Recommended isolated-line profile for representing high-resolution spectroscopic transitions

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Summary

Recommendations of an IUPAC Task Group, formed in 2011 on "Intensities and line shapes in high-resolution spectra of water isotopologues from experiment and theory" (Project No. 2011-022-2-100), on line profiles of isolated high-resolution rotational-vibrational transitions perturbed by neutral gas-phase molecules are presented. The well-documented inadequacies of the Voigt profile, used almost universally by databases and radiative-transfer codes, to represent pressure effects and Doppler broadening in isolated vibrational-rotational and pure rotational transitions of the water molecule have resulted in the development of a variety of alternative line profile models. These models capture more of the physics of the influence of pressure on line shapes but, in general, at the price of greater complexity. The Task Group recommends that the partially-Correlated quadratic-Speed-Dependent Hard-Collision profile should be adopted as the appropriate model for high-resolution spectroscopy. For simplicity this should be called the Hartmann–Tran profile (HTP). This profile is sophisticated enough to capture the various collisional contributions to the isolated line shape, can be computed in a straightforward and rapid manner, and reduces to simpler profiles, including the Voigt profile, under certain simplifying assumptions.

For a full write-up see Tennyson *et al* (2014).

Available line profile models

Table 1: Summary of line profile models considered. N is the number of parameters required to characterize the line shape for a single isolated transition at a given temperature for a given pair of molecules.

Acronym	Profile name	Parameters		Mechanism		
		N		SD[a]	VC[a]	Correlation
DP	Doppler	1	Γ_D	No	No	No
LP	Lorentz	2	Γ, Δ	No	No	No
VP	Voigt	3	Γ_D, Γ, Δ	No	No	No
GP	Galatry	4	Γ_D, Γ, Δ, ν_{VC}	No	Soft	No
RP	Rautian	4	Γ_D, Γ, Δ, ν_{VC}	No	Hard	No
NGP	Nelkin–Ghatak	4	Γ_D, Γ, Δ, ν_{VC}	No	Hard	No
SDVP[b]	speed-dependent Voigt	5	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2	Yes	No	No
SDGP[b]	speed-dependent Galatry	6	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	Yes	Soft	No
SDNGP[b]	speed-dependent Nelkin–Ghatak	6	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	Yes	Hard	No
SDRP[b]	speed-dependent Rautian	6	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	Yes	Hard	No
HTP	Hartmann–Tran	7	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}, η	Yes	Hard	Yes
CSDaRSP[b]	correlated SD asymmetric Rautian–Sobelman	8	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}, χ, η	Yes	Combination	Yes
pCSDKS[b]	partially correlated SD Keilson-Storer	8	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}, γ_{KS}, η	Yes	Combination	Yes

[a] SD = speed-dependent; VC = velocity changes due to collisions.

[b] Parameters for these profiles are all given in the quadratic (q) form of the speed dependence; for hypergeometric models the expansion parameters Γ_0 and Γ_2 (or Δ_0 and Δ_2) are replaced by an amplitude factor and a parameter that is either p, the power-law exponent giving the dependence of the broadening on the relative speed, or q, which describes the power-law dependence of the intermolecular potential on the intermolecular distance.

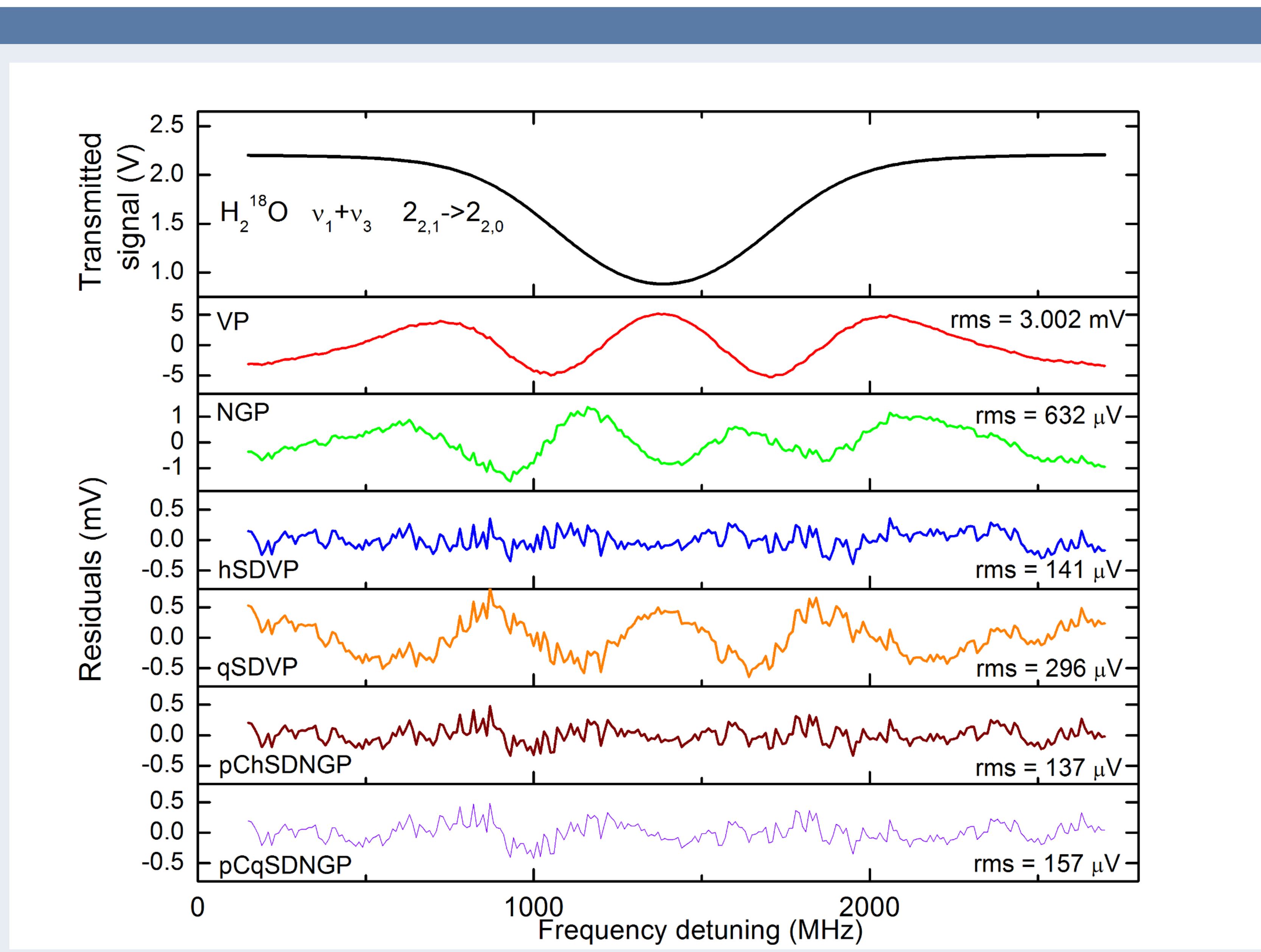

Figure 1: Comparison of line-shape fits to the $H_2{}^{18}O$ absorption feature at 7222.298050 cm^{-1} measured at a pressure of 2.70 Torr and a temperature of 273.16 K (De Vizia *et al.* 2012). Residuals are given in terms of units of the original signal: root mean square (rms) values of about 150 μV simply reflect the noise in the original experiment. Note that pCqSDNGP is equivalent to HTP.

The HTP model

The line profile we recommend is variously described as the partially-Correlated quadratic-Speed-Dependent Hard-Collision Profile (pCqSDHCP) or the partially-Correlated quadratic-Speed-Dependent Nelkin–Ghatak Profile (pCqSDNGP); We recommend that this profile, and its computational implementation, be called the **Hartmann–Tran profile (HTP)**.

In terms of the 7 parameters Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC} and η, it can be expressed as:

$$F_{HTP}(\nu) = \frac{1}{\pi}\mathrm{Re}\left\{\frac{A(\nu)}{1-[\nu_{VC}-\eta(C_0-3C_2/2)]A(\nu)+(\frac{\eta C_2}{v_{a0}^2})B(\nu)}\right\}.$$

The terms $A(\nu)$ and $B(\nu)$ are combinations of the complex probability function

$$w(z) = \frac{i}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-t^2}}{z-t}dt = e^{-z^2}\mathrm{erfc}(-iz),$$

where erfc is the Gauss error function, while

$$A(\nu) = \frac{\sqrt{\pi}c}{\nu_0 v_{a0}}[w(iZ_-)-w(iZ_+)],$$

$$B(\nu) = \frac{v_{a0}^2}{C_2}\left[-1+\frac{\sqrt{\pi}}{2\sqrt{Y}}(1-Z_-^2)w(iZ_-)-\frac{\sqrt{\pi}}{2\sqrt{Y}}(1-Z_+^2)w(iZ_+)\right].$$

In these expressions

$$Z_\pm = \sqrt{X+Y}\pm\sqrt{Y},$$

$$X = \frac{i(\nu_0-\nu)+\tilde{C}_0}{\tilde{C}_2}, \quad Y = \left(\frac{\nu_0 v_{a0}}{2c\tilde{C}_2}\right)^2,$$

where

$$\tilde{C}_0 = (1-\eta)(C_0-\frac{3C_2}{2})+\nu_{VC},$$

$$\tilde{C}_2 = (1-\eta)C_2,$$

with $C_n = \Gamma_n + i\Delta_n$ with $n = 0$ and 2 within the quadratic approximation.

Reduction to simpler models

Table 2: Correspondence between various lower-order models and the limits of the Hartmann–Tran profile.

Acronym	Profile	Parameters	Limit of HTP
DP	Gaussian	Γ_D	$\Gamma_0=\Gamma_2=\Delta_0=\Delta_2=\nu_{VC}=\eta=0$
VP	Voigt	Γ_D, Γ_0, Δ_0	$\Gamma_2=\Delta_2=\nu_{VC}=\eta=0$
RP	Rautian	Γ_D, Γ_0, Δ_0 ν_{VC}	$\Gamma_2=\Delta_2=\eta=0$
qSDVP	speed-dependent Voigt[a]	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2	$\nu_{VC}=\eta=0$
qSDRP	speed-dependent Rautian[a]	Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC}	$\eta=0$

[a] Using the quadratic approximation for the speed-dependence.

HTP and HITRAN

It is our recommendation that HITRAN adopts the HTP to represent beyond-Voigt pressure effects. This profile was proposed to use as the new standard in spectroscopic databases and radiative transfer codes by Ngo *et al.* (2013). A computer program for evaluating the HTP is given by Tran *et al.* (2013).

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References

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