Precise predictions of H₂O line shapes over a wide pressure range

using simulations corrected by a single measurement

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ABTRACT. In this work, we show that precise predictions of the shapes of H₂O rovibrational lines broadened by N₂, 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 H₂O 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 H₂O line shapes for various pressure conditions and thus the simulated spectra can be used to deduce the refined lineshape parameters to complete spectroscopic databases, in the absence of relevant experimental values.

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.

Line	Position (cm⁻¹)	$\gamma_L^{Ref}/\gamma_L^{pcsdKS}$	γ_0 (mk/atm)	γ_2 (mk/atm)	ν_{VC} (mk/atm)	η
$4_{04} \leftarrow 3_{03}$	3837.8692	0.9964	106.469	15.998	3.810	0.039
			105.177	*23.518*	*60.891*	*0.774*
$6_{06} \leftarrow 5_{05}$	3870.1293	0.9930	84.433	20.887	58.508	0.851
			85.057	*19.723*	*46.851*	*0.777*
$9_{19} \leftarrow 8_{18}$	3917.2858	0.9625	42.329	−15.955	81.002	0.873
			44.143	*12.676*	*28.240*	*0.699*
$11_{1\,11} \leftarrow 10_{1\,10}$	3947.4632	0.8611	25.401	1.318	50.582	1.191
			26.205	*8.330*	*22.669*	*0.701*
$13_{1\,13} \leftarrow 12_{1\,12}$	3976.2631	0.7688	16.645	9.336	27.949	1.071
			17.715	*5.589*	*20.047*	*0.567*

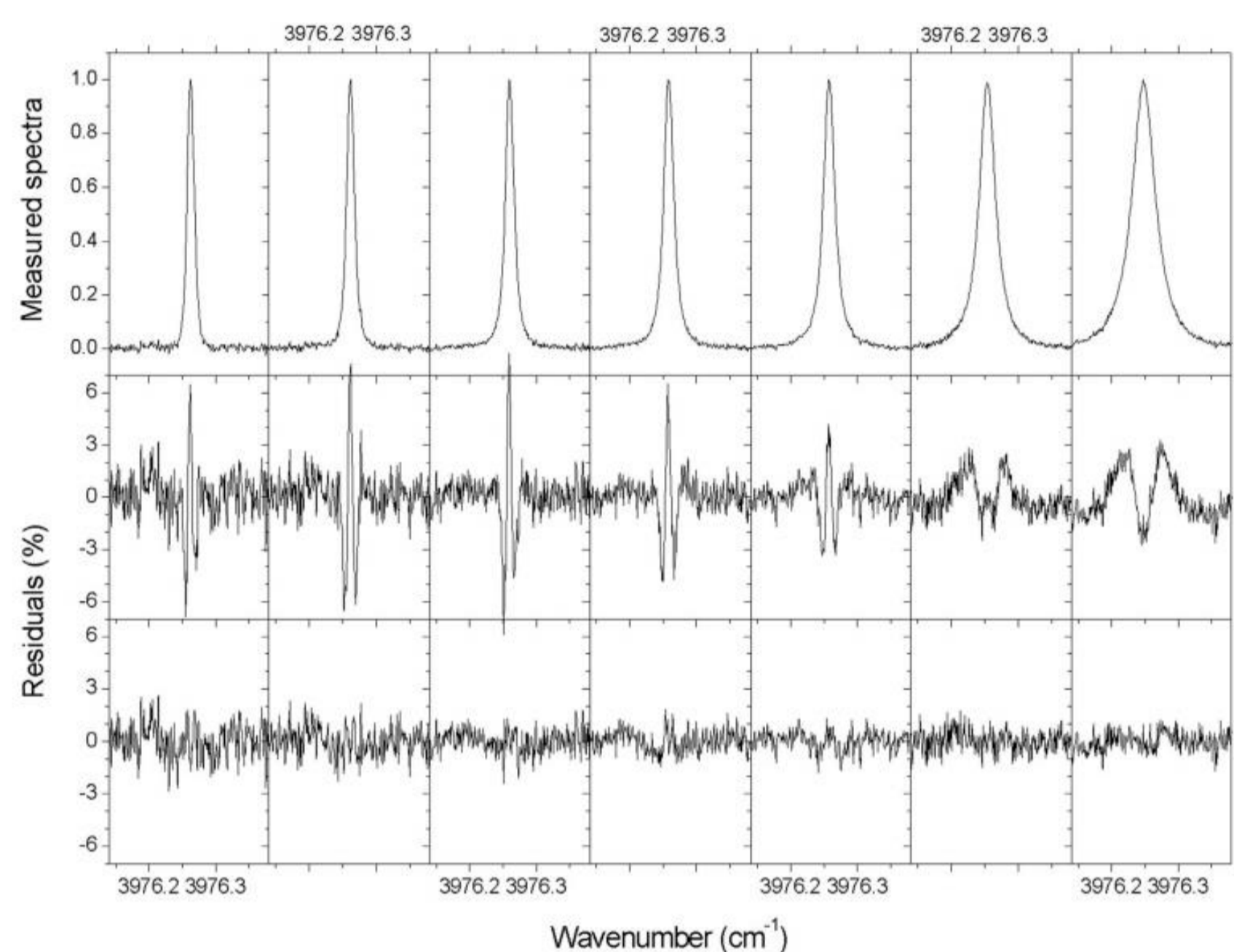**Fig. 1.** Example of measured spectra and their corresponding HT multi-fits. In the top panel are the measured spectra of the H₂O $13_{1\,13} \leftarrow 12_{1\,12}$ line, broadened by N₂ for a total various pressures. In the middle and bottom panels are the fitsresiduals obtained by multi-fitting these measured spectra with the Voigt and with the HT profiles, respectively.
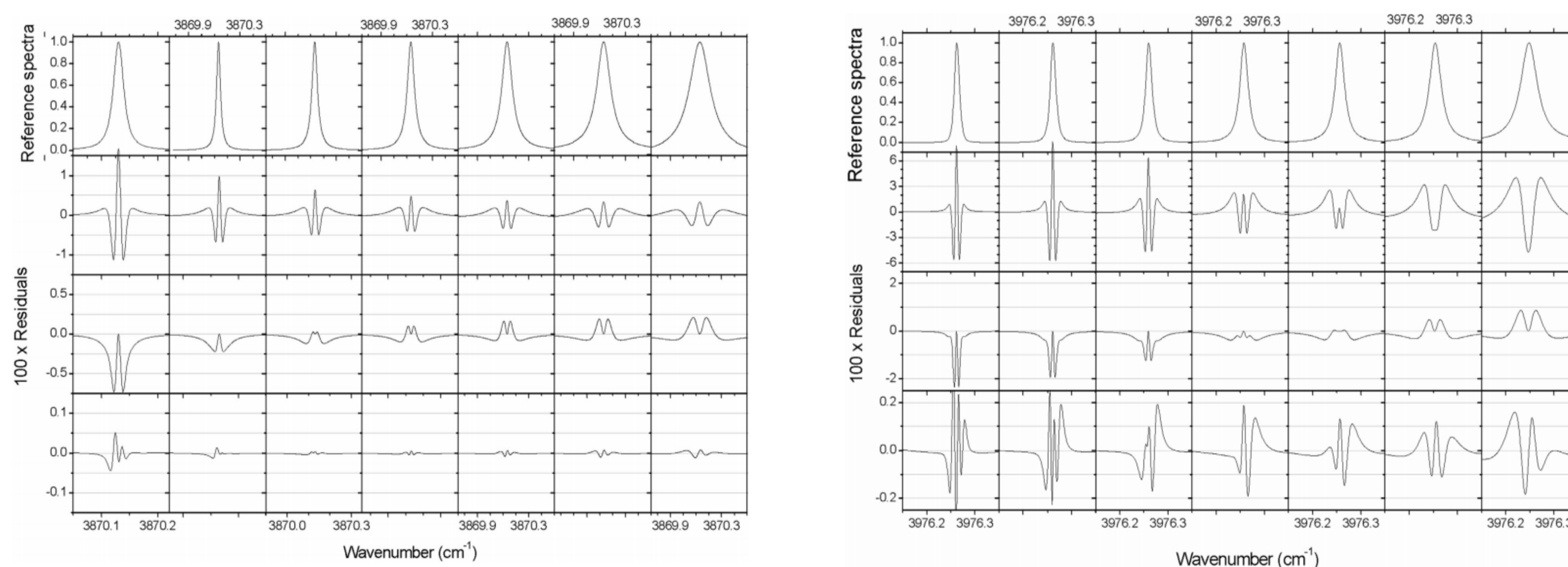
The pcsdKS model, the data used and the correction procedure

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 [1], i.e.:

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

where ω_0 is the unperturbed angular frequency of the optical transition $\bar{d}(t) = \int d(\vec{v},t)d\vec{v}$ with $\vec{v}$ the velocity of the radiator. Within the pcsdKS model, $d(\vec{v},t)$ is the solution of the following kinetic equation [2,5]

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

$\tilde{v}_{VC}(v)$ is the speed dependent (with v the molecular speed) velocity changing collision frequency.

The speed-dependent pressurebroadening and -shifting coefficients for all considered lines were computed using the semi-classical complex Robert–Bonamy formalism [3,4]. All the parameters needed for the computation of N₂-broadened H₂O absorption line shape are thus deduced from CMDS or semi-classical calculations, independently of measurements.
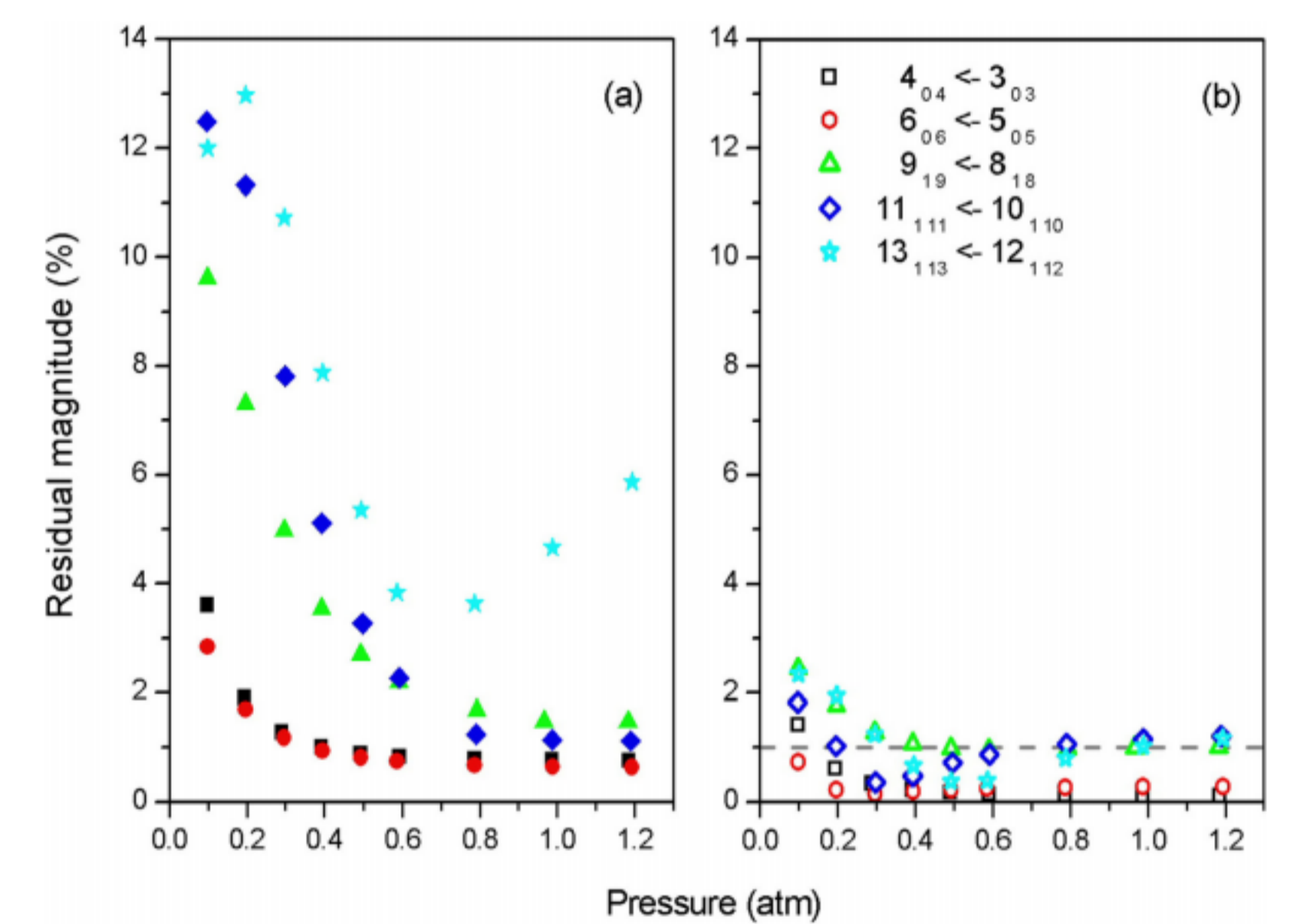

Fig.2; 3. Top panels: Reference spectra for the H₂O $6_{06} \leftarrow 5_{05}$ and $13_{1\,13} \leftarrow 12_{1\,12}$ line, broadened by N₂, for the total various pressures. In the second panels are fits residuals obtained from multi-fitting these reference spectra to the Voigt profile. The differences 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.

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)

Conclusion

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 H₂O 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 H₂O 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, nonlinearity 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.

References

[1] Hartmann J-M , Boulet C , Robert D . Collisional effects on molecular spectra. Laboratory experiments and models, consequences for applications. Amster- dam: Elsevier; 2008 .

[2] Rautian SG , Sobel'man IL . The effect of collisions on the Doppler broadening of spectral lines. Sov Phys Uspekhi 1967;9:701–16 .

[3] Gamache R, Hartmann J. Collisional parameters of H 2 O lines: effects of vibration. J Quant Spectrosc Radiat Transf 2004;83:119–47. doi: 10.1016/ S0 022-4073(02)0 0296-0

[4] Robert D , Bonamy J . Short range force effects in semiclassical molecular line broadening calculations. J. Phys. 1979;40:923–43 .

[5] May AD, Liu WK, Mccourt FRW, Ciuryło R, Sanchez-Fortún Stoker J, Shapiro D, et al. The impact theory of spectral line shapes: a paradigm shift. Can J Phys 2013;895:879–95. doi: 10.1139/cjp- 2012- 0345 .