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# Hyperfine structure effects in Doppler-broadening thermometry on water vapor at 1.4 $\mu\text{m}$

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## Abstract

This article builds upon a previous work dealing with the budget of uncertainties associated to our recent determination of the Boltzmann constant by means of Doppler broadening thermometry. We report on the outcomes of theoretical calculations and numerical simulations aimed to precisely quantify the influence of the unresolved hyperfine structure of a given *ortho* component of the  $\text{H}_2^{18}\text{O}$  spectrum at 1.4  $\mu\text{m}$  on the measurement of the Doppler width of the line itself. We have found that, if the hyperfine structure of the  $4_{4,1} \rightarrow 4_{4,0}$  line of the  $\nu_1 + \nu_3$  band was ignored, the spectroscopic measurement of the Boltzmann constant would be affected by a relative systematical deviation of  $4 \cdot 10^{-8}$ .

Keywords: Doppler broadening thermometry, fundamental metrology, laser spectroscopy

(Some figures may appear in colour only in the online journal)

## 1. Introduction

The best determination of the Boltzmann constant ( $k_B$ ) by means of an optical method has been recently performed by means of a dual-laser absorption spectrometer operating at 1.4  $\mu\text{m}$  on  $\text{H}_2^{18}\text{O}$  molecules in the gas phase [1]. As recently discussed elsewhere [2], the complete budget of uncertainties leads to a global uncertainty of 24 parts over  $10^6$ , which turns to be a factor of 2 better than a previous determination performed on ammonia at 10.35  $\mu\text{m}$  [3].

With its three nuclei and ten electrons, water is classified as an asymmetric rotator belonging to the  $C_{2v}$  symmetry group. The small mass of the molecule leads to large vibrational frequencies and, therefore, to relatively strong absorption features in the near-infrared (NIR) portion of the electromagnetic spectrum. In fact, massive molecules exhibit high-order overtone or combination vibrational bands in the NIR. As it is well known, the transition probabilities rapidly decrease with the increasing order of the overtone band. As a matter of fact, the spectral lines of the  $2\nu_1$  and  $\nu_1 + \nu_3$  bands

occur at 1.4  $\mu\text{m}$ , with an intensity as large as  $10^{-20}\text{cm/mol-ecule}$ , for the strongest component. Due to the presence of two identical nuclei with a nuclear spin of  $\frac{1}{2}$  (the two protons of the hydrogen atoms) the symmetrization postulate applied to the complete wavefunction requires that symmetric spin combinations (with a total nuclear spin,  $I$ , equal to 1) combine with an antisymmetric rovibronic eigenstate, thus leading to the *ortho*-water. Similarly, for *para* water, the antisymmetric spin combination ( $I = 0$ ) combines with a symmetric rovibronic state. Therefore, the water spectrum is characterized by *ortho* and *para* lines, radiative and collisional transitions between *ortho* and *para* states being strongly forbidden [4]. A hyperfine structure is expected only for transitions of the *ortho* type by spin–spin and spin-rotation interactions, while it is totally absent for *para* transitions [5]. Making use of the asymmetric-top notation  $J_{K_a, K_c}$ , *ortho* levels for the fundamental vibrational state are those for which the sum  $K_a + K_c$  is odd. The water transition that was selected for the aims of Doppler-broadening thermometry (DBT) is the  $4_{4,1} \rightarrow 4_{4,0}$  line of the  $\text{H}_2^{18}\text{O}$   $\nu_1 + \nu_3$  band [1]. It offers a number of advantages

for low-uncertainty DBT, being relatively strong, well isolated and sufficiently close to the reference line that is used in the dual-laser approach of [1]. This is a transition of the *ortho* type, thus showing a hyperfine structure. Through a rough estimation of the hyperfine splitting based upon data available in the literature [6, 7], we evaluated that the type *B* component, which is due to the fact that the hyperfine structure is ignored, in the budget of uncertainties for the spectroscopic determination of  $k_B$ , was smaller than  $10^{-6}$  [2, 8].

In this article, we calculate the hyperfine structure of the selected water transition and determine the type *B* uncertainty associated to a line fitting procedure in which the hyperfine splitting is ignored, for the aims of Doppler width retrieval. The hyperfine energy levels and the linestrength of the hyperfine components have been calculated using the theoretical approach reported in the recent literature [5, 9]. Furthermore, absorption spectra at different pressures were simulated adopting the Voigt profile as lineshape model and including the hyperfine structure. The simulated thermodynamic conditions were identical to the experimental ones [1]. Then, the numerically simulated spectra were analyzed by means of a non-linear least-squares fitting procedure, using a Voigt function and ignoring the unresolved hyperfine structure, so as to retrieve the Doppler width and compare it with the expected one.

## 2. Hyperfine structure calculations

A given *ortho* water level with a rotational angular momentum  $J$  is splitted into three sublevels due to spin-rotation and spin-spin interactions. The total angular momentum can take the values  $F = J - 1, J, J + 1$ , while the corresponding energies can be calculated by using the following formula:

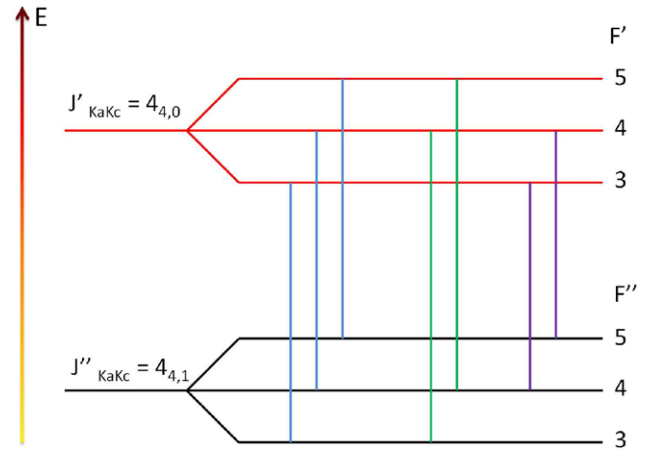
$$E = E_J + \frac{C(J_{Ka,Kc})}{2} [F(F+1) - I(I+1) - J(J+1)] + 4D(J_{Ka,Kc})Y(I, J, F) \quad (1)$$

where  $E_J$  is the unperturbed energy and  $Y(I, J, F)$  is the Casimir function [10]. The spin-rotation  $C(J_{Ka,Kc})$  and spin-spin  $D(J_{Ka,Kc})$  constants, both depending on the rotational level, are defined hereafter [5, 9]:

$$C(J_{Ka,Kc}) = \sum_g \frac{C_{gg} \langle J_g^2 \rangle}{J(J+1)} \quad (2)$$

$$D(J_{Ka,Kc}) = \frac{1}{2} \frac{\mu_N^2 g_I^2}{R^3} \left[ 1 - 3 \sum_g \frac{\alpha_g^2 \langle J_g^2 \rangle}{J(J+1)} \right]$$

where  $\mu_N$  is the nuclear magneton,  $g_I$  is the  $g$ -factor of the two hydrogen nuclei,  $R$  is the distance between the two nuclei,  $\alpha_g$  are the cosine of the angles between the vector joining both equivalent nuclei and the three principal axes of the molecule, while  $\langle J_g^2 \rangle$  are the average values of the square components of  $\vec{J}$  along the principal axes [11]. The calculation of these latter quantities required the values of the energy levels  $E_{Ka,Kc}$  of a rigid rotor, as listed in the appendix IV of [10]. The tensor diagonal elements  $C_{gg}$  change considerably with molecular



**Figure 1.** Hyperfine structure diagram for the  $4_{4,1} \rightarrow 4_{4,0}$  line of  $H_2^{18}O \nu_1 + \nu_3$ .

structure. Moreover, they should vary for interactions between levels belonging to different vibrational states. In this work, we set  $C_{gg} = [35.31 \ 31.31 \ 33.16]$  MHz, as provided by *ab initio* calculations for the  $H_2^{16}O$  molecule [12]. Ignoring a possible dependence on isotopic substitution, these spin-rotation constants were considered valid also for the  $H_2^{18}O$  molecule. Furthermore, we made the assumption that the upper level behaves like the lower one. This approximation is satisfactory for the aims of our calculation, considering that the influence of the hyperfine structure on Doppler width retrieval is expected to be rather small, namely, at the part-per-million (ppm) level [2].

The hyperfine structure of the rovibrational transition  $J'' = 4_{4,1} \rightarrow J' = 4_{4,0}$  of the  $\nu_1 + \nu_3$  band consists of seven components, according to the selection rule  $\Delta F = 0; \pm 1$ , as shown in figure 1. The relative strength of each component is given by the following expression [4, 11]:

$$\frac{S(J''F'' \rightarrow J'F')}{S(J'' \rightarrow J')} = (2F'' + 1)(2F' + 1) \left\{ \begin{matrix} J'' & 1 & J' \\ F' & I & F'' \end{matrix} \right\}^2 \quad (3)$$

where  $\left\{ \begin{matrix} J'' & 1 & J' \\ F' & I & F'' \end{matrix} \right\}$  is the Wigner 6j-symbol and  $S(J'' \rightarrow J')$  is the linestrength of the selected rovibrational transition, without the hyperfine splitting. It should be noted that the total line strength for *ortho* lines increases by a factor of three, proportionally to the statistical weight of the *ortho* states, since

$$\sum_{F''F'} S(J''F'' \rightarrow J'F') = (2I + 1)S(J'' \rightarrow J'). \quad (4)$$

We assume that the sum of all the intensities, which corresponds to the overall strength for the unresolved multiplet of lines, is coincident with the intensity given by the HITRAN database, namely,  $(2I + 1)S(J'' \rightarrow J') = S_{HITRAN}$  [13]. Table 1 reports the calculated central frequency detuning of the hyperfine components with respect to the line center  $\nu_0$  given by HITRAN. Absolute and relative strengths for the various components are also given in the same table. It is worth noting that the HITRAN value is distributed among all the

**Table 1.** Hyperfine components of the selected  $\text{H}_2^{18}\text{O}$  line and relative line strengths calculated at  $T = 296$  K.

$F''$	$F'$	$\Delta\nu = \nu_0^{\text{hf}} - \nu_0$ [kHz]	$S(J''F'' \rightarrow J'F')$ [cm per molecule]	$\frac{S(J''F'' \rightarrow J'F')}{S_{\text{HITRAN}}}$
3	3	14.57	$3.021 \cdot 10^{-24}$	0.2430
3	4	−85.01	$2.014 \cdot 10^{-25}$	0.0162
4	3	111.94	$2.014 \cdot 10^{-25}$	0.0162
4	4	12.36	$3.739 \cdot 10^{-24}$	0.3008
4	5	−225.44	$2.026 \cdot 10^{-25}$	0.0163
5	4	218.41	$2.026 \cdot 10^{-25}$	0.0163
5	5	−19.39	$4.861 \cdot 10^{-24}$	0.3911

components, which will be considered in the simulation of the absorption profiles as illustrated hereafter.

In absorption spectroscopy, the intensity of a light beam passing through an absorbing gas sample decreases according to the well known Beer–Lambert law:

$$I(\nu) = I_0 \exp[-S(T)NL\Phi(\nu)] \quad (5)$$

where  $I_0$  is the incident light intensity,  $N$  is the molecular number density of the absorbing species,  $L$  is the pathlength, and  $\Phi(\nu)$  is the lineshape profile. The line intensity factor,  $S$ , obviously depends on the gas temperature  $T$  [14]. For the sake of simplicity, the lineshape profile is assumed to be a Voigt function, defined in terms of the complex error function  $w(x, y)$ , as specified hereafter:

$$\begin{aligned} \Phi_{\text{VP}}(\nu) &= \frac{1}{2\pi\nu_D\sqrt{\pi}} \text{Re}\{w(x, y)\} \\ w(x, y) &= \frac{i}{\pi} \int_0^\infty \frac{e^{-t^2}}{y^2 + (x - t)^2} dt \\ x &= \frac{\nu - \nu_0}{\nu_D} \quad y = \frac{\nu_L}{\nu_D} \end{aligned} \quad (6)$$

where,  $\nu_0$ ,  $\nu_L$ ,  $\nu_D$  are the line center frequency, the collision width and Doppler width, respectively. The linestrength, the center frequency and the collision broadening coefficient of the  $4_{4,1} \rightarrow 4_{4,0}$  line of the  $\text{H}_2^{18}\text{O}$   $\nu_1 + \nu_3$  band are available from HITRAN, while the Doppler width (HWHM) is given by  $\nu_D = \nu_0 \sqrt{2 \ln 2 k_B T / mc^2}$ , where  $m$  is the molecular mass and  $c$  the speed of light. Numerically simulated spectra are calculated taking the hyperfine structure into account. More particularly, each component leads to an attenuation of the transmitted signal according to the following equation:

$$I_{\text{hf}}(\nu) = I_0 \exp[-S_{\text{hf}}(T)NL\Phi_{\text{VP}}^{\text{hf}}(\nu)] \quad (7)$$

where  $S^{\text{hf}}(T)$  is the linestrength of a given component  $J''F'' \rightarrow J'F'$ . Each component has a Voigt shape,  $\Phi_{\text{VP}}^{\text{hf}}(\nu)$ , with a line center frequency  $\nu_0^{\text{hf}}$  given in table 1. For asymmetric top molecules no collisional coupling between hyperfine components of a single rotational transition is expected [15]. The collision width,  $\nu_L$ , is assumed to be the same for all the components. Past literature has confirmed that this assumption is valid for both pressure broadening and shifting parameters [16, 17]. As a result, the overall transmitted signal can be expressed as:

$$I(\nu) = I_0 \exp\left[-\sum_{\text{hf}} S_{\text{hf}}(T)NL\Phi_{\text{VP}}^{\text{hf}}(\nu)\right]. \quad (8)$$

### 3. Results and discussion

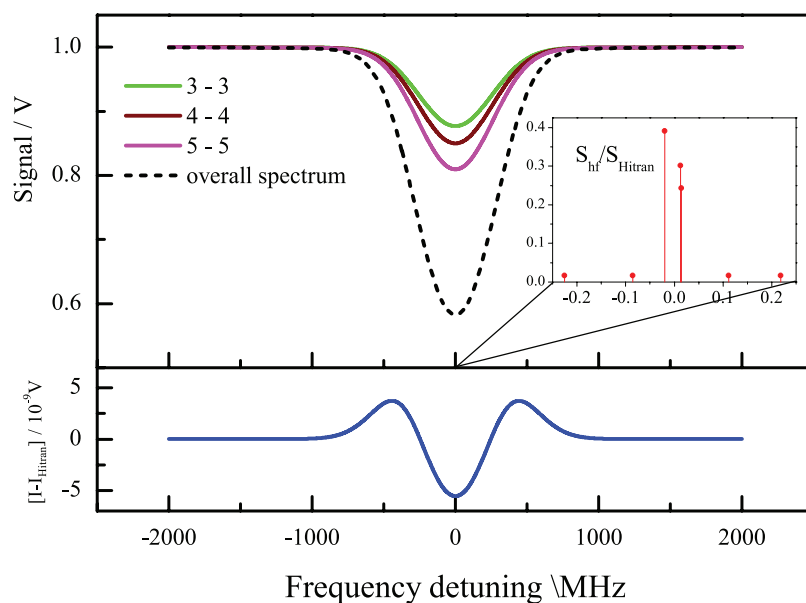
We simulated five absorption spectra at different gas pressures (33, 67, 133, 267 and 400 Pa), with a gas temperature of 273.16 K. The Doppler width was fixed at 285.532 80 MHz, and the collisional-broadening coefficient was set to the value of 0.991 MHz Pa<sup>−1</sup>. For each profile, the number of points was 4000, with the constant frequency step of 1 MHz. An example of numerically simulated spectrum is reported in figure 2, whose upper part also shows the profile of the main hyperfine components contributing to the line. The overall spectrum (dashed black line), which was calculated considering all the components of table 1, results to be very close to that obtained from one line with the parameters of the HITRAN database. The point-by-point difference between the two simulations is reported in the lower part of figure 2 and indicates that the discrepancy between the two is at the level of a few parts over 10<sup>9</sup>.

A non-linear least-squares fitting procedure was then applied to the simulated spectra. In order to quantify the influence of the hyperfine structure on Doppler width retrieval, the fits were performed ignoring the occurrence of an unresolved hyperfine structure underneath each simulated profile. Therefore, each spectrum was fitted to a single Voigt profile, with five free parameters, namely, the line center frequency, the Doppler width, the collision width, the integrated absorbance, and a baseline parameter. As a result of the fit, we could determine the Boltzmann constant by using the following relation:

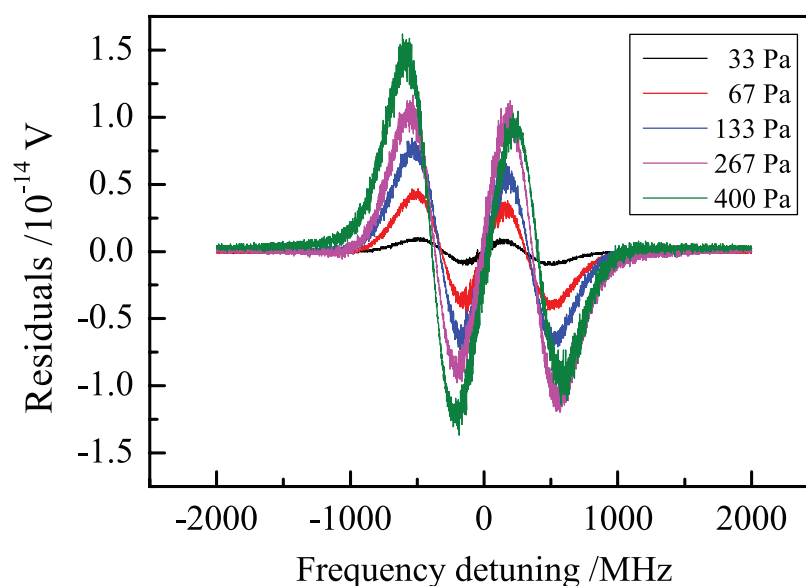
$$k_B = \frac{mc^2}{2T \ln 2} \left( \frac{\nu_D}{\nu_0} \right)^2. \quad (9)$$

We found a relative deviation from the expected (CODATA [18]) value of  $3.7 \cdot 10^{-8}$  (average shift over the pressure range of interest), while the relative standard deviation of the retrieved  $k_B$  values amounts to  $1.3 \cdot 10^{-15}$ . An example of fit residuals is plotted in figure 3 and demonstrates an extraordinary level of agreement, thus confirming the negligible influence of the unresolved hyperfine structure on Doppler broadening thermometry based upon  $\text{H}_2^{18}\text{O}$  molecules. It is worth noting that the noise in figure 3 is apparent, being due to the machine epsilon, which amounts to  $\approx 2 \cdot 10^{-16}$  for a 64-bit system. Adding a realistic white noise on the simulated spectra would prevent the precise quantification of the hyperfine structure effect on the spectroscopic determination of  $k_B$ .

The possible influence of the lineshape model has been investigated. We have repeated the calculations of the hyperfine profiles with the most realistic profile that is the Hartmann–Tran profile (HTP) [19]. Applying the same procedure as before, and doing the fits with a simple HTP profile, we found a relative deviation for  $k_B$  from the expected (CODATA [18]) value of  $3.6 \cdot 10^{-8}$ . The relative standard deviation for the retrieved  $k_B$  values results to be  $2.3 \cdot 10^{-10}$ ,



**Figure 2.** Main components of the hyperfine structure of the selected  $\text{H}_2^{18}\text{O}$  line, calculated at 273.16 K and 133 Pa. The dashed black line is the spectrum resulting from the sum of all the components. The inset shows the pattern of the relative strengths of the various components. The lower plot shows the absolute difference between simulated spectra with and without the hyperfine structure.



**Figure 3.** Absolute residuals resulting from the non-linear least-squares fits of simulated spectra by using a single Voigt profile.

which is much larger than that obtained by the Voigt model. Therefore, we can conclude that the influence of the lineshape model is limited to the dispersion of the data rather than to the values themselves.

#### 4. Conclusion

In conclusion, we have reported a detailed calculation of the hyperfine structure of the *ortho*-type  $4_{4,1} \rightarrow 4_{4,0}$  line of the  $\text{H}_2^{18}\text{O}$   $\nu_1 + \nu_3$  band, in operation conditions identical to the experiment described in [1]. We have confirmed that the

contribution to the uncertainty budget on the Boltzmann constant determination is much smaller than  $10^{-6}$ , being equal to  $3.7 \cdot 10^{-8}$ . This important outcome allows us to state that taking into account hyperfine splitting effects is not necessary for the aims of a spectroscopic determination of  $k_B$  at the ppm level of global uncertainty. This latter would be desired in view of the foreseen redefinition of the unit kelvin, which implies a fixed numerical value for  $k_B$  [20]. In this respect, a spectroscopic determination of  $k_B$  would be of great importance to confirm the highly-accurate values recently obtained by using acoustic gas thermometry [21–23].

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