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Phys. Rev. A 96, 022514 — Published 23 August 2017
DOI: [10.1103/PhysRevA.96.022514](https://doi.org/10.1103/PhysRevA.96.022514)
Title: Broadband, high-resolution investigation of advanced absorption lineshapes at high temperature

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Abstract: Spectroscopic studies of planetary atmospheres and high-temperature processes (e.g. combustion) require absorption lineshape models that are accurate over extended temperature ranges. To date, advanced lineshapes, like the speed-dependent Voigt and Rautian profiles, have not been tested above room temperature with broadband spectrometers. We investigate pure water vapor spectra from 296-1305K acquired with a dual frequency comb spectrometer spanning from 6800-7200cm⁻¹ at a point spacing of 0.0033cm⁻¹ and absolute frequency accuracy of <3.3e-6cm⁻¹. Using a multi-spectral fitting analysis, we show that only the speed-dependent Voigt accurately models this temperature range with a single power law temperature-scaling exponent for the broadening coefficients. Only the data from the analysis using this profile falls within theoretical predictions, suggesting that this mechanism captures the dominant narrowing physics for these high-temperature conditions.

Word Talley

Abstract: 126
Words: 2820
Figures, eqns, tables: 1098
Captions: 186
Total words: 4104
Many fields of research, from planetary/exoplanetary science to combustion, rely on accurate measurements in high-temperature gaseous environments. Absorption spectroscopy is useful for remotely investigating these high-temperature systems [1–3], but its accuracy is entirely linked to the existence of well-vetted spectroscopic databases (e.g. HITRAN2012 [4]) and lineshape models to enable interpretation of measured spectra. Voigt profiles are traditionally used to describe the lineshapes of individual absorption transitions, and opacity models involve summations over many of these transitions. Unfortunately, the Voigt model neglects several collisional effects, such as the frequency of velocity-changing collisions, also known as Dicke narrowing, and speed dependence of the collisional broadening coefficient. These omissions can limit data/model agreement to about 2% at the line center of transitions for pure water [5,6] and up to 10% for air- or N₂-broadened water [7,8]. Additionally, the temperature dependence of the lineshapes is not adequately captured in the simple Voigt profile. Conventionally, temperature scaling has been incorporated through a power law \((296K/T)^n\) to scale broadening and pressure-shift coefficients with temperature. This expression has only been experimentally investigated for high-temperatures in a few studies, and has been shown to produce non-physical, negative values for the transition-specific temperature-scaling exponent \(n\) when using Voigt profiles with air [9,10] and water [11] as the broadening partners above approximately 400K.

In this Rapid Communication, we report on the results of the first broadband, high-resolution, high-temperature study of pure water absorption lineshapes. These results demonstrate that only the speed dependent Voigt lineshape profile accurately captures the correct physical broadening mechanisms for water vapor over our broad temperature range while experimentally confirming an earlier study of theoretically computed temperature-dependent lineshape values [12]. We also show that two other important lineshape profiles, Rautian and Voigt, fail to model the data correctly. The work presented here is useful for both researchers employing the databases to analyze high-temperature systems, and fundamental spectroscopists interested in high temperature lineshape behavior.

Advanced lineshapes incorporating velocity-changing collisions and speed dependence are a potential remedy [13] for more accurate and physically reasonable temperature scaling. However, the efficacy of these higher order collisional mechanisms and scaling over large temperature ranges is largely unexplored in water due to the lack of broadband, high-resolution spectra at high temperatures. For example, prior to the present work, it was unknown if non-physical temperature-scaling exponents would occur for water self-broadening using advanced lineshapes or if a single exponent could model broad temperature ranges. Here we compare the ability of speed dependence and velocity-changing collision mechanisms to model high-temperature spectra. Briefly, velocity-changing collisions reduce the Doppler width of a transition when there are multiple collisions over the distance traveled by a molecule following photon absorption [14,15] and are represented here by the Rautian profile in the hard collision limit [16]. Speed dependence accounts for long-range dipole-dipole coupling and the effect of relative broadener/absorber velocities on the absorber relaxation rate. Absorption profiles are narrowed due the longer lifetimes of slower moving molecules in their excited states relative to fast moving molecules [17]. Here, we compute this profile using a quadratic speed dependent Voigt (qSDVP). It utilizes the quadratic speed dependence model, which is the community standard due to its accurate yet efficient computation [13,18]. These narrowing effects particularly influence the transition- and molecule-dependent collisional broadening parameter \(y_{self}\) and its temperature-scaling exponent \(n_{self}\). These parameters can be predicted by the broadly utilized complex Robert-Bonamy theory.
(CRB) [19], but the accuracy of these predictions was, until now, widely un-validated by experiment. We show that current CRB theory and our data match only when using a qSDVP and that the transition-dependent temperature-scaling exponents clearly trend as expected with the total rotational momentum quantum number \( J'' \). Therefore, this work is a vital first step towards improved theoretical understanding and accurate measurement of high-temperature systems.

Experimental data for temperature-scaling exponents of broadening coefficients is not widely available owing to difficulty of making high-resolution measurements of many transitions over wide temperature ranges. Spectrometers that are capable of broad spectral coverage usually have difficulty measuring high-temperature gases, >400K, due to blackbody contamination [20,21]. Conversely, instruments that can probe high-temperatures are either low resolution [22,23] or cannot investigate many lines at once [11,24], thus limiting their ability to examine trends of various lineshape models. The work presented here is the first broadband, high-resolution data set to separately examine the effectiveness of advanced profiles for high-temperature water vapor, and helps to inform water self-broadening theory at a 3-fold higher temperature range than previous studies. We achieve this using a dual frequency comb spectrometer and high-temperature optical cell facility to measure pure water absorption from 296-1305K, 1-17 Torr, in a 2D matrix (25 total spectra), each spanning 6800-7200cm\(^{-1}\).

Dual comb spectroscopy is an emerging form of high-resolution spectroscopy. Here, we use the technique to probe high-temperature systems with an unprecedented combination of frequency accuracy, resolution, and bandwidth. Our frequency combs are mode-locked lasers that can simultaneously produce 100,000+ distinct frequencies (comb teeth). The spectrometer utilizes two frequency combs with slightly offset repetition rates that are mutually phase locked to an external stable optical cavity. The offset repetition rates create evenly spaced heterodyne beat frequencies when the two combs are combined onto a detector. The intensity of the beat frequencies is proportional to the intensity of the contributing comb teeth, and thus recreates the spectrum of the absorbing molecules on a tooth-by-tooth basis. References [25,26] describe the technique and system in detail, shown in FIG. 1. The collection of the data in this paper was completed prior to the advent of mobile dual comb systems [27,28], so the spectrometer was housed at NIST Boulder and linked to University of Colorado Boulder (CU) via a 3km fiber bundle in the BRAN network [29]. Upon arrival at CU, common mode noise is cancelled [26], the combs are combined, and the light is double passed (pathlength of 91.4cm) through a quartz cell housed inside a uniform tube furnace. The comb light was detected, digitized, and averaged for 90 minutes to reach absorbance SNR of approximately 2000:1. The spectrometer has a point spacing of 0.0033cm\(^{-1}\), absolute frequency accuracy of <3.34e-
7 cm\(^{-1}\), tooth linewidths of \(<3.34\times10^{-6} \text{ cm}^{-1}\), and can span from 5800-7700 cm\(^{-1}\) (filtered here to span 6800-7200 cm\(^{-1}\)) [26].

Extraction of the subtle narrowing effects due to velocity-changing collisions and speed dependence by single-spectrum fitting (i.e. fitting the spectrum for each condition individually) is prone to non-physical results due to correlation among lineshape parameters and the requirement of secondary and tertiary fits to extract pressure- and temperature- dependence. Multispectral fitting routines have therefore been recommended as reliable methods for fitting advanced lineshapes [13]. To analyze the 25 spectra, we employ the multispectral fitting program described in [30,31]. It fits a single set of lineshape parameters for each transition to all of the measured spectra at multiple pressure and temperature conditions simultaneously. The outcome is a single set of transition-dependent parameters that minimize the fit residual across all experimental conditions [30].

The base lineshape function currently employed in the fitting routine is the symmetric quadratic speed-dependent Rautian profile, which can be simplified to the Voigt, Rautian, and speed-dependent Voigt profiles by fixing certain parameters to zero, discussed later. When simplified for a single species without self-shift, the function takes the form:

\[
F(x, y, S, \nu_{vc}) = \frac{2}{\pi^{3/2}} \int_{-\infty}^{+\infty} ve^{-v^2} \arctan \left( \frac{x + v}{y(1 + S(v^2 - 3/2)) + \left(\frac{T_{ref}}{T}\right)\nu_{vc}} \right) dv, \tag{1a}
\]

Where \(v\) is the molecular speed normalized by the most probable speed, \(x = (\sigma - \sigma_o)/\gamma_{Doppler}\) is the optical frequency offset from the line center \(\sigma_o\) normalized to the Doppler width \(\gamma_{Doppler}\) [31,32], \(T\) is the lineshape at the temperature of interest, \(T_{ref}\) is the reference temperature, in this work 296 K, and \(\nu_{vc}\) is the velocity-changing collisions coefficient. \(y\) is the nondimensionalized self-broadening half-width (shown in Eqn. 1b) and \(S\) is the ratio of the speed dependence to collisional self-broadening width.

This form assumes the temperature dependence of \(y\) and \(S\) are equal, as derived in [33] and implemented in [34]. Previous authors have experienced difficulty obtaining reliable temperature dependencies of the speed dependence value when treating self-broadening and speed dependence as independent fitting parameters with separate temperature-scaling exponents due to the dominant influence of self-broadening and inadequate signal-to-noise ratios [11]. Authors with very high signal-to-noise ratio spectrometers have been able to show that separately measured temperature-scaling exponents for self-broadening and speed dependence are similar [35], thus supporting the constraint presented in eqn. (1a).

The temperature dependence of \(\nu_{vc}\) is fixed at \(T_{ref}/T\) as per [36,37] since the temperature dependence of velocity-changing collisions is identical for all transitions of a molecule [14]. The temperature-dependence of the self-broadening and speed dependence (through \(S\)) is captured by:

\[
y = \frac{pY_{self}(T_{ref})/(T_{ref}T)^{n_{self}}}{\gamma_{Doppler}} \tag{1b}
\]

Where \(p\) is system pressure, \(Y_{self}\) is the self-broadening coefficient at \(T_{ref}\), and \(n_{self}\) is the temperature-scaling exponent.

The difference between the velocity-changing collisions and speed dependence narrowing effects require very high SNR to directly discern [38], as the differences are subtle and as there are no
broadly accepted methods of relating/constraining the terms when both are floating in a fit. Therefore, we did not employ the full speed dependent Rautian here. Instead, we explored the qSDVP (eqn. (1a) with $\nu_{pc} = 0$), the Rautian profile (eqn. (1a) with $S = 0$), and the Voigt profile (eqn. (1a) with $\nu_{pc} = S = 0$). We float line center, linestrength, self-broadening coefficient, temperature-scaling exponent, and $S$ or $\nu_{pc}$ for all transitions. HITRAN2012 data was used to supplement the parameters for weak or unfit lines.

FIG. 2 shows examples of the multispectral fit results at 296 and 1305K for each lineshape profile. The qSDVP clearly captures the measured data more accurately across our temperature range than the Voigt and Rautian. As shown in eqn. (1a), our Rautian profile employs a transition-independent $1/T$ temperature scaling of $\nu_{pc}$ [36], while the qSDVP utilizes a transition-specific exponent identical to that used for the self-broadening term. The Rautian fits suggests that additional molecule- or transition-specific broadening temperature exponents may be required, contrary to theory. For all transitions, the qSDVP produced a smaller residual structure than the Rautian or Voigt. The residual for some transitions fit with a Rautian profile matched the qSDVP residual, but for others the result was more similar to the Voigt. This shows that residual analysis in general, and particularly residual analysis on a small number of lines, is not sufficient for determining the dominant narrowing mechanism for our conditions.

To expand the investigation, FIG. 3 shows the 232 extracted temperature-scaling exponents.

![Fig. 2. Dual-comb measurement and multispectral fit results using the qSDVP, Rautian, and Voigt profiles. Panel A shows the full bandwide measurements and fit with the qSDVP at 1305K and 17 torr H$_2$O. Panel B highlights the area indicated in blue on Panel A for 296K and 1305K. The residual structure for the qSDVP is the smallest, while the Rautian and Voigt are similar. The high frequency oscillations on the residual of the 1305K qSDVP are numerical noise and do not influence retrieved parameters.](image)
using the Voigt, Rautian, and qSDVP, organized by $J''$. We use $\Delta n > \sqrt{2(\Delta \gamma / \gamma)}\ln (T_{\text{max}}/T_{\text{min}})$ [39,40], where $\Delta \gamma$ is the accuracy of the transition width measurement, to estimate the systematic uncertainty for our fit. Though the equation was derived for single-spectrum fits, it accounts for the decreased uncertainty for fitting temperature-scaling exponents over a broad temperature range [40]. Using this equation, we estimate a systematic uncertainty range of 0.3% and 3.6% for the extracted exponents. The statistical uncertainty varies depending on the absorption strength and fit uncertainty of each line. We only present lines where the temperature-scaling exponent fit uncertainty (which we approximate as the statistical uncertainty) was less than 25%.

The data are plotted in FIG. 3 together with the upper and lower bounds for the temperature-scaling exponent predicted by CRB theory in Antony et al. [12]. Only the data extracted from the qSDVP agrees with the CRB theory. For the qSDVP lineshapes, the individual temperature-scaling exponents, their average at each $J''$, and standard deviation are all within Antony et al.’s theoretical bounds and closely follow the expected and predicted decrease with increasing $J''$. The Voigt and Rautian resulted in negative exponents that should not occur for water at the $J''$ values explored here [12,41,42]. Furthermore, for 40 of the investigated lines, the multi-spectral fits with the Voigt and Rautian were not stable. These results point toward speed dependence as the most important and dominant narrowing mechanism for our conditions.

FIG. 3. Extracted temperature-scaling exponents using Voigt, Rautian, and qSDVP. Data using the qSDVP clearly follow Antony et al.’s bounds (black traces). $J'' = 0$ falls outside of the trend since there was only a single measured transition. The averages for all plots are offset for clarity and error bars on the averages are standard deviations of all data at each $J''$. 
The ratio of the optical collision radius to the potential radius can also reveal the relative influence of speed dependence over velocity-changing collisions on the lineshape [43]. For water, the potential radius is 2.65 Å based on the Stockmayer potential for polar molecules [36]. We compute an optical collision radius of 4.52 Å from our average measured $\Gamma_2$ values (0.05 cm$^{-1}$/atm across all temperatures). The larger optical collision radius further suggests that speed dependence is the dominant narrowing mechanism at our conditions [43,44].

The large scatter and non-physical results of the Voigt and Rautian results would have a negative impact if a database were created with these data. For example, for a typical $J''=9$ transition examined here, $n_{Voigt} = 0.954$, $n_{Rautian} = 1.37$, and $n_{qSDVP} = 0.604$. Taking the qSDVP as the true value, the percent differences in the broadening width at 1305K are 50%, and 103%, respectively. This illustrates the importance of using the temperature-scaling exponents from this study or from Antony et al. exclusively with the qSDVP, as mixing the exponents with a Voigt profile at elevated temperatures will induce significant error. Therefore, only the qSDVP adequately models temperature behavior of pure water transitions over this temperature range and strongly supports the qSDVP as the preferred advanced lineshape profile of those studied here.

Additionally, we found that the use of a single temperature-scaling exponent to span from 296-1305K adequately modeled the spectra when fit with a qSDVP. The residual structure was almost within noise for the 232 lines that were strong enough to be reliably fit, spanning a linestrength range from 1e-24 to 1.35e-20 (cm$^{-1}$/molecule cm$^{-2}$). The average root mean squared error for all residuals was ~3% lower for the qSDVP as compared to both the Voigt and Rautian. Antony et al.’s results also employ a single temperature-scaling exponent to adequately fit their calculated data from 200-500K.

To account for systems that do not follow the power law, like pure H$_2$ [45], the next version of the HITRAN database will allow up to four broadening temperature-scaling exponents for the following temperature regions: 0-100K, 100-200K, 200-400K, and >400K [46]. Our data shows that this segmentation is not required for pure water over our temperature range. Some authors have postulated that the power law breaks down over large temperature ranges or at high temperatures owing to the complex broadening behavior of water and competing temperature dependent mechanisms [6,11]. Our data suggests this assertion is incorrect within our range (296-1305 K).

Finally, the measurements suggest that the extracted broadening parameters are independent of vibrational band, and thus the trends may carry for vibrational bands not measured here. All of the 232 transitions from six vibrational bands of water investigated here using the qSDVP fall within the Antony et al. prediction (which only studied three of these transitions from the (101)-(000) vibrational band). The results do not show a trend among the vibrational bands. This is expected for pure water collisions, since there are always resonant transitions that facilitate energy transfer and prevent the energy defect thought to be responsible for strong vibrational dependence and anomalous temperature behavior with foreign molecule collisions (like with N$_2$ [12,41,47]).

In conclusion, we utilized a high-resolution, broadband dual frequency comb spectrometer to measure pure water in a uniform furnace at temperatures up to 1305K. We examined the effect of using a Voigt, Rautian, and qSDVP to extract absorption parameters, and in particular the temperature-scaling exponents of the self-broadening coefficient for 232 transitions. These results validate CRB calculations conducted by Antony et al. and show that their theoretical formalism is accurate for $J'' \leq 11$. 
over a much wider temperature range than their original calculations. The temperature-scaling exponents extracted using the qSDVP agree well with the theoretical values, while results obtained using a Voigt or Rautian profile resulted in non-physical and highly scattered values. Additionally, we show that a qSDVP allows accurate fitting over a large temperature range using only a single transition-dependent, power law temperature-scaling exponent. Validity of the power law over such a range for numerous transitions was previously unexplored and this work supports the feasibility of single power law exponents with advanced lineshapes. The systematically better fit and less scattered temperature-scaling exponents suggest that speed dependence is the dominant influence at our conditions despite the effects of velocity-changing collisions and speed dependence narrowing being indistinguishable based solely on residual structure for our SNR of 2000:1.

All lineshapes investigated here are limit cases of the Hartmann-Tran profile so the results are applicable to current and future spectroscopic databases that adopt this formalism. The databases that serve the remote sensing and combustion research communities currently lack temperature dependence information from high-resolution spectra. The line-by-line database extracted from the multispectral fits to our data will be published in an upcoming work, however the results and validation of complex Robert-Bonamy theory lends confidence to the utilization of theoretically computed temperature exponents provided a speed dependent lineshape is also adopted for vibrational bands beyond those studied here. The same is true for the speed dependence and single exponent power-law results.

Overall, the work presented here extends our understanding of high-temperature water vapor absorption, with implications ranging from planetary/exoplanetary science to combustion research.

Support for this work was provided by the National Science Foundation under grants CBET 1336643 and 1454496, and by the Air Force Office of Scientific Research under FA9550-17-1-0224. Portions of the research described in this paper were performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration. Government sponsorship acknowledged.

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