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# Collisional parameters of $H_2O$ lines: Velocity effects on the line-shape

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**Abstract**

This paper is devoted to the effects of velocity on the shapes of six $R(J)$ lines of the $\nu_3$ band of water vapor diluted in $N_2$. The experiments have been made at room temperature for total pressures between 0.1 and 1.2 atm using a tunable infrared laser frequency difference spectrometer. These measurements, which study broad and narrow lines of low and high $J$ values, are first analyzed using the Voigt and the hard collision (HC) model. It is shown that both lead to unsatisfactory results, the Voigt profile being unable to account for the line narrowing whereas the friction (narrowing) parameter deduced using the HC approach has an unphysical dependence on pressure. Furthermore, at elevated pressure where Dicke narrowing and Doppler effects are negligible, deviations between experimental and fitted profiles are still observed, indicating inhomogeneous effects due to the speed dependence of collisional parameters. In order to go further, an approach based on the kinetic impact equation accounting for both the Dicke narrowing and the speed dependence has been applied. It uses velocity-dependent broadening and shifting coefficients calculated with a semi-classical approach and two parameters. The latter, which govern the memory functions of the modulus and orientation of the $H_2O$ velocity are considered as free parameters and determined from experiments. The results show that all profiles, regardless of pressure and of the transition, can be correctly modeled using a single set of memory parameters. This demonstrates the consistency of the approach, which is then used to analyze the different regimes that monitor velocity effects on the line profile.


*Keywords:* Water vapor; Line-shape; Velocity effects

## 1. Introduction

Due to the importance of water vapor in our atmosphere, the broadening and shifting of $H_2O$ absorption lines have been the subject of many experimental and theoretical efforts in the last 20 years (see Refs. [1,2] and

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those cited therein). Deviations of measured $H_2O$ absorption with respect to the Voigt shape have been pointed out a while ago [3], and accounted for or studied in a number of papers [3–20] since then. Nevertheless, for $H_2O$–$N_2$ (and air) mixtures, there are, to our knowledge, few works providing large sets of data on the spectral shape for various lines and pressures [18,19]. In Refs. [3–20], a narrowing of the line-shape is observed that mostly affects rovibrational transitions (of high $J$ and $K_a$ or $K_c$ values), which have small broadening coefficients. It is important to note that in most of these studies, this phenomenon has been attributed only to changes of the $H_2O$ velocity induced by collisions (i.e. confinement or Dicke narrowing) and that the eventual participation of the dependence of collisional parameters (width and shift) on the absolute speed of the radiatively active molecule has seldom been considered. To our knowledge, the only studies that consider this effect for $H_2O$ are those of Refs. [18–20]. They conclude that the speed dependence does have an effect but few results are given and, as will be shown here, empirical and approximate speed dependences of the broadening coefficients are used. Note that an indication of the importance of speed averaging of the line-shape can be found in the "strange" results that may be obtained when only the confinement narrowing is considered. Indeed, the friction parameters $\beta$ deduced from fits of measured absorption then depend on the rovibrational transition and show a non-linear dependence on pressure as demonstrated in this paper and in Ref. [19].

The present paper is the third of a series devoted to the effects of collisions on absorption lines of water vapor diluted in $N_2$ (and air). After studies of the influence of vibration [1] and temperature [21] on the pressure broadening and shifting coefficients, we now study the influence of velocity changes and velocity averaging on the spectral shape and the resulting deviations from the Voigt profile. The experiments were carried out in Madrid using a tunable infrared laser frequency difference spectrometer. Absorption by water vapor highly diluted in nitrogen was measured at room temperature for nine total pressures between 0.1 and 1.2 atm. The spectral transitions under study are six $R(J)$ lines of the $\nu_3$ band with rotational quantum numbers $K_c = J$ (and $K_a = 0$ or 1). These, for $J = 3$, 5, 8, 10, 12, and 14, were chosen since their collisional broadening decreases rapidly with $J$ [1] showing a ratio of about 10 between the broadest and the narrowest. This leads to very different deviations from the Voigt profile for a given pressure as will be shown latter. Furthermore, as demonstrated in Ref. [21], the temperature dependence of the widths varies largely from low to high $J$ lines. This indicates large differences of the velocity dependence from line to line so that significantly different inhomogeneous effects of the speed averaging are expected.

In order to model the line-shapes, the Keilson and Storer 3-dimensional (KS-3D) approach, recently developed and successfully applied to $H_2$ Raman transitions [22,23], is used. This is a powerful approach, self consistent for all pressures from the Doppler to the collisional regime, that includes both the confinement narrowing of the Doppler distribution and the radiator speed dependence of the collisional width and shift. In order to do that, the velocity orientation and velocity modulus memory mechanisms are distinctly considered as explained in Ref. [24]. Starting from the impact kinetic equation, including the Doppler contribution with a convenient bi-parametric 3D radiator velocity memory function, the expression for the line shape is established. It is based on two quantities that parameterize the influence of collisions on the orientation $\gamma_{Ori}$ and modulus $\gamma_{Mod}$ of the $H_2O$ velocity. Using semi-classical predictions [1,21] of the dependences of the broadening and shift on the relative velocity, the values of $\gamma_{Ori}$ and $\gamma_{Mod}$, that are the only adjustable quantities of the model, are determined in order to get agreement with measurements. It is then demonstrated that, with these two parameters only, all measured profiles are correctly reproduced, regardless of the line and total pressure. The model is then used for the analysis of the different mechanisms that govern the line shape.

## 2. Experimental, data treatment, and results

### 2.1. Experiments

Spectra were recorded with the infrared laser frequency difference spectrometer in Madrid [25,26]. For these experiments the $Ar^+$ laser operated at 514 nm, single-mode, actively frequency stabilized and locked to a $^{127}I_2$ hyperfine transition. The ring dye laser used DCM as dye and was frequency stabilized and scanned using its own (commercial) electronics. The wavenumber scale of each scan was linearized and calibrated a posteriori