

Optical Determination of Thermodynamic Temperatures from a C₂H₂ Line-Doublet in the Near Infrared

Antonio Castrillo, Eugenio Fasci, Hemanth Dinesan, Stefania Gravina, Luigi Moretti, and Livio Gianfrani*

Dipartimento di Matematica e Fisica, Università della Campania “Luigi Vanvitelli”, Viale Lincoln 5, 81100 Caserta, Italy



(Received 2 April 2019; revised manuscript received 27 May 2019; published 25 June 2019)

This paper reports the implementation of Doppler-broadening gas thermometry by use of line-shape analysis of a line-doublet. The two spectral components are vibration-rotation transitions belonging to a pair of acetylene combination bands at a wavelength of 1.39 μm . Characterized by an extraordinary spectral fidelity in combination with high resolution, the spectrometer is based on two phase-locked extended-cavity diode lasers, one of them being referenced to an optical-frequency-comb synthesizer. The global analysis of 1180 spectra, which are recorded as a function of the C₂H₂ pressure at the constant temperature of the triple point of water, yields an optical determination of the thermodynamic temperature with a combined relative uncertainty (type A plus type B) of 23 parts per million. Similar results are obtained at the melting point of gallium (approximately 303 K). Furthermore, we apply line-absorbance analysis to the acquired spectra, demonstrating a reduction by a factor of approximately 6 of the statistical uncertainty for the retrieved gas temperature.

DOI: [10.1103/PhysRevApplied.11.064060](https://doi.org/10.1103/PhysRevApplied.11.064060)

I. INTRODUCTION

In November 2018, the 26th General Conference on Weights and Measures (CGPM) unanimously approved new definitions of four base units (kilogram, ampere, kelvin, and mole) in terms of fixed values of fundamental physics constants (the Planck constant, the elementary electric charge, the Boltzmann constant, and the Avogadro constant, respectively). In particular, the new kelvin (the unit of thermodynamic temperature) is based on the following value of the Boltzmann constant k_B : 1.380649×10^{-23} J/K. Reviews of experiments performed worldwide in the last 10 years and relevant for setting the k_B value are provided in Refs. [1,2]. Very recently, research efforts of the international community working in the field of primary gas thermometry have been devoted to the direct realization of the redefined kelvin [3]. In this respect, acoustic gas thermometry and dielectric-constant gas thermometry have been further developed to measure $T - T_{90}$ over a range of temperatures, $T - T_{90}$ being the difference between the thermodynamic temperature and that resulting from the International Temperature Scale of 1990 (ITS-90) [4–6]. Within this framework, Doppler-broadening thermometry (DBT) is widely recognized as a valuable tool for a cross-check with other methods, even though it has not reached yet the same level of accuracy as acoustic gas thermometry and dielectric-constant gas thermometry [7].

DBT consists of retrieving the thermodynamic temperature from the highly accurate observation and analysis of the shape of a given atomic or molecular line in a gas at thermodynamic equilibrium. It exploits the physical relation between the thermodynamic temperature and the Doppler width of an optical absorption line, given by

$$\Delta\nu_D = \frac{\nu_0}{c} \sqrt{2 \ln 2 \frac{k_B T}{M}}, \quad (1)$$

where $\Delta\nu_D$ is the half width at half maximum, ν_0 is the line central frequency, c is the speed of light in a vacuum, and M is the atomic or molecular mass. The history of DBT starts with the proposals of Bordé [8,9], followed by pioneering work on ammonia and carbon dioxide [10,11]. One of the most-accurate implementations of DBT involved an isolated vibration-rotation transition of a water isotopologue (H₂¹⁸O) at 1.39 μm and yielded an optical determination of the Boltzmann constant with a combined uncertainty of 24 parts per million (ppm) [12].

In this paper, we report the development and application of an optical apparatus acting as a primary thermometer based on Doppler-broadened precision spectroscopy of acetylene in the near infrared. This third-generation spectrometer, following those reported in Refs. [11,12], gives a primary realization of the redefined kelvin.

Acetylene has already been used as molecular target for the aims of DBT, as highlighted in Ref. [7]. In particular, Hashemi *et al.* [13] probed the P(25) line of the

*livio.gianfrani@unicampania.it

C_2H_2 $\nu_1 + \nu_3$ band at $1.5 \mu\text{m}$ to perform a spectroscopic determination of k_B with a global uncertainty of 87 ppm. The frequency scale of the absorption spectrum, which was obtained by use of a Fabry-Perot interferometer in conjunction with a wavelength meter, was one of the main factors limiting the accuracy of this experiment. The spectral analysis made use of the so-called speed-dependent Voigt profile (SDVP), accounting for the narrowing effect that is due to the speed dependence of collisional broadening [14].

The line-shape model is a limiting factor for DBT [7,15]. Because of the complexity of *ab initio* line-shape calculations for colliding molecules, one should resort to simplifications and approximations to implement a model into a fitting routine. To overcome this issue, at least partially, one could resort to cavity ring-down spectroscopy so that it would be possible to investigate the low-pressure regime (at the pascal level) and limit as much as possible the influence of collisions, while preserving the advantage of the near-infrared spectral region [16,17]. Alternatively, the thermometric substance can be a low-pressure atomic vapor system, such as rubidium or cesium. In this case, collisional perturbations of the absorption profile can be totally ignored, since the vapor pressure can be extremely small (on the order of 10^{-4} Pa) [18,19]. On the other hand, saturated absorption may occur, thus adding some complexity to the analysis of the spectral profile.

Another option to mitigate the line-shape problem, as described in Ref. [20], consists in using a multispectrum

fitting procedure (MFP) to implement physical constraints between preselected parameters during nonlinear least-squares analysis of a set of spectra across a given pressure range. In this respect, the present paper provided a step forward in DBT since the MFP is applied to the shape of a well-resolved line-doublet. The two C_2H_2 lines can share the thermal energy [namely, the quantity $k_B T$ that enters Eq. (1)] while presenting different collisional widths and shifts, a circumstance that leads to a strong physical constraint in the MFP analysis of a set of spectra as a function of the gas pressure. Thus, temperature metrology is demonstrated with a precision of 22 ppm. Moreover, we apply line-absorbance analysis to the line-doublet. This method exploits the relationship between the line-center absorbance and the integrated absorbance to retrieve the Doppler width of a spectral line from a set of profiles at different gas pressures [21]. Comparison between the results of the two approaches suggests that line-absorbance analysis could be preferred because of the smaller statistical uncertainty.

II. EXPERIMENTAL APPARATUS

A schematic diagram of the DBT spectrometer is depicted in Fig. 1. Essentially, it consists of a probe laser (PL), a frequency-stabilization, measurement, and control unit [including a reference laser (RL) and an

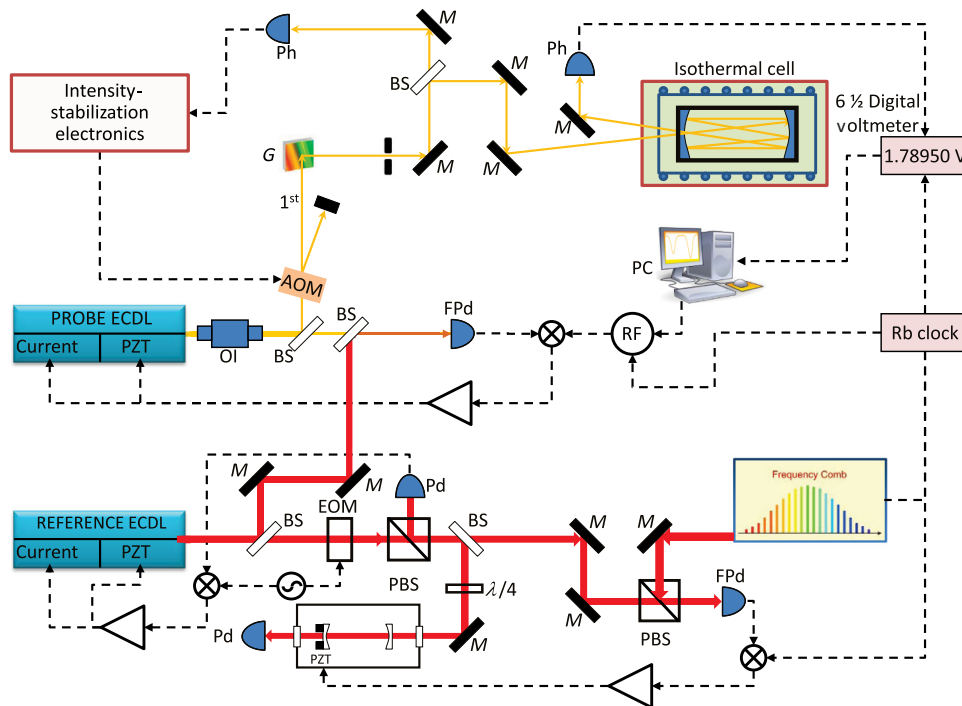


FIG. 1. The experimental setup. BS, beam splitter; EDCL, extended-cavity diode laser; EOM, electro-optic modulator; FPD, fast photodiode; G, diffraction grating; M, mirror; OI, optical isolator; PBS, polarizing beam splitter; PC, personal computer; Pd and Ph stand for photodiode; PZT, piezoelectric transducer; RF, radio-frequency synthesizer.

optical-frequency-comb synthesizer (OFCS)], an intensity-stabilization feedback loop, an isothermal cell, and an acquisition chain.

The PL is an extended-cavity diode laser with an emission wavelength in the range between 1.38 and 1.41 μm , covering well-known vibrational bands of acetylene [22]. An optical phase-locking (OPL) loop guarantees effective PL narrowing, along with precise control of the laser frequency, as explained elsewhere [23]. For this purpose, the PL emission frequency is compared with that of the RL, the beat note being detected by a fast photodiode. The frequency offset, f_{rf} , between the PL and the RL is provided by a radio-frequency synthesizer, which in turn is phase-locked to a Rb clock.

The reference laser consists of an extended-cavity diode laser that is tightly locked to a high-finesse cavity by means of the Pound-Drever-Hall technique. It has an emission width of about 10 kHz over a 1-ms observation time [24]. In turn, the high-finesse cavity is weakly locked to a self-referenced OFCS (model FC1500-250-WG, Menlo Systems). This further technical expedient ensures an absolute frequency scale for the acquired spectra. It also enables us to correct for possible frequency drifts of the high-finesse cavity during the spectral acquisitions. Thus, the beat note between the RL and the nearest tooth of the OFCS is properly processed to generate a correction signal that actively controls the length of the high-finesse cavity through a piezoelectric actuator.

The in-loop relative stability of the beat note is 2.7×10^{-7} for an integration time of 1 s as determined from a modified Allan deviation analysis whose results are shown in Fig. 2. The upper part of Fig. 2 shows the fluctuations of the beat-note frequency (f_{beat}) over a time span of about 5 h. In the lower part, the modified Allan deviation plot exhibits a trend that is typical of a white-type phase noise

for integration times of less than 1 min. What is more important is the absence of any drift for about 1 h. Obviously, this study cannot be sensitive to possible frequency drifts of the Rb clock to which the OFCS is referenced. The RL absolute frequency, f_{RL} , can be determined from the equation $f_{\text{RL}} = N \times f_{\text{rep}} \pm f_{\text{ceo}} \pm f_{\text{beat}}$, where N is the comb-tooth order, f_{rep} the repetition rate (250 MHz), and f_{ceo} the carrier-envelope offset frequency (20 MHz). The correct signs could be easily determined by slightly changing f_{rep} and f_{ceo} while observing the consequent variation on the beat-note frequency. The relative stability of the RL frequency with respect to the OFCS is 2×10^{-14} at 1 s.

The comb-referenced dual-laser approach is preferred to direct phase locking of the probe laser against the OFCS since the width of each comb tooth is about 120 kHz against the 10 kHz width of the reference laser.

Highly linear and accurate frequency scans of the PL around a given central frequency are done by tuning, step by step, the rf offset frequency, f_{rf} . The absolute frequency of the probe laser can be determined as follows: $f_{\text{PL}} = f_{\text{RL}} + f_{\text{AOM}} \pm f_{\text{RF}} = N \times f_{\text{rep}} \pm f_{\text{ceo}} \pm f_{\text{beat}} + f_{\text{AOM}} \pm f_{\text{rf}}$, where f_{AOM} is the radio frequency (of about 80 MHz) driving the acousto-optic modulator (AOM). In our configuration the scan width is approximately 4.4 GHz and results from 786 steps of 5.6 MHz each, with a step-by-step acquisition time of 100 ms. The scan width is close to the maximum value (approximately 5 GHz) that is allowed by the OPL loop to maintain the phase-lock between the two lasers. The AOM is used as an actuator within an intensity-control feedback loop that stabilizes the PL power. Two low-noise In-Ga-As detectors are used: one of them produces the reference signal entering the intensity-stabilization loop, while the other monitors the output beam from the isothermal cell. This latter has a first-order low-pass filter with a 3-dB point at 320 Hz. A $6\frac{1}{2}$ -digit voltmeter, connected to a personal computer, is used for data acquisition with the required levels of linearity and accuracy.

A portion of the first-order AOM-diffracted beam, with an optical power that does not exceed 50 μW , is sent to a spherical, Herriott-type, multiple-reflection cell, where laser-gas interaction occurs. The multipass cell is built entirely from stainless steel, with electropolished inner and outer surfaces. The optical path length is variable between 6 and 12 m in a volume of about 400 cm^3 . Two capsule-type standard platinum resistance thermometers (SPRTs) are placed at 180° to each other, at the front and rear ends of the cell. Calibrated at the National Institute for Research in Metrology, the two SPRTs are used for temperature control and measurement. The cell's temperature is actively stabilized by a sophisticated system that is similar to that described in Refs. [25,26]. To guarantee acoustic and thermal insulation, the multipass cell is housed inside a cylindrical vacuum chamber. Temperature stability (as determined over one full day at any temperature between

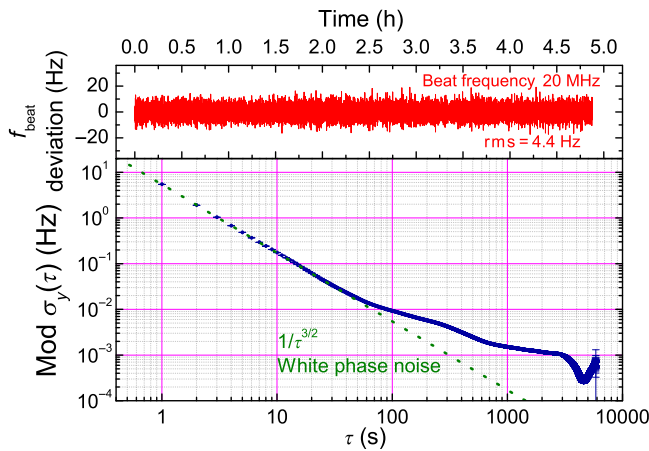


FIG. 2. RL-OFCS beat-note-frequency (f_{beat}) fluctuations (upper panel), and modified Allan deviation as a function of the integration time for the time series reported in the upper panel (lower panel).

the triple point of water and the melting point of gallium) is on the order of 0.1 mK, while temperature homogeneity is better than 1 mK. A 100-Torr capacitance manometer measures the gas pressure inside the cell with an accuracy of 0.25% of the reading. The acetylene sample is in a commercial bottle with a quoted concentration of 99.6%. A turbomolecular pump is used to periodically evacuate the isothermal cell and create high-purity conditions.

III. RESULTS AND DISCUSSION

Acetylene is a centrosymmetric, linear, nonpolar molecule with five fundamental modes of vibration. It shows interesting absorption features at $1.39 \mu\text{m}$ that are due to combination vibrational bands [22]. Details about the selected line pair are given in Table I. This doublet is a good choice for the aims of DBT. Firstly, the frequency separation is sufficiently large to resolve the doublet but, at the same time, small enough such that it is possible to acquire the tails of the two lines within a frequency span of up to approximately 5 GHz. Also, the collisional width at C_2H_2 pressures between 10^2 and 10^3 Pa is expected to vary in the range from 4 to 40 MHz. Therefore, it is significantly smaller than the frequency separation of the two lines (approximately 2 GHz). This condition should be sufficient to ignore the collisional mixing effect between the two lines due to population exchanges caused by inelastic collisions [28]. The occurrence of this effect would imply that the absorption spectrum from the line-doublet could not be considered as the superposition of two isolated line shapes.

Transmission spectra were acquired at the constant temperatures of the triple point of water (T_0) and the melting point of gallium (T_1) for many different values of the sample pressure (59 at T_0 and 73 at T_1) in the range between 60 and 1100 Pa. For each pressure, 20 repeated acquisitions were performed. Example spectra are shown in Fig. 3.

A. Spectral analysis

One of the major efforts of this work is the simultaneous analysis of a manifold of experimental profiles. A nonlinear least-squares fitting code is developed within the MATLAB environment with use of the Levenberg-Marquardt optimization algorithm. The spectra are compared with the following function:

$$P(\nu) = (P_0 + P_1\nu)e^{-[A_P(g(\nu-\nu_{0P})+Rg(\nu-\nu_{0R}))]}, \quad (2)$$

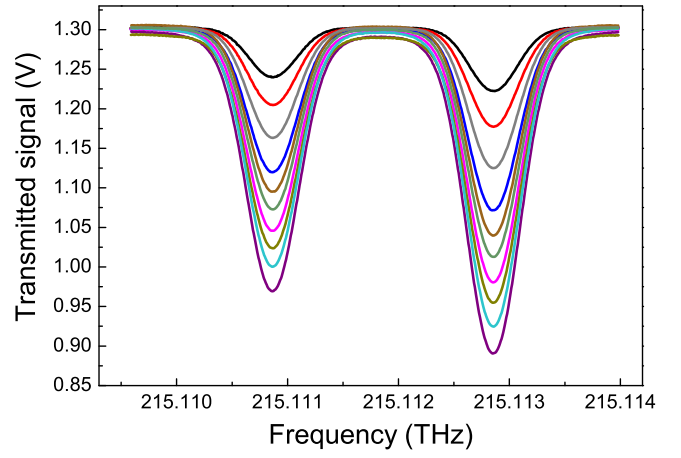


FIG. 3. Example of absorption spectra for the R(15) and P(17) transitions acquired as a function of the gas pressure at the triple point of water. The x axis represents the absolute frequency as measured by means of the OFCS.

where $g(\nu - \nu_{0X})$ is the line-shape function (the subscript X standing for either R or P), the parameters P_0 and P_1 take into account a possible residual variation of the PL power, ν is the PL frequency, ν_{0R} and ν_{0P} are the central frequencies of the R(15) and P(17) lines, respectively, A_P is the integrated absorbance for the P(17) line, and R is the line-intensity ratio of the doublet, namely, $S_{R(15)}/S_{P(17)}$. We use the partially correlated quadratic speed-dependent hard-collision profile [29], in which the speed dependence of collisional broadening and shifting is considered in a quadratic form [30]. Also known as the ‘‘Hartmann-Tran profile’’ (HTP), this model has been proposed as a sort of universal profile to be used for high-resolution spectroscopy in the gas phase [29,31]. The HTP model is sophisticated enough to consider the various collisional perturbations of an isolated C_2H_2 line, as already experienced elsewhere [23,32]. For the complete HTP equations, we refer the reader to Ref. [29]. In the MFP, we retain P_0 , P_1 , and A_P as free parameters that are characteristic of individual spectra, while ν_{0R} , ν_{0P} , γ_{0R} , γ_{0P} , δ_{0R} , δ_{0P} , and R are shared across spectra in the whole pressure range. Here γ_{0X} and δ_{0X} are the self-broadening and shifting parameters, respectively. Furthermore, in the HTP implementation, the Doppler width is written in the form of Eq. (1). Thus, it is possible to share the product $k_B T$ for the two lines across the spectra. This is a sort of twofold constraint that is expected to make DBT more robust and reliable. In fact, if

TABLE I. Spectroscopic parameters for the selected line pair as given by the HITRAN database [27].

Component	Vibrational band	Central frequency (cm^{-1})	Lower energy level (cm^{-1})	Self-broadening coefficient ($\text{cm}^{-1}/\text{atm}$)	Line strength ($10^{-23} \text{ cm}^2/\text{molecule}$)
R(15)	$\nu_2 + \nu_3 + \nu_5$	7175.326220	282.30150	0.135	2.660
P(17)	$2\nu_2 + \nu_4 + \nu_5$	7175.392570	359.90160	0.132	3.528

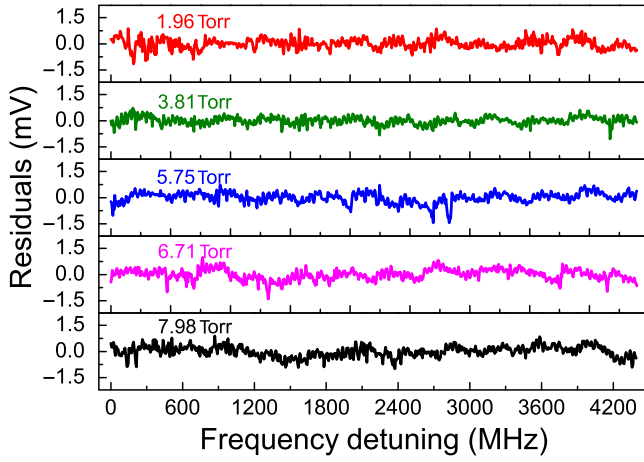


FIG. 4. Example of residuals resulting from the application of the MFP by use of the HTP model.

we consider the statistical correlation index of the thermal energy with γ_{0R} and γ_{0P} , we observe a reduction by a factor of approximately 4 as compared with Ref. [33], where the MFP was applied to numerically simulated profiles in coincidence with a single and isolated line.

Finally, six other parameters are shared among the spectra: the velocity-changing collision frequency per unit pressure (one parameter for each of the two lines, β_R and β_P) and the parameters accounting for the quadratic speed dependence of the collisional width and shift of each line. The parameter η , taking into account the partial correlation between velocity- and phase-changing collisions, is fixed to a proper value, whose identification requires a detailed study, as explained in the next subsection. We anticipate that the best choice is $\eta = 0.029$ for all the spectra at either T_0 or T_1 .

In total, for those spectra acquired at the lowest temperature (T_0), the fitting procedure manages 191 parameters and 46 374 experimental points in the simultaneous analysis of 59 spectra, looking for the minimum of a global chi-squared function (χ^2) [20]. For the spectral analysis at T_1 , we have 233 parameters, 57 378 experimental points, and 73 spectra. Figure 4 shows a few examples of residuals, whose root-mean-square value amounts to about 0.2 mV at any pressure. This quantity provides an indication of the achieved signal-to-noise ratio, which ranges between 1000 and 6000 for the strongest line, limited by periodic modulations of the baseline. These modulations are due to spurious etalon effects. No signs of a collisional mixing effect or interfering lines are evidenced in the residuals.

B. Temperature determinations

The global analysis, which is applied to 20 sets of spectra, yields the spectroscopic determinations of the gas temperature that are plotted in Fig. 5. The weighted mean of these values gives 273.159(6) K, in perfect agreement

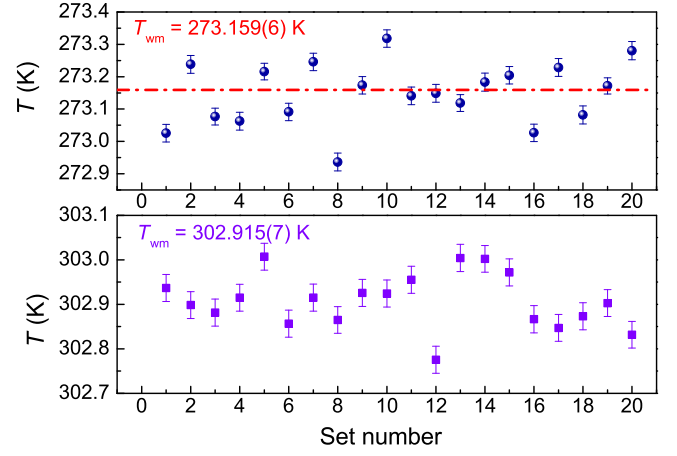


FIG. 5. The upper panel reports the spectroscopic determination of the thermodynamic temperature around the triple point of water. Each point is the output of the MFP that is applied to a set of 59 spectra, acquired as a function of the C_2H_2 pressure. The dashed line represents the weighted mean. Error bars correspond to one standard deviation. For a detailed explanation of the calculation of the uncertainty, the reader is referred to Refs. [20,33]. The lower panel reports the same as the upper panel but close to the melting point of gallium.

with the set point. More particularly, it agrees with the mean value of the SPRT temperatures that are recorded over the time span necessary for the spectral acquisitions (of about 1 month), namely, 273.1604(3) K. The same level of agreement is found near the melting point of gallium. Here the spectroscopic temperature is 302.915(7) K, while the SPRT temperature is 302.9135(3) K. The measurement precision is not sufficiently high to quantify the deviation from the ITS-90. In fact, the current estimate of $T - T_{90}$ at the melting point of gallium is 4.38 mK [34].

The residuals in Fig. 4 result from the use of the HTP model with $\eta = 0.029$. We test many other values of η in the interval between 0 and 0.2, each time applying the MFP to the same set of spectra. We carefully search for the η value leading to the minimum χ^2 . In the interval explored, the global chi-squared function shows a second-order polynomial dependence on η , with a minimum for the reduced χ^2 (namely, the chi-squared function per degree of freedom) of 1.078 for $\eta = 0.029 \pm 0.007$. We also test simplified models such as the SDVP and the speed-dependent hard-collision profile (SDHCP). At the triple point of water, the SDVP provides a thermodynamic temperature that is underestimated, namely, 273.141(6) K, as expected. This simplified model takes into account only the narrowing due to speed dependence, ignoring that associated with the Dicke effect. For the SDHCP, the results are quite close to the results we obtained, with a retrieved temperature of 273.160(6) K, with a relative deviation of 3.6 ppm, which is well within the type-B uncertainty

TABLE II. Uncertainty budget (in terms of relative contributions, corresponding to one standard deviation) related to the spectroscopic determination of the thermodynamic temperature.

Contribution	Type A (ppm)	Type B (ppm)
Reproducibility	22–23	
Frequency scale		< 2
Line central frequency		< 10^{-4}
Laser emission width		< 0.1
Optical saturation effects		Negligible
Detector nonlinearity		≈ 2
AM modulation effects		≈ 1
Hyperfine structure		Negligible
Line-shape model		7
Finite detection bandwidth		1.1
Relativistic effects		Negligible
Optical zero		< 0.2
Overall combined uncertainty	23–24	

associated with the line-shape model (of 7 ppm, as reported in Table II). Moreover, the SDVP and SDHCP did not provide the same performance as the HTP model, leading to a reduced χ^2 of 1.116 and 1.081, respectively. Another argument that confirms the optimum performance of the HTP model with $\eta=0.029$ is the retrieved value of the Dicke narrowing parameter, which is 0.473(3) and 0.304(2) MHz/Torr, respectively, for the R(15) and P(17) transitions at the temperature of the triple point of water. These values are reasonably smaller than the diffusive value resulting from kinetic theory (namely, 1.6 MHz/Torr at the temperature of the triple point of water). Moreover, $\beta - \eta\gamma$ is positive for each line, a circumstance that gives another indication about the optimum operation of the line-shape function [35]. It is worth noting that if η is treated as a free parameter, the results of the fitting procedure are not physically meaningful, since negative values for β_P , β_R , and η are returned.

As a result of the MFP, we also determine the line-strength ratio of the two transitions, which is 0.771866 at the temperature of the triple point of water, with a relative statistical uncertainty of 16 ppm. At the melting point of gallium, the measured ratio is 0.743082(8). This latter value is in good agreement with the value calculated with the data reported in the HITRAN database [27], the relative difference being on the order of 0.5%. Our determinations of R can be of interest for a first test of the line-strength-ratio thermometry method proposed by Santamaria *et al.* [36].

Table II provides the complete uncertainty budget for the spectroscopic determination of the thermodynamic temperature. In building this table, we obviously benefited from past experience regarding the various sources of type-B uncertainties (including systematical deviations) in the determination of the Boltzmann constant [37,38].

The most-important contribution is the statistical (type-A) uncertainty, which amounts to 22 ppm at T_0 and 23 ppm at T_1 . The signal-to-noise ratio on the beat note between the two lasers determines the uncertainty on the frequency scale, which is smaller than 2 ppm. The uncertainty associated with the line central frequency is significantly smaller than 10^{-10} because of the use of the OFCS technology. For the laser emission width, the use of the OPL technique made it possible to reduce this contribution to the level of 0.1 ppm. Optical saturation, hyperfine structure, and relativistic effects are found to be fully negligible. As reported in Ref. [38], the contribution from detector nonlinearity and amplitude modulation (AM) of the baseline (arising from spurious etalon effects) amounts to about 2×10^{-6} and 1×10^{-6} , respectively. The influence of out-of-resonance radiation transported by the probe laser, which may lead to a difference between the optical zero and the electrical zero of the detector, contributes a negligible amount. The unavoidably limited bandwidth of the detection chain should be considered, according to the findings in Ref. [39]. Particularly, one can easily calculate that the scan rate of 56 MHz/s, in conjunction with the filter time constant of 4 ms (which results from a first-order low-pass filter with -6 dB per octave roll-off), leads to an extra broadening and, consequently, to a temperature shift of 1.1 ppm. Finally, the uncertainty associated with the line-shape model is 7 ppm. To make this estimate, we determine the variation of the mean temperature associated with the uncertainty on the η value. Systematic deviations due to the possible occurrence of collisional line-mixing effects are negligible, as obtained from the application of the multispectrum fitting procedure to numerically simulated spectra in which realistic line-mixing coefficients are used, their values being close to those in Ref. [28] for transitions involving similar rotational quantum numbers.

C. The line-absorbance method

According to the Lambert-Beer law, the absorbance at the line center, in coincidence with a given spectral line, is $\delta = Ag(0)$, where $g(0)$ is the line-shape function calculated at the line central frequency. Whatever model describes the absorption profile, the quantity $g(0)$ depends on the collisional width of the line and, consequently, on the molecular density, N . Since the integrated absorbance is proportional to N , a Taylor expansion of $g(0)$ in terms of the variable A can be performed. Therefore, it is possible to write the following equation [21]:

$$\delta = A(c_0 + c_1A + c_2A^2 + c_3A^3 + c_4A^4 \dots). \quad (3)$$

At very low pressures, close to the zero value, the profile function of any molecular vibration-rotation transition reduces to a Gaussian function, provided that the natural width is sufficiently small. This is surely the case for a spectral component of an overtone or combination

vibrational band. In this limit, the relationship between δ and A reduces to

$$\delta = A \frac{1}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}}. \quad (4)$$

If we compare Eq. (3) with Eq. (4), it is possible to conclude that c_0 is inversely proportional to the Doppler width. Consequently, a polynomial fit of experimental absorbance data enables one to retrieve the Boltzmann constant or the thermodynamic temperature. Experimental absorbance data for each of the two acetylene lines are plotted in Fig. 6 for all the spectral acquisitions. We perform a fourth-order polynomial fit to retrieve the Doppler width of each line, from which the temperature can be determined. More particularly, 20 polynomial fits are simultaneously performed for each line, sharing the c_0 coefficient from Eq. (3). The weighted mean of the two values is 302.9133(11) K, which is surprisingly close to the ITS-90 value. The statistical uncertainty is roughly 4 ppm, namely, a factor of 6 smaller than that of conventional DBT, which is a quite-remarkable result. Similarly, the results are very promising at the triple point of water, where the line-absorbance method yields 273.1591(18) K, which is in perfect agreement with the set point. For the polynomial order of the fit in Fig. 6, it is worth noting that the change in the reduced χ^2 that results from the addition of the fifth-order term is not statistically significant, as clearly indicated by an F -test performed with a confidence level of 5%.

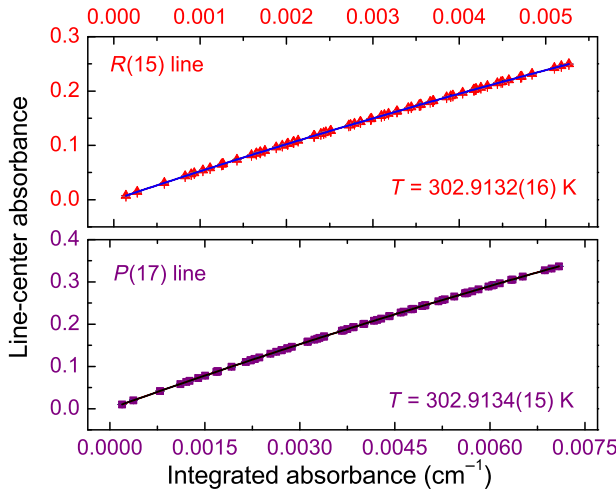


FIG. 6. The upper panel shows line-center absorbance data plotted as a function of the integrated absorbance. Data are retrieved from the MFP applied to the spectral acquisitions at the melting point of gallium at different C_2H_2 pressures for the R(15) line. Fourth-order polynomial fits, forced to pass through zero, yield the value of $\Delta\nu_D$ according to Eq. (4). Repeating the fits with a fifth-order polynomial, the c_4 coefficient turns out to be consistent with zero. The lower panel shows the same as the upper panel but for the P(17) transition.

The complete uncertainty budget for the line-absorbance method requires a specific study that will be the subject of future work. Here we anticipate that the most-important component is the line-shape model. Similarly to what was described in the previous subsection, the line-shape contribution is given by repeating the absorbance analysis for the datasets that result from η values in the range from 0.022 and 0.036. The corresponding variation of the retrieved temperature is 6 ppm.

IV. CONCLUSIONS

In conclusion, we report a significant step forward for low-uncertainty Doppler-broadening gas thermometry. Firstly, the use of a line-doublet rather than a single and isolated line is a good choice since it provides a strong physical constraint for the thermal energy, thus reducing statistical correlation issues. The third-generation spectrometer described in this paper shows many improvements as compared with previous implementations: use of a phase-locking loop; calibration of the frequency axis by means of a self-referenced optical frequency comb; a more-advantageous molecular target; adoption of a more-refined line-shape model and fitting procedure. As a result, the uncertainty budget shows type-B components that are significantly smaller than those in Ref. [38]. Thermodynamic temperature determinations are demonstrated near two fixed points; namely, the triple point of water and the melting point of gallium. The combined uncertainty is 23 ppm at the lowest temperature and is dominated by the statistical component. This latter can be reduced to a few parts per million when the temperature is retrieved from the line-absorbance analysis. When the type-B uncertainty associated with the line-shape model is added, the uncertainty is less than 10 ppm. This opens the door to the best DBT implementation, with a solid perspective toward thermodynamic temperature determinations at the parts-per-million level.

ACKNOWLEDGMENTS

This work received funding from the EURAMET-EMPIR program cofinanced by the participating states and from the European Union's Horizon 2020 research and innovation program through the InK2 project, coordinated by Graham Machin. The authors gratefully acknowledge Andrea Merlone and the Istituto Nazionale di Ricerca Metrologica for providing the periodic traceability to the fixed points.

- [1] J. Fischer *et al.*, The Boltzmann project, *Metrologia* **55**, R1 (2018).

- [2] L. Pitre, M. D. Plimmer, F. Sparasci, and M. E. Himbert, Determinations of the Boltzmann constant, *C. R. Phys.* **20**, 129 (2018).
- [3] G. Machin, The kelvin redefined, *Meas. Sci. Technol.* **29**, 022001 (2018).
- [4] R. M. Gavioso, D. M. Ripa, P. P. M. Steur, C. Gaiser, T. Zandt, B. Fellmuth, M. de Podesta, R. Underwood, G. Sutton, L. Pitre, F. Sparasci, L. Risegari, L. Gianfrani, A. Castrillo, and G. Machin, Progress towards the determination of thermodynamic temperature with ultra-low uncertainty, *Philos. Trans. R. Soc. A: Math. Phys. Eng. Sci.* **374**, 20150046 (2016).
- [5] G. Machin, J. Engert, R. Gavioso, M. Sadli, and E. Williams, Summary of achievements of the European Metrology Research Programme project implementing the new kelvin (InK 1), *Measurement* **94**, 149 (2016).
- [6] G. Machin, J. Engert, L. Gianfrani, H. McEvoy, and F. Sparasci, The European metrology programme for innovation and research project: Implementing the new kelvin 2 (InK 2), *J. Phys.: Conf. Ser.* **1065**, 122002 (2018).
- [7] L. Gianfrani, Linking the thermodynamic temperature to an optical frequency: Recent advances in Doppler broadening thermometry, *Philos. Trans. R. Soc. A: Math. Phys. Eng. Sci.* **374**, 20150047 (2016).
- [8] C. J. Bordé, Atomic clocks and inertial sensors, *Metrologia* **39**, 435 (2002).
- [9] C. J. Bordé, Base units of the SI, fundamental constants and modern quantum physics, *Philos. Trans. R. Soc. A: Math., Phys. Eng. Sci.* **363**, 2177 (2005).
- [10] C. Daussy, M. Guinet, A. Amy-Klein, K. Djerroud, Y. Hermier, S. Briaudeau, C. J. Bordé, and C. Chardonnet, Direct Determination of the Boltzmann Constant by an Optical Method, *Phys. Rev. Lett.* **98**, 250801 (2007).
- [11] G. Casa, A. Castrillo, G. Galzerano, R. Wehr, A. Merlone, D. Di Serafino, P. Laporta, and L. Gianfrani, Primary Gas Thermometry by Means of Laser-Absorption Spectroscopy: Determination of the Boltzmann Constant, *Phys. Rev. Lett.* **100**, 200801 (2008).
- [12] L. Moretti, A. Castrillo, E. Fasci, M. D. De Vizia, G. Casa, G. Galzerano, A. Merlone, P. Laporta, and L. Gianfrani, Determination of the Boltzmann Constant by Means of Precision Measurements of H_2^{18}O Line Shapes at $1.39\ \mu\text{m}$, *Phys. Rev. Lett.* **111**, 060803 (2013).
- [13] R. Hashemi, C. Povey, M. Derksen, H. Naseri, J. Garber, and A. Predoi-Cross, Doppler broadening thermometry of acetylene and accurate measurement of the Boltzmann constant, *J. Chem. Phys.* **141**, 214201 (2014).
- [14] R. Ciuryło, Shapes of pressure- and Doppler-broadened spectral lines in the core and near wings, *Phys. Rev. A* **58**, 1029 (1998).
- [15] A. Cygan, D. Lisak, R. S. Trawiński, and R. Ciuryło, Influence of the line-shape model on the spectroscopic determination of the Boltzmann constant, *Phys. Rev. A* **82**, 032515 (2010).
- [16] C.-F. Cheng, J. Wang, Y. R. Sun, Y. Tan, P. Kang, and S.-M. Hu, Doppler broadening thermometry based on cavity ring-down spectroscopy, *Metrologia* **52**, S385 (2015).
- [17] R. Gotti, L. Moretti, D. Gatti, A. Castrillo, G. Galzerano, P. Laporta, L. Gianfrani, and M. Marangoni, Cavity-ring-down Doppler-broadening primary thermometry, *Phys. Rev. A* **97**, 012512 (2018).
- [18] G.-W. Truong, D. Stuart, J. D. Anstie, E. F. May, T. M. Stace, and A. N. Luiten, Atomic spectroscopy for primary thermometry, *Metrologia* **52**, S324 (2015).
- [19] G.-W. Truong, J. D. Anstie, E. F. May, T. M. Stace, and A. N. Luiten, Accurate lineshape spectroscopy and the Boltzmann constant, *Nat. Commun.* **6**, 8345 (2015).
- [20] P. Amodio, L. Moretti, A. Castrillo, and L. Gianfrani, Line-narrowing effects in the near-infrared spectrum of water and precision determination of spectroscopic parameters, *J. Chem. Phys.* **140**, 044310 (2014).
- [21] A. Castrillo, M. D. De Vizia, L. Moretti, G. Galzerano, P. Laporta, A. Merlone, and L. Gianfrani, Doppler-width thermodynamic thermometry by means of line-absorbance analysis, *Phys. Rev. A* **84**, 032510 (2011).
- [22] D. Jacquemart, N. Lacombe, J.-Y. Mandin, V. Dana, H. Tran, F. Gueye, O. Lyulin, V. Perevalov, and L. Regalia-Jarlot, The IR spectrum of $^{12}\text{C}_2\text{H}_2$: Line intensity measurements in the $1.4\ \mu\text{m}$ region and update of the databases, *J. Quant. Spectrosc. Radiat. Transfer* **110**, 717 (2009).
- [23] E. Fasci, T. A. Odintsova, A. Castrillo, M. D. De Vizia, A. Merlone, F. Bertiglia, L. Moretti, and L. Gianfrani, Dual-laser absorption spectroscopy of C_2H_2 at $1.4\ \mu\text{m}$, *Phys. Rev. A* **93**, 042513 (2016).
- [24] H. Dinesan, E. Fasci, A. D'Addio, A. Castrillo, and L. Gianfrani, Characterization of the frequency stability of an optical frequency standard at $1.39\ \mu\text{m}$ based upon noise-immune cavity-enhanced optical heterodyne molecular spectroscopy, *Opt. Express* **23**, 1757 (2015).
- [25] A. Merlone, F. Moro, A. Castrillo, and L. Gianfrani, Design and capabilities of the temperature control system for the Italian experiment based on precision laser spectroscopy for a new determination of the Boltzmann constant, *Int. J. Thermophys.* **31**, 1360 (2010).
- [26] A. Merlone, L. Iacomini, A. Tiziani, and P. Marcarino, A liquid bath for accurate temperature measurements, *Measurement* **40**, 422 (2007).
- [27] I. Gordon *et al.*, The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer* **203**, 3 (2017).
- [28] C. Povey, A. Predoi-Cross, and D. R. Hurtmans, Line shape study of acetylene transitions in the $\nu_1 + \nu_2 + \nu_4 + \nu_5$ band over a range of temperatures, *J. Mol. Spectrosc.* **268**, 177 (2011).
- [29] N. Ngo, D. Lisak, H. Tran, and J.-M. Hartmann, An isolated line-shape model to go beyond the Voigt profile in spectroscopic databases and radiative transfer codes, *J. Quant. Spectrosc. Radiat. Transfer* **129**, 89 (2013).
- [30] F. Rohart, H. Mader, and H.-W. Nicolaisen, Speed dependence of rotational relaxation induced by foreign gas collisions: Studies on CH_3F by millimeter wave coherent transients, *J. Chem. Phys.* **101**, 6475 (1994).
- [31] J. Tennyson *et al.*, Recommended isolated-line profile for representing high-resolution spectroscopic transitions (IUPAC technical report), *Pure Appl. Chem.* **86**, 1931 (2014).
- [32] D. Forthomme, M. Cich, S. Twagirayezu, G. Hall, and T. Sears, Application of the Hartmann-Hran profile to precise experimental data sets of $^{12}\text{C}_2\text{H}_2$, *J. Quant. Spectrosc. Radiat. Transfer* **165**, 28 (2015).
- [33] P. Amodio, M. D. De Vizia, L. Moretti, and L. Gianfrani, Investigating the ultimate accuracy of Doppler-broadening

- thermometry by means of a global fitting procedure, *Phys. Rev. A* **92**, 032506 (2015).
- [34] J. Fischer, M. de Podesta, K. D. Hill, M. Moldover, L. Pitre, R. Rusby, P. Steur, O. Tamura, R. White, and L. Wolber, Present estimates of the differences between thermodynamic temperatures and the ITS-90, *Int. J. Thermophys.* **32**, 12 (2011).
- [35] D. A. Shapiro, R. Ciurylo, R. Jaworski, and A. D. May, Modeling the spectral line shapes with speed-dependent broadening and Dicke narrowing, *Can. J. Phys.* **79**, 1209 (2001).
- [36] L. Santamaria Amato, M. S. de Cumis, D. Dequale, G. Bianco, and P. Cancio Pastor, A new precision spectroscopy based method for Boltzmann constant determination and primary thermometry, *J. Phys. Chem. A* **122**, 6026 (2018).
- [37] A. Castrillo, L. Moretti, E. Fasci, M. D. Vizia, G. Casa, and L. Gianfrani, The Boltzmann constant from the shape of a molecular spectral line, *J. Mol. Spectrosc.* **300**, 131 (2014).
- [38] E. Fasci, M. D. D. Vizia, A. Merlone, L. Moretti, A. Castrillo, and L. Gianfrani, The Boltzmann constant from the H_2^{18}O vibration-rotation spectrum: Complementary tests and revised uncertainty budget, *Metrologia* **52**, S233 (2015).
- [39] F. Rohart, S. Mejri, P. L. T. Sow, S. K. Tokunaga, C. Chardonnet, B. Darquié, H. Dinesan, E. Fasci, A. Castrillo, L. Gianfrani, and C. Daussey, Absorption-line-shape recovery beyond the detection-bandwidth limit: Application to the precision spectroscopic measurement of the Boltzmann constant, *Phys. Rev. A* **90**, 042506 (2014).