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The Boltzmann constant from the shape of a $H_2{}^{18}O$ vibration-rotation line

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Abstract **– We report on the recent determination of the Boltzmann constant, k_B, by means of Doppler broadening thermometry, performed at the Second University of Naples, providing complementary information, as compared to previous papers. This relatively new method of primary gas thermometry was implemented by using a pair of offset-frequency locked extended-cavity diode lasers at 1.39 μm, to probe a particular vibration-rotation transition of the $H_2{}^{18}O$ molecule. Adopting a rather sophisticated and extremely refined line shape model in the spectral analysis procedure, we were able to determine the Doppler width from high-quality absorption spectra with unprecedented accuracy. Our spectroscopic determination of k_B exhibits a combined (type A plus type B) uncertainty of 24 parts over 10^6.**

I. INTRODUCTION

The expression of the Doppler width of a given atomic or molecular line, valid for a gaseous sample at the thermodynamic equilibrium, represents a powerful tool to link the thermodynamic temperature to an optical frequency, passing through the Avogadro number and the Boltzmann constant. This is the basis of a relatively new method of primary gas thermometry, known as Doppler broadening thermometry (DBT), which is currently at the stage of further development and optimization in a few labs, all over the world.

As it is well known, k_B is the basic constant of statistical mechanics and thermodynamics, appearing in several fundamental laws of physics. The renewed interest towards k_B arises from the possible redefinition of the International System of Units (SI). In fact, the International Committee for Weights and Measures (CIPM) has proposed new definitions for the kilogram, ampere, kelvin, and mole, based upon the assignment of fixed numerical values to a set of fundamental constants, namely Planck constant, elementary charge, Boltzmann constant, and Avogadro number. The changes proposed for the SI units will be adopted only after a further refinement of the experimental results on these constants. A refined value of k_B should ideally be determined by at least three different methods, at a combined uncertainty of 1 part per million (ppm) or better [1]. Presently, the most accurate and consolidated methods to access the value of k_B are known as Acoustic Gas Thermometry (AGT) and Dielectric Constant Gas Thermometry (DCGT). The former essentially consists in measuring the speed of sound in a noble gas inside an acoustic resonator and it has recently provided a k_B determination with a relative uncertainty of 0.71 parts over 10^6 [2]. Based upon the Clausius–Mossotti equation, DCGT deals with measurements of the electric susceptibility of helium as a function of the gas pressure and it has recently led to a k_B value with a combined uncertainty of 4.3 ppm [3].

DBT consists in retrieving the Doppler width ($\Delta\omega_D$) from the highly accurate observation of the spectral profile corresponding to a given atomic or molecular line in a gas sample at the thermodynamic equilibrium [4]. If implemented at the temperature of the triple point of water (namely, T = 273.16 K), pursuing the highest levels of precision and accuracy for laser absorption spectroscopy in the linear regime of interaction, DBT can provide an optical determination of the Boltzmann constant, by inverting the following equation [5]:

$$\Delta\omega_D = \frac{\omega_0}{c}\sqrt{2\ln 2\frac{k_B T}{M}}, \qquad (1)$$

being ω_0 the line center frequency, c the speed of light, and M the molecular mass.

In the present paper, we report complementary information regarding our determination of the Boltzmann constant, discussing possible sources of systematical deviations that were ignored in previous publications, such as relativistic effects and possible distortions of the absorption line shape resulting from the finite bandwidth of the detection system.

II. EXPERIMENTAL APPARATUS

Figure 1 shows a block diagram of the laser absorption spectrometer. It basically consists of an extended cavity diode laser (namely, the probe laser) with an emission wavelength in the range between 1.38 and 1.41 μm, a frequency control system, an intensity stabilization feed-

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back loop, and an isothermal cell. Precise control, stabilization and synchronization of the laser frequency is achieved by using the technique of offset frequency locking, in which the probe laser is forced to maintain a precise frequency-offset from a reference laser [6]. This offset is provided by a radio-frequency (rf) synthesizer, which in turn is phase-locked to an ultra-stable Rb oscillator. The reference laser presents a sub-kilohertz absolute stabilization of its central frequency, being locked to an ultra-narrow saturated absorption signal, resulting from the nonlinear interaction that occurs inside a high-finesse optical resonator, in coincidence with a particular vibration-rotation line of a water isotopologue. Hence, the beat note between the two lasers is first detected by means of a fast photodiode, properly amplified, scaled in frequency, and subsequently compared with the rf signal, so as to produce an error signal driving the probe laser. By tuning the rf frequency, it is possible to perform continuous, highly linear and highly accurate frequency scans of the probe laser around a given center frequency. An example of beat note between the two lasers, as acquired by means of a spectrum analyzer with a 10 Hz resolution bandwidth, is shown in Figure 2.

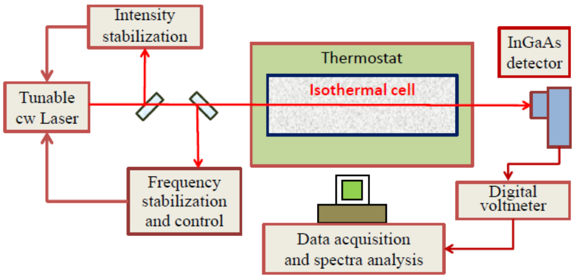

Fig. 1. Sketch of the laser absorption spectrometer.

The most subtle source of systematic deviations, namely, amplitude variation in the background baseline, is essentially removed by implementing an intensity control feedback loop, based upon an acousto-optic modulator, which effectively compensates for any power variation associated to a laser frequency scan, as well as for the periodic modulation of the power arising from spurious etalon effects.

Equipped with a pair of antireflection-coated BK7 windows, the isothermal cell is 150-mm long and it is referenced to the triple point of water (TPW), with temperature accuracy, uniformity and stability at the level of 0.1 mK, as extensively described elsewhere [7].

Finally, the transmitted beam is detected by means of a ultralow-noise, preamplified, InGaAs photodiode (see the beam path drawn in Figure 1), whose electrical bandwidth is set to 1 kHz. The preamplifier consists of a transimpedance amplifier, which also acts as a first-order active low-pass filter. Absorption spectra are acquired using a data acquisition board with a 16-bit resolution and a sampling rate of 10^6 samples per second. The possible nonlinearity of the whole detection chain was estimated to be well below the noise level. A LABVIEW code allows us to control the whole setup, to perform step-by-step frequency scans and to acquire, for each step, the transmitted signal.

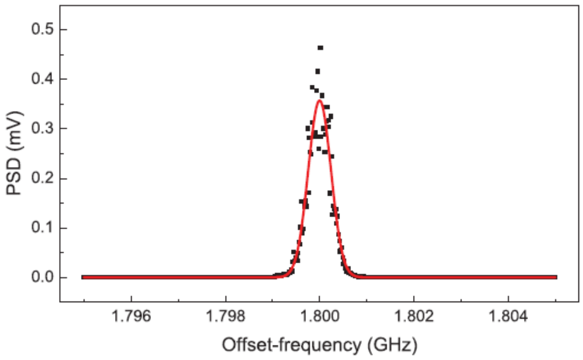

Fig. 2. Electrical spectrum of the beat note between probe and reference lasers. The red line represents the best-fit curve, given by a Gaussian function with a FWHM of 570 kHz.

III. RESULTS

The isothermal cell was filled with a 97.7% enriched ^{18}O water sample at variable pressures, ranging between 150 and 500 Pa. The total number of acquired spectra was 718, in coincidence with the $4_{4,1} \rightarrow 4_{4,0}$ line of the $H_2^{18}O$ $\nu_1 + \nu_3$ band, recorded at the TPW temperature as a function of the total gas pressure.

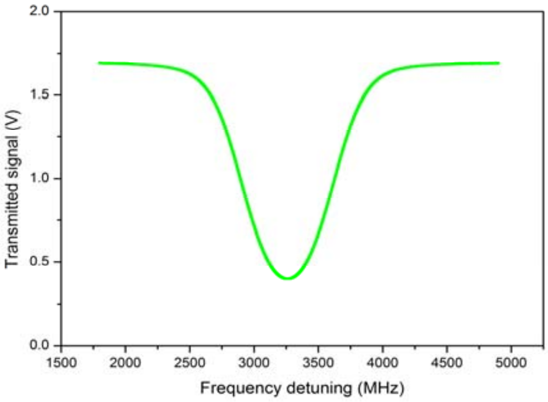

Fig. 3. Example of an absorption spectrum. The x-axis represents the frequency detuning from the center of the $4_{4,0} \rightarrow 4_{4,1}$ line of the $H_2^{18}O$ $\nu_1 + \nu_3$ band that is used for the absolute stabilization of the reference laser.

Figure 3 shows an example spectrum, recorded at a pressure of about 410 Pa. The laser scan was 3.1 GHz wide and resulted from 3100 steps of 1 MHz each, with a step-by-step acquisition time of 100 ms. The signal-to-noise ratio was measured to be about 5000.

It is worth noting that the finite bandwidth of the detection system can cause distortions to the measured line shape. Very recently, a theoretical model has been developed in order to consider the influence of the detection bandwidth properties on the observed line shapes in laser absorption spectroscopy [8]. The model predicts artificial frequency shifts, extra broadenings and line asymmetries which must be taken into account in order to obtain accurate line parameters. The theoretical model has been validated by experiments performed on H_2O and NH_3 molecular lines recorded by precision laser spectroscopy, in the near- and mid- infrared spectral regions. Furthermore, it has been possible to figure out the detection bandwidth adjustments required to perform a spectroscopic determination of the Boltzmann constant at the 1 ppm level of accuracy. In this respect, an important parameter is the so-called frequency constant, ν_D, which is given by the product between the filter time constant, τ_D, and the scan rate, $\dot{\nu} = \Delta\nu / \Delta t$, $\Delta\nu$ being the frequency step and Δt the time interval for each step. Numerical simulations have shown that the frequency constant must be about 700 times smaller than the Doppler width (half-width at 1/*e* of the maximum), while the ratio $\tau_D/\Delta t$ should be smaller than 0.25. In our experimental configuration, this latter quantity amounts to about 0.0016, while ν_D results to be about 2 kHz (namely, more than five orders of magnitude smaller than the Doppler width), conditions that are very favorable to completely ignore possible effects related to the finite detection bandwidth.

A major effort in our work was devoted to line shape modeling, which is far from being trivial for self-colliding water molecules. In fact, deviations from the Voigt model are clearly observed even in the case of pure H_2O samples at relatively small pressures [9]. In this respect, the molecular confinement alone was revealed to be unable to explain entirely these departures, while the speed dependence of pressure-induced broadening and shifting should be taken into account. Therefore, speed-dependent and Dicke narrowing effects were jointly considered by adopting the so-called partially correlated speed-dependent hard-collision (pcSDHC) model in the nonlinear least-squares fits of the recorded spectra [10]. Recent theoretical and experimental studies have demonstrated that this model is the most appropriate one to describe the physical situation of self-colliding water molecules, even in the Doppler regime [11, 12].

The power distribution P(ω), describing the shape of the isolated absorption spectrum of Figure 3, centered at ω_0, is given by the well known Beer-Lambert law, namely:

$$P(\omega) = (P_0 + P_1\omega)\exp[-Ag(\omega - \omega_0)], \quad (2)$$

where A represents the integrated absorbance, the parameters P_0 and P_1 account for a residual, linear variation of the incident power, and $g(\omega\text{-}\omega_0)$ is the line shape function, as provided by the pcSDHC model. The non-linear, least-squares, fitting procedure was implemented under the MATLAB environment, using the trust region optimization algorithm, and involved a single spectrum at a time. A total of seven quantities were considered as free parameters, including A, P_0, P_1, the Doppler width, the collision frequency, the collisional shift and width, this latter being averaged over the absorbers' speed. Fit residuals associated to the spectrum of Figure 3 are shown in Figure 4.

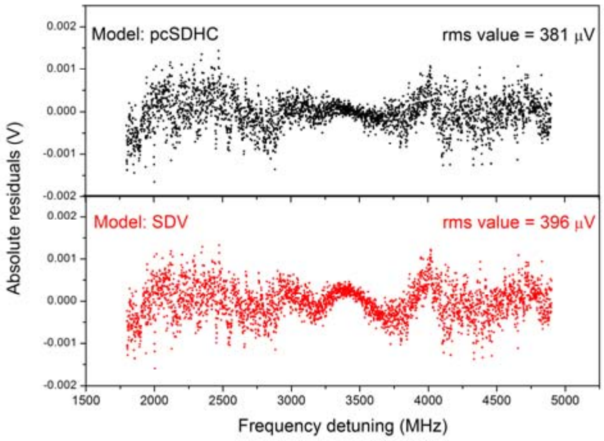

Fig. 4. Fit residuals by using the pcSDHC model (upper plot) and the speed-dependent Voigt (SDV) profile (lower trace). Root-mean square values are also reported.

The noise level is smaller around the line center, as the transmitted signal is significantly reduced at those frequencies (see Figure 3). The pcSDHC model allowed us to successfully fit the measured profiles within the experimental noise, with a root-mean-square (rms) value of the residuals of 0.381 mV. One might be interested in understanding which performance would have been obtained by adopting a simplified model, such as the symmetric version of the speed-dependent Voigt profile. This model allows one to consider line narrowing due to the speed dependence of collisional broadening, ignoring the averaging effect of velocity changing collisions as well as the speed dependence of pressure shift. Looking at the residuals of the lower trace of Figure 4, a w-shaped structure is visible around the line center. This is a clear consequence of the fact that line narrowing effects are not properly accounted for, when using a simplified line shape model. It is also true that the difference between the rms values of the residuals amounts to only 15 μV. Nevertheless, this is sufficient to add a measurable systematical deviation in Doppler width retrieval.

Given the unprecedented quality and fidelity in the observation of the absorption spectra, one may wonder whether the relativistic Doppler effect should be considered. At the TPW temperature, the most probable speed of the absorbing molecules (v_m) amounts to about 500 m/s, which gives a β-value (namely, the ratio v_m/c) of about 1.6 10^{-6}. In a recent paper, a relativistic formulation for the Voigt profile has been provided [13]. A comparison with the classical Voigt profile has revealed that the relativistic deformation, expressed in terms of peak-to-peak relative variation between relativistic and classical Voigt profile, is of the order of few parts over 10^8, for $\beta=10^{-6}$ [14]. This is nearly four order of magnitude below the noise level affecting our spectra. Even though a relativistic version of the pcSDHC model is not available, yet, a similar behavior is likely to be observed. Therefore, we can conclude that relativistic effects can be neglected, at the present precision level.

As a result of the spectral analysis, the Boltzmann constant could be retrieved with a relative statistical uncertainty of about 16 ppm. The complete uncertainty budget gives a combined uncertainty of 24 ppm, our value being (1.380631 ± 0.000033) 10^{-23} J/K. The uncertainty is a factor of 6 better than the best result obtained so far, by using an optical method [14]. The main sources of systematic deviations are ascribed to the line shape model and to the frequency-modulation (FM) broadening effect [15].

Our determination, however, is in full agreement with the current recommended CODATA value, namely, 1.3806488 (13) 10^{-23} J/K.

Repeating the complete analysis by using the SDV model, we obtain a different value for k_B, which results to be underestimated by about one part over 10^3. Therefore, it is confirmed that the choice of the line shape model is of the utmost importance for a successful low-uncertainty DBT experiment, circumstance that was already hypothesized elsewhere [5, 16].

IV. CONCLUSIONS

We have reported on recent advances towards the development of low-uncertainty Doppler broadening thermometry, based upon precision molecular spectroscopy in the near-infrared region, for the aims of the spectroscopic determination of the Boltzmann constant. The dual-laser approach enabled us to reach unprecedented fidelity in the observation of the shape associated to a given vibration–rotation transition of the $H_2{}^{18}O$ molecule. The uncertainty budget shows that the achievement of a global uncertainty at the ppm level is a realistic possibility. In fact, the statistical uncertainty can be reduced by increasing the number of spectra, possibly enlarging the pressure interval. The limitation arising from FM broadening has been already removed, by implementing noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) for the highly sensitive detection of the sub-Doppler line, on which the reference laser is stabilized [17]. In this respect, we exploit the fact that NICE-OHMS provides a dispersion signal without dithering the optical cavity.

As for the uncertainty associated to the line shape model, we believe that it will be significantly reduced once a global analysis approach will be used to simultaneously fit a manifold of profiles across a given range of pressures, sharing a restricted number of unknown parameters, including the Doppler width [18].

It is worth noting that absorption spectra, when acquired with the highest metrological qualities, can provide information on other physical quantities, besides the Doppler width. For instance, the integrated absorbance is proportional to the molecular number density. Therefore, the same set-up can be employed for highly accurate determinations of the amount of substance. Similarly, it is possible to perform isotope ratio measurements for the stable isotopologues of water (namely, $^{17}O/^{16}O$, $^{18}O/^{16}O$ and D/H in water) [19]. This latter application requires a proper selection of the wavelength of the probe laser, so as it is possible to catch a pair of vibration-rotation transitions for the isotopologues of interest, within a single scan of the laser itself [20].

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