Title: Metrology for broadband ro-vibrational spectroscopic thermometry

Abstract
Accurate gas temperature measurements are critical in modern science. Spectroscopic thermometry is particularly advantageous for applications such as environmental science, industrial process control and combustion research, but is often hampered by the uncertainties in molecular spectral parameters and their adoption at elevated temperatures. Recent advances in quantum mechanical calculations in combination with metrological comb/FT-based spectrometric techniques offer novel routes towards highly accurate spectral parameters and provides an opportunity for the development of a novel broadband rotation-vibrational spectroscopic gas thermometry system which addresses these challenges.

Keywords
Spectroscopic thermometry, primary temperature standard, molecular line parameter, quantum mechanical calculation, Fourier transform spectroscopy, comb-based FTS, comb-assisted cavity ring-down spectroscopy, carbon dioxide, water vapour, oxygen

Background to the Metrological Challenges

Currently, within the thermodynamic temperature range of 13.8033 K to 1234.93 K, T_{90} is disseminated with platinum resistance thermometers (PRTs). Even after the redefinition of Kelvin planned in 2018, PRTs will continue to serve as the main means to disseminate T_{90} until more rugged, stable and cost effective alternatives are developed. However, gas temperature measurement in intermediate to high temperature conditions poses a number of challenges to PRTs. These challenges include the poor thermal conductivity of gas compared to solids; the need in many applications for accurate temperate measurement in remote locations for which the optical method is the only feasible choice; the limited accuracy of PRTs in field applications due to external radiation interference; and the preference of optical thermometers in ultra-high temperature (>3000 K) applications.

In contrast to PRTs, spectroscopic methods are more rugged, stable under harsh conditions and more responsive for low density gases. Nevertheless, spectroscopic methods have stringent requirements on the accuracy of the input spectral line parameters. For example, assuming the relative sensitivity of the measured line area is 4 %/K, a 25 mK targeted accuracy would require at least 0.1 % accuracy on knowledge of line intensity parameters. However, such accurate data is currently not available, for instance, the widely used HITRAN database quotes at best 1-2 % accuracy for line intensities.

Recent significant improvements in fundamental quantum mechanical calculations offer a novel route towards determination of accurate fundamental molecular parameters for an increasing number of small molecules which are often impossible to prepare experimentally. To exploit these improvements in measurement accuracy there is a need to link the quantum mechanical theory experts and the metrological lab-spectroscopy groups to enable the most accurate spectral parameters determination for important temperature probing molecules such as CO_2, H_2O and O_2.

The current state of the art accuracies for experimental line intensities are typically 1-3 %. Recent developments in spectroscopic measurement techniques allow for dramatically more accurate determination of line shape parameters by employing comb-assisted CRDS (CA-CRDS) and comb-based FTS which could potentially allow for an accuracy target of 0.1 % for line intensity to be achieved.

The conventional spectroscopic methods of temperature measurements utilize the ratio of line strengths of two transitions. It is possible instead to use the entire molecular cold and hot bands to determine gas temperature with much improved accuracy. This would involve a comb source needing to be implemented in the existing FTS infrastructure to benefit from the accuracy and precision offered by this source.

None of the spectroscopic temperature methods based on intensity measurement has been compared to a primary gas standard. To rectify this there is a need to design dedicated experiments to validate the proposed spectroscopic method with various primary temperature standards, and any new methodology would also need to be rigorously tested under metrologically controlled laboratory conditions.

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 the definition of an accurate and traceable primary spectroscopic gas temperature measurement infrastructure.

The specific objectives are

1. To perform high accuracy quantum mechanical calculations on essential line parameters (line intensity parameter and its rotational and vibrational dependence) of selected ro-vibrational bands of candidate molecules (CO_2, H_2O, O_2) in a large temperature range (100 - 2000 K).
2. To perform high accuracy measurements of selected molecular transitions of CO_2, H_2O and O_2 with existing NMI Fourier transform spectroscopy (FTS) infrastructure, and with more accurate comb-assisted cavity ring-down spectroscopy (CA-CRDS) and comb-based FTS techniques to validate the FTS results; to retrieve essential line parameters with high accuracy using refined line shape models; to compare and validate the *ab initio* results from objective 1 using the best experimental values.
3. To develop the methodology of multi-band ro-vibrational spectroscopic thermometry and to test it under metrologically controlled laboratory conditions using optimum spectral parameters from objectives 1 and 2; to develop the infrastructure for primary temperature measurements by updating the existing NMI FTS infrastructure with the frequency comb technique, to an accuracy of 25-50 mK (0.1 % - 0.2 % in relative line intensities of the probed molecules).
4. To validate the developed spectroscopic thermometry (objective 3) against other primary temperature methods maintained at NMIs; during the validation process to identify potential accuracy barriers in both theory and experiment in order to point out directions for future improvements towards primary broadband ro-vibrational thermometry and its applications in industry and environmental science.

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 JRP 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 to the project.

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, 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.