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Impact of ab initio line-intensity ratios on primary spectroscopic thermometry

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ABSTRACT

Line-intensity-ratio thermometry (LRT) is a spectroscopic primary thermometry method whose accuracy depends critically on the quality of the reference molecular line intensities. We investigate the impact of reference spectroscopic data on LRT by reanalyzing previously measured cavity mode-dispersion spectroscopy spectra of ten CO (3–0) band transitions at 296 K using newly available *ab initio* line-intensity ratios [Science Advances 11, eadz6560 (2025)]. Keeping the experimental data and analysis procedure unchanged allows the contribution of the reference data to be isolated from other uncertainty sources. The updated line-intensity ratios improve the consistency of temperatures retrieved from different line pairs by an order of magnitude compared to the result reported in [Physical Review Letters 135, 103201 (2025)]; for seven out of nine line pairs, the statistical standard error of the mean (SEM) of retrieved temperatures is 1.3 mK. The weighted mean spectroscopic temperature agrees with the independently measured gas-cell temperature within a few mK. The combined standard uncertainty of the mean spectroscopic temperature is 19 mK (62 ppm at 296 K), with the dominant contribution arising from spectral line-shape modeling rather than reference line intensities.

1. Introduction

The redefinition of the International System of Units (SI) separated unit definitions, based on fixed fundamental constants, from their practical realizations, placing increased emphasis on the validation and uncertainty analysis of primary measurement methods [1]. In the case of thermodynamic temperature, methods that determine temperature directly from the thermal energy scale kT are now used for primary thermometry, shifting attention from calibration chains to the accuracy of the underlying physical models and reference data [2].

Spectroscopic thermometry in gases is a prominent example of this shift. Among optical primary thermometry methods, Doppler broadening thermometry (DBT) and rovibrational line-intensity-ratio thermometry (LRT) are widely studied because they enable contact-free temperature measurements with direct traceability to SI-defining constants [3–6]. In LRT, the gas temperature is inferred from the ratio of integrated spectral line intensities, which depends on temperature, primarily through the Boltzmann distribution of the population of molecular energy levels. As a result, LRT retrieves temperature from the thermodynamic energy scale kT and is therefore considered a primary thermometry method.

From a measurement perspective, LRT offers several practical advantages over DBT. Because it relies on integrated line areas rather than detailed line-shape analysis, LRT remains applicable at elevated pressures, where collisional effects complicate the retrieval of Doppler widths. Furthermore, the temperature sensitivity of the line-intensity ratio can be significantly enhanced by selecting transitions with a large difference in lower-state rotational energies, increasing robustness against random measurement noise. This enhanced sensitivity also enables the precise testing of the reference spectroscopic data used in temperature retrieval.

In particular, the accuracy of LRT critically depends on the reference line-intensity ratios employed to relate the measured intensity ratio to temperature. For absolute LRT, these reference ratios are typically obtained from *ab initio* molecular calculations and constitute an essential element of the traceability chain in spectroscopic thermometry. Any systematic error in the reference line intensities propagates into the inferred temperature, independently of experimental precision. Despite this, the influence of uncertainties and potential biases in reference spectroscopic data on LRT-based temperature measurements has received comparatively limited experimental scrutiny.

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In our previous work [7], we demonstrated a high-precision implementation of LRT using frequency-based cavity mode dispersion spectroscopy (CMDS) [8] of carbon monoxide, obtaining highly reproducible measurements of rovibrational line intensities. The spectroscopic temperatures inferred from these measurements, however, showed a clear deviations from the temperature measured by a calibrated contact thermometer, dependent on the choice of rovibrational lines. Uncertainty analysis confirmed that experimental effects and data processing uncertainties could not account for this discrepancy, indicating that limitations in the reference line-intensity ratios were a likely dominant source of systematic error.

In the present study, we revisit the same experimental dataset as in our earlier work [7] and perform new data analysis. Specifically, we replace the previously used reference line-intensity ratios with a newly published set of *ab initio* calculations, verified against ultra-accurate line-intensity ratios measured using dual-wavelength CMDS [9]. This strategy allows us to isolate the contribution of the reference spectroscopic data to the overall temperature measurement result. With these updated reference data, the temperature values from different line pairs are approximately an order of magnitude closer to each other and to the independently measured contact-thermometer temperature.

These results demonstrate that the dominant limitation in the earlier LRT-based temperature measurements originated in the reference spectroscopic data rather than in the experimental method itself. From a measurement science standpoint, this finding highlights the importance of critically assessing theoretical input data in primary thermometry and quantifies their impact on measurement bias and traceability. More broadly, the present work illustrates how improvements in reference spectroscopic parameters can directly enhance the accuracy of spectroscopic temperature measurements and provides experimental guidance for the use of LRT in practical thermometric applications.

2. Principle and experimental method

The spectral line intensity at given temperature, $S(T)$, depends on thermal energy, kT, [10]

$$S(T) = S(T_r)\,\frac{Q(T_{\mathrm{ref}})}{Q(T)}\,\frac{e^{-E''/(kT)}\left[1-e^{-h\nu/(kT)}\right]}{e^{-E''/(kT_r)}\left[1-e^{-h\nu/(kT_r)}\right]} \tag{1}$$

Here, E'' is the lower-state energy, ν is the transition frequency, T_r is an arbitrary reference temperature, k is the Boltzmann constant, h is the Planck constant, and $Q(T)$ is the total internal partition function at temperature T for a given molecule. Taking the ratio $R_S = S_b/S_a$ of two line intensities, S_a and S_b, involving different rotational energy states, one obtains an equation for the temperature of the gas sample [5,7],

$$T = \frac{\Delta E''}{k\,\ln[R_S/\xi(T)]}\,, \tag{2}$$

in which $\xi(T)$ is specific to the used molecular transitions,

$$\xi(T) = R_S(T_r)\,e^{-\Delta E''/(kT_r)}\,\frac{1-e^{-h\nu_a/(kT_r)}}{1-e^{-h\nu_b/(kT_r)}}\,\frac{1-e^{-h\nu_b/(kT)}}{1-e^{-h\nu_a/(kT)}}\,, \tag{3}$$

where ν_a and ν_b are the transition frequencies, and $\Delta E'' = E''_a - E''_b$. For overtone transitions, such as CO (3-0) band lines and temperatures up to several hundred kelvins, the induced emission is negligibly small and $\xi(T)$ can be well approximated by a constant value,

$$\xi \approx R_S(T_r)\,e^{-\Delta E''/(kT_r)}. \tag{4}$$

A key advantage of LRT is that the temperature sensitivity of the measured line-intensity ratio can be tailored through the choice of spectral lines. The sensitivity, η, of the LRT, defined as a ratio of fractional changes of R_S and T, depends on the lower-state energy difference $\Delta E''$,

$$\eta = \frac{\mathrm{d}R_S/\mathrm{d}T}{R_S/T} \approx -\frac{\Delta E''}{kT}. \tag{5}$$

Therefore, a trade-off between high sensitivity and a large difference in the line intensities must be considered to minimize LRT uncertainty. Alternatively, each line can be measured at different gas pressures to minimize the integrated line-area uncertainties as demonstrated in [7]. Such an approach relies on the linearity of the gas pressure measurement.

Our spectroscopic dataset [11] used for LRT [7] covers ten lines of the CO (3-0) band measured using CMDS; i.e., the dispersive molecular line shapes are obtained from the measured cavity mode resonant frequencies shifted by molecular lines. This dispersive mode frequency shift $\Delta\nu_d$ is associated with line intensity, S, and gas concentration, n, by the relation [8,12]

$$\Delta\nu_d(\nu-\nu_0) = (4\pi n_0)^{-1}\,n\,S(T)\,\Phi_I(\nu-\nu_0)\,, \tag{6}$$

where ν_0 is the line center frequency, n_0 is the non-resonant broadband gas sample refractive index, and $\Phi_I(\nu-\nu_0)$ is the imaginary part of the complex line shape model. Each line was measured at $T_{\mathrm{cell}} = 296.00(3)$ K and at three to five pressures, selected from a range (0.05–20) kPa to maximize the signal-to-noise ratio. The actively-stabilized gas cell temperature, T_{cell}, was measured using three 10-kΩ thermistors placed along the cell and calibrated to a reference-grade thermometer traceable to SI, with an expanded (2σ) uncertainty of 2 mK at 296 K. Details of the experimental setup are given in Refs. [7,11].

3. Data analysis procedure

Advancing the accuracy of spectroscopic approaches to thermometry requires a proper description of the spectral line shapes, as was indicated in the case of DBT [13–15] and LTR [7,16,17]. Use of molecular transitions requires analysis, which includes speed-dependence of collisional broadening and shifting [18,19] as well as velocity changing collisions [20,21] simultaneously [22,23]. The satisfactory compromise between adequate description of physical process forming spectral line shape and the efficiency of line profile evaluation was reached [23–25] using the hard collision model [21,26] for description of velocity changing collisions and quadratic speed dependence of collisional broadening and shifting [19,27]. Such a description, called the Hartmann–Tran profile (HTP) [25,28,29] is especially attractive because it can be improved by introduction correction [30,31] based on comparison with a more physically accurate speed-dependent billiard-ball profile (SDBBP) [12,32,33]. Finally, line intensity determination could be affected by the nonlinearity of line area with pressure induced by the nonimpact effects [34,35], as well as line-mixing going beyond first-order approximation [36–38], however, these effects do not play a noticeable role in our study [7].

To determine the integrated line areas, the CMDS spectra of the CO (3–0) band were fitted using HTP [25,28], which accurately reproduces the experimental spectra at signal-to-noise ratios ranging from 6000 to 19,000. There was no need to use the correction described in Refs. [30, 31]. The high linearity of the gas pressure sensor enabled us to convert the fitted line areas, measured at different pressures, into line-intensity ratios. This linearity was independently confirmed by spectroscopic means, with a standard deviation of 0.023% [7]. For LRT, nine line ratios, R_S, were selected; each measured line was paired with that leading to the highest temperature sensitivity, η (between 3.9 and 7.6). Spectroscopic temperatures for every experimental R_S were calculated using Eqs. (2) and (4) in which $\Delta E''$ were taken from HITRAN [10] and the reference $R_S(T_r)$ were taken from *ab initio* calculations described in the next section.

4. Reference line-intensity ratios

In our previous LRT [7], we used *ab initio* absolute line intensities of CO (3-0) band published in Ref. [39] (which we refer to as UCL2022) as a reference. They were experimentally validated independently in several laboratories [11,39], with sub-promille uncertainty

level, comparable to the level of agreement between different experimental results. In the present reanalysis of the LRT experiment, we use line intensity ratios published in Ref. [9] (which we refer to as UCL2025), in which they were verified against ultra-accurate line intensity ratios measured using dual-wavelength CMDS and having relative standard uncertainties at a 0.003% level. These new *ab initio* line ratios agree with the experimental ratios at a 0.02% level [9]. However, we note that the new *ab initio* calculations, contrary to the previous one [39], exhibit a systematic bias of about 0.7%, relative to the experimental results of [11,39]. Such a common multiplicative bias does not limit LRT, which depends on the ratio $R_S = S_b/S_a$. Writing the calculated intensities as $S_a^{\text{calc}} = (1+\epsilon_a)S_a$, and $S_b^{\text{calc}} = (1+\epsilon_b)S_b$, gives

$$R_S^{\text{calc}} = R_S \frac{1+\epsilon_b}{1+\epsilon_a}. \tag{7}$$

Therefore, a common error, $\epsilon_a = \epsilon_b$, cancels exactly, whereas for small transition-dependent errors the relative error of the calculated line-intensity ratio,

$$\frac{\delta R_S}{R_S} \simeq \epsilon_b - \epsilon_a. \tag{8}$$

For example, biases of +0.71% and +0.69% in two absolute line intensities correspond to an error of only approximately 0.02% in their ratio. This illustrates why the UCL2025 calculations can provide more accurate line-intensity ratios despite a larger common bias in the absolute intensities.

The effect of an error in the reference line-intensity ratio on the retrieved temperature can be estimated directly from the LRT sensitivity defined in Eq. (5). For small deviations, $\delta T/T \approx \delta R_S/(\eta R_S)$. For the line pairs used here, $|\eta| = 3.9 - 7.6$, so that at 296 K a 0.1% error in R_S corresponds to a temperature error of approximately 39 – 76 mK. In comparison, a 0.02% error in R_S, corresponding to the reported level of agreement of the UCL2025 ratios with experiment [9], gives approximately 8–15 mK. This illustrates quantitatively why relatively small transition-dependent errors in the reference ratios can lead to the temperature discrepancies observed in LRT.

As it could be seen from the results of [9] and this paper, UCL2025 calculations are significantly more accurate for the theoretical evaluation of the line intensities ratio, than UCL2022. As it was described in [9,39], the calculation of UCL2025 intensities used significantly lower level of quantum chemical theory to calculate the DMC of CO molecule, than UCL2022. This behavior indicates a substantial cancellation of common theoretical errors in the calculated line intensities, leading to a significantly higher accuracy of relative intensities than of their absolute values. We conclude from it that on one hand unless the full convergence of all factors in the calculations is achieved, different *ab initio* models have to be tried when the corresponding experimental accuracy requires it. On the other hand we continue our work of the inclusion of all factors presently omitted, like full allowance for the relativistic corrections, non-adiabatic corrections and recent improvements of the Davidson size extensivity corrections [40] and some other minor corrections which will explain the presently observed cancellation of errors.

5. Results and uncertainty analysis

Fig. 1 compares spectroscopic temperatures measured using LRT with the UCL2022 reference reported in [7] and new temperature results obtained from the same experimental data and the UCL2025 reference. The new results show a temperature consistency between line pairs that is over an order of magnitude higher than the previous results. To compare repeatability of the T_{LRT} obtained from different rovibrational lines pairs we use the statistical standard error of the mean T_{LRT}, defined as a ratio of the standard deviation to the square root of the number, N, of T_{LRT} results from different line pairs, SEM = $\sigma/\sqrt{N}$. With UCL2025, the SEM is 6 mK for all data points and 1.3

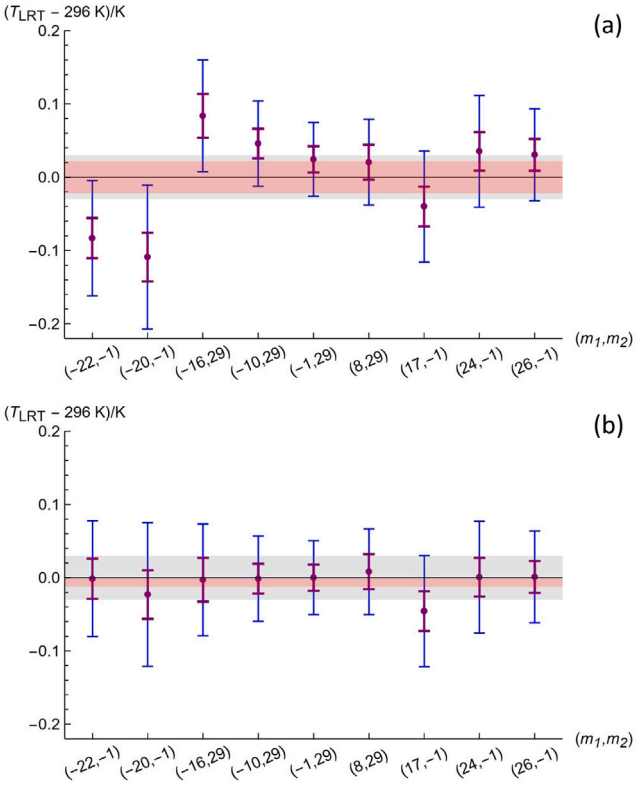


Fig. 1. Differences between spectroscopic gas temperature, T_{LRT}, and the reference temperature of the gas cell (T_{cell} = 296.00(3) K) for different spectral line pairs (m_1/m_2) obtained with: UCL2022 *ab initio* line ratios (panel a), and UCL2025 *ab initio* line ratios (panel b). The m index equals $-J''$ and $J''+1$ for the P and R branch lines, respectively, where J'' is the lower-state rotational quantum number. The error bars correspond to combined (blue) and statistical (purple) standard uncertainties. The colored bands correspond to the ± statistical standard error of the mean (SEM) of T_{LRT} (red), and the combined standard uncertainty of T_{cell} (gray).

mK for 7 out of 9 data points, while with UCL2022, the SEM was 22 mK. This result clearly shows that the main repeatability limitation of the previous result [7] was the reference line intensities. The absolute temperature differences between the mean spectroscopic and a gas cell temperature T_{cell} and their statistical standard uncertainties are (-7 ± 9) mK for all nine line pairs and (-2 ± 9) mK for seven line pairs, which are well below the 30 mK standard uncertainty of the T_{cell}.

The complete uncertainty budget of spectroscopic temperature is shown in Table 1. The first three uncertainty components are identical to those reported in Ref. [7], where they were evaluated. In contrast, the previously dominant contribution arising from the reference line intensities decreases from up to 0.28×10^{-3} for the UCL2022 reference to 0.039×10^{-3} for the UCL2025 reference, and thus becomes nearly negligible in the present uncertainty budget. As a result, the largest systematic uncertainty component is now associated with the spectral fitting and modeling. This contribution is a conservative combined estimate encompassing both residual experimental structures, primarily weak etalon fringes, and possible imperfections of the fitted Hartmann–Tran line-shape model [25]. The HTP reproduces the present spectra at signal-to-noise ratios of 6000–19,000, and no improvement requiring the SDBBP-based correction discussed in Refs. [30,31] was found necessary. Therefore, the present uncertainty budget does not allow the contributions from residual experimental structure and line-shape-model inadequacy to be separated unambiguously. However, the corresponding errors in line-area ratios are expected to differ among transitions and therefore contribute largely as uncorrelated components

Table 1
Uncertainty components (1σ) of spectroscopic gas temperature measurements. The values (average over line pairs) correspond to T obtained from the two-line ratio, except for the "(all line pairs)", which correspond to the weighted mean from all used line pairs. The uncertainty of T_{cell} is used only for comparison of spectroscopic and contact-thermometer based measurements. The labels (A) and (B) denote uncertainty components evaluated using Type A statistical methods and Type B methods based on other available information, respectively.

Uncertainty component	$u(T)/T$ (10^{-3})
Line area fit (A)	0.036
Spectrum model (B)	0.160
A vs p linearity (A)	0.082
Reference S (B)	0.039
Stat. (one line pair)	0.089
Combined (one line pair)	0.186
Stat. (all line pairs)	**0.030**
Combined (all line pairs)	**0.062**
Reference T_{cell} (B)	0.11

to temperatures retrieved from different line pairs. Consequently, averaging over multiple line pairs effectively suppresses this uncertainty contribution. The final combined standard uncertainty of the mean T_{LRT} value, of 19 mK ($u(T_{LRT})/T_{LRT} = 62$ ppm) was therefore evaluated from the weighted mean of all line-pair temperatures, using weights equal to the inverse squared uncertainties of the temperatures obtained from the individual line pairs. We note here that the statistical and combined standard uncertainties of T_{LRT} averaged over all line pairs are smaller than individual uncertainty components for one line pair given in Table 1.

Fig. 1 shows that the observed scatter of the individual T_{LRT} values is substantially smaller than predicted by their combined standard uncertainties (blue error bars). This indicates that the uncertainty budget may be too conservative. A plausible explanation is the presence of correlations between line-intensity errors of the two transitions forming a given line pair, arising from common spectral-model imperfections. Such correlations would partially cancel in the line-intensity ratio, thereby reducing the actual uncertainty of the retrieved temperature. Further experimental studies would be required to quantify this effect.

6. Discussion

The results presented have several consequences for the spectroscopic primary thermometry. Contrary to fully experimental temperature difference measurements from line ratios at known and unknown T, the use of *ab initio* reference enables the primary thermometry method, i.e., from the definition of T without using any other reference thermometer. The LRT consistency of the results obtained from different rovibrational lines shows that *ab initio* UCL2025 can be treated as a reliable reference for thermometry with mK-level accuracy. It also shows prospects for further accuracy improvement by using more line pairs from both branches of the CO (3-0) band, because the dominant uncertainty component, associated with a spectrum modeling, becomes random for different line pairs. Contrary to DBT, achieving its best performance at very low gas pressures [41,42], LRT can be used in a much wider pressure range, which extends its applications in metrology and applied measurements, e.g. in fully optical primary gas pressure and concentration measurements [7] based on real-gas state equation and temperature-dependent absolute line intensities.

7. Conclusions

We demonstrated an improved implementation of primary line-ratio thermometry (LRT) using CO (3–0) band transitions measured with cavity mode dispersion spectroscopy. By reanalyzing previously reported spectra with newly available *ab initio* reference line-intensity ratios verified earlier against ultra-accurate dual-wavelength CMDS measurements, we isolated the influence of the reference spectroscopic data on the thermometric performance of LRT.

The updated UCL2025 reference data improved the consistency of spectroscopic temperatures obtained from different line pairs by more than an order of magnitude (except for one outlier) compared with the earlier UCL2022 reference. While millikelvin-level agreement between LRT temperatures derived from two line pairs was previously demonstrated in Ref. [9], the present results show that such agreement is maintained across seven independent line pairs spanning a wide range of rotational energies. The weighted mean spectroscopic temperature agrees with the independently measured gas-cell temperature within a few millikelvin, well below the uncertainty of the reference contact thermometer based result.

The uncertainty analysis shows that the previously dominant uncertainty contribution associated with reference line intensities becomes nearly negligible with the new dataset. The remaining dominant contribution is associated with spectral fitting and modeling, including residual experimental structures and possible line-shape-model imperfections and behaves largely as a random component for different line pairs, enabling uncertainty reduction through averaging over multiple transitions.

These results demonstrate that the main limitation of the earlier LRT realization originated from the reference spectroscopic data rather than from the experimental method itself. More broadly, the work highlights the importance of accurate theoretical spectroscopic line intensity parameters in primary thermometry and confirms the strong potential of LRT for precision thermometry and optical gas metrology.

CRediT authorship contribution statement

Daniel Lisak: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Szymon Wójtewicz:** Writing – review & editing, Methodology, Investigation. **Agata Cygan:** Writing – review & editing, Methodology, Investigation. **Piotr Wcisło:** Writing – review & editing, Methodology, Investigation. **Roman Ciuryło:** Writing – review & editing, Methodology, Investigation. **Oleg L. Polyansky:** Writing – review & editing, Methodology, Investigation. **Nikolai F. Zobov:** Writing – review & editing, Methodology, Investigation. **Jonathan Tennyson:** Writing – review & editing, Methodology, Investigation. **Katarzyna Bielska:** Writing – review & editing, Methodology, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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