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High precision line shape studies in low pressure ammonia for an accurate determination of the Boltzmann constant

C Lemarchand, M Triki, B Darquié, P L T Sow, S Mejri, C Chardonnet,
Ch J Bordé and C Daussy

Université Paris 13, Sorbonne Paris Cité, Laboratoire de Physique des Lasers, CNRS,
UMR 7538, F-93430, Villetaneuse, France

E-mail: christophe.daussy@univ-paris13.fr

Abstract. In this paper, we present the progress performed in an experiment dedicated to the determination of the Boltzmann constant by an accurate measurement of the Doppler absorption profile of a line of ammonia in the gas phase in thermal equilibrium. We have recorded the hyperfine structure of the ν_2 saQ(6,3) rovibrational line by saturation spectroscopy and determined very precisely the induced broadening of the absorption line in linear absorption. In addition, we present an accurate analysis of the shape of the probed self-broadened line. Experimental spectra are confronted to various models that take into account Dicke narrowing or speed-dependent effects. Our results show a deviation from the Voigt profile dominated by speed-dependent broadening and shift. We also theoretically demonstrate that there is strictly no additional broadening from finite transit time across the laser beam. Finally, from the reported analysis, we anticipate that a first optical determination of the Boltzmann constant with a competitive accuracy of 1.8 parts per million is now reachable.

1. Introduction

A renewed interest in the Boltzmann constant, k_B , is related to the possible redefinition of the International System of Units (SI) [1-4]. A new definition of the kelvin would fix the value of the Boltzmann constant to a value determined by The Committee on Data for Science and Technology (CODATA) [5]. Since 2004 we have developed a new approach based on laser spectroscopy for the Boltzmann constant determination. The principle [6, 7] consists in recording the Doppler profile of a well-isolated absorption line of a molecular gas in thermal equilibrium in a cell. This profile reflects the Maxwell-Boltzmann distribution of velocities along the laser beam axis. In a first experiment we demonstrated the potential of this approach [8-12] on an ammonia rovibrational line. We were soon followed by at least four other groups who started similar experiments on CO₂, acetylene, H₂O and rubidium [13-17].

In this paper, we present the spectrometer developed to record the ν_2 saQ(6,3) rovibrational line of ammonia both by linear and saturated absorption spectroscopy. We give an evaluation of the effect of the hyperfine structure on the Doppler width measurement accuracy. We also present an accurate line shape analysis of the probed self-broadened absorption transition, recorded by linear absorption laser spectroscopy. Spectra are analyzed using various models which enable to clearly identify the profile which best matches the data as the speed-dependent Voigt profile (SDVP). We present a determination of the impact of collisional effects on the Doppler width measurement accuracy. Finally, we

theoretically demonstrate that there is strictly no additional broadening from finite transit time across the laser beams. The molecular recoil and the second-order Doppler effect are included in this analysis following a complete quantum treatment.

2. The spectrometer

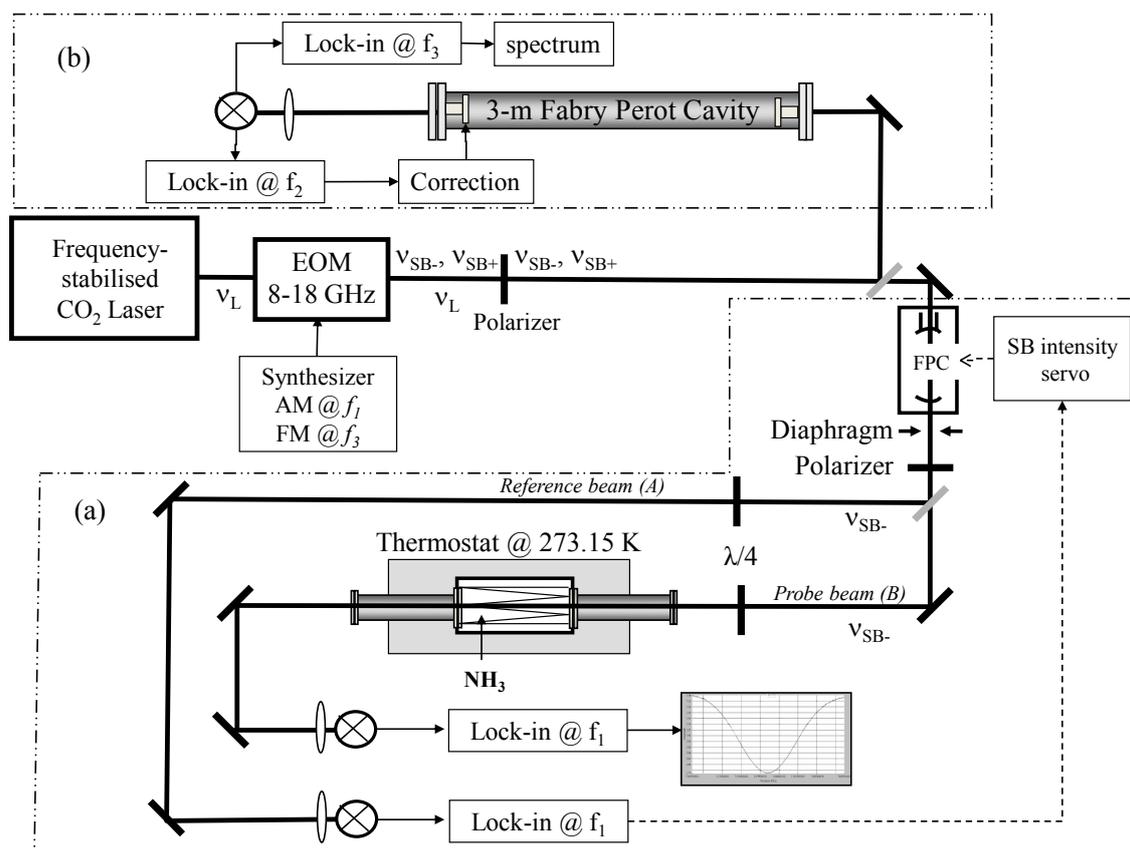


Figure 1. Experimental setup for (a) linear absorption spectroscopy and (b) saturated absorption spectroscopy (AM: amplitude modulation, FM: frequency modulation, EOM: electro-optic modulator, FPC: Fabry Perot cavity, SB: sideband, Lock-in: lock-in amplifier).

The spectrometer (figure 1) is based on a CO₂ laser source which operates in the 8-12 μm range. The laser frequency stabilisation scheme is described in reference [18]: a sideband generated with a tunable electro-optic modulator (EOM) is stabilized on an OsO₄ saturated absorption line detected on the transmission of a 1.6-m long Fabry-Perot cavity (FPC). Since its tunability is limited to 100 MHz, our CO₂ laser source is coupled to a second EOM which generates two sidebands SB- and SB+ on both sides of the fixed laser frequency. Their frequency is tunable from 8 to 18 GHz with respect to the carrier frequency. The intensity ratio between these two sidebands and the carrier is about 10⁻⁴. After the EOM, a grid polarizer attenuates the carrier by a factor 200 but not the sidebands which are cross-polarized. Figure 1.b represents the saturated absorption spectrometer used for recording the hyperfine structure of the rovibrational line. The modulation f₂ is used to stabilize the resonator frequency and can be applied either on one mirror mounted on a piezoelectric transducer or directly on the sideband frequency via the synthesizer that drives the 8–18 GHz EOM. The hyperfine components of the molecular line are detected in transmission of a 3-m long Fabry Perot cavity after demodulation at f₃, a modulation applied on the sideband frequency via the EOM. Figure 1.a represents the linear absorption spectrometer. An FPC is used to drastically filter out the residual carrier and the unwanted

SB+ sideband and to stabilise the intensity of the transmitted sideband SB-. A 50/50 beamsplitter splits the transmitted beam in two parts. Beam A intensity is compared and locked to a very stable voltage reference by acting on the length of the FPC, which results in beam B probing NH₃ in the 37-cm long absorption cell with a constant incident laser power. Both the reference beam (A) and the probe beam (B) are amplitude-modulated at f_1 via the 8-18 GHz EOM for noise filtering and signals are obtained after demodulation at f_1 . The sideband is tuned close to the desired molecular resonance and scanned to record the Doppler profile.

3. The hyperfine structure analysis

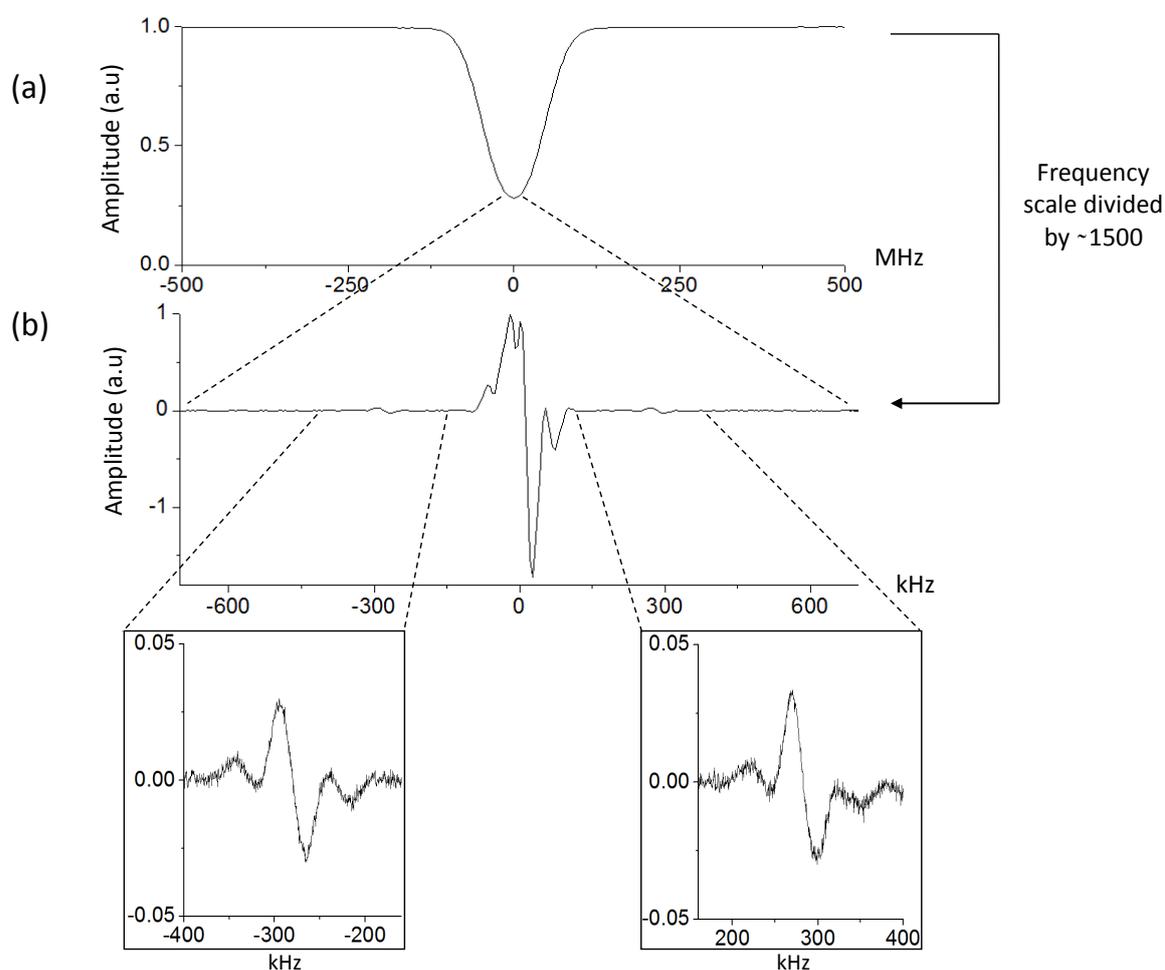


Figure 2. ¹⁴NH₃ saQ(6,3) absorption line recorded by linear absorption (a) and at higher resolution by saturated absorption spectroscopy (b). At about 300 kHz on both sides of the central components Doppler-generated level crossings are observed.

The selected absorption line is the ν_2 saQ(6,3) rovibrational line of the ammonia molecule ¹⁴NH₃ at the frequency $\nu = 28\,953\,693.9(1)$ MHz. This well-isolated transition has been chosen to avoid any deformation of the profile due to line mixing with neighbouring lines. Owing to the non-zero spin values of the nitrogen and hydrogen nuclei, an unresolved hyperfine structure is present in the Doppler profile of this rovibrational line. Figure 2 compares (a) the ν_2 saQ(6,3) linear absorption signal

recorded in transmission of the 37-cm long absorption cell (see figure 1.a) and (b) the saturated absorption signal recorded in transmission of the 3-m long Fabry-Perot cavity (see figure 1.b). Saturated absorption spectroscopy displays Doppler-generated level crossings, clearly visible around ± 300 kHz from the central components.

Combined with microwave spectroscopy data, an analysis of saturated absorption spectra led to an accurate determination of the hyperfine constants of the ν_2 saQ(6,3) line [19] and to the estimation of the impact of the hyperfine structure on the Doppler width measurement. The global spread of the overall hyperfine structure and the relative intensities of hyperfine components of the linear absorption spectrum (and the respective uncertainties) result in a very precise determination of the correction to be applied on the value of the Doppler width: -4.356(13) parts per million, leading to an uncertainty of 0.026 part per million on k_B .

4. The self-broadened line shape analysis

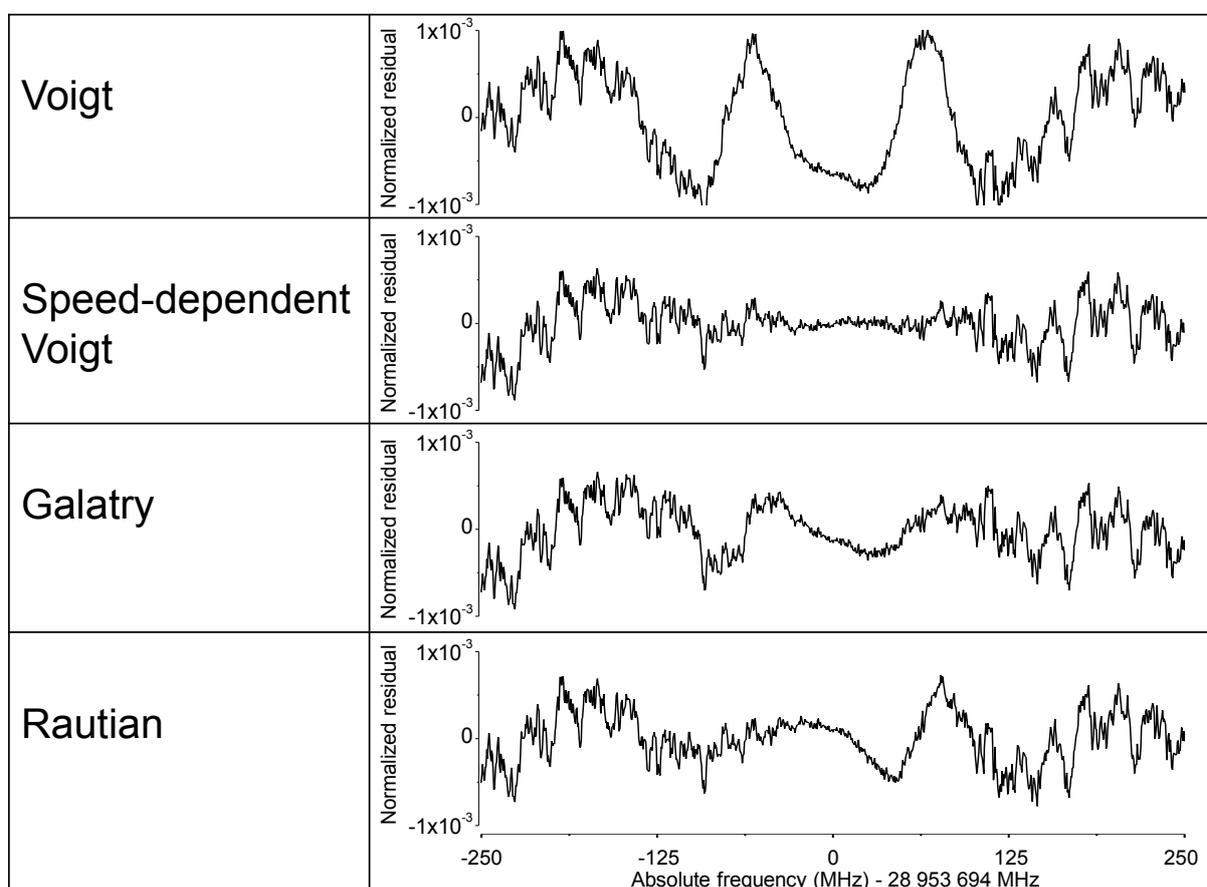


Figure 3. Normalized residuals for non-linear least-squares fits of spectra recorded at 17.3 Pa, with a VP (Voigt Profile), SDVP (Speed-Dependent Voigt Profile), GP (Galatry profile) and RP (Rautian Profile). The frequency scale is offset by 28 953 694 MHz.

In the very low pressure regime explored, the line shape can be described simply by a Voigt profile (VP). With respect to the VP, the line shape can be narrowed either by speed-dependent or Lamb-Dicke-Mössbauer (LDM) effects. On the one hand, the SDVP takes into account a dependence of the relaxation mechanism on molecular speed through a speed-dependent collisional shift and broadening.

On the other hand the LDM effect results in a reduction of the Doppler width due to velocity changing collisions. Assuming soft – resp. hard – collisions between molecules then leads to the Galatry – resp. Rautian – profile (GP – resp. RP) [20, 21].

Spectra recorded around 17 Pa have been fitted with a VP, SDVP, GP and RP. Residuals obtained are displayed on figure 3. For the VP, GP and RP, residuals clearly indicate that these profiles do not match the experimental data. By contrast, analysis of spectra with the SDVP clearly demonstrates a good agreement between this model and experimental line shapes. Based on our analysis (reported in detail in ref [22]) we can state that the deviation from a VP of the ν_2 saQ(6,3) line of NH_3 is most probably caused by speed-dependent effects and not LDM effects, in the explored pressure range.

The impact of collisional effects on the Doppler width measurement has been estimated. The associated uncertainty is only limited by our knowledge on the SDVP collisional parameters [22]. In order to reduce the impact of this source of uncertainty, the measurement of the Boltzmann constant is performed at low pressure, below 2 Pa. Simulated spectra corresponding to these experimental conditions have been fitted taking into account uncertainties on the SDVP parameters. Following the line-absorbance based analysis recently proposed by A. Castrillo et al. [23] an experimental uncertainty of 0.9 part per million is obtained on the Doppler width measurement, leading to an uncertainty of 1.8 parts per million on k_B .

5. The theory of linear absorption line shape: case of the speed-dependent Voigt profile

The purpose of this paragraph is to outline the derivation given in [21] of a line shape including the modal structure of the laser beams, with an explicit introduction of a speed-dependent broadening and shift (besides the second-order Doppler shift), in order to investigate possible contributions of transit-time effects. The starting point is the expression for the dimensionless absorbance in the momentum representation:

$$A_\nu = 2\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_{a\beta}}}{Z_{int}} \frac{\omega}{V} \int d^3k \alpha^*(\vec{k}) \alpha(\vec{k}) \bar{f}_{ba}(\vec{k}, \omega) + c. c. \quad (1)$$

where α is the fine structure constant, $n^{(0)} \frac{e^{-E_{a\beta}}}{Z_{int}}$ the population of the lower level, d_{ba} the dipole moment of the transition divided by the elementary charge, L the absorption length, $V = LS$ the laser mode volume. The normalized line shape for each plane wave component $\alpha(\vec{k})$ of the laser mode is the velocity average $\bar{f}_{ba}(\vec{k}, \omega) = \int f_{ba}(\vec{v}, \vec{k}, \omega) d^3v$ where $f_{ba}(\vec{v}, \vec{k}, \omega)$ is proportional to the first-order off-diagonal density matrix element $\rho_{ba}^{(1)} = i\Omega_{ba} f_{ba}$ through the Rabi frequency Ω_{ba} and satisfies the integral equation:

$$\begin{aligned} & [i(\omega - \omega_{ba}(1 - v^2/2c^2) - \Delta_{ba}(v) - \vec{k} \cdot \vec{v} - \delta) + \gamma_{ba} + \Gamma_{ba}(v)] f_{ba}(\vec{v}, \vec{k}, \omega) \\ & = F_M(\vec{v}) + \int d^3v' W_{ba}(\vec{v}' \rightarrow \vec{v}) f_{ba}(\vec{v}', \vec{k}, \omega) \end{aligned} \quad (2)$$

which includes the second-order Doppler shift, the recoil shift δ , a velocity-dependent shift $\Delta_{ba}(v)$ and broadening $\Gamma_{ba}(v)$, the natural linewidth γ_{ba} , and where $F_M(\vec{v})$ is the Maxwell-Boltzmann distribution of velocities and $W_{ba}(\vec{v}' \rightarrow \vec{v})$ is the collision kernel describing the probability for a velocity change from \vec{v}' to \vec{v} .

The wave vector appears in this equation only through the projection $\vec{k} \cdot \vec{v}$ so that, thanks to the isotropy of the velocity distribution and of collisions, there is no privileged direction (except for that of gravity whose influence needs to be carefully evaluated). Thus \bar{f}_{ba} cannot depend on the direction of \vec{k} but only on its modulus $|\vec{k}|$ and finally, due to the dispersion relation $k = \omega/c$, \bar{f}_{ba} results in a function of ω only. The mode volume V cancels with $\int d^3k \alpha^*(\vec{k}) \alpha(\vec{k})$ and any dependence on the laser mode content disappears. This gives for the absorbance:

$$A_\nu = 4\pi\alpha n^{(0)} d_{ba}^2 L \frac{e^{-E_{a\beta}}}{Z_{int}} \omega \text{Re} \bar{f}_{ba}(\omega) \quad (3)$$

which is independent of the structure of the light beam and hence has strikingly no additional transit-time broadening as we shall illustrate below in a specific case.

In this paper we consider more specifically the case where velocity-changing collisions are ignored and hence the integral term of equation (2) is neglected:

$$2\text{Re}\bar{f}_{ba}(\omega) = 2 \frac{\sqrt{\pi}}{\Delta\omega_D} \text{Re} z(\omega) \quad (4)$$

where

$$\begin{aligned} z(\omega) &= \int d^3v \frac{F_M(\vec{v})}{i(\omega - \omega_{ba}(1 - v^2/2c^2) - \Delta_{ba}(v) - \vec{k} \cdot \vec{v} - \delta) + \gamma_{ba} + \Gamma_{ba}(v)} \\ &= \frac{4}{\sqrt{\pi}\Delta\omega_D} \int_0^{+\infty} d\theta \theta e^{-\theta^2} \tan^{-1} \left(\frac{i\theta}{\zeta(\theta)} \right) \end{aligned} \quad (5)$$

is a generalized speed-dependent Voigt profile which, thanks to the isotropy of $F_M(\vec{v})$, depends on \vec{k} only through the Doppler width $\Delta\omega_D = ku$ ($u = \sqrt{2k_B T/m_{NH_3}}$ is the most probable speed of molecules) and the recoil shift and hence has been expressed as a single quadrature on $\theta = v/u$, with $\zeta(\theta) = (\omega - \omega_{ba}(1 - \theta^2 u^2/2c^2) - \Delta_{ba}(\theta) - \delta + i(\gamma_{ba} + \Gamma_{ba}(\theta))) / \Delta\omega_D$.

In section 4, we followed the formalism developed by Berman, Ward and Pickett for the SDVP leading to the collisional parameters [24-26]:

$$\Gamma_{ba}(\theta) = \frac{\Gamma_{ba}}{2^{m/2}} {}_1F_1\left(-\frac{m}{2}, \frac{3}{2}, -\theta^2\right) \text{ and } \Delta_{ba}(\theta) = \frac{\Delta_{ba}}{2^{n/2}} {}_1F_1\left(-\frac{n}{2}, \frac{3}{2}, -\theta^2\right) \quad (6)$$

where ${}_1F_1(a, b, z)$ is the Kummer confluent hypergeometric function, and $m = 0.360(7)$ and $n = -3.8(3)$ are parameters related to the intermolecular potential [22].

More generally equation (2) cannot be solved without a numerical calculation of the collision kernels [27, 28]. There are however simple cases where it can be solved analytically e.g. when the integral term in (2) is a convolution product [29, 30]. Another example is the model of Rautian, Nelkin and Ghatak [31, 32] in which each collision is assumed to be strong enough to redistribute the velocities according to the Maxwell-Boltzmann distribution:

$$W_{ba}(\vec{v}' \rightarrow \vec{v}) = \nu_c F_M(\vec{v}) \quad (7)$$

where ν_c is an adjustable collision frequency. We obtain the generalized speed-dependent Rautian profile:

$$2\text{Re}\bar{f}_{ba}(\omega) = 2 \frac{\sqrt{\pi}}{\Delta\omega_D} \text{Re} \frac{z(\omega)}{1 - \nu_c (\sqrt{\pi}/\Delta\omega_D) z(\omega)} \quad (8)$$

If velocity-changing collisions are neglected, $\nu_c = 0$ and the generalized speed-dependent Rautian profile reduces to the generalized speed-dependent Voigt profile which is considered in this paper. Other models for the collision kernels are presently under study but as long as these are isotropic no transit-time effect will occur.

6. Conclusion

This paper presents a study of the influence of the hyperfine structure on the measurement of the Doppler broadening of the ν_2 saQ(6,3) rovibrational line of ammonia close to 273.15 K. Its role cannot be neglected at a level of a few parts per million but it can now be taken into account with a negligible residual uncertainty. We have reported on an accurate analysis of self-broadened ν_2 saQ(6,3) line shape of NH_3 . The deviation from a Voigt profile of the present line shape seems dominated by speed-dependent effects. We have also demonstrated the absence of any additional transit broadening whatever the optical quality of the laser beam wave fronts and effective diameters, even in presence of relaxation effects dependent on molecular speed. Finally, from the accurate knowledge of the absorption line shape we anticipate that a first determination of k_B with a competitive accuracy of 1.8 parts per million by measurement of the Doppler width in ammonia is now reachable.

Acknowledgments

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