Ro-Vibrational Spectroscopic Gas Thermometry (RVSGT):
A new primary method for gas thermometer calibrations?

Gang Li, *Volker Ebert*
Physikalisch-Technische Bundesanstalt (PTB),38116 Braunschweig, Germany,
Corresponding Author: gang.li@ptb.de, volker.ebert@ptb.de

Summary:

Gas temperature measurements play an important role for industrial process control, combustion technology, but also for environmental and climate science. Absolute calibration of contact gas thermometers is difficult and has a number of practical challenges when aiming on high accuracies. Rovibrational spectroscopic gas thermometry RVSGT, directly employs molecules as smallest possible "sensors", can be "read out" remotely using light absorption and can serve as a primary reference method for direct gas thermometer calibrations. Here, we present a new methodology to extract the gas temperature from a ro-vibrational spectrum of a "sensor" molecule measured by FT-spectrometry.

Keywords: gas temperature, spectroscopic thermometry, FT spectrometry, molecular spectral data

Introduction

Accurate gas temperature measurements are critical in modern science, but often hampered by the intrusive character of the contact-based techniques or the low thermal conductivity of gases causing multiple complications when calibrating contact gas thermometers. An ideal gas thermometry approach is versatile, non-intrusive, compatible with low to mid gas pressures, avoids the introduction of significant energy into the sample, allows a "remote" read-out and covers a wide temperature range. Broadband ro-vibrational spectroscopic gas thermometry (RVSGT) combines all requirements by using the gas molecules itself as temperature "sensor" and infrared spectroscopy as the remote temperature read out technique. For this RVSGT detects groups of rotationally resolved molecular transitions, preferentially in the near or the mid IR. RVSGT has the potential to derive absolute temperatures, just requiring a complete set of traceable spectral parameters as targeted in the EUMETRISPEC initiative (https://www.eumetrispec.org/). Rotationally resolved rovibrational spectra also contain a lot of "orthogonal" information, e.g. gas temperature from line intensity distribution, gas pressure from collisional or Doppler width, absorber number density from line area or band intensity, thus promising a consistent set of thermodynamic gas parameters from a single measurement. RVSGT thus can become particularly advantageous for numerous industrial as well as metrological applications, even has the potential to become a primary gas thermometry method. Until recently this was to some extend hampered by large uncertainties in the required molecular spectral parameters or their adoption to elevated temperatures. Recent advances in quantum chemical calculations now offer novel routes towards highly accurate spectral parameters and thus highly accurate non-contact gas temperature measurements. Furthermore, RVSGT can serve as primary reference method and allow a direct primary calibration of the ubiquitous contact gas thermometers without the need for assumption/corrections for possibly ill-described thermal coupling of the contact sensor and the gas.

Methodology

The relationship between intensities (S_i) of rotational lines within a vibrational band and the thermal dynamic temperature T at a local thermal equilibrium (LTE) condition is described by:

$$S \propto \ \cdot v \cdot \frac{1}{Q_T} \cdot HL \cdot g_I \cdot exp^{(-E_{Low}/k_B T_{rot})} \cdot \left(1 - exp^{(-hcv/k_B T_{rot})}\right) \cdot |\langle vJ'|M(x)|0J''\rangle|^2$$

where v is the frequency of the transition, Q_T is the partition sum at temperature T, HL is the Hönl-London Factor, g_I is the statisitical weights, E_{Low} is the lower state energy of the transition, h is the Planck constant, c is the speed of light, T_{rot} is the thermal dynamic temperatue assuming a LTE condition, $M(x)$ is the Matrix element. The equation shows three

terms influencing the temperature: Q_T, $exp^{(-E_{Low}/k_B T_{rot})}$, $\left(1 - exp^{(-hcv/k_B T_{rot})}\right)$. making the direct analytical determination of T_{rot} impossible.

Here, we propose a simple pseudo-T-fit approach. This method has mainly three prerequisites:

a) Accurate knowledge of the relative rotational line intensity distributions within a vibrational band from ab initio calculations or semi-empirical fits to the best experiments.

b) A probe molecule whose spectrum is measured with signal-to-noise ratio (SNR) of at least a few hundred or better.

c) Suitable high-resolution line shape model (Hartmann-Tran profile and its derivatives) adequate to model the high-SNR spectrum.

The pseudo-T-fit approach starts from assuming a trial temperature, T_{ini}. Doppler width of a spectral line, Q_T, $exp^{(-E_{Low}/k_B T_{rot})}$, $\left(1 - exp^{(-hcv/k_B T_{rot})}\right)$ are calculated using T_{ini}. The relative distribution of line intensities, i.e. C_v, D_v, …, is fixed, e.g. by the HITRAN database or ab initio spectral data [1,2]. The fit is implemented via an optimization algorithm, Gauss-Newton or Levenberg-Marquart, to optimize other spectral parameters and to reduce the global root mean square (rms) of the fitted residual. After the fit is converged, the rms sum, f_T^2, is registered. Subsequently, other temperatures are iterated. f_T^2 as a function of T is then modeled with a third order polynomial function. The optimum temperature T_{opt} is extracted as the minimum on the polynomial curve. figure 1 shows an an example. A second iteration with finer T grid around the T_{opt} is preferred for a more accurate T_{opt} determination.

Results

Figure 1 shows the variations of the sum of the fitting residual squared at different input temperatures for a measured FTIR spectrum of the 2.3 µm band of N_2O [3] using speed-dependent Voigt line shape model – a subgroup of the Hartmann-Tran profile. The minimum of the red curve corresponds to the determined temperature of T(spec)=296.10(6) K, which is in agreement with the traceably measured temperature T(ref)=296.0(1) K using two PT100 sensors. The major T(ref) uncertainty comes from the spatial T inhomogeneity between top and bottom of an 80 cm long absorption cell.
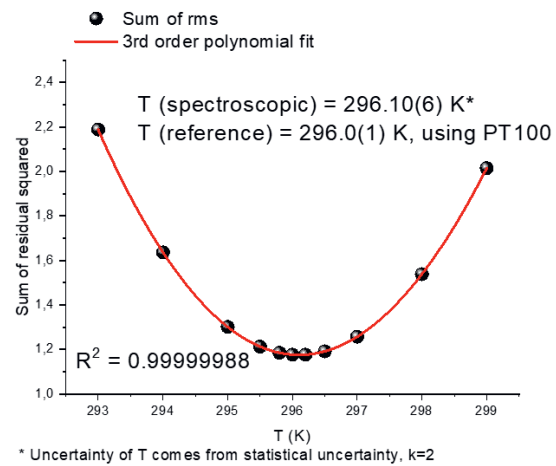

Fig. 1. Example of a pseudo-T-fit approach to extract the optimum spectroscopic gas T. The sum of the squared fit residuals between observed and calculated spectrum at different "assumed" gas T's are fitted with a cubic function. The gas T corresponding to the minimum of the fitted curve is the fitted T derived from our approach. The uncertainty of the spectroscopic T quoted in the figure arises from the statistical uncertainty of the polynomial fit. Other sources of uncertainty are still to be analysed.

RVSGT [4] has the advantage of utilizing the full spectral information for higher accuracy, compared to laser-based Doppler-width-thermometry or two-line ratio thermometry. We employ a full spectroscopic model and follow the GUM to study the accuracy requirements on different input parameters for a highly accurate spectroscopic gas thermometry from Doppler limit to atmospheric pressure at LTE conditions. These parameters include Herman-Wallis factor, line shape models, accessible temperature range, and others. The full potential and optimum uncertainty of RVSGT needs to be further studied and experimentally verified using other primary (gas) temperature realizations.

References

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