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Recommended Isolated-Line Profile for Representing High-Resolution Spectroscopic Transitions (IUPAC Technical Report)

Jonathan Tennyson

Peter F. Bernath
Old Dominion University, pbernath@odu.edu

Alain Campargue

Attila G. Császár

Ludovic Daumont

See next page for additional authors

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Authors
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IUPAC Technical Report

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Abstract: The report 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 is presented. The well-documented inadequacies of the Voigt profile (VP), 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

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***Corresponding author: Jonathan Tennyson,** Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK, e-mail: j.tennyson@ucl.ac.uk
Peter F. Bernath: Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA
Alain Campargue: Université Grenoble 1/CNRS, UMR5588 LIPhy, Grenoble, F-38041, France
Attila G. Császár: Institute of Chemistry, Loránd Eötvös University, H-1117 Budapest, Pázmány sétány 1/A, Hungary; and MTA-ELTE Research Group on Complex Chemical Systems, H-1518 Budapest 112, P.O. Box 32, Hungary
Ludovic Daumont: GSMA, UMR CNRS 7331, Université de Reims Champagne Ardenne U.F.R. Sciences Exactes et Naturelles Moulin de la Housse, B.P. 1039, 51687 Reims Cedex 2, France
Robert R. Gamache: Department of Environmental, Earth, and Atmospheric Sciences University of Massachusetts Lowell Lowell, MA 01854, USA
Joseph T. Hodges: National Institute of Standards and Technology, Gaithersburg, MD, USA
Daniel Lisak: Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
Olga V. Naumenko: Institute of Atmospheric Optics, Russian Academy of Sciences, Tomsk, Russia
Laurence S. Rothman: Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA
Ha Tran and Jean-Michel Hartmann: Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris Est Créteil, Université Paris Diderot, Institut Pierre-Simon Laplace, 94010 Créteil Cedex, France
Nikolai F. Zobov: Institute of Applied Physics, Russian Academy of Sciences, 46 Uljanov Street, 603950 Nizhny Novgorod, Russia
Jeanna Buldyreva: Institut UTINAM UMR CNRS 6213, Université de Franche-Comté, 16 route de Gray, 25030 Besançon, France
Chris D. Boone: Department of Chemistry, University of Waterloo, 200 University Ave W, Waterloo, Ontario, N2L 3G1, Canada
Maria Domenica De Vizia and Livio Gianfrani: Department of Mathematics and Physics, Second University of Naples, Caserta, Italy
Robert McPheat and Damien Weidmann: Space Science and Technology Department, Rutherford Appleton Laboratory, Harwell Oxford Campus, Didcot, OX11 0QX, UK
Jonathan Murray: Space and Atmospheric Physics, Imperial College London, London, Prince Consort Road, London SW7 2BW, UK
Ngoc Hoa Ngo: Faculty of Physics, Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Hanoi, Vietnam
Oleg L. Polyansky: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK; and Institute of Applied Physics, Russian Academy of Sciences, 46 Uljanov Street, 603950 Nizhny Novgorod, Russia

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 (pCqSD-HCP) should be adopted as the appropriate model for high-resolution spectroscopy. For simplicity this should be called the Hartmann–Tran profile (HTP). The HTP 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.

Keywords: high-resolution spectroscopy; IUPAC Physical and Biophysical Chemistry Division; line profiles; line shifts; water vapor.

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1 Introduction

Characterization of an isolated spectral line measured under high resolution requires three pieces of information: the transition frequency, the transition integrated intensity, and the parameters that describe the line profile. A previous IUPAC Task Group (hereafter called TG1), comprising several of the current authors, has critically evaluated the line frequency data available for all the major isotopologues of water [1–4]. A summary of this work along with recommendations of TG1 were recently presented in this journal [5].

The full characterization of the high-resolution spectrum of water vapor from the microwave to the ultraviolet is a prerequisite for modeling and understanding of various processes in many fields in chemistry, physics, earth sciences and engineering. The diverse areas of interest include:

1. Atmospheric modelling, with emphasis on the definitive understanding of global warming as water vapor is responsible for about 70 % of the known absorption of sunlight and the majority of the greenhouse effect;
2. Atmospheric remote sensing and environmental monitoring, since it is generally necessary to remove the spectral signature of water in order to interpret correctly the signatures from trace species;
3. Satellite communication, as the performance of satellites in the Earth's atmosphere is sensitive to water absorption between about 3 and 400 GHz;
4. Active remote sensing such as radar and lidar that is affected by water vapour attenuation;
5. Studies of planetary and exoplanetary atmospheres;
6. Astronomy, for example, that of cool stars, where hot water is a major constituent; water lasers and masers, which are widespread in outer space, and the study of comets based on fluorescence spectroscopy;
7. Combustion research, such as rocket exhausts, forest fires, and turbine engines, as hot steam is a major product of most combustion processes.

One of the recommendations of TG1 was the urgent need to identify and adopt a reference line profile for high-resolution spectroscopic studies which improved upon the current standard, the so-called Voigt profile (VP). The present paper reports the related recommendation of another IUPAC Task Group (hereafter called TG2) on "Intensities and line shapes in high-resolution spectra of water isotopologues from experiment and theory" (Project No. 2011-022-2-100). TG2 limited itself to considering gas-phase transitions which occur in neutral environments as the pressure effects in plasmas need a somewhat different treatment.

The line profile of an isolated spectroscopic transition is usually defined as being normalized to unit area and can be attributed to the following three physical factors:

1. The Heisenberg time-energy uncertainty principle, or, equivalently, the spontaneous emission of radiation, is responsible for the natural lifetime broadening or *intrinsic line width*. This component of the

overall line shape is described by a Lorentzian profile which is, however, sufficiently narrow to be safely neglected in favour of the next two contributions in all but the most specialized situations and ultra-low temperatures.

2. The thermal translational motion of the spectroscopically active molecule at velocity v_a gives the incident radiation, of frequency ν_0, a frequency shift of $\Delta\nu = \pm (v_a/c)\nu_0$ in the molecular frame of reference (where c is the speed of light in vacuum): the well-known *Doppler effect*. The corresponding Doppler profile (DP) is expressed in terms of the Doppler half-width, Γ_D, by a Gaussian function:

$$F_D(\nu-\nu_0) = \sqrt{\frac{\ln(2)}{\pi}}\frac{1}{\Gamma_D}\exp\left(-\ln(2)\left(\frac{\nu-\nu_0}{\Gamma_D}\right)^2\right). \quad (1)$$

For temperature T, in K, and molecular mass m, in kg, the Doppler half-width, in Hz, is

$$\Gamma_D = \sqrt{\frac{2\ln(2)kT}{mc^2}}\nu_0 = 1.4593136(7)\times 10^{-20}\sqrt{(\mathrm{kg/K})}\sqrt{(T/m)}\nu_0, \quad (2)$$

or equivalently in terms of the molar mass, m_m in g mol^{-1}, $\Gamma_D = 3.581163(2)\times 10^{-7}\sqrt{\frac{\mathrm{g}}{\mathrm{mol}}\frac{1}{K}}\sqrt{(T/m_m)}\nu_0$.

3. Individual collisions of molecules lead to energy exchanges between radiators and perturbers. These exchanges shorten the lifetime of the initial and final states of the optical transition and yield what is called pressure or *collisional broadening*. These collisions also induce pressure-dependent shifts in the central frequency of the transition. Assuming the independence of the pressure-broadened line half-width at half-maximum, Γ, and of the pressure-induced line shift, Δ, from the molecular speeds (mean thermal velocity approximation), one obtains, for the associated profile, a homogeneous Lorentzian function:

$$F_L(\nu-\nu_0) = \frac{1}{\pi}\frac{\Gamma}{(\nu-\nu_0-\Delta)^2+\Gamma^2}. \quad (3)$$

At low pressures the Doppler effect dominates, and as the pressure increases the effects of collisions become increasingly important. As a first approximation to get the resulting line shape, the convolution of an inhomogeneous Doppler profile with a homogeneous Lorentzian profile is commonly used. It defines the so-called VP, which contains Doppler and Lorentzian shapes as limiting cases. The three parameters, Γ_D, Γ and Δ, characterizing the Voigt profile are routinely employed in standard spectroscopic information systems [6, 7]. Γ_D is independent of the gas mixture composition and has a known temperature dependence, see eq. 2. For Γ and Δ, their values in a mixture are simply obtained, assuming binary collisions, through model fraction-weighted average of the individual values for each collision partner. The temperature dependence of Γ and Δ is commonly assumed to be a power law for the broadening [6, 7] but remains to be found for the pressure shift. Although the Voigt profile involves an integral that cannot be evaluated analytically, there are readily available, fast computational procedures for doing this, see, e.g., Refs. [8, 9], which make this function suitable for use in complex radiative-transfer codes.

There is now a widespread recognition that the VP does not give a fully accurate representation of the spectral line shape [10] and its use can lead, e.g., to a systematic underestimation of experimental line intensities [11–13]. Use of the VP for modelling spectra of water vapour recorded in both the laboratory and the atmosphere under high resolution leads to characteristic W-shaped residuals in any high-precision fit to the line absorption coefficient. See, e.g., Refs. [14–17] for laboratory work and Refs. [18, 19] for atmospheric studies. In particular, large W-shaped residuals were observed in the analysis of H_2O lines from the Atmospheric Chemistry Experiment [19], an effect that appears to occur only for H_2O and not for other molecules in the spectra. Deviations from the Voigt line shape contribute to the large residuals for H_2O lines, although there are likely other contributions relating to the high variability of the H_2O column in the Earth's atmosphere and the rapid change of H_2O volume mixing ratio as a function of altitude in the troposphere, particularly in the tropics.

The W-shaped residuals arise, and their amplitude may reach 10 % of the peak absorption [16, 20], as the observed lines are typically higher and narrower than predicted by the VP. Deviations from the VP are generally ascribed to the effect of velocity changes (VCs) due to collisions, which reduce Γ_D, and/or to the speed dependence (SD) of the relaxation rates, which corrects the simple Lorentzian shape for different velocity-classes of active molecules. Inclusion of these velocity effects in line-profile models has led to the development of a variety of possible line shape functions which can be characterized by their increasingly sophisticated representation of the underlying physics and an increasing number of parameters. Several of these models are briefly considered in Section 3.

2 Objectives of the task group

There are many suggested models for the line profile which move beyond the VP [21–27]; see chapter III of the book by Hartmann et al. [10] for a more general discussion. These profiles are more sophisticated in that they include more physical effects than are accounted for by the VP and, as a consequence, require additional model parameters. At present, databases and most major radiative-transfer codes use Voigt profiles, despite their well-documented deficiencies. The implementation of profiles beyond the Voigt approximation in databases and codes represents a major task and will only be undertaken once there is some reasonable consensus as to which line profile to use. This has become particularly timely as increased sensitivity of remote sounding instruments and better knowledge of geophysical parameters has increased the relative significance of line-profile issues for observing systems. The aim of TG2 and of this article is therefore to recommend the use of a single functional form suitable for line profiles representing high-resolution spectroscopic transitions.

To achieve this goal the following points need to be considered:

1. What single functional form from those available is most appropriate to replace the VP? The chosen function should have a sound theoretical basis and behave in an appropriate manner as a function of pressure and temperature.
2. Is the chosen functional form computationally tractable? Radiative-transfer models which perform line-by-line calculations for large numbers of lines demand a functional form that can be evaluated reliably and efficiently.
3. What are the consequences of replacing Voigt functions in databases and models? There should be a straightforward path from the current situation which relies on Voigt functions to the newly recommended function.

To answer these questions, the water molecule serves as a suitable benchmark. As detailed in the Introduction, water line profiles are of great importance for a number of applications. Furthermore, water has a large permanent dipole moment which leads to strong long-range interactions, making the line shape of its transitions particularly challenging to model from the purely theoretical point of view. TG2 therefore aimed to make a recommendation for water which would also be appropriate and adopted for other molecules.

Finally, we note that collision-induced mixing of nearby lines also alters line profiles, see chapter IV of Ref. [10] for a general discussion of this process. This effect has been observed in water transitions [28, 29] but was not explicitly considered by TG2. Nevertheless, the significance of the TG recommendations for the inclusion of line mixing and for the water continuum is discussed below.

3 Line-profile models: a brief review

The theory of molecular line shapes is rather complicated and has been studied over many years [30]. It is not possible to review it all here, and instead the reader is pointed to two recent books on the topic [10, 31].

Atoms and molecules obey the laws of quantum mechanics and ab initio quantum mechanical treatments of water line broadening are available for low-temperature collisions [32], but more approximate treatments

are required at higher temperatures [33]. This is because at atmospheric temperatures a molecule such as water has too many relaxation channels for a fully quantal treatment of the problem to be practicable. The discussion below will therefore be limited to semi-classical studies.

When considering the various models, it is also important to remember that as the models become more sophisticated they have more free parameters which almost automatically results in better fits of measured spectra. However, a high-quality fit to a set of spectral lines is not a guarantee of the validity of the line-shape model used; in particular, in the binary-collision regime the fitted parameters have to be linear functions of the pressure [15, 16, 34–36]. At the same time, multispectral fits [37, 38] of lines recorded at several pressures of the perturbing gas are particularly useful for testing and characterizing complicated line-profile functions. Compared to spectrum-by-spectrum adjustments, multispectrum fits have the great advantage that they reduce correlations between model parameters, decrease their uncertainties and make convergence easier. Table 1 lists some of the key line-profile models developed and orders them in terms of the number of parameters required to characterize a single spectral transition at a given temperature for a given absorber and a given perturbing gas. The standard three-parameter VP, as already mentioned above, is the simplest line shape accounting for the pressure and Doppler effects.

The effect of collision-induced velocity changes on spectral line shape is usually known as Dicke narrowing [39]. In this case the strength of the collisions, i.e., their efficiency at changing the velocity, becomes important. Hard-collision models assume that molecular velocities before and after each collision are completely decorrelated, i.e., each collision is so violent that the molecule loses completely the memory of its previous velocity and its new velocity simply follows a Maxwell distribution. The corresponding line profile is referred to as a Rautian profile (RP) [23] or equivalently the Nelkin–Ghatak profile (NGP) [22]. The hypothesis of soft collisions, in which many collisions are necessary to change the molecular velocity significantly, leads to the Galatry profile (GP) [21]. Both hard- and soft-collision models introduce one extra parameter, ν_{VC}, to quantify the frequency of VC-collisions.

The speed-dependence of the relaxation rates, considered as the single source of line narrowing, leads to the speed-dependent Voigt profile (SDVP) [25, 40]. It should be noted that this speed-dependence can be

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	$\Gamma_D, \Gamma, \Delta, \nu_{VC}$	No	Soft	No
RP	Rautian	4	$\Gamma_D, \Gamma, \Delta, \nu_{VC}$	No	Hard	No
NGP	Nelkin–Ghatak	4	$\Gamma_D, \Gamma, \Delta, \nu_{VC}$	No	Hard	No
SDVP[b]	Speed-dependent Voigt	5	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2$	Yes	No	No
SDGP[b]	Speed-dependent Galatry	6	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{VC}$	Yes	Soft	No
SDNGP[b]	Speed-dependent Nelkin–Ghatak	6	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{VC}$	Yes	Hard	No
SDRP[b]	Speed-dependent Rautian	6	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{VC}$	Yes	Hard	No
HTP	Hartmann–Tran	7	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{VC}, \eta$	Yes	Hard	Yes
CSDaRSP[b]	Correlated SD asymmetric Rautian–Sobelman	8	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{VC}, \chi, \eta$	Yes	Combination	Yes
pCSDKS[b]	Partially correlated SD Keilson-Storer	8	$\Gamma_D, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{VC}, \gamma_{KS}, \eta$	Yes	Combination	Yes

See text for further details and citations. All profiles except the simple Lorentz profile include the Doppler broadening effect.

[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.

introduced in more than one way. The most popular choice considers a simplified r^{-q} long-range interaction potential, r being the intermolecular distance and q = 3, 4, 5, etc., for leading dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, etc., interactions, respectively. This approximation results in an absolute speed-dependence expressed analytically using a confluent hypergeometric function (often denoted by "h" in the model acronym) [41]. However, the cost associated with this model is too high for routine computations, and thus it is common practice to use a much simpler, quadratic form (given by a "q" in the acronym) [41–44]. In this case the pressure-broadening width and shift are given by

$$\begin{aligned} \Gamma(v_a) &= \Gamma_0 + \Gamma_2[(v_a/v_{a0})^2 - 3/2], \\ \Delta(v_a) &= \Delta_0 + \Delta_2[(v_a/v_{a0})^2 - 3/2], \end{aligned} \tag{4}$$

where Γ_0 and Δ_0 are, respectively, the collisional width and shift averaged over all speeds, and the phenomenological rate parameters Γ_2 and Δ_2 characterize the dependence on the active-molecule speed v_a (v_{a0} is its most probable value). The Boone–Walker–Bernath algorithm [19] allows the calculation of a SDVP from two VPs.

Ascribing the line narrowing solely to the VC-collisions frequently leads to aberrant values of the ν_{VC} parameter which can show unrealistic non-linearities as a function of pressure [15, 16]. For example, when just the linear part of this pressure-dependence is used with a GP to deduce the narrowing coefficient (the slope), the latter demonstrates higher values than those allowed by the kinetic diffusion [35, 36]; conversely, a similar analysis using a RP leads to smaller values of ν_{VC} [15]. This behavior means that other treatments of narrowing are needed; in particular, SD should be accounted for. To this end, speed-dependence has been introduced in the soft-collision model, leading to the SDGP [45]. The SDGP reduces to the GP in the absence of the speed-dependence ($\Gamma_2 = 0$ for qSD) and to the SDVP in the absence of velocity-changing collisions ($\nu_{VC} = 0$). Similarly, the SD introduced in the RP provides the speed-dependent Rautian profile (SDRP) [46]. For both the SDGP and SDRP there are functional advantages if the quadratic SD, see eq. 4, is assumed [47, 48].

Both the SDGP and SDRP models assume that the velocity-changing and the rotational-state-changing aspects of a collision are independent. In practice this is not true: a change of the velocities is balanced by a change of the internal states of the colliders, according to the energy conservation law. Therefore, VC and SD mechanisms can operate simultaneously and their respective model parameters are correlated. The profile models accounting for the correlation of these two collisional effects are described by functions involving supplementary fitting parameters. To achieve this correlation requires the introduction of further parameters. An example is the speed-dependent dispersive Rautian–Galatry profile (SDDRGP) [49], which is used to explain the line-shape asymmetries due to correlation, hardness and collision duration. The SDDRGP is a non-analytic line-shape model with many parameters, which have to be adjusted simultaneously, and therefore this treatment requires multispectrum fits.

An alternative method of introducing correlation is via the partially correlated hard-collision model for velocity- and state-changing collisions [42, 50, 51]. Such a model, based on the use of hypergeometric SD, was recently employed for a spectroscopic determination of the Boltzmann constant [52]. However, this hypergeometric form is difficult to use. A related, but easier-to-apply model considers the speed-dependence only quadratically, yielding the partially Correlated quadratic-Speed-Dependent Hard-Collision Profile (pCqSD-HCP) [48]. This model is flexible and has the major advantage that it can be represented using a relatively simple form, which allows rapid computational evaluation [53], an essential prerequisite for the adoption of a model by databases and modellers. This model is discussed in detail in the following section.

There are more sophisticated profiles which allow for intermediate strength collisions, of which the Keilson–Storer (KS) [54] and the Rautian–Sobelman (RS) [23] profiles are the most widely used. These more sophisticated profiles have an additional parameter η, the correlation parameter. In the KS model there is also a memory parameter, γ_{KS}, which goes to zero for no memory (a hard collision) and unity for full memory (a soft collision) [54, 55]. The RS model instead uses the hardness parameter χ [23].

Of course, the choice of an appropriate line shape function is not a purely theoretical excercise and must be guided by fits to high accuracy measurements, which also need to consider the appropriate instrumental line shape function.

4 The HTP model

The line profile recommended by the TG 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). This line-shape model has been considered by a number of authors [42, 48–51, 53], and has been used successfully for the analysis of ultra-high accuracy experimental water line shapes [15, 56, 57], although not all of these studies considered the speed dependence in quadratic form. The quoted acronyms represent an attempt to capture the physics behind the profile but they are hard to remember and convey little meaning to the non-specialist. The TG therefore recommends that this profile, and its computational implementation which we describe below, be called the Hartmann–Tran profile (HTP) after the authors of Refs. [48, 53].

In terms of the 7 parameters Γ_D, Γ_0, Δ_0, Γ_2, Δ_2, ν_{VC} and η, the HTP functional form can be expressed as [48, 53, 58, 59]:

$$F_{HTP}(\nu)=\frac{1}{\pi}\mathrm{Re}\left\{\frac{A(\nu)}{1-[\nu_{VC}-\eta(C_0-3C_2/2)]A(\nu)+\left(\frac{\eta C_2}{\nu_{a0}^2}\right)B(\nu)}\right\}. \tag{5}$$

The terms $A(\nu)$ and $B(\nu)$ can be expressed as combinations of the complex probability function

$$w(z)=\frac{i}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-t^2}}{z-t}dt=e^{-z^2}\mathrm{erfc}(-iz), \tag{6}$$

where erfc is the Gauss error function, while

$$\begin{aligned}A(\nu)&=\frac{\sqrt{\pi}c}{\nu_0\nu_{a0}}[w(iZ_-)-w(iZ_+)],\\ B(\nu)&=\frac{\nu_{a0}^2}{\tilde{C}_2}\left[-1+\frac{\sqrt{\pi}}{2\sqrt{Y}}(1-Z_-^2)w(iZ_-)-\frac{\sqrt{\pi}}{2\sqrt{Y}}(1-Z_+^2)w(iZ_+)\right].\end{aligned} \tag{7}$$

In these expressions

$$\begin{aligned}Z_\pm&=\sqrt{X+Y}\pm\sqrt{Y},\\ X&=\frac{-i(\nu_0-\nu)+\tilde{C}_0}{\tilde{C}_2},\ Y=\left(\frac{\nu_0\nu_{a0}}{2c\tilde{C}_2}\right)^2,\end{aligned} \tag{8}$$

where

$$\begin{aligned}\tilde{C}_0&=(1-\eta)\left(C_0-\frac{3C_2}{2}\right)+\nu_{VC},\\ \tilde{C}_2&=(1-\eta)C_2,\end{aligned} \tag{9}$$

with $C_n=\Gamma_n+i\Delta_n$ with $n=0$ and 2 within the quadratic approximation, see eq. 4. Finally, the most probable speed can be expressed in terms of the Doppler half-width as $\nu_{a0}=\frac{c}{\sqrt{\ln 2}\nu_0}\Gamma_D$. Note that the HTP is normalized to unit area and is generally asymmetric, even if only slightly, due to the correlation and the speed dependence of the line shift. Furthermore, in the far wing, when $|\nu-\nu_0|$ is much larger than all other terms, the HTP reduces to a Lorentzian of half-width Γ_0.

The physics underlying the 7-parameter HTP profile is as follows. The speed-dependences of the relaxation rates are represented by four parameters: two, (Γ_0, Γ_2), to represent the line broadening and two, (Δ_0, Δ_2), to represent the line shift. Γ_0 and Δ_0 are the mean relaxation rates, while Γ_2 and Δ_2 are the quadratic terms describing the speed dependence of relaxation [43, 44], see eq. 4. Velocity changes are represented within the

Nelkin–Ghatak hard collision model, which requires a single parameter, ν_{VC}. Finally, parameter η represents the partial correlation between velocity and rotational state changes due to collisions. The assumptions of quadratic speed dependences and hard collisions are approximations but, as illustrated below, some of the errors introduced by these approximations are actually compensated for by the inherent flexibility of the parameter fits. This model has been extensively tested both for water transitions and for those of other molecules [48] using accurate calculated spectral shapes [20, 60–62].

As discussed in the literature [48], there are a number of advantages the HTP model offers.

The first is that F_{HTP} can be expressed in terms of two (complex) Voigt (or complex probability) functions, see $w(z)$ as given in eq. 6. Tran et al. [53] provide a routine for evaluating the HTP built on the Voigt routine of Humliček [8]. Numerical tests have shown that the relative accuracy of this routine is always better than 10^{-4} and that the computer time requirement is at most only five times that required for the computation of a VP.

Second, in the case where not all the parameters have been or can be determined, HTP reduces in a very straightforward fashion to a number of simpler, standard profiles. These limiting cases are listed in Table 2. In particular, given that the present databases are largely populated with parameters for the VP, it is advantageous that the HTP reduces to the VP if all the high-order correction terms are set to zero. This is an extremely useful property, but one note of caution is in order. The parameters used to determine these profiles are not independent; this means that once beyond-Voigt parameters are introduced into the fit it is no longer possible to use the parameters to give a correct VP.

Third, we should mention the Van Vleck–Weisskopf (VVW) line shape function [63], see page 184 of Bernath [64] for a short discussion. This simple form includes an anti-resonant Lorentzian function. It is used for low-frequency microwave work [65–67] and in all models of mm-submm radiation propagation [68]. By analogy with the VVW profile, the anti-resonant contribution, which is only significant at very long wavelengths, could be taken into account using an HTP after changing the signs of the transition frequency and the pressure shift.

Finally, line-mixing can be easily included in the model provided that two approximations are made [48]. The first is the use of the so-called (Rosenkranz) first-order approximation [69]. The second is the neglect of the speed-dependence of the line-mixing. These approximations are routinely used in practical treatment of line-mixing, for example the implementation in the HITRAN database [70].

5 Discussion

The recommendation by the TG of the HTP as the new standard for representing the profile of high-resolution spectroscopic transitions raises a number of issues which should be considered.

First, use of this more complex parameterization to characterize the pressure line shape has a consequence not mentioned so far: collisional parameters for gas mixtures are no longer simple linear combinations of the parameters for the various active molecule-perturber pairs [48]. This means that, for example, in the terrestrial atmosphere, it will be necessary for databases to separately specify collisional parameters for perturbations by N_2 and O_2 rather than just for "air" so that separate profiles can be computed and then

Table 2 Correspondence between various lower-order models and the limits of the Hartmann–Tran profile (HTP) [48].

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

[a]Using the quadratic approximation of eq. 4 for the speed dependence.

added. As a result of this it will become necessary for all significant perturbers to be added individually to the databases.

Second, the discussion above has not addressed the temperature dependence of parameters in the line-profile models considered. Even for studies of the Earth's atmosphere it is necessary to consider line profiles in the temperature range of approximately 200–300 K. Much larger temperature ranges are required for other modelling studies. For example, water line profiles are required for the atmosphere of hot Jupiter exoplanets (T = 1000 – 1500 K) [71] and probably also for brown dwarfs ($T \leq 3000$ K). Available experimental studies usually span ranges of about 100 K to about room temperature, see Refs. [72, 73], for example. Obviously, it would be desirable to have experimental studies over more extended temperature ranges, but these are unlikely to be forthcoming in the immediate future. Conversely, ab initio spectral shapes calculated by molecular dynamics simulations [61, 62] should be reliable at temperatures above the quantum limit and can easily be repeated for many temperatures. So far such studies on water seem to have focused heavily on the room temperature regime [20, 74–76]. Extending molecular dynamics simulations to probe the effects of temperature would clearly be very useful. In the absence of experimental determinations, this would allow predictions of the temperature dependence of the narrowing and correlation parameters. We expect the latter to be reliable, in view of the quality of calculations at room temperature. Furthermore, the temperature dependences of Γ_2 and Δ_2, like Γ and Δ, can be investigated by using semi-classical calculations [74, 76].

Third, other tests, both experimental and numerical, would also be useful. Issues that should be probed include: (a) signal-to-noise limits that the HTP (and other profiles) are reliable for; (b) tests of extreme heavy – light collisions such as water perturbed by He (or H_2), such collisions are normally considered to be "soft"; (c) tests of extreme light — heavy collisions such as water with Xe or SF_6; and (d) tests of whether collisions with open-shell systems, such as O_2, introduce any new features.

Finally, the HTP is based on an approximate quadratic treatment of the speed dependence and of velocity changes. The approximate treatment of SD can be tested against the more physically-based and more complicated pChSDNGP, which uses the hypergeometric SD, albeit still with an approximate treatment of the potential. Such tests have recently been completed by De Vizia et al. [78], see Fig. 1. They found that the HTP and pChSDNGP fitted their benchmark, measured, high-precision water line profiles almost equally well. Furthermore, they found that the retrieved broadening and shifting parameters were unchanged in the two fits, something not completely found, for example, when using the SDGP (speed-dependent Galatry profile) to fit the same data [77]. However, values for the parameter ν_{VC}, which can be related to the diffusion coefficient of the molecule in the perturbing medium, were found to be physically meaningful for the pChSDNGP fits but not the HTP ones [78]. Under these circumstances ν_{VC} must just be regarded as a useful fit parameter, and nothing more. From Fig. 1, one can see that the residual of the fit with the VP varies between about ±0.5 % of the peak absorption. These data are for a specific line and pressure, but much larger effects are observed [16, 20] for other transitions and gas densities.

6 Final recommendations and conclusions

The IUPAC Task Group formed by the first 12 authors of this paper makes the recommendation that the pCqSDHCP [48, 53, 58, 59] should be adopted as the appropriate line-profile model of high-resolution spectroscopy moving beyond the VP. For simplicity we propose calling this the Hartmann–Tran profile (HTP).

The proposed line shape is based on six temperature-dependent, collisional parameters for each line and perturber plus the Doppler width, Γ_D, fixed to its theoretical value. These parameters give the model the flexibility to include all the major "non-Voigt" effects. HTP involves parameters with known pressure dependences that can be stored in databases. HTP has been demonstrated to lead to an accurate description (0.1 % or better) of the line shapes for a number of combinations of absorbers and perturbers [48], with the exception of H_2, which is a known difficult case. Furthermore, HTP can be computed accurately using only moderate

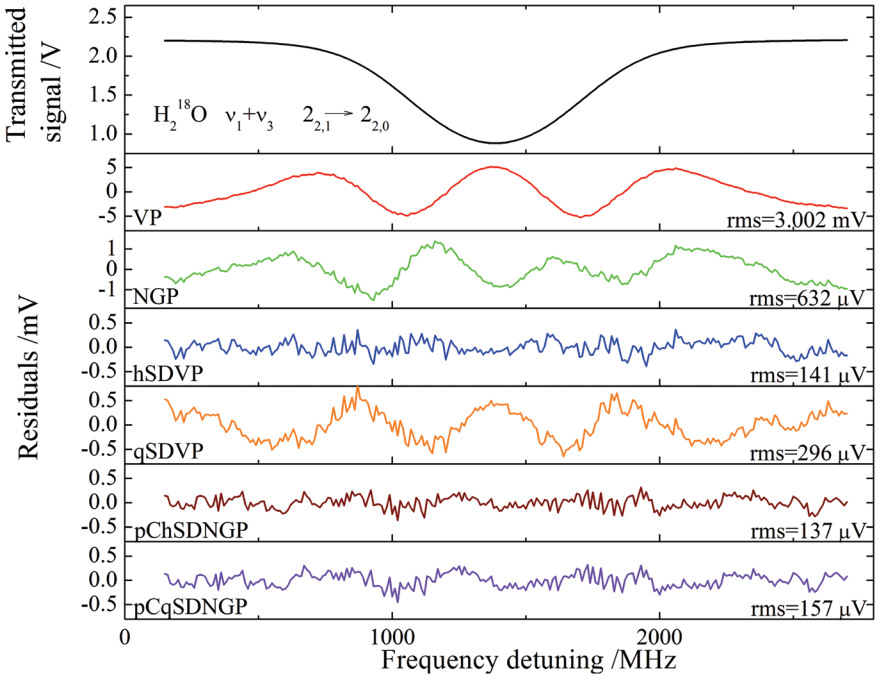

Fig. 1 Comparison of line-shape fits to the $H_2{}^{18}O$ absorption feature at 7222.298050 cm^{-1} measured at a pressure of 2.70 Torr and a temperature of 273.16 K. Residuals are given in terms of units of the original signal: root mean square (rms) values of about 150 μV simply reflect the noise in the original experiment [77]. Note that pCqSDNGP is equivalent to HTP.

computer time requirement [53], it is compatible with current implementations of line mixing, and it can be initially parameterized using the Voigt parameters already available in standard data compilations.

Considering the relatively large number of parameters required for the full HTP model and the correlations between them, fitting measured individual spectra is unlikely to yield a well-constrained parameter set. This means that a multispectrum procedure [37] must be used. Furthermore, to remove the partial correlations between the various parameters, it is essential to use spectra recorded in a broad pressure range and with a high signal-to-noise ratio.

There are some open questions about the use of the HTP. The most pressing of these concerns the temperature dependence of the model parameters. These have not been the subject of serious testing over extended temperature ranges with temperature-dependent data from either laboratory measurements or numerical (molecular dynamics and semi-classical) simulations. Furthermore, very high signal-to-noise ratio measurements, combined with multispectrum fits of data recorded at a number of pressures, would help to better define the underlying accuracy of the model. Finally, tests need to be performed with a variety of collision partners to determine, e.g., the effects of different mass ratios and collisions with open-shell species such as O_2.

One issue not discussed so far is that of the so-called water continuum [79]. The water vapor continuum is characterized by absorption that varies smoothly with wavelength, from the visible to the microwave. It is present within the rotational and vibrational-rotational bands of water vapour, and in the many "windows" between these bands. The precise relationship between the water continuum with the far wings of the line profile for individual transitions and with dimer contributions remains a matter for discussion. It is clear that changing the model for the line profile about the line center has possible consequences on the determination of the continuum. However, these should be small as local line contributions are only calculated in a narrow interval before subtraction from the measured absorption. Changing the line shape thus has only a local effect with minor consequences on the broad and slowly varying continuum. Furthermore, the main uncertainties in the continuum determination remain more to do with uncertainties in the line intensity and broadening coefficients than the line profile. Nevertheless, for consistency, a continuum should be used in radiative transfer calculations which has the same local line shape as the one used in its experimental determination.

Finally, we note that adoption of the HTP will require significant alteration to the data structures used in databases. Work in this direction has already started [80]. Although TG2 was set up explicitly to consider water, our recommendations and the modernizations should apply to the line shape used for all molecular species.

7 Membership of sponsoring body

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