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Precise predictions of H_2O line shapes over a wide pressure range using simulations corrected by a single measurement

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Abstract

In this work, we show that precise predictions of the shapes of H_2O rovibrational lines broadened by N_2, over a wide pressure range, can be made using simulations corrected by a single measurement. For that, we use the partially-correlated speed-dependent Keilson-Storer (pcsdKS) model whose parameters are deduced from molecular dynamics simulations and semi-classical calculations. This model takes into account the collision-induced velocity-changes effects, the speed dependences of the collisional line width and shift as well as the correlation between velocity and internal-state changes. For each considered transition, the model is corrected by using a parameter deduced from its broadening coefficient measured for a single pressure. The corrected-pcsdKS model is then used to simulate spectra for a wide pressure range. Direct comparisons of the corrected-pcsdKS calculated and measured spectra of 5 rovibrational lines of H_2O for various pressures, from 0.1 to 1.2 atm, show very good agreements. Their maximum differences are in most cases well below 1%, much smaller than residuals obtained when fitting the measurements with the Voigt line shape. This shows that the present procedure can be used to predict H_2O line shapes for various pressure conditions and thus the simulated spectra can be used to deduce the refined line-shape parameters to complete spectroscopic databases, in the absence of relevant experimental values.

1. Introduction

Thanks to the development of advanced spectroscopic-measurement techniques, extremely high resolution and high signal-to-noise absorption spectra for many molecular species are nowadays possible. Analyses of these spectra enable to investigate various characteristics of the absorbing molecule and of its interaction with radiation. High quality spectra are also obtained by a large number of atmospheric remote-sensing experiments (e.g. [1–4]). However, it is now well known that the widely-used Voigt profile is not able to describe the measured spectra within the experimental accuracy, its deviation with the observed line shape being of several percent of the peak absorption (see [5,6] and references therein, for instance). A precise line-shape model beyond the Voigt profile is thus required to meet the experimental accuracy and to fulfil the precision requirements of many applications such as atmospheric remote sensing (e.g. [2,7–10]), or metrology (e.g. [11–14]). Recently, the Hartmann-Tran (HT) profile [6,15] was retained by a spectroscopy task group of IUPAC [16] as the new reference line-shape model to be used for high resolution spectroscopy. This model takes into account several effects which are neglected in the Voigt profile, i.e.: the velocity changes due to collisions [17,18], the speed dependences of the collisional width and shift [19] and the correlation between velocity-changing collisions and internal-state changing collisions [17]. It was shown that [6,16] this model is capable to describe the measured line shapes of

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various molecular systems within a precision of a few 0.1%. A very efficient method for its calculation was also developed [20,21]. The HITRAN spectroscopic database [22] now enables the storage of the HT parameters and provide them for a few lines. Moreover, the correct use of the HT profile in spectra analyses requires several conditions. Firstly, due to the large number of its parameters, a multi-spectrum fitting technique applied to spectra measured for a large pressure range is recommended in order to decrease correlations between various parameters. Secondly, high signal-to-noise ratio spectra are needed to accurately retrieve all the line-shape parameters. Fulfilling all these conditions for many molecular systems in wide spectral ranges under various pressure and temperature conditions is not an easy task. Tremendous efforts will thus have to be made before spectroscopic databases are completed with HT parameters and this profile can be used in the treatment of high accuracy atmospheric observations.

In [23], Ngo and Hartmann demonstrated that this issue can be solved by using *ab initio* calculated spectra and very little experimental information. Indeed, it was shown that requantized classical molecular dynamics simulations (rCMDS) (e.g.[24–28]) enable accurate predictions of non-Voigt effects on the line shapes of linear molecules. Starting from a precise intermolecular potential, the time evolution of a molecular system can be simulated. The auto-correlation function of the dipole moment, responsible for the optical transition can thus be computed. Its Fourier transform directly yields the spectral shape. Comparisons between the rCMDS-calculated spectra and measurements were made by fitting both the calculated and measured spectra with the Voigt profile. The retrieved (Lorentz) broadening coefficients, their evolutions with pressure as well as the fit residuals are then compared. It was shown that the broadening coefficients retrieved from rCMDS-calculated spectra agree within a few percent those deduced from measurements. However, the non-Voigt effects on the measured spectra (expressed through the pressure dependences of the broadening coefficient and of the Voigt-fit residuals) are in very good agreement with those obtained from rCMDS-calculated spectra. Based on these characteristics, Ngo and Hartmann have corrected the rCMDS by using the difference $\Delta\gamma$ between the pressure-broadening coefficients obtained from a spectrum measured at a single pressure P_0 and that deduced from rCMDS, calculated under exactly the same condition. The rCMDS auto-correlation of the dipole moment for pressure P is then corrected by multiplying it by the factor $\exp(-2\pi c P \Delta\gamma t)$ with $(P\Delta\gamma)$ in cm^{-1}. Direct comparisons (without any other adjustable parameter) between these calculations and spectra of two lines of CO, diluted in He, Ar and Kr, measured for large pressure ranges show very good agreements [23]. The calculations are able to predict spectra for all considered pressures within a precision better than 1%, much better than the best fits of the measurements with the Voigt profile [23]. This shows that, from only one measured broadening coefficient and by using this corrections procedure, one can produce "reference spectra" for various pressure conditions, and thus provide HT line-shape parameters for the considered line.

In this work, we applied a similar procedure to H_2O lines, broadened by N_2. H_2O being a key molecule in the Earth atmosphere, a precise knowledge of the spectroscopic parameters of its lines is obviously needed. In [29–31], we showed that the partially-correlated speed dependent Keilson-Storer (pcsdKS) model enables accurate predictions of the non-Voigt effects on measured H_2O spectra. This model is based on the Keilson-Storer (KS) [32] function for collision-induced velocity changes. The parameters of the KS function were directly deduced from classical molecular dynamics simulations (CMDS) [25,26], together with the correlation between velocity- and internal-state-changing collisions. The speed-dependent line width and shift were calculated using the complex Robert-Bonamy formalism [33,34]. The spectral shape was then computed by solving a kinetic equation taking into account all these contributions. Comparisons between calculated and measured spectra of several lines of H_2O diluted in N_2 and of pure H_2O, made using their Voigt-fits, showed that the pcsdKS model correctly predicts non-Voigt effects [29-31]. Similarly to Ref. [23], here we first correct the pcsdKS model by

using the ratio $\gamma_L^{Meas}/\gamma_L^{Calc}$ between the Lorentz broadening coefficient obtained from a single spectrum measured for a given pressure and that deduced from the pcsdKS-spectrum, calculated under exactly the same condition. The correction was then made by multiplying the speed-dependent line width involved in the pcsdKS function by $\gamma_L^{Meas}/\gamma_L^{Calc}$. Spectra of five ro-vibrational lines of H_2O diluted in N_2, measured for various total pressure (from 100 to 1200 mbar) were retained for the test of this procedure. For that, the corrected pcsdKS-calculated line shapes were directly compared with the measured spectra. The HT parameters obtained from fits of experimental spectra and of corrected pcsdKS-calculated spectra are also compared and analysed.

The remainder of this paper is divided into 3 sections. In section 2, we briefly describe the pcsdKS model, the experimental data used. The correction procedure applied to the pcsdKS model is also detailed in this section. The comparisons between the calculated spectra and measured ones are made in Sec. 3 in which results obtained by fitting the calculated and measured spectra with the HT profile are also presented and discussed. Conclusions and perspectives to this work are drawn in Sec. 4.

2. The pcsdKS model, the data used and the correction procedure

Since a detailed description of the pcsdKS line-shape model used here is given in [29–31], only the main equations are recalled in the following. The profile of an isolated line (no line-mixing) is given by the Fourier transform of the auto-correlation function $\bar{d}(t)$ of the dipole moment responsible for the transition [5], i.e.:

$$I(\omega) = \frac{1}{\pi}\, Re\left[\int_0^{+\infty} dt\; e^{i(\omega-\omega_0)t}\; \bar{d}(t)\right], \tag{1}$$

where ω_0 is the unperturbed angular frequency of the optical transition and $\bar{d}(t) = \int d(\vec{v},t)d\vec{v}$ with $\vec{v}$ the velocity of the radiator. Within the pcsdKS model, $d(\vec{v},t)$ is the solution of the following kinetic equation [17,35]

$$\frac{\partial}{\partial t} d(\vec{v},t) = -\tilde{\nu}_{VC}(v)d(\vec{v},t) + \tilde{\nu}_{VC}(v)\int f_{KS}(\vec{v}\leftarrow\vec{v}')\, d(\vec{v}',t)d\vec{v}' - [i\vec{k}\vec{v} + \Gamma(v) + i\Delta(v)]d(\vec{v},t)\,. \tag{2}$$

The term $i\vec{k}\vec{v}$ in Eq. (2) represents the dephasing due to the Doppler effect, with $\vec{k}$ the wave vector. $\tilde{\nu}_{VC}(v)$ is the speed-dependent (with v the molecular speed) velocity changing collision frequency, given by

$$\tilde{\nu}_{VC}(v) = \nu_{VC} - \eta[\Gamma(v) + i\Delta(v)], \tag{3}$$

where $\Gamma(v)$ and $\Delta(v)$ are the speed dependent collisional width and shift, η is the parameter characterizing the correlation between velocity- and internal-state-changing collisions. ν_{VC} is the frequency of velocity-changing collisions assuming no temporal correlation between velocity and states changes. $f_{KS}(\vec{v}\leftarrow\vec{v}')$ is the probability of a velocity change from $\vec{v}'$ to $\vec{v}$, modeled by the Keison-Storer function [32], i.e.:

$$f_{KS}(\vec{v}\leftarrow\vec{v}') = \frac{1}{(1-\alpha^2)^{3/2}}\, f_{MB}\left(\frac{\vec{v}-\alpha\vec{v}'}{\sqrt{1-\alpha^2}}\right) \tag{4}$$

where $f_{MB}(\,)$ is the Maxwell-Boltzmann distribution, and α $(0 \le \alpha \le 1)$ is a parameter characterizing the correlation between the velocity before and after a collision, also called the memory parameter [32,36].

The parameters of the KS function, ν_{VC} and α, were fixed to their values determined from CMDS for H_2O in N_2 [30]. The correlation parameter η for each considered line was also fixed to the value obtained from CMDS [30]. The speed-dependent pressure-broadening and -shifting coefficients for all considered lines were computed using the semi-classical complex Robert-Bonamy formalism [33,34]. All the parameters needed for the computation of N_2-broadened H_2O absorption line shape are thus deduced from CMDS or semi-classical calculations, independently of measurements.

Measured spectra of 5 lines of H_2O broadened by N_2, already presented in [30,37], were retained in this study for the test of the proposed procedure. These spectra were measured by a difference-frequency laser spectrometer. The measurements were made in large pressure ranges and for various rotational quantum numbers (Table 1) thus enabling meaningful tests. Indeed, the set of considered H_2O lines is interesting since, as values of the rotational quantum number J are increasing, the corresponding broadening coefficients are strongly decreasing, which involves an increasing influence of velocity-changing collisions. Therefore, very large non-Voigt effects were observed for the high J lines [30,37]. In a first steps, measured spectra of each considered line were fitted with the HT profile using a multi-spectrum fitting procedure [38,39]. The various line parameters of the HT model, i.e. the line position, the pressure-broadening and -shifting coefficients and their speed dependent components, the Dicke narrowing as well as the correlation parameters were imposed to be the same for all considered pressures with the exception of line intensity which was floated for each pressure. A linear base line for each single spectrum was also fitted. The retrieved line parameters are reported in Table 1. Note that due to the relatively small signal-to-noise ratio of the considered measurements and the correlation between the various line-shape parameters, some retrieved values of γ_2 and ν_{VC} (see Table 1) could be correlated and should be considered as effective only. The quality of the fit is very good as can be observed in the example of Figure 1 and in [40], the residuals being almost always within the experimental noises. The corresponding HTp spectra can thus be used to represent the measurements, without the problem of experimental noises and base line stability. These spectra, from now on called "reference spectra", are then retained for comparisons with those calculated by the pcsdKS model. Since no simple experimental information can be used to correct the calculated speed dependent line shifting of the pcsdKS model, the speed dependence of the line shift is disregarded in the following. Furthermore, as shown in [41,42] for instance, the retrieved quadratic speed-dependent component of the line shift is almost independent on the line-shape model used. Therefore, contrary to the other parameters of the HT profile, this parameter can be easily obtained from fits using the quadratic speed dependent Voigt profile, for instance.

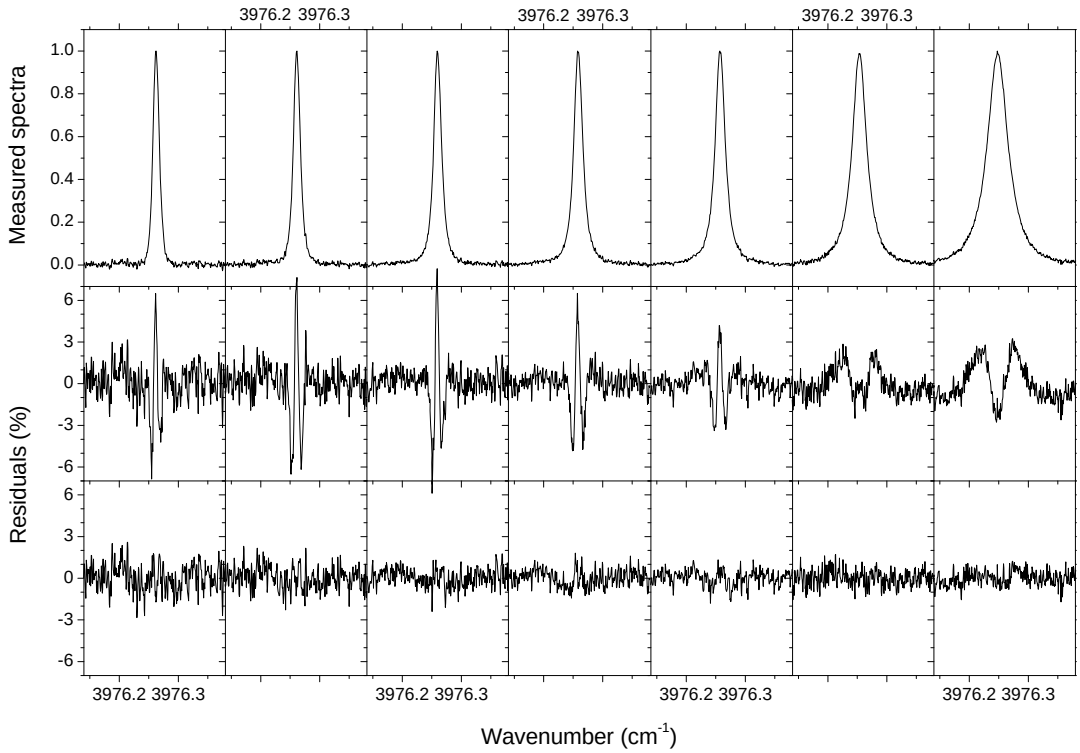

Fig. 1: Example of measured spectra and their corresponding HT multi-fits. In the top panel are the measured spectra of the H_2O $13_{1\,13} \leftarrow 12_{1\,12}$ line, broadened by N_2 for a total pressure, from the left to the right, of 100.6, 200.0, 300.3, 401.1, 499.8, 797.0, and 1208.7 mbar, respectively. In the middle and bottom panels are the fits residuals obtained by multi-fitting these measured spectra with the Voigt and with the HT profiles, respectively.

For each considered line, the highest pressure spectrum was retained in order to determine the correction factor for the pcsdKS model. For this, the reference spectrum and the pcsdKS-one, calculated at exactly the same pressure were both fitted with the Voigt profile. We then compare the Lorentz broadening coefficients obtained from these fits, i.e. γ_L^{Ref} and γ_L^{pcsdKS}. For the five considered lines, $\gamma_L^{Ref}/\gamma_L^{pcsdKS}$ varies from 0.78 to 0.99 (see Table 1) demonstrating the quite good quality of the complex Robert-Bonamy calculations used in the pcsdKS model. However, these errors on the calculated broadening coefficients are too large and would lead to inacceptable errors in spectra calculations and to deviations of several % between the measured and calculated spectra. Note that, since the ratio $\gamma_L^{Ref}/\gamma_L^{pcsdKS}$ is almost constant with pressure (see Fig. 6 of [30]), this correction procedure can be done using any pressure value. The pcsdKS calculations were then corrected by multiplying the $\Gamma(v)$ term of Eqs. (2,3) by the ratio $\gamma_L^{Ref}/\gamma_L^{pcsdKS}$, for each considered line. The pcsdKS model, corrected by this way, was then used to calculate absorption spectra for all considered pressure conditions. Comparisons between the reference spectra and those calculated with this corrected-pcsdKS model are presented in the following section.

3. Comparison between calculated and reference spectra

Figures 2 and 3 show comparisons between the reference spectra and the corrected-pcsdKS ones for the $6_{0\,6} \leftarrow 5_{0\,5}$ and $13_{1\,13} \leftarrow 12_{1\,12}$ lines, respectively. Recall that there is no

adjustment in these comparisons, since all the parameters needed for the calculations by the pcsdKS-corrected model were determined as explained previously. Residuals obtained from multi-fitting the reference spectra with the Voigt profile are also plotted for comparison.

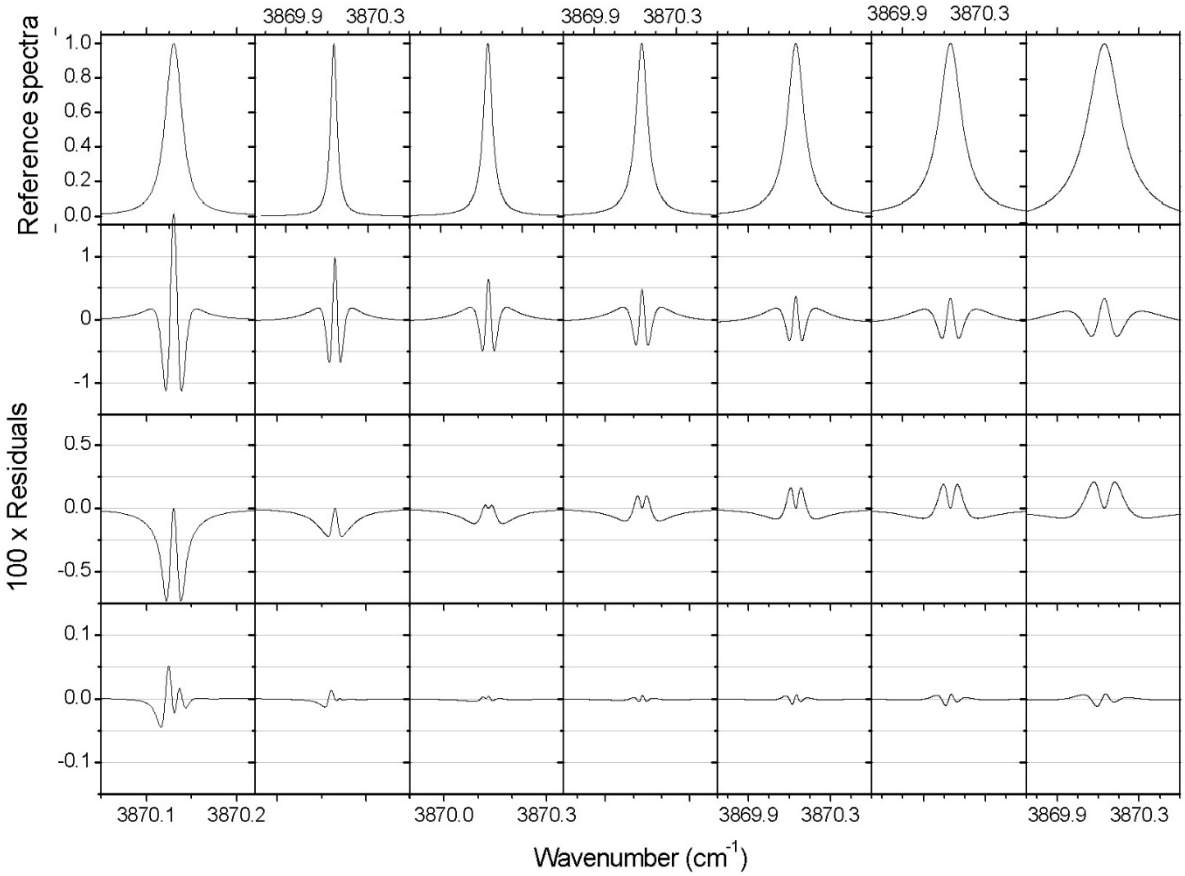

Fig. 2: Top panels: Reference spectra for the H_2O $6_{0\,6} \leftarrow 5_{0\,5}$ line, broadened by N_2, for the total pressure, from the left to the right, of 100.6, 200, 300.3, 401.1, 594, 797 and 1208.7 mbar. In the second panels are fits residuals obtained from multi-fitting these reference spectra to the Voigt profile. The differences between the reference spectra and the corrected-pcsdKS ones, calculated at the same pressure conditions, are plotted in the third panels. In the last panels are fit residuals obtained from multi-fitting the corrected-pcsdKS spectra to the HT profile.

As can be observed on these figures, the corrected-pcsdKS model leads to a good agreement with the reference spectra for all considered pressure conditions. In most cases, their maximum differences are well below 1% of the peak absorption. This is much smaller than the residuals obtained when fitting the reference spectra with the Voigt line shape, which can reach several percent of the peak absorption.

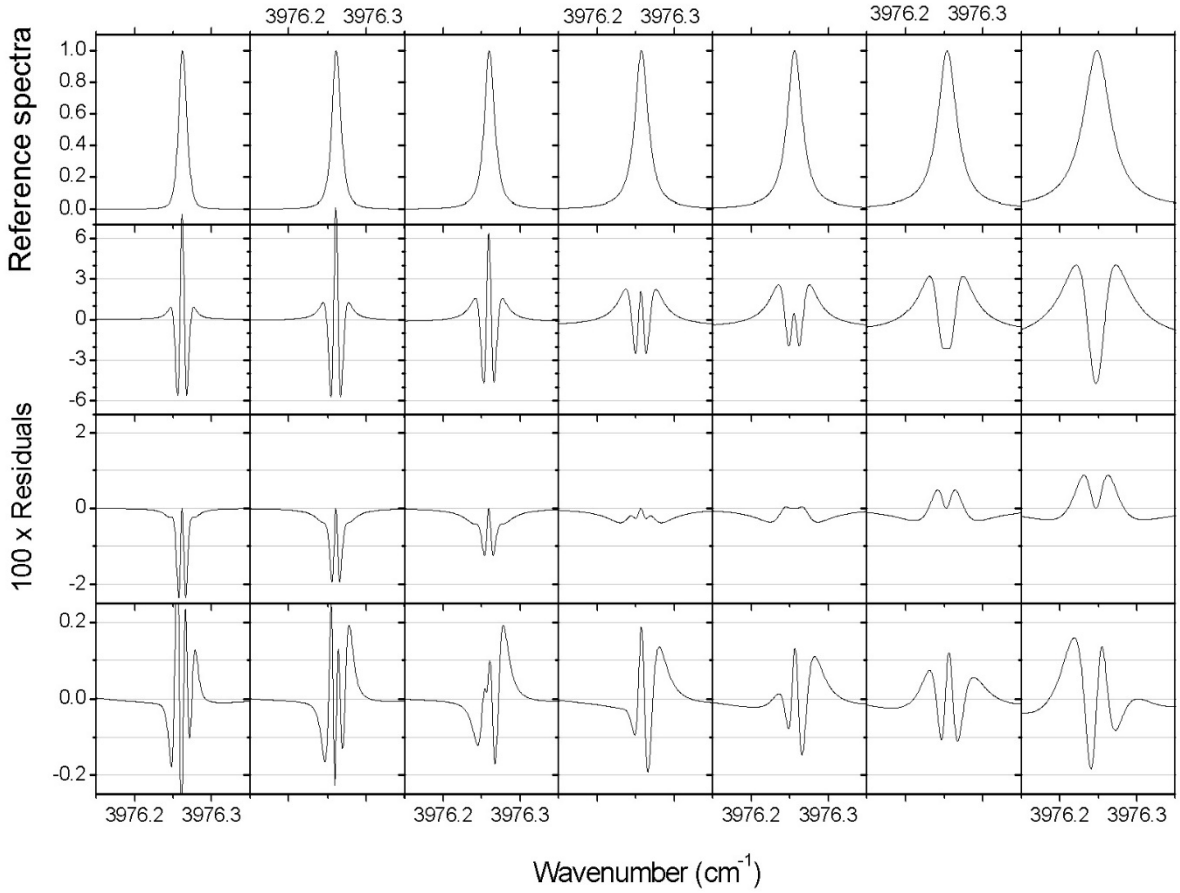

Fig. 3: The same as Fig. 2 but for the $13_{1\,13} \leftarrow 12_{1\,12}$ line with a different scale for bottom panels. From the left to the right, the total pressure is 100.6, 200.0, 300.3, 401.1, 499.8, 797.0, and 1208.7 mbar.

In order to have an overview of the quality of the predictions, the full amplitude (maximum-minimum) of the residuals between the reference spectra and the pcsdKS-corrected ones was determined for each line and pressure. The obtained values are plotted versus pressure in the right panel of Fig. 4. In the left panel of Fig. 4 are plotted those obtained with the Voigt fit residuals (see the second panels of Figs. 2, 3). These results show a large improvement brought by the corrected-pcsdKS calculations, confirming that non-Voigt effects are correctly predicted. Note that, for lines which present very strong non-Voigt effects (those of high *J* values), although in much better agreement with the reference spectra than the Voigt profile, the corrected-pcsdKS model leads to residual amplitudes which can reach 2% of the peak absorption, especially at low pressures where the influence of velocity-changes effect is the most important. This is probably due to the use of the Keilson-Storer function to model the velocity changes due to collisions. Although significantly more sophisticated than the simple hard [17,18] or soft [43] collisions model, the KS function may be not realistic enough to accurately predict the effect of velocity changes on the line shape, as shown for the case of H_2 [44,45]. Nevertheless, a very good overall improvement is observed with respect to the Voigt profile, for all considered lines at all pressure conditions.

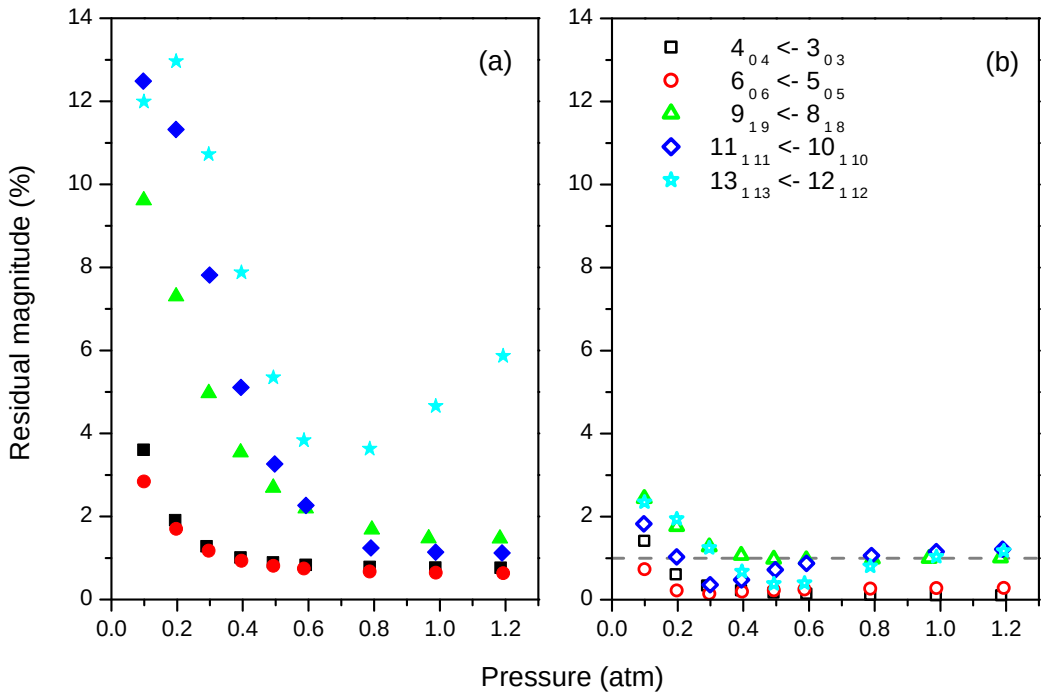

Fig. 4: Peak-to-peak magnitude of the residuals between the reference spectra and their Voigt multi-fits (left panel) and between the reference spectra and the corrected pcsdKS-calculated ones (right panel).

Since the aim of this exercise is to provide the parameters of a refined line-shape model, the corrected-pcsdKS spectra were multi-fitted with the HT profile. Note that the same exercise can be done for other phenomenological line shapes [5,6]. Here, with the HT profile, we used exactly the same multi-fitting procedure as that applied to the measured spectra (see Sec. 2). The quality of the fit is excellent, fit residuals are almost always smaller than ±0.2 % of the peak absorption (see the last panels of Figs. 2, 3). The corresponding parameters obtained by these fits are listed in Table 1 together with those obtained from the corresponding fit of the measured spectra. As can be observed in this table, there is a reasonable agreement between the values of γ_0 retrieved from the corrected-pcsdKS spectra and those obtained from the measurements. However, significant differences can be observed for γ_2, ν_{VC} and η. This is probably due to the fact that the pcsdKS model is built from physical assumptions which are not at all the same as those of the HT profile (e.g. Keilson-Storer function *vs* hard collision for velocity changes, semi-classical approach *vs* quadratic law for the speed dependence). However, as discussed in Ref. [23], the comparisons between measured and calculated spectra are the only relevant benchmark when one wants to generate data that enable to accurately calculate the absorption. From this point of view, the HTp parameters retrieved from the corrected-pcsdKS spectra can be used to calculate the absorption since they lead to a very good agreement with the reference spectra (see Fig. 4b).

Line	Position (cm^{-1})	γ_L^{Ref} / γ_L^{pcsdKS}	γ_0 (mk/atm)	γ_2 (mk/atm)	ν_{VC} (mk/atm)	η

$4_{0\,4} \leftarrow 3_{0\,3}$	3837.8692	0.9964	106.469 *105.177*	15.998 *23.518*	3.810 *60.891*	0.039 *0.774*
$6_{0\,6} \leftarrow 5_{0\,5}$	3870.1293	0.9930	84.433 *85.057*	20.887 *19.723*	58.508 *46.851*	0.851 *0.777*
$9_{1\,9} \leftarrow 8_{1\,8}$	3917.2858	0.9625	42.329 *44.143*	-15.955 *12.676*	81.002 *28.240*	0.873 *0.699*
$11_{1\,11} \leftarrow 10_{1\,10}$	3947.4632	0.8611	25.401 *26.205*	1.318 *8.330*	50.582 *22.669*	1.191 *0.701*
$13_{1\,13} \leftarrow 12_{1\,12}$	3976.2631	0.7688	16.645 *17.715*	9.336 *5.589*	27.949 *20.047*	1.071 *0.567*

Table 1: Comparison between the HTp parameters used to calculate the reference spectra and those (in *italic*) obtained from fitting the corrected-pcsdKS spectra with the HT profile for the five considered lines. The value of $\gamma_L^{Ref}/\gamma_L^{pcsdKS}$ (see text) for each line is also reported.

Since the correction factor (i.e. $\gamma_L^{Ref}/\gamma_L^{pcsdKS}$) is applied to the $\Gamma(v)$ term [see Eq. (2)], on can assume that only γ_0 and γ_2 among the various HT parameters will be significantly affected by this correction. In this case, the pcsdKS model (without correction) can be used to predict all other HT parameters (i.e. the Dicke narrowing ν_{VC}, the correlation η) while γ_0 and γ_2 can be directly scaled using the same value as the correction factor $\gamma_L^{Ref}/\gamma_L^{pcsdKS}$. In order to check this assumption, we performed the following test for the two lines, $6_{0\,6} \leftarrow 5_{0\,5}$ and $13_{1\,13} \leftarrow 12_{1\,12}$ which present significantly different non-Voigt behaviours (see Figs. 2-4). First, we apply a correction factor A=1.1 to the $\Gamma(v)$ term in the pcsdKS model [see Eq. (2)] which is then used to calculate spectra for a wide pressure range. These spectra (calculated using the corrected-pcsdKS profile) are then multi-fitted with the HT profile. The corresponding retrieved HT parameters (denoted by $\gamma_0^*, \gamma_2^*, \nu_{VC}^*, \eta^*$) are then compared to those obtained by directly using the scaling factor (i.e. $A\gamma_0,\ A\gamma_2,\ \nu_{VC}, \eta$). The obtained results are listed in Table 2.

Line	γ_0 (mk/atm)	γ_2 (mk/atm)	ν_{VC} (mk/atm)	η
$6_{0\,6} \leftarrow 5_{0\,5}$	93.559* *93.563*	22.085* *21.695*	49.998* *46.851*	0.786* *0.777*
$13_{1\,13} \leftarrow 12_{1\,12}$	19.491* *19.487*	6.352* *6.148*	20.494* *20.047*	0.593* *0.567*

Table 2: Comparison between the HTp parameters resulted from multi-fitting the corrected-pcsdKS calculated spectra (*) and those obtained by directly using the scaling factor for γ_0 and γ_2 (in *italic*).

As can be observed in Table 2, the values ν_{VC}^* and η^* are very close to the original ones (i.e. before the correction) ν_{VC}, η while γ_0^* and γ_2^* are also very close to $A\gamma_0$ and $A\gamma_2$. We also compute absorption spectra of these two lines using the two sets of HTp parameters (Table 2) for various pressures, from 0.1 to 1 atm. Comparisons between these calculated spectra show that their maximum differences are always smaller than 0.2%. This result demonstrates that the pcsdKS model can be used to predict the HTp parameters for H_2O transitions and the correction

can be simply made directly on the obtained values of γ_0 and γ_2. This procedure is thus quite simple and efficient to provide refined line-shape parameters.

4. Conclusions

In this paper, we have shown that the partially-correlated speed-dependent Keilson-Storer model can be used to generate refined line-shape parameters for H_2O rovibrational transitions. This model takes into account the collision-induced velocity-changes effects, the speed dependences of the collisional line width and shift as well as the correlation between velocity and internal-state changes. All the parameters of the pcsdKS model were deduced from *ab initio* calculations and not adjusted from measurements. Using a simple correction from a measured value of the Lorentz line width, the corrected-pcsdKS model can predict the measured profiles with a precision better than 1% for a wide pressure range. This simple procedure can thus be used to simulate spectra of H_2O lines for various pressures, and then fit them in order to deduce their refined line-shape (HT for instance) parameters to complete spectroscopic databases, in the absence of relevant experimental values. Note that the measured value retained for the correction must be very accurate and should not be affected by errors due to inaccurate knowledge of the temperature and pressure, non-linearity of the detection scheme, instrument line-shape function. In addition, spectra simulated in order to retrieve the needed correction should be calculated at the exact same conditions of the experiments. Then, they should be fitted exactly as done for the measurements. It is worthy to note that data obtained from fits of measurements with any model can be used to get the correction factor provided that the same model is used to fit the simulated spectra. Also, from the corrected-pcsdKS model, one can generate line-shape parameters for any model and not only for the HT profile.

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