions (minimally for CO_2, and H_2O molecules) with high resolution FTS infrastructure. To validate the FTS results with accurate CA-CRDS or comb-based FTS techniques. To retrieve essential line parameters with high accuracy using refined line shape models (e.g. IUPAC recommended Hartmann-Tran profile). To compare and validate the *ab initio* results from objective 1 using the best experimental values.
3. To develop the methodology of multi-line RVSGT. To evaluate its performance for temperature range (200 - 400) K and for variable pressures based on optimised spectral parameters from objectives 1 and 2. To develop the infrastructure for primary gas temperature measurements with target accuracy 30 mK, to correspond with accuracy better than 0.2 % in relative line intensities of the probed molecules absorption lines.
4. To cross-validate the spectroscopic gas thermometry developed in Objective 3 against other methods for the determination of thermodynamic temperatures (e.g. DBT, AGT, RIGT, dielectric constant gas thermometry (DCGT), or via ITS-90 referenced SPRTs and $T-T_{90}$) and identify potential accuracy barriers of RVSGT in both theory and its experimental applications
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (thermal metrology, molecular spectroscopy, long range distance metrology), standards developing organisations (CCT) and end users (remote sensing, automobile industry, aerospace industry).

Proposers shall give priority to work that aims at excellent science exploring new techniques or methods for metrology and novel primary measurement standards, and brings together the best scientists in Europe and beyond, whilst exploiting the unique capabilities of the National Metrology Institutes and Designated Institutes.

Proposers should establish the current state of the art, and explain how their proposed project goes beyond this. In particular, proposers should outline the achievements of the EMRP project ENV06 EUMETRISPEC and how their proposal will build on those.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 1.5 M€, and has defined an upper limit of 1.8 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 40 % of the total EU Contribution across all selected projects in this TP.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the “end user” community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the Spectroscopic Thermometry sector.

You should detail other impacts of your proposed JRP as specified in the document “Guide 4: Writing Joint Research Projects (JRPs)”

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically, the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work.

Time-scale

The project should be of up to 3 years duration.