Highly-accurate line shape studies in the near-IR spectrum of $\text{H}_2^{18}\text{O}$: Implications for the spectroscopic determination of the Boltzmann constant

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Abstract. The outcomes of a specific study on line shape deviations from the usual Voigt profile, in the near-IR spectrum of water, will be discussed. Particularly, a great attention is paid to the role of speed-dependence of collisional broadening. From the experimental point of view, high spectral fidelity has been reached by using the technique of offset-frequency locking between two extended-cavity diode lasers. In such a system, the master laser is frequency stabilized against a narrow sub-Doppler molecular line, while the slave laser is actively controlled so that its emission frequency maintains a given offset with respect to the frequency of the master. This method allows one to perform highly accurate and reproducible frequency scans of the slave laser around a given vibration-rotation line. I will present recent findings on the speed dependence of collision parameters, influencing the shape of $\text{H}_2^{18}\text{O}$ absorption lines. Finally, I will discuss the implications for the spectroscopic determination of the Boltzmann constant.

1. Introduction
The General Conference on Weights and Measures (CGPM) agreed at its 24th meeting in October 2011 on new definitions of the kilogram, ampere, kelvin, and mole in terms of fixed numerical values of the Planck constant ($\hbar$), elementary charge ($e$), Boltzmann constant ($k_B$), and Avogadro constant ($N_A$), respectively [1]. The changes proposed for the International System of units (SI) will be adopted only after a further refinement of the experimental results on the new definitional constants. Meanwhile, the CGPM encourages scientists to continue their work and efforts for the aims of a better determination of the $\hbar$, $e$, $k_B$, and $N_A$ constants. The new definition for the unit kelvin would require precision measurements of $k_B$ by at least three fundamentally different methods. Presently, the most accurate way to access the value of the Boltzmann constant is from measurements of the speed of sound in a noble gas. In fact, acoustic gas thermometry has recently provided a $k_B$ determination with a relative standard uncertainty of 1.24 parts in $10^6$ [2]. Another approach is known as dielectric constant gas thermometry and it is based upon the Clausius-Mossotti equation. A relative standard uncertainty of 9.2 parts in $10^6$, at the temperature of the triple point of water, has been recently demonstrated by using this method [3]. Other upcoming primary thermometry techniques, which are currently at the stage of further development and optimization, include Doppler broadening thermometry (DBT) and quantum voltage calibrated electrical noise thermometry [4]. Based upon precision laser spectroscopy in the linear regime of interaction, DBT consists in retrieving the Doppler width from the highly-accurate observation of the absorption profile corresponding to a
given atomic or molecular line in a gaseous sample at the thermodynamic equilibrium. In addition to a very well designed experiment allowing for extremely high fidelity in observing the absorption profile of the selected line, the spectroscopic determination of the thermodynamic temperature requires a very reliable physical understanding of line shape that may present quite strong departures from the usual Voigt profile. Besides the Doppler effect, other mechanisms can influence the line profile and they all contribute to the overall width [5]. Collisions between particles increases the relaxation rate (thus giving rise to the collision broadening), but they also have an averaging effect on the velocity of the particles, leading to a narrowing of the line, usually referred to as the Dicke effect. Collisional narrowing and collisional broadening effects can be correlated, as velocity-changing collisions and internal state perturbations may occur simultaneously. Furthermore, speed dependence can be evidenced, consisting in the fact that the relaxation rate of a given energy level presents a dependence on the relative velocity of the absorber-perturber system. In some cases, it is also necessary to consider collision time asymmetry, because of the finite duration of each collision [5].

As a result, the retrieval of the Doppler width from high quality absorption spectra is far from being trivial. A true calculation of the spectral line shape would require the density-matrix formalism of quantum mechanics that leads to a Boltzmann-like transport/relaxation equation [6]. A similar approach is still prohibitively complex for molecular systems. As a consequence, one should resort to semiclassical models, whose physical interpretation is often dubious. Since a perfect representation of reality is not available yet, there is presently a wide consensus on the fact that retrieval of the Doppler width at a given gas temperature requires spectra acquisitions at different gas pressures, with the aim of determining a possible dependence on the pressure and, eventually, extrapolating the zero-pressure value of the Doppler width [7].

Alternatively, instead of probing weakly absorbing molecules in a diffusive regime, it is possible to use a low-pressure atomic vapor system, like Rb [8]. In this case, being the atomic motion effusive, collisions are extremely rare so that pressure-induced variation of the absorption line shape can be completely neglected. This removes the need to extrapolate results to an equivalent zero-pressure value. On the other hand, Doppler-width determinations from atomic transitions are significantly affected by systematic deviations due to effects such as magnetic sensitivity and optical pumping. In reason of that, the most accurate determinations of the Boltzmann constant by means laser spectroscopy have been performed on molecular systems, like ammonia and carbon dioxide, despite the difficulties in modeling the line shape [9, 10].

Another interesting molecular target for DBT experiments is water, due to the occurrence of relatively strong absorption features in the spectral window around 1.4 µm [11]. This is a telecom wavelength whose technical benefits can be fully exploited for the aims of an optimum implementation of DBT. Similarly, it is worth noting the extremely high linearity in the response of standard InGaAs photodiodes, which is a further important ingredient for a highly-accurate spectroscopic measurement of the Boltzmann constant [12].

In this paper, I will resume the outcomes of a recent investigation on the spectral profile of individual vibration-rotation lines of the H$_2^{18}$O molecule at 1.4 µm. High spectral fidelity was ensured by the use of a dual-laser absorption spectrometer, expressly designed and developed with the ambitious goal of reaching the target uncertainty of $10^{-6}$, in the spectroscopic determination of $k_B$. Pushing the experimental precision to extreme levels, it was possible to provide new insights towards a better physical understanding of the line shape problem in the near infrared spectrum of water.

2. Experimental details

Figure 1 shows a block diagram of the laser absorption spectrometer, which has been already described elsewhere [13]. It basically consists of an extended cavity diode laser with an emission wavelength in the range between 1.38 and 1.41 µm, a frequency control system, an intensity stabilization feed-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
The probe laser (usually referred to as the slave laser) is forced to maintain a precise frequency-offset from a reference laser (namely, the master laser). This offset is provided by a radio-frequency (rf) synthesizer, which in turn is phase-locked to an ultra-stable Rb oscillator. The master laser presents a subkilohertz 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. For this purpose, the optical cavity is filled with a water-vapor sample at very low pressures, either enriched in $^{17}$O and $^{18}$O, or characterized by a natural abundance, depending on the selected reference line. Hence, the beat note between master and slave 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 a double-servo system, which in turn acts on the diode injection current and on the extended-cavity length of the slave laser. By tuning the rf frequency, it is possible to perform continuous, highly linear and highly accurate frequency scans of the slave laser around a given center frequency.

![Figure 1. Sketch of the absorption spectrometer which has been developed for a highly-accurate spectroscopic determination of $k_B$.](image)

The most subtle source of systematic deviations, namely, amplitude variation in the background baseline, is essentially removed by implementing an intensity control feedback loop, 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 [14].

![Figure 2. Correction of the laser power variation associated with a laser frequency scan around a pair of H$_2$^{16}O and H$_2$^{18}O lines.](image)
This technical development represents a further element of novelty, as compared to previous works dealing with line shape studies by means of diode laser absorption spectroscopy. It also cancels out any influence of absorption from water molecules along the path of the beam in air. This is clearly shown in figure 2, where a typical absorption spectrum is shown without (upper trace) and with (lower trace) the action of the servo loop. Intensity stabilization at the level of $10^{-4}$ is achieved by using an AOM as an actuator, thus controlling continuously the amount of laser power that is deflected from the primary beam to the first diffracted order, which is used for the spectroscopic experiment. This method of background flattening is more effective compared to other approaches based on background subtraction procedures or the use of balanced dual-beam detection strategies. In fact, the optoelectronic control of the laser intensity ensures a better stability of the background signal and, consequently, a better experimental reproducibility and accuracy, because of the active nature of its operation, in a relatively large electronic bandwidth (~50 kHz).

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 [15].

3. Line shape investigations

Speed-dependent (SD) effects may take place regardless of the gas pressure and usually lead to an absorption line shape that is asymmetric and narrower than the Voigt profile. Characterized by very different physical origins, the two narrowing effects, namely, optical diffusion and speed-dependence of collisional broadening, can occur simultaneously. Past experiments have shown that SD effects are particularly important in the case of large perturber-to-absorber mass ratios [16].

A recent experimental and theoretical analysis of the $^2\text{H}_2^{18}\text{O}$ line shapes at 1.38 $\mu$m has revealed that SD effects in self-colliding water molecules cannot be ignored [17]. More specifically, it has been demonstrated that the molecular confinement alone is unable to explain entirely the departures from the Voigt profile and that the speed dependence of pressure-induced broadening and shifting has to be considered, even in the case of pure water samples at relatively small pressures (between 10 and 500 Pa). In fact, absorption spectra were successfully interpolated using the uncorrelated version of the speed-dependent Galatry profile, with a hypergeometric dependence on the absorber speed for both pressure broadening and shifting parameters, thus reaching an agreement between theory and experiment at the level of $5 \times 10^{-5}$. This outcome agrees with what we expect when comparing the Lenard-Jones radius with the collision diameter retrieved from the relaxation parameter. It is worth noting that the hypergeometric speed dependence results from the application of the formalism developed by Berman and Pickett [18, 19].

Since the confluent hypergeometric function entails long numerical calculations for line fitting, a quadratic approximation is often employed, leading to the so-called quadratic speed-dependent models [20]. In this approximation, the collisional width is given by:

$$\Gamma(v_a) = \Gamma_0 \left[ 1 + a_w \left( \frac{v_a}{v_{a0}} \right)^2 - \frac{3}{2} \right],$$

where $v_a = \left| \vec{v}_a \right|$ is the speed of the absorbing molecule, $v_{a0}$ is the most probable speed, $\Gamma_0 = \langle \Gamma(v_a) \rangle$ is the average collisional width over molecular speeds, and $a_w$ is a coefficient characteristic of the speed dependence, which is independent on the pressure. A similar equation holds for the pressure shifting parameter. Figure 3 shows the absolute residuals resulting from line fitting to the quadratic and hypergeometric speed-dependent Voigt (SDVP-Q and SDVP-HG) and speed-dependent Galatry profiles (SDGP-Q and SDGP-HG) of an experimental spectrum as acquired in coincidence with the $2_{2,1}\rightarrow 2_{2,0}$ line of the $^2\text{H}_2^{18}\text{O} v_1 + v_3$ band, at 1.3846 $\mu$m. The gas pressure was 500 Pa, while the temperature was kept at the constant value of the triple point of water. It is clear that the quadratic approximation, either used alone or considered in conjunction to the Dicke narrowing effect, fails to
 reproduce the experimental spectrum. In particular, the best agreement between theory and experiment was found when using the speed-dependent Galatry profile, with a hypergeometric dependence (SDGP-HG).

This failure can be ascribed to the fact that the perturber-to-absorber mass ratio, $\alpha$, is equal to exactly 1, the perturber being identical to the absorber. In fact, Ciurylo and co-workers, in a previous work, argued that the quadratic approximation, in a model describing simultaneously the two narrowing effects, is compatible with a soft-collision assumption, which implies $\alpha \ll 1$ [21].

4. Consequences for the spectroscopic determination of the Boltzmann constant

In proof-of-principle experiments, performed on ammonia and carbon dioxide molecules, respectively at ~10.3 and ~2 $\mu$m, spectroscopic determinations of the Boltzmann constant were performed with a combined relative uncertainty of 1.9 $10^{-6}$, for the NH$_3$ spectrometer, and 1.6 $10^{-6}$, for the CO$_2$ spectrometer [22, 10]. At that time, spectral analysis was performed by using Gaussian and Voigt profiles, respectively. In the last few years, with the ambitious goal of approaching the target accuracy of one part over $10^{6}$, technical improvements of the experimental setups have been accompanied by more and more refined modeling of the line shapes, also involving other molecular targets, like water and oxygen [23, 24]. As a consequence, it has been possible to look for speed-dependent collisional effects even in those cases in which their influence on the experimental line shapes is expected to be rather small. This is the case of self-colliding molecules in the very low pressure regime (namely, $p < 100$ Pa), as already discussed in the previous section. In this respect, I should also mention the recent work performed on ammonia by Triki et al. [25].

Coming back to water, the implications for the spectroscopic determination of the Boltzmann constant have been deeply investigated both theoretically and experimentally. A careful analysis of numerically simulated spectra has demonstrated that the choice of the line shape model is a key factor to reach low uncertainties in DBT [23]. A large number of simulations were done by accurately calculating the SDGP-HG function through numerical integration, adopting the Berman-Pickett model for a quadrupole-quadrupole interaction. The narrowing parameter per unit pressure was fixed at a reasonable value, taking into account the upper limit to the effective frequency of velocity changing collisions, provided by diffusion theory. A random noise was added to the simulated spectra so as to
reproduce the observed signal-to-noise ratios. A non-linear least-squares fitting procedure was applied to the simulated spectra, using Voigt, Galatry and speed-dependent Voigt models, in order to retrieve the Doppler width as a function of the simulated $\text{H}_2^{18}\text{O}$ pressure, at the temperature of the triple point of water. In any case, the Doppler width values exhibited a clear pressure dependence, which could be modeled by using a second-order polynomial function, at the aims of extrapolating the zero-pressure value ($\Delta v_0^D$). It turned out that, for Voigt and Galatry fits, $\Delta v_0^D$ underestimates the real Doppler width, with a relative systematic deviation of about $10^{-4}$, for a signal-to-noise ratio of 10000 (calculated with respect to the maximum transmitted signal of the simulated spectra). The SDVP-HG model did much better in the fits of simulated spectra. More particularly, as a result of the analysis of 1050 simulated spectra, characterized by a signal-to-noise ratio of 50000, the extraordinary accuracy of $3\times10^{-7}$ was demonstrated [23].

Experimental results seem to confirm the outcomes of the simulations. Figure 4 shows the Doppler widths as retrieved from the analysis of 150 spectra, recorded in coincidence with the $2_{2,1}\rightarrow2_{2,0}$ line of the $\text{H}_2^{18}\text{O} v_1+v_3$ band, as a function of the gas pressure, at the temperature of the triple point of water.

![Figure 4. Examples of Doppler-width retrieval by means of non-linear least-squares fits of absorption spectra at different pressures (between 10 and 400 Pa). The black line represents the expected value (286.4530 MHz).](image)

Of the tested models, the speed-dependent Voigt profile with hypergeometric dependence on both pressure broadening and shifting coefficients gives the best results, being the extrapolated zero-pressure value of the Doppler width equal to 286.469 (22) MHz, which differs from the expected one by less than 6 parts in $10^5$ (in terms of relative difference between measured and expected values). Instead, both Voigt and Galatry profiles (VP and GP) give smaller values (as compared to the expected one), with relative deviations of the order of $10^{-3}$. It is worth noting that the quadratic model, even doing better than VP and GP, does not reach the performance of the SDVP-HG model.

5. Conclusions
Recent advances in precision molecular spectroscopy enable one to reach unprecedented fidelity in the observation of the shape associated to a given vibration-rotation transition. Consequently, interesting investigations can be carried out, aimed at a better understanding of the physical mechanisms...
determining the spectral profiles. This is of utmost importance for improving the capabilities of quantitative laser absorption spectroscopy, for a variety of applications, including primary gas thermometry. I have shown and discussed the outcomes of recent studies on the H$_2^{18}$O near-IR spectrum. The experimental accuracy is so high that it is possible, for the first time, to recognize the influence of a restricted number of molecules, moving at the highest velocities, for which the quadratic approximation departs from the actual behavior of the relaxation rate as a function of the molecular speed. Experimental tests of DBT at the triple point of water confirm that the SDVP-HG model is superior to the others. This is an important step-forward towards a spectroscopic determination of the Boltzmann constant with a combined uncertainty at the ppm (part per million) level.

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