Precise predictions of H$_2$O 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$_2$O 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$_2$O 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$_2$O 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
(expresssed 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$_2$O lines, broadened by N$_2$. H$_2$O 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$_2$O 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$_2$O diluted in N$_2$
and of pure H$_2$O, 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 $\gamma_L^{\text{Meas}}/\gamma_L^{\text{Calc}}$ between the Lorentz broadening coefficient obtained from a single spectrum measured for a given pressure and that deduced from the psdKS-spectrum, calculated under exactly the same condition. The correction was then made by multiplying the speed-dependent line width involved in the psdKS function by $\gamma_L^{\text{Meas}}/\gamma_L^{\text{Calc}}$. Spectra of five ro-vibrational lines of H$_2$O 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 psdKS-calculated line shapes were directly compared with the measured spectra. The HT parameters obtained from fits of experimental spectra and of corrected psdKS-calculated spectra are also compared and analysed.

The remainder of this paper is divided into 3 sections. In section 2, we briefly describe the psdKS model, the experimental data used. The correction procedure applied to the psdKS 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 psdKS model, the data used and the correction procedure

Since a detailed description of the psdKS 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 $\tilde{d}(t)$ of the dipole moment responsible for the transition [5], i.e.:

$$ I(\omega) = \frac{1}{\pi} \text{Re} \left[ \int_{-\infty}^{+\infty} \text{d}t \, e^{i(\omega-\omega_0)t} \, \tilde{d}(t) \right], $$

where $\omega_0$ is the unperturbed angular frequency of the optical transition and $\tilde{d}(t) = \int d(\tilde{v}, t) d\tilde{v}$ with $\tilde{v}$ the velocity of the radiator. Within the psdKS model, $d(\tilde{v}, t)$ is the solution of the following kinetic equation [17,35]

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

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

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

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

$$ f_{KS}(\tilde{v} \leftarrow \tilde{v}') = \frac{1}{(1-\alpha^2)^{3/2}} f_{MB}(\frac{\tilde{v}'-\alpha \tilde{v}}{\sqrt{1-\alpha^2}}), $$

where $f_{MB}(\ )$ is the Maxwell-Boltzmann distribution, and $\alpha$ ($0 \leq \alpha \leq 1$) 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, $v_{VC}$ and $\alpha$, were fixed to their values determined from CMDS for H$_2$O in N$_2$ [30]. The correlation parameter $\eta$ 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$_2$O absorption line shape are thus deduced from CMDS or semi-classical calculations, independently of measurements.
Measured spectra of 5 lines of H$_2$O 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$_2$O 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 $\gamma_2$ and $\nu_{VC}$ (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$_2$O 13 1 13 $\leftrightarrow$ 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. $\gamma_L^{\text{Ref}}$ and $\gamma_L^{\text{pcsdKS}}$. For the five considered lines, $\gamma_L^{\text{Ref}}/\gamma_L^{\text{pcsdKS}}$ 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 unacceptable errors in spectra calculations and to deviations of several % between the measured and calculated spectra. Note that, since the ratio $\gamma_L^{\text{Ref}}/\gamma_L^{\text{pcsdKS}}$ 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 $\Gamma(\nu)$ term of Eqs. (2,3) by the ratio $\gamma_L^{\text{Ref}}/\gamma_L^{\text{pcsdKS}}$, 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 $\leftrightarrow$ 5 0 5 and 13 1 13 $\leftrightarrow$ 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$_2$O $6_{0.6}$ ← $5_{0.5}$ 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.
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 $\gamma_0$ retrieved from the corrected-pcsdKS spectra and those obtained from the measurements. However, significant differences can be observed for $\gamma_2$, $\nu_{VC}$ and $\eta$. 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).

<table>
<thead>
<tr>
<th>Line</th>
<th>Position (cm$^{-1}$)</th>
<th>$\gamma_L^{Ref}$ / $\gamma_L^{pcsdKS}$</th>
<th>$\gamma_0$ (mk/atm)</th>
<th>$\gamma_2$ (mk/atm)</th>
<th>$\nu_{VC}$ (mk/atm)</th>
<th>$\eta$</th>
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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 $\gamma_L^{\text{Ref}}/\gamma_L^{\text{pcsdKS}}$ (see text) for each line is also reported.

<table>
<thead>
<tr>
<th>Line</th>
<th>$\gamma_0$ (mk/atm)</th>
<th>$\gamma_2$ (mk/atm)</th>
<th>$\nu_{VC}$ (mk/atm)</th>
<th>$\eta$</th>
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<tr>
<td>$4_0 4\leftrightarrow 3_0 3$</td>
<td>3837.8692</td>
<td>0.9964</td>
<td>106.469</td>
<td>0.9964</td>
</tr>
<tr>
<td>$6_0 6\leftrightarrow 5_0 5$</td>
<td>3870.1293</td>
<td>0.9930</td>
<td>84.433</td>
<td>0.9930</td>
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<tr>
<td>$9_{19}\leftrightarrow 8_{18}$</td>
<td>3917.2858</td>
<td>0.9625</td>
<td>42.329</td>
<td>0.9625</td>
</tr>
<tr>
<td>$11_{111}\leftrightarrow 10_{110}$</td>
<td>3947.4632</td>
<td>0.8611</td>
<td>25.401</td>
<td>0.8611</td>
</tr>
<tr>
<td>$13_{113}\leftrightarrow 12_{112}$</td>
<td>3976.2631</td>
<td>0.7688</td>
<td>16.645</td>
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Since the correction factor (i.e. $\gamma_L^{\text{Ref}}/\gamma_L^{\text{pcsdKS}}$) is applied to the $\Gamma(v)$ term [see Eq. (2)], on can assume that only $\gamma_0$ and $\gamma_2$ 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 $\nu_{VC}$, the correlation $\eta$) while $\gamma_0$ and $\gamma_2$ can be directly scaled using the same value as the correction factor $\gamma_L^{\text{Ref}}/\gamma_L^{\text{pcsdKS}}$. In order to check this assumption, we performed the following test for the two lines, $6_0 6\leftrightarrow 5_0 5$ and $13_{113}\leftrightarrow 12_{112}$ 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 $\gamma_0^\ast, \gamma_2^\ast, \nu_{VC}^\ast, \eta^\ast$) 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.

<table>
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<tr>
<th>Line</th>
<th>$\gamma_0$ (mk/atm)</th>
<th>$\gamma_2$ (mk/atm)</th>
<th>$\nu_{VC}$ (mk/atm)</th>
<th>$\eta$</th>
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<tbody>
<tr>
<td>$6_0 6\leftrightarrow 5_0 5$</td>
<td>93.559*</td>
<td>22.085*</td>
<td>49.998*</td>
<td>0.786*</td>
</tr>
<tr>
<td>$13_{113}\leftrightarrow 12_{112}$</td>
<td>19.491*</td>
<td>9.336*</td>
<td>27.949*</td>
<td>0.593*</td>
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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 $\gamma_0$ and $\gamma_2$ (in italic).

As can be observed in Table 2, the values $\nu_{VC}^\ast$ and $\eta^\ast$ are very close to the original ones (i.e. before the correction) $\nu_{VC}, \eta$ while $\gamma_0^\ast$ and $\gamma_2^\ast$ 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$_2$O transitions and the correction
can be simply made directly on the obtained values of $\gamma_0$ and $\gamma_2$. 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$_2$O 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-csdKS 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$_2$O 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-csdKS model, one can generate line-shape parameters for any model and not only for the HT profile.

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Benner DC, Rinsland CP, Devi VM, Smith MAH, Atkins D. A multispectrum nonlinear least squares fitting technique. J Quant Spectrosc Radiat Transf


