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Linestrength ratio spectroscopy as a new primary thermometer for redefined Kelvin dissemination

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Abstract. Experimental methods for primary thermometry, after Kelvin unit redefinition on May 2019, become based on a known value of the Boltzmann constant rather than by measuring temperature with respect to a reference point. In this frame, we propose Linestrength Ratio Thermometry (LRT) as a candidate method for primary thermometry in the 9-700 K temperature range. Temperature accuracies at the ppm level are prospected for LRT applied to optical transitions of the CO molecule in the range 80-700 K and of a rare-earth-doped crystal in the 9-100 K one. Future implementations of this technique can contribute to measure the calibration-discrepancies in the ITS-90 metrological scale of thermodynamic temperature which can have a measurable impact in applications ranging from fundamental-physics to meteorology and climatology.

Keywords: Molecular spectroscopy, primary thermometry, laser spectroscopy, carbon monoxide, rare earth doped crystal, Kelvin dissemination

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1. Introduction

Nowadays, the measurement of thermodynamic temperature T of physical systems plays a fundamental role in experimental science ranging from fundamental physics [1, 2, 3, 4] to chemical physics [5, 6, 7, 8, 9], cold atoms physics [10, 11, 12], meteorology and climatology [13, 14] and control of industrial processes. Accuracy and reproducibility of such measurements depends on the international standard of temperature: the Kelvin unit and its precise traceability.

Up to now, the International System (SI) of units has defined the Kelvin in terms of the temperature of the triplet point of "pure" water, which was assigned the exact value of T_{TPW}= 273.16 K. It was the absolute reference value for each accurate thermodynamic temperature measurement, traceable trough the primary thermometers (PT's). In these thermometers, there is a basic relation between the observable and T that can be written down explicitly without having to introduce unknown, temperature-dependent quantities. The PT's are impractical for most part of the applications that need accurate T measurements due to their size, measurement speed and cost. Instead, secondary thermometers (ST's), as the platinum resistance temperature detector (RTD), are the practical-instrumentation used to measure precisely thermodynamic temperature. But such a thermometers must be calibrated against a defined fixed temperature points to ensure worldwide accuracy and primary traceability. Indeed, the International Temperature Scale of 1990 (ITS-90 [15]) and the Provisional Low Temperature Scale of 2000 (PTLS-2000 [16]) were established by the Consultative Committee for Thermometry (CCT) of the International Committee for Weights and Measures (CIPM) as a practical reference scales for dissemination of the Kelvin unit. These scales have a number of fixed temperature values defined by the reproducible freezing or melting temperature of pure substances measured against T_{TPW} by means of accepted primary thermometers.

On May 2019, the CIPM has anticipated the most radical revision of the definition of the SI base units in terms of exact fundamental constants, and in particular the Kelvin unit in terms of the assigned exact value of the Boltzmann constant, k [17, 18]. The *mise en pratique* for the Kelvin redefinition (*MeP-K-19*) establishes, as first, that the accurate methods used to determine k [19, 20, 21, 22, 23], become PT's [24] because in their basic equations T always appears as thermal energy kT. Recently, we proposed Linestrength Ratio Thermometry (LRT) [25] to determine Boltzmann constant with accuracy comparable or even better than other primary techniques. Consequently, we propose the LRT method as a potential candidate as a primary thermometer, prospecting its accuracy and precision performances to measure some reference temperatures of the ITS-90, and by extending the application towards the low T range where other optical techniques are not available. Secondly, by *MeP-K-19*, the worldwide dissemination of Kelvin will be provided equally by those PT's and through the defined scales ITS-90 and PLTS-2000. In this way the practice of thermometry will remain largely unchanged with a smoothed impact in the calibration

of secondary thermometers and the T-measurement-based applications. The first immediate implication on the scales of the new definition is that the T_{TPW} would lose its status of reference temperature of the primary thermometry, becoming just another fixed T point. The uncertainty of such point would be the order of 10^{-4} K transferred by the k uncertainty at the moment of the redefinition. Because T_{TPW} still remains the reference point for the ITS-90, this uncertainty will be propagated to the other fixed points of the scale with a larger impact in the extreme T's. The new PT's are called to calibrate these uncertainties as first issue.

Equally important for a proper Kelvin dissemination is to calibrate systematic discrepancies, T-T_{90} between temperature points of the ITS-90 (T_{90}) and the measured T by using the new defined PT's [26, 27]. Although such systematic errors seem to be small if compared with precision of secondary thermometers, they can produce measurable effects in applications that need precise temperature determinations. For example measured shift of 1.5×10^{-4} of T-T_{90} for temperatures in the range of meteorological relevance (-50 to 90 °C), even if smaller than the T-variations of the ST's in the short time due to other environment factors, might be just detectable in homogenisation procedures using annual or decadal means [27]. More important, the metrological relevance of these discrepancies prospects a possible future revision of the ITS-90, where current scale errors will certainly be removed if they takes place, and the temperatures estimated according the new ITS will be likely to be much closer to true (i.e. thermodynamic) temperature T than at the present.

In this framework, new accurate thermometry methods as LRT are welcome. To this aim, we report the prospected accuracy performances of LRT to measure absolute T's in the range between 9 and 700 K. The temperature uncertainties of some fixed points of the ITS-90 between triple point of argon (83.8058 K) and freezing point of zinc (692.677 K) were systematically evaluated by applying LRT to ro-vibrational transitions of the CO molecule. In addition, the applicability of LRT to measure T's in the low range of ITS-90 (9-100K) by laser spectroscopy in a rare-earth-doped crystal is proposed. Similar accuracy performances are also prospected in this temperature range

LRT method for primary thermometry

LRT method is based on the precise measurement of the linestrength ratio, R of two transitions a and b of the targeted specie at two different temperatures, T and T_r: $R(T) = \frac{S_b(T)}{S_a(T)}$, $R(T_r) = \frac{S_b(T_r)}{S_a(T_r)}$, with $S_{a,b}$ linestrengths of the a, b transitions, respectively [25]. Laser absorption spectroscopy experiments in highly controlled temperature environment can be used to measure these ratios with high precision (few ppm). Other techniques [28, 29] based on the same principle but with different experimental implementation have been used to measure high temperatures with lower accuracy.

In LRT, a determination of the temperature T with respect to the other T_r is

obtained by:

$$T(ln(F), T_r, \nu_a) = \frac{T_r h\nu_a}{T_r k\ ln(F) + h\nu_a} \quad (1)$$

with $F(T, T_r) \equiv \frac{R(T)}{R(T_r)}$, k Boltzmann constant and ν_a the frequency corresponding to the energy of the lower level of the a transition, and by considering b as a ground state transition (ν_b=0) for simplicity . This equation was deduced by considering the relationship between the linestrengths of a transition at two different temperatures [30]. Hence, LRT can be considered to fulfill the *MeP-K-19* criteria of relative primary thermometry: Eq.1 is the simple equation to measure thermodynamic temperatures with respect to a reference one, in a wide temperature range with a low uncertainty δT:

$$\delta T = \sqrt{\delta T_r^2 + \delta F^2 + \delta \nu_a^2} \quad (2)$$

where $\delta T_r = \frac{\partial T}{\partial T_r} dT_r$, $\delta F = \frac{\partial T}{\partial F} dF$ and $\delta \nu_a = \frac{\partial T}{\partial \nu_a} d\nu_a$.

The experimental implementation of LRT uses two cells, highly stabilized at the T, T_r temperatures to perform simultaneous absorption spectroscopic detection of the a, b transitions with high resolution and signal-to-noise ratio (S/N). In this way, a precise measurement of F is achieved by numerical integration of the detected signals. Moreover, common systematic experimental effects present in individual spectroscopic measurements of linestrengths are removed by using the ratio approach, and hence improving the final uncertainty, dF. Nevertheless, it actually turns to be the limiting factor of the final error of T in LRT even if the functional dependence of T on F, according with Eq.1, shows a large slope and mitigates the F-error propagation: an uncertainty δF on F measurement corresponds to a small uncertainty δT on T. This is the strength of LRT as thermometric method which can be able to provide precise T measurements even if measuring a challenge parameter as the linestrength ratios of optical transitions.

The key criteria for LRT applicability as PT is to individuate the best combination of the transitions which minimize the total error given by eq. 2. In our previous paper [25], we did this evaluation with the aim of an accurate determination of k by LRT of the CO molecule at two known temperatures: the T_r=T_{TPW} and the triplet point temperature of Argon, T=T_{TPAr}. If LRT is used as PT, the individuated CO transitions in that case could be appropriated to measure T_{TPA} against T_{TPW} (or the contrary), but not for other temperature points of the ITS-90 scale. In view of a real PT applicability of LRT, now, we do a more esaustive analysis both in terms possible transitions and targeted species to cover all T_{90} points in the range 9-700 K.

LRT on CO molecule: primary thermometry in the 80-700 K range

To illustrate the performances of LRT as PT in this range, we have selected which is probably the most promising molecule: carbon monoxide. The reasons of that are the following:

- low freezing point (68.13 K) enabling wide range of applicability for LRT thermometry.

- As biatomic molecule, it shows a simple ro-vibrational spectrum in the mid-infrared (MIR) spectral region. As a consequence it is feasible to find target transitions with negligible interference effects by off-resonance absorptions of CO.

- ro-vibrational transitions in the MIR with large dipole moment, allowing strong absorption at low pressure.

In addition, the current availability of narrow linewidth laser sources [31, 32, 33] and high performance detection technology [34] in the MIR allow to perform high-resolution spectroscopy of CO transitions with very high S/N, as required to get low uncertainty on F.

Selection of the LRT transitions

In the following we describe the procedure to individuate the best transition of CO (a transition) to perform LRT primary thermometry in *defined points* of ITS-90 scale between 83.8058 and 692.677 K by considering T_r=T_{TPW} as reference temperature. The analysis is made in terms of minimum error δT evaluated by propagating the prospected errors in dT_r, dF and $d\nu_a$ for each considered CO transition. The R(0) of the (2-0) band of CO at 4263.837197 cm^{-1} (having ν_b=0) is the b transition, common to all temperatures. Our algorithm downloads a list of linestrenghts for the CO molecule in 1000-10000 cm^{-1} wavenumber range [35] and the corresponding energy (divided by h) of lower state, ν_a [36, 37] for each analyzed temperature, and calculates δT by using eq.2. In this calculation, we consider an experimental uncertainty on T_r of dT_r= 0.3 mK, easily achievable by using temperature-controlled commercial cells. We assume to achieve a S/N of the CO spectra to allow a R measurement uncertainty at the best reported for absorption spectroscopy [23], i.e. dR/R=dR$_r$/R$_r$ = 2.8 ppm or dF/F= 4 ppm.

For ν_a, $d\nu_a$ is evaluated taken into account the error due to pressure shift for each transition in the pressure range of a practicable LRT experiment (around 10 Pascal) [37]. As shown in the following, this contribution should be considered negligible to the total T-error.

Let first analyzed the behaviour of T error with the spectral region by considering CO transitions from different vibrational bands. In Fig.1, the relative error $\delta T/T$ for T$_{TPAr}$= 83.8058 K calculated for the CO ro-vibrational transitions of the fundamental, first and second overtone bands is shown, as well as the partial contributions $\delta T_r/T$, $\delta F/T$ and $\delta\nu_a/T$. In all cases, the final error is dominated by the linestrength ratio uncertainty as expected. We note that similar relative temperature errors were found for transitions in the fundamental and overtone bands.This is fundamental in view of a practical implementation of LRT, because of the major availability of the laser, optics and optics and electro-optics technology at the wavelengths of overtone bands. Between them, the (2-0) band transitions are preferred to those of the (3-0) band due to the strong intensity of the former by considering the same final T-error level. For that, the

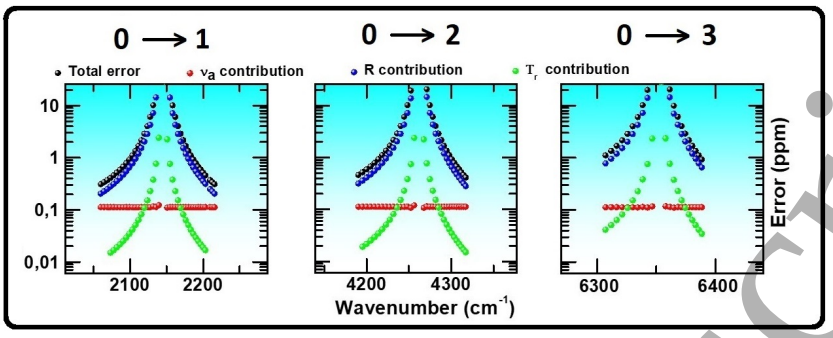

Figure 1. Relative error $\delta T/T$ (black points) in ppm on temperature measurement of T_{TPAr} by LRT with T_{TPW} as reference temperature and by using different rotational transitions of the fundamental ($0 < J < 16$) (left graph), first overtone ($0 < J < 15$) (center graph) and second overtone ($0 < J < 10$) (right graph) vibrational bands. Green, red and blue points for each graph are the partial contribution to this error due to the uncertainties of the reference temperature, frequency of the lower level of the transition and F ratio measurement, respectively (δT_r, $\delta\nu_a$ and δF contribution in eq.2).

final best a transition candidates were chosen from the first overtone (2-0).

The same procedure was applied to calculate δT for all the other analysed T_{90}'s: triple point of mercury, T_{TPHg} = 234.3156 K; melting point of gallium, T_{MPGa}= 302.9146 K; freezing point of indium, T_{FPIn}= 429.7485 K; freezing point of tin, T_{FPSn}= 505.078 K; freezing point of zinc, T_{FPZn}= 692.677 K.

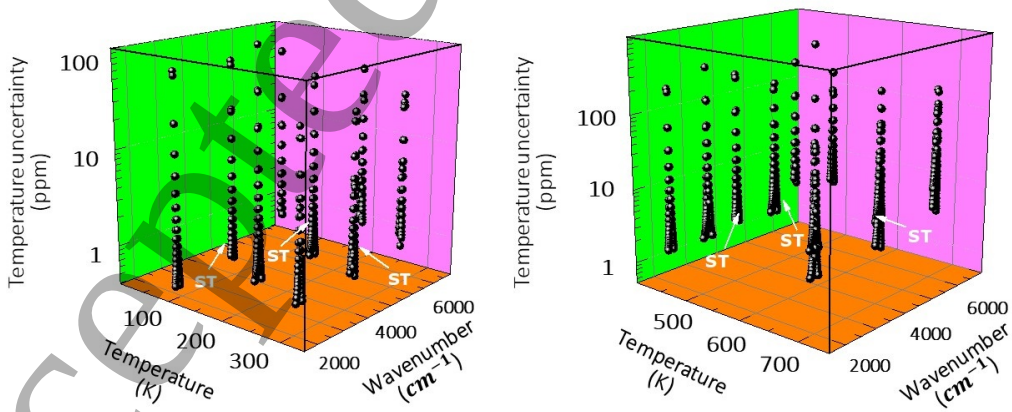

Figure 2. Total relative errors $\delta T/T$ (z axis) for the entire temperature range (x axis: 80-350 K left graph, 350-700 K right graph) as function of transition wavenumber (y axis). The best transition for each ITS-90 in the 80-700 K range fixed point is indicated by ST and is proposed for LRT-temperature measurement with ppm accuracy.

The results are shown in Fig.2 in two three dimensional graphs with the calculated

Table 1. Prospected total relative temperature error of a LRT-measurement of ITS-90 fixed points in the range 83.8058-692.677 K with respect to the reference temperature T_{TPW}=273.1600 (3) K. dF/F= 4 ppm was considered in this calculation

T (K)	a wavenumber (cm^{-1})	$10^{-22}S_a$(T) (cm/mol)	b wavenumber (cm^{-1})	$10^{-22}S_b$(T) (cm/mol)	δT/T (ppm)
83.8058	4303.623335	2,004	4263.837197	2.459	0.79
234.3156	4324.409820	1.491	4263.837197	8.855	0.87
302,915	4328.878516	1.797	4263.837197	6.854	0.96
429,7485	4328.878516	4.942	4263.837197	4.831	1.3
505,078	4328.878516	6.827	4263.837197	4.105	1.6
692,677	4328.878516	10.42	4263.837197	2.964	2.2

$\delta T/T$ in the z-axis as function of the measured thermodynamic temperature T (x-axis) and the wavenumber of the transition (y-axis). All the three CO vibrational bands (fundamental and 1st and 2nd overtones) haven been considered. The best transition for LRT determination of the T_{90}'s at the ppm level (signed as ST in the Fig.2) was selected taking into account the criteria of minimum δT for transitions of the first overtone band, excluding those with linestrength lower than 10^{-22} cm/mol. For the ST transitions, high S/N spectra can be allowed at low CO gas pressure in a technically better spectral region.

Considering these ST as the a transition candidates for LRT primary thermometry at the ITS-90 fixed temperatures between 80-700 K, we report in detail in Fig. 3 and Table 1, the prospected relative uncertainty $\delta T/T$ by considering the T_{TPW} as reference temperature. Data about linestrengths and wavenumbers of the a and b transitions for each temperature are included in Table 1. In Fig. 3, in addition, the main temperature error contributions due to dT_r and dF are shown. The F-contribution is the dominant source of error and it is almost constant in all considered temperature range. Instead, the T_r-contribution begin to be consistent for T above 300 K, and it is almost negligible at low temperatures. Nevertheless, the total error is always lower than 2.5 ppm and becomes lower than 1 ppm for T under 300 K.

Uncertainty analysis on spectroscopic measurement of F ratios

All the above analysis about uncertainties at ppm level on LRT primary thermometry are supported if the considered experimental errors on ν_a, T_r and F are achieved. The ν_a frequencies of the ST transitions are known with a relative accuracy of about 0.1 ppm (see Fig.1) for the experimental conditions of the CO samples in LRT, and hence we consider a negligible contribution of $d\nu_a/\nu_a$ on T's at the ppm level. For T_r, temperature stability at the 0.3 mK level can be achieved with commercial control systems. Only for above 300 K temperatures where the dT_r becomes a significative contribution to the δT, a further technological effort in the T-stability should be realised if the dF/F

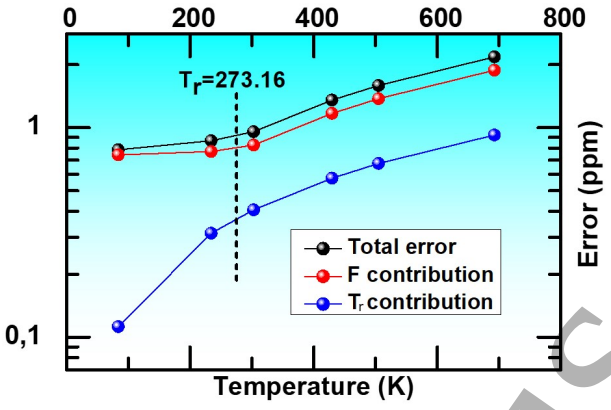

Figure 3. Total relative error on temperature measurement using LRT (black points), contribution due to T_r uncertainty(blue points) and contribution due to the F uncertainty (red points). The errors were calculated at ITS-90 fixed points using the ST transitions.

contribution will be improved better than 4 ppm. Finally for F, we evaluate that a few ppm F-measurement can be achieved by numerical integration of the absorption area for the spectra with S/N of thousands [25].

As a preliminary experimental support of this estimation on error in F, a spectroscopic measurement in the 4.5 μm wavelength region was performed. Because we have not yet available a laser source resonant with the CO transitions in this spectral region, the test was realised on the ($0^2$01-$0^0$00) R(16)e transition of N_2O molecule at 2209.0854 cm^{-1}, which has similar spectroscopic characteristics to those the CO transitions at these wavelengths. Linear absorption spectroscopy of this transition was performed by interaction of a Quantum Cascade Laser (QCL) at 4.5 μm with the N_2O gas contained in a cell of 18 cm of length at 1.1 mbar of pressure. Eleven consecutive transmission spectra were recorded by scanning the QCL frequency in an interval of about 500 MHz around N_2O resonance at acquisition times of 50 ms per spectrum. The results are reported in fig. 4 in terms of absorbance. Then, the integrated absorption (IA) area for each spectrum has been calculated by using numerical Romberg integration method and the area ratio R with respect to the mean value were calculated, as well as the standard deviation. As a result a relative uncertainty on the absorbance area of about 1.1% was measured, only two times larger than we have prospected for spectra with a noise level ϵ=0.05 and a QCL linewidth of about 500 kHz [25] . We ascribe this discrepancy to temperature, pressure and absorption path fluctuations whose do not particularly taken care in this simple experimental set-up, differently of a real LRT set-up which provides simultaneous measurement of both transitions in a cell at a highly controlled temperature. In these conditions, error contributions due to absorption path and gas pressure fluctuations should be cancelled and highly minimised those due to temperature fluctuations. Hence, we are confident to achieve the prospected

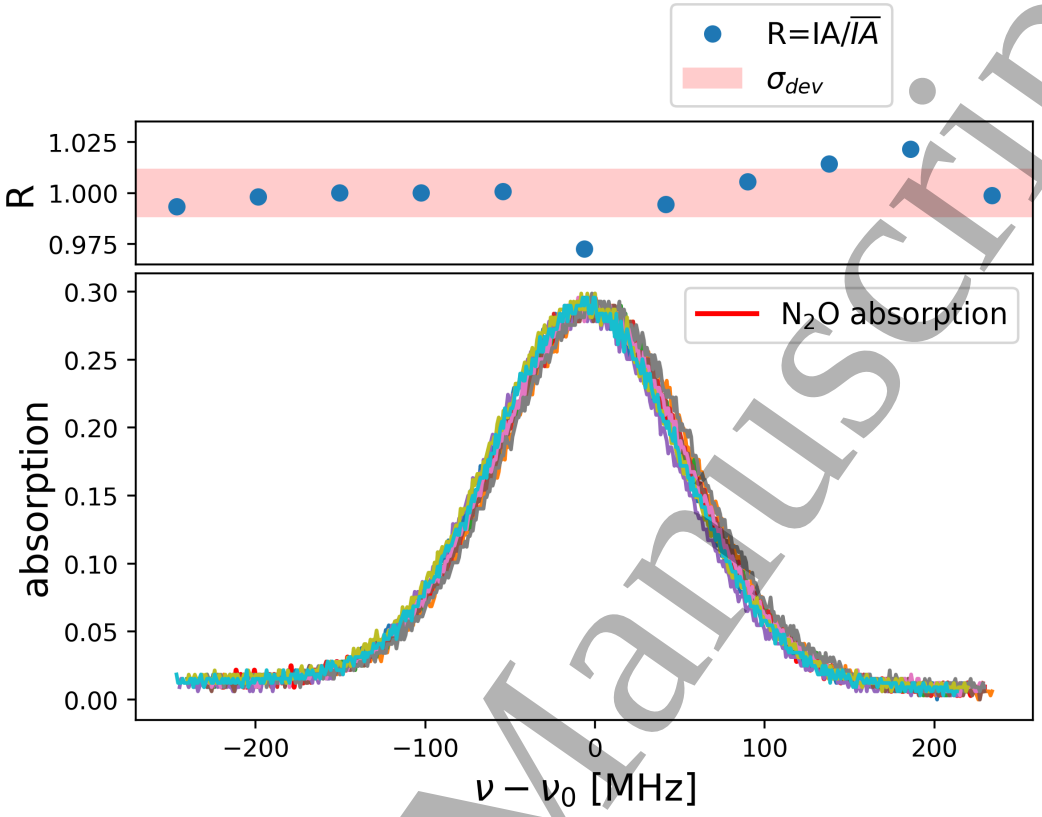

Figure 4. Absorption spectra of N_2O at 2209.0854 cm^{-1} in a 18 cm cell with a 1.1 mbar pressure when probed by a QCL at 4.5 μm. The laser was frequency scanned around the resonance frequency and eleven different scans were recorded at 50 ms acquisition time. The integrated absorption (IA) area was calculated by using numerical Romberg integration method and the area ratio R (blue points) with respect to the mean value are plotted at the top of the figure, with the red bar indicated one standard deviation of such values.

F uncertainties when the experiment will be performed in the conditions of the LRT method. Nevertheless, F measurement can be affected by systematic effects on the measured area due to the limited spectral range detected for each spectrum or due to the presence of off-resonance molecular absorbances different of the targeted ones. In the following, we evaluate the contributions of these systematics in view of a practical realisation of LRT in CO.

A benefit of LRT spectroscopy is the measurement of the absorbance of the different spectra without requiring a sophisticated line shape model, but just by numerical integration. In order to guarantee the few ppm F-accuracy in LRT methods, we evaluate that a scan bandwidth of about 2 GHz is sufficient to numerically capture the entire absorption area with a systematic error below ppm. The CO transition line-shapes in the thermodynamic conditions of the sample gas relevant for LRT experiments are due to Doppler broadening and pressure broadening.

The line shape $I_D(\nu)$ due to Doppler broadening effect is given by:

$$I_D(\nu) = I_0 \sqrt{\frac{4\,ln(2)}{\pi}} \frac{1}{\Delta\nu_D}\; Exp\left(-4\,ln(2)\frac{(\nu-\nu_0)^2}{\Delta\nu_D^2}\right) \tag{3}$$

$$\Delta\nu_D = \frac{2\nu_0}{c}\sqrt{\frac{2kTln(2)}{m}} \tag{4}$$

where ν_0 is the line center frequency, m the CO mass, c vacuum light velocity and $\Delta\nu_D$ FWHM Doppler linewidth contribution. Acquiring a 2 GHz absorption spectrum is sufficient to capture entire Doppler contribution, even in the case of the largest Doppler-broadening at the highest analysed temperature ($\Delta\nu_D$=450 MHz at 692.677 K). In fact, the difference between $\int_{\nu_0-1GHz}^{\nu_0+1GHz} I_D(\nu)d\nu$ and $\int_{-\infty}^{\infty} I_D(\nu)d\nu$ is 0.2 ppm in this case, and it decreases for the other temperatures in the analyzed range.

The pressure broadening generates a Lorentzian contribution to the line-shape:

$$I_L(\nu) \propto \frac{\gamma P}{(\nu-\nu_o)^2 + (\gamma P)^2} \tag{5}$$

where γ is pressure broadening coefficient [35]. For our analysis, we consider this profile at pressure P of about 10 Pascal, sufficient to have an adequate S/N of the absorption spectra of the ST and b transitions. If we consider each spectral profile separately to calculate S_a and S_b at T and T_r, a 2 GHz scan bandwidth is not sufficient to measure their area with the required precision because of the truncated-wings contribution. The error in this case is:

$$\frac{|\int_{-\infty}^{\infty} I_L(\nu)d\nu - \int_{\nu_0-1GHz}^{\nu_0+1GHz} I_L(\nu)d\nu|}{\int_{-\infty}^{\infty} I_L(\nu)d\nu} \simeq 336ppm \tag{6}$$

Even more, the error on R and R_r by considering $R(T) = S_b(T)/S_a(T)$, recorded with a 2 GHz scan, is:

$$\frac{|\int_{\nu_0-1GHz}^{\nu_0+1GHz} R_r(\nu)d\nu - \int_{-\infty}^{\infty} R_r(\nu)d\nu|}{\int_{-\infty}^{\infty} R_r(\nu)d\nu} \simeq$$
$$\simeq \frac{|\int_{\nu_0-1GHz}^{\nu_0+1GHz} R(\nu)d\nu - \int_{-\infty}^{\infty} R(\nu)d\nu|}{\int_{-\infty}^{\infty} R(\nu)d\nu} \simeq 60ppm \tag{7}$$

and hence very far from the requested ppm. But the method is based on the ratio between to linestrength ratios, F. If the CO pressure P for the measurement of R was be exactly equal to the P for R_r, the error on F should be 0 even with a limited 2 GHz scan. If the P for measurement of R was be different to the P for R_r, the error on F should be 0 by using an infinite integration bandwidth. Assuming an error of 1% on the pressure gauge, the pressure broadening for R will be different of the pressure broadening of R_r and the error on F in the case of 2 GHz scan bandwidth is:

$$\frac{|\int_{\nu_0-1GHz}^{\nu_0+1GHz} F(\nu)d\nu - \int_{-\infty}^{\infty} F(\nu)d\nu|}{\int_{-\infty}^{\infty} F(\nu)d\nu} \simeq 0.59ppm \tag{8}$$

that is nearly one order of magnitude lower than error we considered on F of 4ppm across the present analysis. We can conclude that a 2 GHz scan bandwidth and an error of one per cent on the pressure gauge can be sufficient to candidate LRT as a ppm level primary thermometry technique.

The possible influence of interferent off-resonance absorptions to the measured area in the scan bandwidth is now evaluated. Thanks to the simple ro-vibrational spectrum of the biatomic molecule of CO, the chosen b transition at 4263.837197 cm^{-1} and the ST transitions (see Table 1) are very far apart of possible interfering absorptions. In the worst case, the nearest unwanted transition is the R(17) component of (3-1) band at 4263.635524 cm^{-1} (x-line) about 6.6 GHz apart from ν_b and with a linestrength of $6.261*10^{-23}$ cm/mol[35]. To estimate the contribution of the x transition wings to the integrated absorption of the b transition in a range of 2 GHz around ν_b, we calculate the ratio between the expected contribution for the x and b absorptions when considering not interference from x:

$$x_{wing} = \frac{\int_{\nu_{0b}-1GHz}^{\nu_{0b}+1GHz} I_x(\nu)d\nu}{\int_{\nu_{0b}-1GHz}^{\nu_{0b}+1GHz} I_b(\nu)d\nu} \simeq 0.8ppm \tag{9}$$

which is again a contribution one order of magnitude lower than the prospected 4 ppm on F.

Finally, let us consider the uncertainty consequences on the F measurement when numerical integration of the spectra instead of lineshape fit is used to measure it. This consideration is not only important in terms that LRT is a line-shape model independent, avoiding, in this way, to accurately consider all velocity-changing collision effects, normally present in spectroscopy of gas species. Even in terms of how the uncertainty of the numerical integrated area is lower than fitted one. To evaluate it, we have simulated a Voigt profile of an absorption transition with a Doppler width contribution, ω much larger than the collisional one and with an area A. This is the usual situation in optical spectroscopy-based thermometric techniques: LRT and Doppler Broadening Thermometry, DBT [38][38, 39]. A random white noise of the 1% was added to the spectral profile to simulate a real experimental spectrum of the transition. Then, we have determined the relevant spectral parameters for thermometry by using a fit procedure to measure ω_F and A_F, and a numerical integration to measure A_I. The fit and numerical integration is repeated a significant number of times to get a normal statistical distribution of the measured parameters. As a result, the standard deviations of the fitted area (σ_{A_F}) and Doppler linewidth contribution (σ_{ω_F}) are one order of magnitude worst than the numerical integrated area (σ_{A_I}). Consequently, even if with an adequate line-shape model, better accurate results could be expected for LRT if compared with DBT due F is measured by the numerical integration and ω by the fit procedure.

LRT on Er:YLF crystal: primary thermometry in the 9-100 K range

The use of the carbon monoxide for LRT is limited in the range 80 - 700 K because of technical issues. Below 80 K, high resolution CO absorption spectroscopy is limited by the gas sample vapour pressure at these T's. Above 700 K instead, the not negligible absorption of interferences from off-resonance neighbour transitions limits the LRT-application. A possible system useful to extend LRT range towards few Kelvin is a rare-earth-doped crystal. In such materials, the shielding of f electrons by closed shells makes possible optical transitions between these quasi-unperturbed f levels[40] with very narrow achieved linewidths as, for example, the transitions of Erbium doped $YLiF_4$ ($Er^{3+}:YLF$) in the near-IR region[41, 42]. For this reason, we propose this crystal as a target specie to perform LRT in the low temperature range of ITS-90.

In $YLiF_4$, erbium ions substitute yttrium ions in one crystallographic site of S4 point symmetry. Since Er^{3+} has an odd number of electrons, all crystal field levels are doubly degenerate. In each $^{2S+1}L_J$ multiplet, crystal field levels are characterized by the absolute value of the projection of J number along crystal field axis, for example the ground state energy level $^4I_{15/2}$ is splitted by crystal field interaction in $^4I_{15/2,|M_J|}$ where $|M_J| = 5/2, 15/2, 3/2, 1/2, 9/2, 7/2, 11/2, 13/2$ each level is doubled degenerate $|M_J| = |\pm M_J|$ and the degeneracy is removed if a magnetic field is applied.

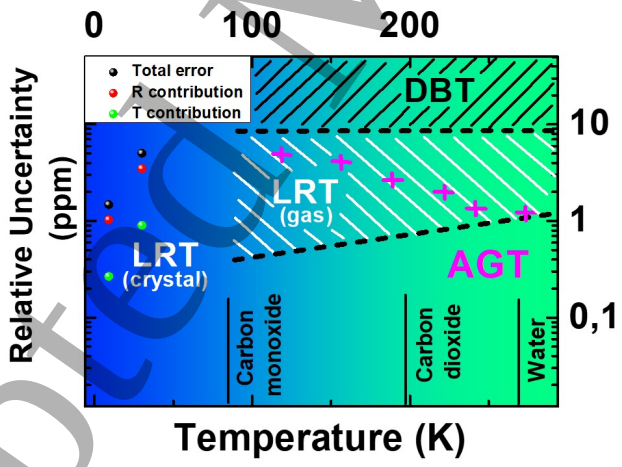

Figure 5. Relative T uncertainty (black points) and their partial contributions due to δT_r (green points) and δR for LRT applied to hyperfine transitions of Erbium doped $YLiF_4$ crystal around 800 nm at T of 30 and 9 K with respect to the 100 K reference temperature. Uncertainty performances of AGT, DBT and LRT in the 80-300 K range are shown. Freezing points of CO, CO_2 and H_2O are also indicated.

In order to evaluate the practical realization of LRT at the low temperatures of ITS-90 scale, we estimated the errors contributing to the final temperature measurement by considering the transitions $^4I_{15/2,5/2} \rightarrow ^4 I_{9/2,9/2}$ and $^4I_{15/2,15/2} \rightarrow ^4 I_{9/2,9/2}$ around 800 nm as the b and a LRT-transitions, respectively. The starting level of the b transition is the ground state and the starting level of a transition is 17 cm^{-1} above, equivalent to a temperature of 24.5 K. Taking into account the $S(T)$ values for the a an b transitions [43],

we calculate the ratios: $R(T_r = 100K) = \frac{S_b(T_r)}{S_a(T_r)}$ and $R(T) = \frac{S_b(T)}{S_a(T)}$ for T=30 and 9 K. Consequently , as done above for the CO, the T and its total relative uncertainty from eqs. 1-2 and the partial uncertainties $\delta T_r/T$ determination and $\delta F/T$ were estimated (as for CO, $\delta\nu_a/T$ is negligible if compared with the others) . The results are shown in the left part of fig. 5. The same values and criteria as in CO are used for the dF, dT_r and $d\nu_a$ in this calculation. As a result, the total T uncertainty is few ppm proving the validity of LRT as primary thermometry technique also in few Kelvin range. This would be, to the best of our knowledge, the first optical primary thermometry technique working in this low temperature range. Indeed, in fig. 5 is also shown the range of applicability of the optical spectroscopy based PT's: DBT and LRT. DBT uses Doppler broadening due to the T of gas samples, and, in principle, a low temperature applicability up to 80 K could be prospected if CO is used‖. LRT is also down limited to this T if CO is used, but its range of applicability can be extended up to 9 K if transitions in rare-earth doped materials as Erbium doped $YLiF_4$ crystal are measured.

Comparison with the most accurate primary thermometry, Acoustic Gas Thermometry (AGT), in the range of 80-300 K is also shown in fig. 5. Similar accuracies to the AGT ones are prospected for T's around water triplet point and even better for low temperatures.

Discussion

On the frame of the Kelvin unit dissemination prospected by *MeP-K-19* by using the ITS-90 scale corrected by the new PT's, we are advancing the LRT method as candidate for a no-contact primary thermometer. The thermometric capabilities of LRT envisage accuracies of thermodynamic temperature at the ppm level when applied to transitions of the CO molecule and of the Erbium doped $YLiF_4$ crystal in a temperature range between 80 and 700 K and between 9 and 100 K, respectively. This accuracy makes LRT comparable even with the most precise PT's as those based in AGT. Even more, if compared with the other optical-based thermometry, the DBT [38], an accuracy improvement of a factor of 15 for T$\simeq$300 K is prospected. Discrepancies under mK level of T-T_{90} in 9-700 K range can be tested by this accurate LRT thermometry, and in particular, the T range of meteorological interest [27]. In addition, LRT technique would be, to the best of our knowledge, the first optical based primary thermometry working at few kelvin with ppm accuracies. For the above discussion, crucial for LRT success as a primary thermometer is to achieve experimental accuracy at the few ppm level in the spectral measurements of F in a LRT experiment. The experimental feasibility of LRT is enabled by technological development of laser sources in near-infrared and mid-infrared with linewidths at the few kHz level (and less) reachable using different stabilization techniques as those based on ultra-stable cavities [44, 32] or whispering gallery mode

‖ A constant relative uncertainty of about 9 ppm was considered in all the range of applicability corresponding to that reported for CO_2 at 300 K [38]. Different values could be achieved with different sample gases at other T's.

microresonators [45, 46]. In addition, optical frequency comb (OFC) disciplined laser sources [47, 31] or directly OFC's as spectroscopic sources [48, 49, 50, 51] provide sub Hz control level of the absolute frequency.

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Additional information

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