Primary Gas Thermometry by Means of Laser-Absorption Spectroscopy: Determination of the Boltzmann Constant

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We report on a new optical implementation of primary gas thermometry based on laser-absorption spectrometry in the near infrared. The method consists in retrieving the Doppler broadening from highly accurate observations of the line shape of the $R(12)$ $\nu_1 + 2\nu_2^0 + \nu_3$ transition in CO_2 gas at thermodynamic equilibrium. Doppler width measurements as a function of gas temperature, ranging between the triple point of water and the gallium melting point, allowed for a spectroscopic determination of the Boltzmann constant with a relative accuracy of $\sim 1.6 \times 10^{-4}$.

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Atomic and molecular spectroscopy have played a major role in fundamental metrology since the advent of highly monochromatic, tunable laser sources. Spectroscopic experiments with a metrological goal mostly consist in precision measurements of absolute frequencies, such as the center frequency of the hydrogen 1s-2s line [1,2] and the strontium intercombination line [3]. Recently, high resolution laser-absorption spectroscopy has been proposed for a direct determination of the Boltzmann constant [4]. In this case, a frequency interval has to be measured accurately: The method relies on a determination of the width of a Doppler-broadened absorption line in a rarefied gas at thermodynamic equilibrium. The current value of k_B, $1.380\,650\,4(24) \times 10^{-23}\ \mathrm{J\,K^{-1}}$, recommended by the Committee on Data for Science and Technology (CODATA) [5], comes from the ratio between the molar gas constant R and the Avogadro number N_A [6]. Its relative uncertainty, 1.7×10^{-6}, is mostly due to the uncertainty on R, whose accepted value is that obtained in 1988 by Moldover *et al.* [7] using acoustic gas thermometry in argon. There is presently a strong interest in new and more direct determinations of k_B in view of a possible new definition of the unit kelvin [8]. In the current International System of Units (SI), the unit kelvin is linked to an artifact, which is far from being invariant in space and time. As already done for the unit meter by fixing the speed of light c, the unit kelvin could be redefined through the thermal energy by fixing the Boltzmann constant. This new definition would be independent of any material substance, technique of implementation, and temperature. However, before fixing its value, k_B must be determined with an improved uncertainty, possibly using different methods based on radically different principles. For this reason, the experimental investigation of new primary thermometric methods is strongly encouraged by the Consultative Committee for Thermometry of the International Committee for Weights and Measures, as reported in its Recommendation T 2 of 2005.

Doppler-broadened laser-absorption spectroscopy can serve as a primary thermometric method, with the advantage of being conceptually simple, applicable to any gas at any temperature, in whatever spectral region. In contrast to other methods based on electromagnetic radiation measurements, such as total radiation thermometry [9], this new approach does not require absolute radiation determinations. It is well known that the Doppler width, $\Delta\nu_D$ (FWHM), of a line (with a center frequency ν) in an absorbing molecular gas at thermodynamic equilibrium depends on the temperature T through the equation

$$\Delta\nu_D = 2\frac{\nu}{c}\sqrt{2\ln 2 k_B \frac{T}{m}}, \tag{1}$$

where m is the mass of the molecule.

The first spectroscopic determination of k_B has been recently performed in the midinfrared by Daussy *et al.* on the ν_2 as Q(6,3) rovibrational line of $^{14}NH_3$ at a frequency of 28 953 694 MHz [10]. The absorption profile was observed with a maximum signal-to-noise ratio (S/N) of 10^3, in the pressure range between 1 and 10 Pa, at a temperature of 273.15 K, using a CO_2 laser, frequency stabilized on an OsO_4 line. Under these low-pressure conditions, close to the Doppler limit, by measuring the width of the absorption line as a function of the pressure and extrapolating to zero pressure, it was possible to deduce the Boltzmann constant with a relative uncertainty of 1.9×10^{-4} [10]. This approach allows for a very simple spectral analysis but requires an accurate determination of the gas pressures.

Here we report on a radically different implementation of laser-absorption spectroscopy for primary gas thermometry. In particular, we demonstrate that it is possible to retrieve the gas temperature from a molecular absorption profile even when the gas pressure is sufficiently high that the line shape is far from the Doppler limit, but sufficiently small that one can neglect the averaging effect of velocity-changing collisions, so that the line shape is given by the exponential of a Voigt convolution. We perform absorption spectroscopy in the near-infrared on a CO_2 gas sample at thermodynamic equilibrium using a distributed feedback (DFB) diode laser, probing the $R(12)$ component of the

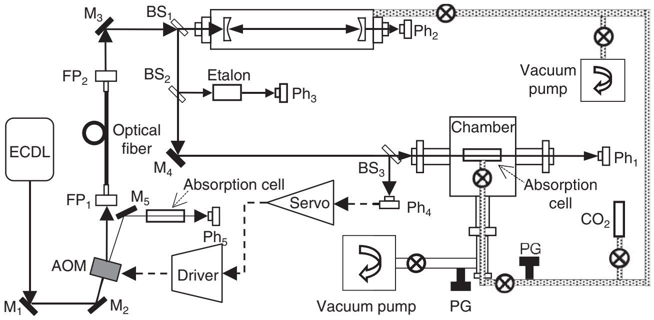

FIG. 1. A sketch of the intensity-stabilized laser-absorption spectrometer. ECDL: extended-cavity diode laser; M: mirror; BS: beam splitter; FP: fiber port; Ph: photodetector; PG: pressure gauge. The cell is closed by an oil-free solenoid valve, placed inside the chamber.

$\nu_1 + 2\nu_2^0 + \nu_3$ combination band. In contrast to NH_3, our molecular target does not exhibit any hyperfine structure.

The experimental setup is depicted in Fig. 1. The diode laser, emitting on a single mode at 2.006 μm with a maximum power of 3 mW, is mounted in a mirror extended-cavity configuration, which provides optical feedback for line narrowing down to $\sim$1 MHz. This is sufficiently small for the aims of the present experiment. Collimated by a double-aspheric lens, the laser beam first passes through an acousto-optic modulator (AOM) and then is injected into a single-mode, polarization-maintaining optical fiber. The latter is employed as a high-quality spatial filter to produce an optimum TEM_{00} transverse mode. The AOM is used as an actuator within a servo loop in order to keep the intensity of the laser beam constant. Driven by a 1 W radio-frequency signal at 80 MHz, the AOM deflects about 70% of the laser power from the primary beam to the first diffracted order, which is used for the experiment. The intensity control feedback loop ensures a stability level better than 10^{-4}, over a laser frequency span of about 0.5 cm^{-1}. The servo loop is active within an electronic bandwidth of 50 kHz. After being collimated again, the laser beam is divided into four parts by a series of beam splitters. The first beam is sent to a high-finesse, confocal optical resonator that provides accurate frequency markers for calibration purposes. The second goes to a 5 cm tick germanium etalon, which allows for a coarse check of the frequency calibration. The third beam impinges on a monitor photodiode, whose output signal is used as the input signal to our servo to control the rf power driving the AOM. Finally, the remaining portion of the laser beam passes through a homemade, temperature-stabilized sample cell, closed at each end by an AR-coated BK7 window. Temperature-stabilized, extended-wavelength, InGaAs photodetectors are employed to monitor the laser radiation. The optical resonator consists of a pair of identical, high-quality, dielectric mirrors, with a radius of curvature of 50 cm and a reflectivity of 99.5%. The mirror mounts, tightly locked over a stainless steel base, fit into the two ends of a glass tube, which is periodically evacuated. The absorption cell is 10.5 cm long and is housed inside a stainless steel vacuum chamber, which is equipped with a pair of optical windows of the same type as those of the cell. Consisting of a cylindrical cavity inside an aluminum block, with inner and external surfaces carefully polished, the cell is temperature stabilized by means of four Peltier elements. Three precision platinum resistance thermometers (Pt100) measure the temperature of the cell's body while a proportional integral derivative controller is used to keep the temperature uniform along the cell and constant within 40 mK, over a time interval of $\sim$2 h. This active system also allows us to vary the gas temperature between 270 and 330 K. The Pt100 thermometers were calibrated at the triple point of water and at the gallium melting point with an overall accuracy better than 0.01 K. Both during the calibration and when placed in the absorption cell, the thermometers are fed by a 1 mA current and the correction due to the self-heating effect is applied together with the associated uncertainty.

The sample cell is filled with CO_2 gas (with a nominal purity of 99.999%) at a pressure between 70 and 130 Pa, measured using a 1300 Pa full-scale capacitance gauge with a 0.25% accuracy. A turbomolecular pump periodically evacuates the sample cell and creates high-purity conditions. Data acquisition is performed by means of a digital oscilloscope (Tektronix TDS7104), with a 13-bit vertical resolution (on the voltage range covered by the absorption signal) and a total number of points for each spectrum equal to 5000. Spectral averaging over 25 consecutive scans is performed, the scan rate being 5 Hz. The resulting spectrum is then transferred to a personal computer. Simultaneously, the transmissions from both the optical resonator and the etalon are recorded.

An example spectrum is shown in Fig. 2. The observed S/N was 1600:1, with an equivalent noise detection bandwidth of 600 Hz and a power incident upon the cell of 50 μW. A MATLAB code is used to carry out the line shape fitting and retrieve the Doppler width in a fully automated way for any set of repeated acquisitions. Particular attention is paid to the frequency calibration of the spectra. In fact, prior to each fit, the same code analyzes the transmission spectrum from the confocal resonator in order to construct a linear frequency scale that has to be matched to the corresponding absorption spectrum. This is done by means of a cubic spline interpolation of the peak frequencies versus their index in the data array. Obviously, an accurate determination of the cavity free-spectral-range f_{FSR} is also necessary. For that purpose, two different methods were implemented, whose results were in total agreement. The first was based on simultaneous detection of absorption on both the zero- and first-order beams as provided by the AOM, once the former was sent to a second absorption cell (see Fig. 1). The two cells were filled with CO_2 gas at the same pressure and at room temperature. Because of the frequency shift between the

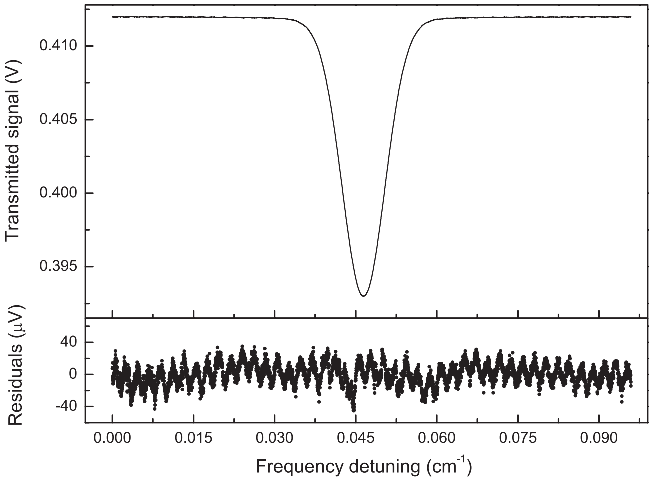

FIG. 2. Transmission spectrum for the $R(12)$ line at ~100 Pa and 275.12 K. The absolute residuals are also shown, as a result of a nonlinear least-squares fit to a Voigt convolution. The retrieved Doppler width was 268.01 MHz.

two beams (80 517.42 ± 0.12 kHz, as measured by a universal counter), the center frequencies of the two line profiles, recorded along with the transmission comb from the optical cavity, are separated by an exactly known quantity. The second method consisted in making a broad laser frequency scan ($\sim 0.5\ \mathrm{cm}^{-1}$) in order to observe a pair of CO_2 absorption lines, namely, the $R(8)\ \nu_1 + 2\nu_2^0 + \nu_3$ and $R(27)\ \nu_1 + 3\nu_2^1 - \nu_2^1 + \nu_3$ transitions, whose center frequencies are accurately known. These frequencies, as well as that of the $R(12)$ line, were taken from Ref. [11]. Thus, as a result of a weighted mean between the two values, f_{FSR} was found to be 149.56 ± 0.01 MHz. In our operation conditions, the effects of temperature variations and changes in the cavity alignment on f_{FSR} could be neglected. As will be shown, the relative uncertainty on the cavity free-spectral-range, multiplied by a factor of 2, will contribute to the overall accuracy of the spectroscopic determination of k_B. The linearity of the frequency scale was periodically checked using the transmission spectra from the germanium etalon. Deviations from linearity, which could affect the symmetry of the absorption profiles, were found to be negligible at the present experimental accuracy. Coming back to the fit of the absorption line shape, the normalized Voigt function was computed using the approximation of Weideman [12]. It was confirmed that this approximation is equal to the Voigt convolution, as tabulated in Ref. [13], to better than 1 part in 10^6. The nonlinear least-squares fitting code was based on a Levenberg-Marquardt algorithm. The code was tested on simulated spectra, assuming a gas pressure of 130 Pa at a temperature of 296 K, and adding a random noise to the computed line shape. As one could expect, the relative accuracy in the retrieval of the Doppler width strongly depends on the signal-to-noise ratio. In fact, relative deviations between the real value and the retrieved one of 2.6×10^{-5} and 5.2×10^{-6} (mean values over 10 simulations) were found for $S/N = 1600$ and 1.6×10^4, respectively.

The exponential of a Voigt function is able to fit our measured spectra within the experimental noise, as shown in Fig. 2. Reported in the bottom part of the figure, the residuals evidence that the noise is dominated by periodic fluctuations due to spurious etalon effects, whose root-mean-square value is of the order 10^{-5} V. Owing to our intensity stabilization procedure, a constant background factor optimally represented the baseline for the Voigt fit. Apart from this factor, the remaining free parameters were the line center frequency, the homogeneous and Doppler widths and an amplitude factor, the latter representing the product of the line strength factor, the gas pressure and the absorption path length. In our experimental configuration, saturation and transit time broadening could be neglected. It is worth noting that the scan goes quite far into the line wings, as demonstrated *a posteriori* by the area under the normalized fitting function, which was found to be larger than 0.99.

In Fig. 3, example determinations of the gas temperature, over a time interval of ~4 min are reported. The histogram on the right side of Fig. 3 shows that the distribution is Gaussian. Simultaneously to the spectral acquisitions, the Pt100 temperatures were also recorded, providing a mean value of 298.68 K with a standard deviation of ~10 mK. With very few exceptions, a good agreement was found between the spectroscopic and Pt100 temperatures, typical deviations being much smaller than 1 K.

Doppler width determinations were repeated as a function of the gas temperature, in the range between the triple point of water and the gallium melting point. This approach was mainly adopted to cancel out possible systematic errors arising from residual etalon effects due to the cell's windows. In Fig. 4, the experimental values of the

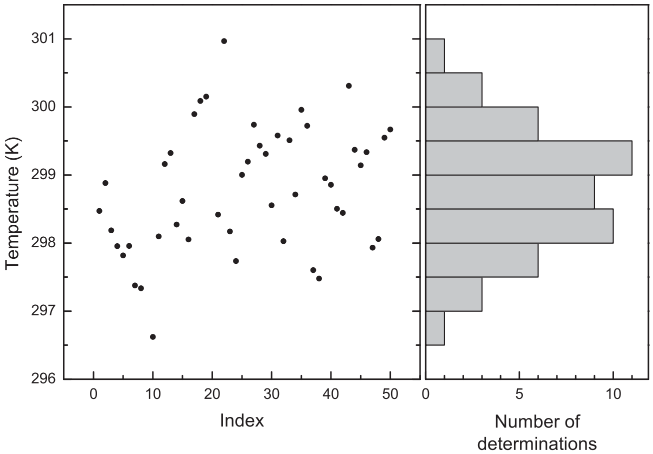

FIG. 3. Repeated spectroscopic measurements of the absolute temperature and a histogram of the determinations. The mean value is 298.77 K, the standard deviation 0.89 K, and the standard error 0.13 K.

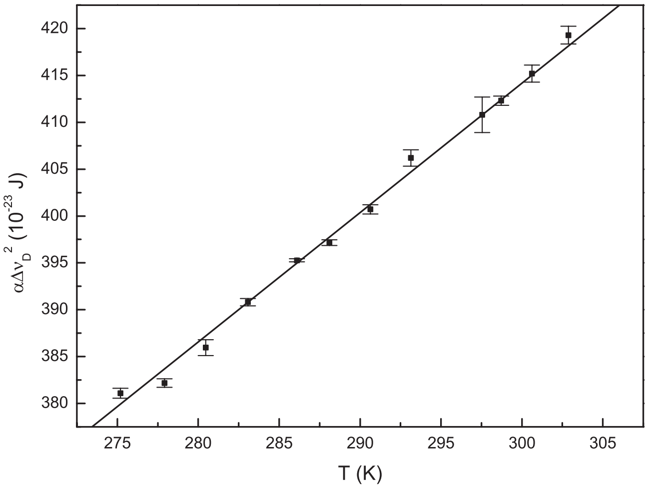

FIG. 4. A plot of the quantity $\alpha\Delta\nu_D^2$ as a function of the gas temperature, where $\alpha = mc^2/(8\nu^2 \ln 2)$ and $\alpha\Delta\nu_D^2$ represents the thermal energy. The slope of the weighted best-fit line directly provides the value of k_B. Each point represents the mean value over a number of repeated determinations, the error bars being the standard error (3σ). These data resulted from more than 1500 spectra, acquired over five consecutive weeks.

quantity $\frac{m}{8\ln 2}\frac{c^2}{\nu^2}\Delta\nu_D^2$ and the corresponding Pt100 temperatures are plotted. The molecular mass was calculated from the relative atomic masses of ^{16}O and ^{12}C, the molar mass constant, and the Avogadro number [6]. A linear fit of these data directly provides the spectroscopic value for the Boltzmann constant, namely $k_B = 1.380\,58(13) \times 10^{-23}$ J K^{-1}. The relative uncertainty in the Pt100 temperatures, also including the short-term fluctuations, was found to be at least a factor of 10 smaller than the relative error of a typical spectroscopic determination of the temperature. For this reason, the Pt100 errors were ignored in the linear fit. The 1-σ uncertainty on k_B increases up to 22×10^{-28} J K^{-1} once the uncertainty on the frequency scale is also considered. Our determination agrees with the CODATA value.

In conclusion, we have demonstrated that highly accurate, intensity-stabilized, laser-absorption spectrometry in the near-infrared represents an extremely powerful tool for primary gas thermometry. We have provided a spectroscopic measurement of the Boltzmann constant, with an overall relative accuracy of 1.6×10^{-4}. Our molecular target in the spectral region around 2-μm represented a very good choice mainly because of the insensitivity of the retrieved Doppler width from the gas pressure. More precisely, for CO$_2$ pressures below a few hundred Pa, we did not observe any influence from Dicke narrowing or speed-dependent effects. This is true at the present precision level. Once, in the near future, we will be able to retrieve the Doppler width with a much smaller uncertainty, it will be necessary to confirm its behavior as a function of the gas pressure.

Future developments include a pair of phase-locked extended-cavity diode lasers to improve our capability of measuring laser frequency variations, as well as a new detection method based on fast amplitude modulation of the laser beam and phase-sensitive detection to enhance the signal-to-noise ratio. We are also building a new temperature-stabilized cell, which should ensure a constant and homogeneous gas temperature within 1 mK. After these significant improvements, our method could contribute to the new definition of the kelvin, in the near future. In fact, we will no longer be limited by the accuracy of the frequency scale. On the other hand, the S/N is expected to increase by a factor of 25, provided that spurious etalon effects are eliminated. We also plan to exploit the excellent linearity of standard InGaAs detectors by shifting the operation wavelength down to 1.4 μm. According to our simulations, it should be possible to reach an accuracy level of a few parts in 10^6.

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