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Line shapes, positions and intensities of water transitions near 1.28 μm



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ABSTRACT

We present measurements of approximately 70 isolated, self-broadened, water vapor lines which are assigned to the (1,0,1)-(0,0,0), (0,0,2)-(0,0,0), (1,2,0)-(0,0,0), and (2,0,0)-(0,0,0) vibrational bands and which occur in the transparency window region from 7710 cm⁻¹ to 7920 cm⁻¹. We acquired absorption spectra on room-temperature, water samples over the pressure range 150-800 Pa with the frequency-stabilized cavity ringdown spectroscopy technique. In order to optimize measurement accuracy, we integrated mK-level temperature control and SI-traceable pressure measurements into our cavity ring-down spectroscopy measurements. This technique yielded relative uncertainties of 0.04% and 0.20% in sample density and measured line intensity, respectively. We also referenced our spectrum frequency axes to a Cs clock, which provided vacuum line positions with a combined standard uncertainty of 3 MHz. Comparison of our measured intensities, positions and self-broadening parameters with literature values reveals that the present work substantially reduces uncertainty in these line parameters. For the (1,0,1)-(0,0,0) vibrational band, the measured line intensities agree at the 1%-level with published ab initio calculations. Our spectra exhibited signal-to-noise ratios up to \approx 20,000:1 to enable stringent tests of theoretical line profiles through multispectrum least-squares data analysis. We show that the partially correlated, quadratic-speeddependent Nelkin-Ghatak profile gives a quality of fit that is commensurate with the high spectrum signal-to-noise ratio, and unlike most other profiles considered here, reproduces the measured line shapes without systematic residuals over the entire pressure range. Our results confirm that mechanisms of (1) collisional narrowing, (2) speed-dependent effects and (3) partial correlation between velocity-changing and dephasing collisions, contribute to the self-broadened line shape of isolated water vapor transitions.

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1. Introduction

Water plays a key role in radiative energy transfer in the atmosphere of the Earth because it has an enormous number of rotation-vibration bands that span the visible and infrared regions. In measurements of transmitted solar

http://dx.doi.org/10.1016/j.jqsrt.2014.10.020 0022-4073/Published by Elsevier Ltd. radiation from ground- or satellite-based spectrometers, absorption by water vapor can enable remote sensing of tropospheric water vapor [1,2]. Water vapor may also interfere with the spectra of other target species. These and other spectroscopic applications require accurate assignments, frequencies and intensities for water transitions. Although there has been much progress in fundamental, quantum-mechanics-based calculations of these quantities [3–6], low uncertainty spectroscopic line parameter data are necessary to confirm theoretical

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predictions. The water transitions considered herein are of particular importance because they interfere with the $(a^{1}\Delta_{g}-X^{3}\Sigma_{g}^{-}(0,0))$ rovibronic band of oxygen (O₂) at 7880 cm⁻¹. In this spectral region and at atmospheric abundances, the respective amounts of light absorption by water vapor and oxygen are of comparable magnitude. These interferences are particularly relevant to the Total Carbon Column Observing Network (TCCON) [7], which is a global network of ground-based, solar-observing Fourier-transform spectrometers for high-precision measurements of atmospheric carbon dioxide (CO₂) and other greenhouse gases. TCCON uses this band as an internal standard for oxygen column abundance and relies on HITRAN as well as hundreds

of supplemental, empirically determined water lines to account for spectral interferences by water.

Presently most of the studies on the water vapor spectrum in the 1.28 um spectral region were made by Fourier transform spectroscopy (FTS) in which the positions and intensities are reported [8–16]. Recently a high-sensitivity cavity ring-down spectroscopy (CRDS) experiment was used by Mikhailenko et al. [17] to record the absorption spectrum of the water vapor in the 1.28 µm spectral region. In this work, the authors report a more complete line list than that provided by the 2009 update to HITRAN 2008 [18]. Mikhailenko et al. [17] measured 4600 lines of the isotopologues of water, reporting intensities as low as 2×10^{-29} cm/molecule. However, these measured intensities were found to be systematically smaller than those obtained from the ab initio potential energy [19] and dipole moment surfaces [20] calculated by Schwenke and Partridge. This discrepancy was attributed to inaccuracy in the pressure gauge used in the CRDS experiment [17], which caused a few % error in all measured line intensities. Thus for water vapor intensities in this region, databases like HITRAN 2012 [21] still mostly use the results of Toth [13] and values for relatively weak transitions which are based on theoretical calculations [3].

Accurate spectroscopic data for water vapor are also highly relevant to improving semi-empirical lists of transition frequencies. A recent example includes the line list based on the measured active rotational-vibrational energy levels (MARVEL) algorithm [11]. MARVEL compiles, critically evaluates and uniquely assigns measured transition frequencies, and subsequently weights and inverts this set of observations to yield the rotation-vibration energy levels of the water molecule. The line positions used in MARVEL for the present region come from the experiments of Toth [13], Tolchenov et al. [12], Zobov et al. [22] and [14] Mikhailenko et al. [17], the first three data sets of which were measured with FTS. For the FTS measurements the reported standard uncertainties are 10^{-4} cm^{-1} (3 MHz) [13], 10^{-3} cm^{-1} (30 MHz) [12], and 0.02 cm^{-1} [22]. In the CRDS study of Mikhailenko et al. [17] the probe laser frequency was measured with a wavelength meter having a standard uncertainty of 20 MHz. Notably, although the self-pressure shifting of water can be quite strong [≈ 15 kHz/Pa (0.05 cm⁻¹ atm⁻¹) for example] none of these previous studies were corrected to the zero-pressure position value [16]. Recently, Tennyson et al. [11] completed a comprehensive review of the measured $H_2^{16}O$ transition frequencies upon which the MARVEL analysis of energy levels is based. They showed that more than 25% of the assigned transitions in MARVEL differ in frequency by more than 30 MHz by comparison to the corresponding HITRAN 2004 values [23].

Systematic departures of water line shapes from the Voigt profile are well documented, with a representative summary being Refs. [1–25] of Ngo et al. [24]. Line narrowing in the ν_2 band water transitions was reported over 40 years ago by Eng et al. [25] and was assigned to the effect of molecular diffusion. This early work was followed by many laser- [26–29] and FTS-based [30,31] observations of collisional line narrowing in isolated rotation–vibration transitions of water vapor.

The role of speed-dependent effects in the narrowing of water lines was reported first by Claveau et al. [31] and subsequently by Lisak et al. [32]. In another study, Lisak et al. [33] observed collisional narrowing and speed dependent effects in CRDS spectra of nitrogen-broadened water transitions near 925 nm. These spectra were modeled using a rigid-sphere model of collisions called the speed dependent billiard-ball profile (SDBBP) [34]. Tran et al. [35] also observed collisional narrowing and speed dependent effects in nitrogen-broadened lines of the ν_3 band of water vapor. Their analysis involved numerical solution of the kinetic equation for the transition moment autocorrelation function [36], calculation of absorber velocity changes with the Keilson–Storer function [37], and a memory parameter [38] which ranges from zero to unity with limiting values that correspond to the purely hardand soft-collision cases, respectively. Speed-dependent effects were also found to be important in remote sensing of tropospheric water spectra [39], thus also motivating the need for advanced line shape analyses in measurements outside of the laboratory.

In addition to collisional narrowing and speed-dependent effects, correlations between velocity-changing and dephasing collisions [40] are known to influence line shapes of isolated water transitions. Asymmetric spectra (see Grossmann and Browell [28]) and differences between the optical frequency of velocity-changing collisions and the molecular-diffusionbased narrowing frequency (see Lisak et al. [33]) were assigned to these correlations. In a recent FS-CRDS study where correlations between velocity-changing and dephasing collisions were not considered, Lisak et al. [41] measured a collisional narrowing frequency that was a factor of five less than the value corresponding to the mass diffusion coefficient of water. More recently, Ngo et al. [42] and Tran et al. [43] introduced correlation effects in water line shapes using the partially correlated speed dependent Keilson-Storer profile (pCSDKSP). This generalization of the Keilson-Storer model given in Ref. [35] was in good agreement with observed spectra and illustrated the importance of considering correlation effects in the analysis of water line shapes.

Recent advances in laboratory measurements that yield extremely high signal-to-noise-ratios (SNRs) for absorption spectra [44] now enable increasingly stringent tests of fundamental line shape theories [45,46]. For water vapor, the identification and validation of accurate line shape models to reproduce both the pressure- and composition-dependence of isolated transitions, has been the focus of several recent studies [41–43]. Lisak et al. [41] used CRDS to

measure nitrogen-broadened spectra with SNRs exceeding 1000. Fitting the Voigt profile (VP), Galatry profile (GP), Nelkin–Ghatak profile (NGP) and speed-dependent Voigt profile (SDVP) to this high-fidelity measurement yielded systematic residuals exceeding the measurement noise. The largest residuals were those of the VP, which exhibited Wshaped values that were at most about 5% of the absorption signal. Lisak et al. [41] also implemented multispectrum fits of the quadratic-speed dependent Nelkin-Ghatak profile (qSDNGP) to FS-CRDS spectra obtained over a range of pressure. Their multispectrum analysis constrained the broadening and narrowing widths to vary linearly with pressure and eliminated correlation between the optical frequency of velocity-changing collisions and the speeddependence parameter (which occurs when fitting spectra acquired at a single pressure). This study confirmed that profiles that do not model both collisional narrowing and speed-dependent effects cannot always describe the observed line shapes of isolated water lines.

The pCSDKSP is probably one of the most rigorous and general line profiles to be implemented and compared to measurements of water spectra. Unfortunately, the pCSDKSP is computationally demanding and cannot be reduced to a simple, parameterized functional form. These complications usually make this profile unsuitable for fitting to measured spectra or for parametric incorporation into spectroscopic line lists. In this context, Ngo et al. [24] concluded that compared to the many other models which have been considered, the partially correlated, quadraticspeed-dependent hard-collision profile (pCqSDHCP) is most suitable for calculating the line shape of isolated water transitions over a wide range of pressure. This line profile recently was recommended by the IUPAC task group on "Intensities and line shapes in high-resolution spectra of water isotopologues from experiment and theory" (Project no. 2011-022-2-100) as a generalized alternative to the Voigt profile for use in spectroscopic databases because it captures the physical complexity of real line profiles without introducing undue computational burden [47]. For simplicity, the authors of this study suggested that the pCqSDHCP be called the Hartmann-Tran profile.

The relatively large uncertainties in intensities, positions and fundamental uncertainty in the line shapes of water vapor spectra motivate the present set of measurements. In the remainder of this article, we report new measurements of approximately 70 self-broadened H_2^{16} O transitions in the wave number range 7710–7920 cm⁻¹ corresponding to a transparency window region. We begin by describing the experimental apparatus, and then we present formulas for line profiles in the hard-collision limit, and we investigate the fidelity with which various line profiles model the observed line shapes. Finally, we present measured intensities, positions and line widths, and we compare these to literature values.

2. Experimental apparatus

These measurements were based on the frequencystabilized cavity ring down spectroscopy (FS-CRDS) technique and were made using a custom apparatus located at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, USA. Extensive details regarding FS-CRDS can be found in Refs. [48–50], and therefore only a brief description is given here. The length-stabilized cavity ring-down resonator consists of two identical, spherical mirrors of diameter 7.5 mm and radius of curvature equal to 1 m. The mirrors are held in stainless-steel flexure mounts bolted to steel angle plates, which are connected by four invar (2.5 cm diameter, 50 cm length) rods. These mirrors are lightly glued with epoxy to metal supports and mounted within an evacuated sample chamber having an internal volume of 0.2 L. The cavity length (75 cm) is adjustable with a piezo-electric transducer (pzt) which is coupled to one mirror through a vacuum bellows mounted outside of the vacuum chamber. Apart from the mirror materials and small quantity of adhesive, all wetted internal surfaces of the vacuum system are stainless steel. This configuration eliminates unwanted surface interactions of water that would occur if the pzt and connecting wire assembly were mounted within the sample volume.

We use dichroic cavity mirrors in order to produce two geometrically overlapping but optically distinct resonators, the first of which has high finesse (F=60,000) at the probe wavelength (1.28 µm) and the second of which has low finesse (F=60) at the reference laser wavelength of 0.633 µm. These two beams are combined/separated before/after the cavity using dichroic beam splitters. As described by Hodges et al. [48], the ring-down cavity length is servoed by maintaining constant transmission of the reference laser beam through the low-finesse cavity. For the frequency reference, we use a frequency-stabilized HeNe laser with a long-term stability of 800 kHz. With the cavity length stabilized, this performance leads to a stability of approximately 400 kHz for cavity mode frequencies at the probe wavelength.

The probe laser consisted of an external cavity diode laser (ECDL) with a tuning range of 1330 nm (7519 cm⁻¹) to 1260 nm (7936 cm⁻¹). The beam from this laser was inserted into a fiber-coupled, C-band InP/InGaAsP booster optical amplifier, which was followed by a fiber-coupled acousto-optic modulator (AOM). The AOM served as an optical switch (50 dB extinction ratio) for initiating ring-down decay events. The first-order diffracted beam exiting the AOM passed through two free-space isolators (30 dB) and was mode-matched into the ring-down cavity. This configuration yielded approximately 20 mW of power incident on the ring-down cavity. The decay signals were measured with an InGaAs photoreceiver which had a bandwidth of 1 MHz and a noise-equivalent-power of $0.3 \text{ pW Hz}^{-1/2}$.

With the cavity length stabilized against the reference laser, the probe laser frequency was tuned to a local TEM_{00} cavity resonance and was actively locked with a lowbandwidth (200 Hz) servo by proportional-integral feedback to the fine frequency input (pzt-actuated mirror) of the ECDL. We quantified detuning between the probe laser frequency and local cavity mode by sweeping the laser frequency over a range of approximately 5 MHz and by measuring the distribution of average transmitted signals. For the absolute frequency determinations discussed below, it was necessary to improve precision of the locking scheme. To this end, we incorporated into this servo a high-bandwidth wavelength meter with a 400 Hz update rate. This approach enabled measurement of the laser frequency detuning with a precision of about ± 2 MHz: a value that was commensurate with the long-term stability of the locked cavity and better than the manufacturer's stated 10 MHz resolution for this wavelength meter. Also, we note that although the probe laser lock eliminated frequency drift and increased the average rate of transmission bursts and hence ring-down acquisition rate, the servo bandwidth was not high enough to narrow the instantaneous laser line width. Consequently, the peak amplitude of the transmitted probe beam signal was largely unaffected, being driven by rapid phase fluctuations in the laser.

Decay signals were acquired by turning off the AOM when the transmission signal exceeded a preset threshold value, and signals were digitized with a 12-bit A/D board sampling at 25 M samples/s and fit in real time to give the cavity decay time. The peak signal value corresponded to about 5 µW of transmitted power. This scheme gave acquisition rates of up to 100 Hz, relative standard deviations of 0.1% in the measured decay times and a noiseequivalent absorption coefficient of 7×10^{-11} cm⁻¹ Hz^{-1/2}. Spectra were acquired by stepping from mode-to-mode of the cavity, relocking and acquiring up to 200 decays at each lock point. We note that the step size of our acquired spectra equals the cavity free-spectral range (FSR). For the empty-cavity case, we determined the FSR to be 201.455 (3) MHz by stepping through a large number of cavity modes and by recording the frequency shift of the laser with a wavelength meter as described in Ref. [51].

Measurements were made on a static, distilled water sample at natural isotopic abundance. The water sample was cooled to -20 °C, pumped on to remove impurities, and then re-heated at room temperature. We repeated this freeze-pump-thaw cycle several times to remove expected impurities such as carbon dioxide (CO₂) or molecular oxygen (O_2) . We determined the carbon dioxide molar fraction in the water vapor sample by measuring the (30013)-(0001) P24 ¹²C¹⁶O₂ line near 6207.246 cm⁻¹ with another CRDS setup, obtaining a maximum carbon dioxide molar fraction of 2×10^{-5} . Similarly, the amount of O_2 impurity was investigated by scanning over the spectral region corresponding to one of the strongest lines of the $a^1 \Delta_g O_2$ band (Q7Q7 at 7881.3137 cm⁻¹ having an intensity of 1.095×10^{-25} according to HITRAN 12 [21]). This survey vielded no evidence of absorption, from which we estimate an upper bound of 0.01% for the O_2 molar fraction. We also investigated the possibility of fractionation of the heavier isotopologues of water vapor. To quantify this effect, we analyzed the spectra of four H_2^{18} O transitions acquired in the present study. Based on natural isotopic abundance levels, these measurements resulted in H_2^{18} O intensities that were on average within 12% of those given in HITRAN 2012. Assuming that these published intensities are correct, these observed differences in spectrum areas would lead to an uncertainty of about 0.02% in the $H_2^{16}O$ concentration.

We measured the sample temperature (standard uncertainty 0.02 K) with a NIST-calibrated thermistor that was in good thermal contact with the ring down cavity. The transitions reported here were recorded at several pressures. For lines with an intensity between 4×10^{-25} cm/molecule and 8×10^{-25} cm/molecule, the pressure ranged from slightly below 130 Pa (≈ 1 Torr) up to 530 Pa (4 Torr). For the weaker lines (1×10^{-26} cm/molecule to 4×10^{-25} cm/molecule) the maximum pressure was 800 Pa (6 Torr). Only the lines stronger than 8×10^{-25} cm/molecule were recorded at just one pressure which was below 130 Pa.

In a previous CRDS study involving static charges of pure water vapor, Tran et al. [43] found it necessary to actively stabilize the cell pressure using a servo-actuated valve. Their approach resulted in sample pressures that varied by up to 1% during spectrum acquisition. For our experiments, after the pressure was changed inside the cell, the sample was allowed to stabilize for two days before performing any measurement. The combination of high temperature stability (better than 0.1 K over a measurement period) and long term equilibration times resulted in sample gas pressures that never varied by more than 0.25 Pa during the time to measure the spectrum of a single line (about 30 min). We measured a leak rate of about 70 mPa day⁻¹ under vacuum conditions. Thus, over the course of a typical 30-min-long scan, changes in the pressure caused by leaks were at most only about one part in 10^5 of the measured pressure and therefore were negligible.

The pressure was monitored by a capacitance diaphragm gauge (1.33 kPa full scale,), which was calibrated *in situ* in terms of a NIST pressure standard having a relative combined standard uncertainty less than 0.03% over the entire pressure range. We accounted for non-ideal gas effects using an appropriate equation of state for the water vapor density (maximum relative deviation from the ideal gas law value of 0.04% at 296 K and 800 Pa.) Based on the calibration uncertainties and measured drift in gas pressure and maximum sample temperature difference (0.05 K), we estimate the relative combined standard uncertainty the water vapor density to be less than 0.04%.

In addition to the extremely linear and precise spectrum detuning axis provided by the FS-CRDS technique, we linked the laser frequencies to an optical frequency comb (OFC) to place this axis on an absolute scale. The OFC was a commercial, self-referenced, octave-spanning (1–2 μ m) system with a repetition rate of 250 MHz and carrier-envelope offset (CEO) frequency of 20 MHz, both of which were actively locked to a Cs clock. This absolute reference had a long-term relative frequency stability better than 1 × 10⁻¹⁴.

We made an initial and approximate determination of our spectrum frequency axis by measuring the frequency of the external cavity diode laser with our wavelength meter, which had an absolute uncertainty of 20 MHz. The absolute response of the wavelength meter was also verified by measurements of known $^{12}C^{16}O_2$ transition frequencies in the 1.6 μ m region. In order to obtain more accurate, absolute determinations of the frequency axis, on the first point of every scan we measured the heterodyne beat signal between the locked probe laser and the OFC with a frequency counter. The heterodyne beat signal was averaged for 30 s, yielding a standard uncertainty of 500 kHz. This measurement gave us the probe laser frequency in terms of the average beat frequency, OFC repetition rate, CEO and the mode order of the nearest OFC mode based on the wavelength meter measurement. Subsequent spectrum points were tied to the first point by known integral multiples of the FSR. The frequency range of each scan was about15 GHz. Based on the reproducibility of these measurements over a few month interval we estimate the standard uncertainty in the measured frequency to be approximately 2 MHz. Because of the low-bandwidth laser lock to the cavity, this uncertainty was dominated by imprecision in the measurement of the detuning between the mean, locked laser frequency and the local cavity resonance frequency.

3. Line shape models

The pCqSDHCP, which was proposed by Ngo et al. [24] as the model of choice to go beyond the well-known limitations of the widely used Voigt profile, incorporates adjustable parameters which are suitable for describing the effects of collisional narrowing, speed dependence and correlations between velocity-changing and dephasing collisions. As discussed below, in limiting cases this profile reduces to simpler forms such as the Voigt profile (VP), the Nelkin–Ghatak profile (NGP) (hard collision case), the speed dependent Voigt profile (SDVP) and the speed dependent Nelkin-Ghatak profile (SDNGP). As mentioned in Ref. [24], the pCqSDHCP can be represented in terms of the VP, which makes it amenable to rapid curve fitting of spectra. For completeness, we note that the NGP is also referred to as the Rautian profile (RP) [52,53] and the SDNGP is sometimes called the speed dependent Rautian profile (SDRP).

As an alternative representation of the pCqSDHCP given in Ref. [24], we start with the complex representation of the area-normalized, speed-dependent Voigt profile (SDVP) given by [54]

$$\tilde{I}_{SDVP}(u) = \frac{2}{\pi^{3/2}} \int_{-\infty}^{\infty} dx e^{-x^2} x \left\{ \tan^{-1} \left[f(u,x) \right] + \frac{i}{2} \ln \left[1 + f(u,x)^2 \right] \right\}$$
(1)

where $u = (\omega - \omega_0)/\omega_D$ is the reduced spectral detuning, which is given in terms of the angular frequency ω_0 , unperturbed angular transition frequency ω_0 , and the 1/eDoppler width ω_D . In Eq. (1) the variable of integration is the reduced absorber speed $x = v/v_p$, where $v_p = \sqrt{2k_BT/m_A}$, m_A is the absorber mass, T is the gas temperature, and k_B is the Boltzmann constant. Defining the collisional relaxation rate Γ , and the shift of line center Δ , then $f(u, x) = [u - dB_s(x) + x)]/[gB_w(x)]$ in which $g = \Gamma/\omega_D$, $d = \Delta/\omega_D$, and $B_w(x)$ and $B_s(x)$ are the reduced speeddependent collisional width and shift functions, respectively. Assuming quadratic dependences for the collisional broadening then

$$B_w(x) = 1 + a_w(x^2 - 3/2)$$

and
$$B_s(x) = 1 + a_s(x^2 - 3/2)$$
 (2)

define the broadening speed-dependence parameter a_w , and the shifting speed-dependence parameter a_s . These

two terms typically are treated as fitted parameters in the data analysis. At fixed temperature, a_w and a_s are expected to be independent of gas pressure.

The speed dependent Nelkin–Ghatak profile (SDNGP) can be expressed in terms of the SDVP as [53]

$$\tilde{I}_{SDNGP}(u) = \frac{\tilde{I}^*_{qSDVP}(u)}{1 - \pi z \tilde{I}^*_{qSDVP}(u)}$$
(3)

where $z = \omega_{eff} / \omega_D$ and $\tilde{I}^*_{SDVP}(u)$ is the function $\tilde{I}_{SDVP}(u)$ with $gB_w(x) + z$ substituted for $gB_w(x)$. Here ω_{eff} is the effective frequency of velocity-changing collisions, which may be associated with the diffusion constant of the absorber in the buffer gas, *D*. In dimensions of angular frequency, this rate is given by

$$\omega_{eff} = \frac{k_B T}{m_a D},\tag{4}$$

and at fixed temperature it is proportional to pressure p, since $D \propto 1/p$. In order to account for partial correlation between velocity-changing and dephasing collisions, one can define the optical angular frequency of velocity-changing collisions as a complex quantity equal to [32,55]

$$\omega_{opt} = \omega_{eff} - \eta (\Gamma_0 + i\Delta_0), \tag{5}$$

where η is the correlation parameter, (here assumed to be the same for the broadening and shifting terms). Evaluating $\tilde{I}^*_{SDVP}(u)$ with the complex-valued parameter $z = \omega_{opt}/\omega_D$ gives the partially correlated quadratic-speed-dependent Nelkin–Ghatak profile (pCqSDNGP)

$$I_{pCqSDNGP}(u) = Re\left\{\frac{\tilde{I}^*_{SDVP}(u; gB_w + \omega_{opt}/\omega_D)}{1 - \pi z \tilde{I}^*_{SDVP}(u; gB_w + \omega_{opt}/\omega_D)}\right\},\tag{6}$$

which is equivalent to the partially correlated quadraticspeed-dependent, hard-collision profile (pCqSDHCP) which can be calculated in terms of the VP [24]. We note further that Eq. (6) is based on the SDVP, which can be easily numerically evaluated using Eq. (1), thus making calculation of the pCqSDNGP also relatively straightforward.

The pCqSDNGP and the pCqSDHCP both have seven parameters, quantifying the effects of collisional narrowing, speed dependent broadening and shifting or partial correlation between velocity-changing and dephasing collisions. In the notation of Ngo et al. [24] the parameters of the pCqSDHCP are unperturbed angular frequency ω_0 , correlation-free frequency of velocity-changing collisions ν_{vc} , correlation parameter η , mean relaxation rate over all speeds Γ_0 , empirical relaxation rate Γ_2 , mean line center shift over all speeds Δ_0 , and empirical shift Δ_2 . Based on the preceding definitions and assuming that $\omega_{eff} = \omega_{vc}$ the two sets of parameters are interrelated by

$$a_{w} = \Gamma_{2}/\Gamma_{0}$$

$$a_{s} = \Delta_{2}/\Gamma_{0}$$

$$Re\{\omega_{opt}\} = \omega_{vc} - \eta\Gamma_{0}$$

$$Im\{\omega_{opt}\} = -\eta\Delta_{0}$$
(7)

Consistent with limits of pCqSCHCP given in Table 2 of Ref. [24], the pCqSDNGP reduces to the VP, NGP, qSDVP and qSDNGP [42] for $Im\{\nu_{opt}\} = 0$ and when

 $(a_w, a_s, Re\{\omega_{opt}\}) = (0, 0, 0)$ $(a_w, a_s) = (0, 0)$, $(Re\{\omega_{opt}\} = 0)$, and $(Re\{\omega_{opt}\} = \omega_{eff})$, respectively.

In the case when the absorber–perturber interaction potential is modeled as an inverse power law $V(r) = C_q r^{-q}$, then the speed-dependence functions are equal to [56]

$$B_{w}(x; m_{p}/m_{a}, q) = B_{s}$$

= $(1 + m_{p}/m_{a})^{-(q-3)/(2q-2)} M\left(-\frac{q-3}{2q-2}, \frac{3}{2}, -(m_{p}/m_{a})x^{2}\right)$
(8)

where m_p/m_a is the perturber/absorber mass ratio and M(a, b, c) is the confluent hypergeometric function. Incorporating this model for the speed-dependence functions into the above analysis results in the partially correlated hypergeometric-speed-dependent Nelkin–Ghatak profile (pChSDNGP) which has the parameters ω_0 , Γ_0 , Δ_0 , $Re\{\omega_{opt}\}$, $Im\{\omega_{opt}\}$ and q.

4. Experimental results

4.1. Measurements of line shapes

We began our analysis by focusing on a few of the most isolated transitions in order to determine the optimal line profile for data reduction. To this end, we fitted the following seven profiles to our measured spectra: VP, Galatry profile (GP) [57], NGP, qSDVP, qSDNGP, pCqSDNGP and pChSDNGP. A useful figure-of-merit to compare the results is the quality-of-fit (*QF*) parameter defined by Cygan et al. as [44]

$$QF = (\alpha_{max} - \alpha_{min})/S_R \tag{9}$$

where \tilde{S}_R is the standard deviation of the fit residuals given by

$$\tilde{S}_R = \sqrt{\frac{\sum_{i=1}^{M} \left[\alpha_{\exp}(\nu_i) - \alpha_{fit}(\nu_i)\right]^2}{M - k}}$$
(10)

and in which α_{exp} and α_{fit} are the measured and fitted absorption coefficient, respectively, ν_i is the *i*th frequency in the measured spectrum, M is the number of measured spectrum points and M-k is the degrees of freedom with kequal to the number of adjusted line shape parameters. Fig. 1 shows a representative series of fits to a measured selfbroadened spectrum for the $[(\nu'_1, \nu'_2, \nu'_3) - (\nu''_1, \nu''_2, \nu''_3)]$ $[(J'_{\lambda}K'_{a},K'_{c})-(J'',K''_{a},K''_{c})]=[(0,0,2)-(0,0,0)] [(10,5,6)-(9,2,7)]$ H_2^{16} O transition measured at 666 Pa (5 Torr). It was found that the VP always results in the lowest QF parameter of all profiles considered. In this example QF for the VP fit is 590, which is typical for the strongest lines measured here. With VP fits to the spectra, prominent W-shaped residuals are clearly evident, and for transitions with intensities greater than approximately 5×10^{-26} cm/molecule we found that fitting the VP to the measured spectra consistently yields areas which are about 0.5% smaller than those obtained using the other profiles. This result is consistent with a recent theoretical analysis of Wcisło et al. [58].

Generalizing the profile to include the effects of collisional narrowing via soft- (GP) or hard- (NGP) collisions



Fig. 1. Measurements and fit results for the [(0,0,2)-(0,0,0)] (10,5,6)–(9,2,7) H₂¹⁶ O transition at $\tilde{\nu}_0$ =7892.30195 cm⁻¹. The sample was pure water vapor at 296 K at a pressure of 666 Pa (5 Torr). The intensity for this transition is nominally 1.89 × 10⁻²⁵ cm/molecule. Uppermost panel. Measured (symbols) and fitted (line) absorption spectrum. The bottom panels show the fit residuals and the *QF* values for the indicated profiles.

reduces the peak fit residuals substantially and increases the *QF* parameter approximately six-fold compared to the VP, but does not eliminate all systematic discrepancies. Nearly identical residuals to the GP fit were obtained by modeling speed dependent effects with the qSDVP, whereas fitting the qSDNGP nearly doubles the *QF* compared to the GP or SDVP fits. Our results are consistent with Lisak et al. [33,41] and Tran et al. [43] who concluded that both collisional narrowing and speed dependence must be considered to reduce fit residuals below the baseline noise level of the measurement, although as can be seen in Fig. 1 the spectrum signal-to-noise ratio is high enough that there remain relatively prominent systematic residuals for the qSDNGP fit.

Because of the limited pressure range in this study, it was not possible to determine the speed dependent shifting with good confidence, and therefore, we neglected this term in all fits by setting $a_s = 0$. This assumption is justifiable because pressure shifting tends to be nominally an order of magnitude smaller than pressure broadening and given that we did not see strong evidence of asymmetry in our spectra.

Fitting either the pCqSDNGP or pChSDNGP (which both incorporate collisional narrowing, speed-dependent effects and correlation between velocity- and phasechanging collisions) eliminates systematic residuals, giving *QF* values of \approx 11,000 which are dominated by baseline noise. In this study we report the line parameters obtained by fitting the pCqSDNGP to our measured spectra because of the relatively high *QF* and because we expect this profile to be incorporated into databases and analytical representations that extend beyond the VP.

4.2. Multispectrum fitting method

Multispectrum analysis is a robust method for eliminating spurious correlation between line profile parameters which can occur in least-squares fits to singlepressure spectra [41,59]. For quadratic, speed-dependent models which also incorporate collisional narrowing, correlation between a_w and ω_{opt} can be removed by treating the former as being independent of pressure and the latter as being proportional to pressure. In the present analysis, we treated the pressure-normalized quantities, Γ_0/p , Δ_0/p , $Re\{\omega_{opt}\}/p$, $Im\{\omega_{opt}\}/p$, as fitted quantities in our multispectrum fits.

Assuming an isolated transition, we modeled each pressure-dependent cavity ring-down spectrum as

$$\frac{1}{c\tau_i} = n(p, T)S(T)I(\nu_i - \nu_0) + \alpha_{bl}(\nu_i) = A(p, T)I(\nu_i - \nu_0) + \alpha_{bl}(\nu_i)$$
(11)

where c is the speed of light, n is the number density of absorbers at pressure p and temperature T, τ_i is the measured ring-down time constant at the *i*th frequency step ν_i , S(T) is the temperature-dependent line intensity, and I is the normalized line profile which satisfies $\int_{-\infty}^{\infty} I(\nu - \nu_0) d(\nu - \nu_0) = 1$. The last term α_{bl} is the baseline signal of the ring-down spectrometer, which generally accounts for the effective mirror reflectivity and residual etalons caused by coupled-cavity effects [60]. When it is necessary to account for weak interfering water vapor transitions, additional lines are included in Eq. (11) using line parameters constrained by HITRAN 2012 values. Each component spectrum comprised nominally 50 frequency steps, thus providing sufficient sampling of the line core and wings and spectrometer baseline. Fig. 2 shows a typical multispectrum fit and corresponding residuals at each pressure. As with the single-spectrum fit in Fig. 1,



Fig. 2. Multispectrum fit for the self-broadened [(0,0,2)–(0,0,0)] (10,4,6)–(9,3,7) H₂⁰ 0 transition at $\tilde{\nu}_0 = 7799.99696 \text{ cm}^{-1}$. The top panel shows the measured spectra (symbols) and pCqSDNGP fit (solid lines), with the values offset in the vertical direction by multiples of 0.2 units for clarity. The bottom panels show the corresponding fit residuals for spectra which were acquired at the indicated pressure. The quality of fit parameter given by Eq. (9) can be generalized for the multispectrum fit case to give QF_{ms} by evaluating the standard deviation of the fit residuals as, $\tilde{S}_R = \sqrt{\frac{\sum_{j=1}^{N} \sum_{i=1}^{M} (a_{exp}(\omega_{ij}))^2}{\sum_{j=1}^{N} M_j - k}}$.

there is little evidence of systematic deviations above the spectrometer baseline noise level, with the global fit giving a *QF* of \approx 18,000.

4.3. Measured line intensities

Our measured line intensities extracted from multispectrum fits of the pCqSDNGP are given in Table 1. They

Table 1

Summary of measured line parameters for self-broadened H_2^{16} O transitions measured in this study. The assignments are specified by $[(v'_1, v'_2, v'_3) - (v'_1, v'_2, v'_3)]$ $[(J', K'_a, K'_c) - (J^*, K^*_a, K^*_c)]$, position \tilde{v}_0 , intensities S(296 K) (weighted by the natural abundance of water isotopologues), broadening parameter $\gamma_{self} = \Gamma_0/(2\pi p)$, pressure shifting parameter $\delta_{self} = \Delta_0/(2\pi p)$, and other fitted parameters of the pCqSDNGP. With a few indicated exceptions, all parameters were obtained from multispectrum fits of spectra involving at least three pressures. For the line positions the numbers in parentheses represent the combined standard measurement uncertainty. The remaining values in parentheses are the relative standard uncertainties in % (of the corresponding quantity to the left) reported by the fitting algorithm. Note that the factor 1 cm⁻¹/ atm=295.872 kHz/Pa can be used to convert some of these line shape parameters to conventional units.

Assignment from HITRAN 12		$\tilde{\nu}_0 \ (\mathrm{cm}^{-1})$	S (10 ⁻²⁵ cm/molecule)		γ _{self} (kHz/Pa)		δ_{self} (kHz/Pa)		$Re\{\omega_{opt}\}/2\pi p$ (kHz/Pa)		a _w		$Im\{\omega_{opt}\}/2\pi p$ (kHz/Pa)	
101-000	11 3 8-10 1 9	7714.81227(8)	5.9673	(0.25%)	102.88	(0.2%)	-7.4	(20%)	7.69	(4%)	0.0919	(2%)	0.110	(3%)
101-000	11 6 6-10 4 7	7715.02046(8)	5.2621	(0.23)	92.34	(0.2)	-3.55	(42)	8.40	(4)	0.0870	(2)	1.14	(6)
101-000	10 3 8-9 1 9	7722.13518(10)	12.235ª	(0.37)		. ,		. ,		. ,		. ,		
002-000	955-844	7723.14611(10)	7.6288	(0.20)	115.80	(0.3)			5.86	(8)	0.0875	(3)	1.25	(10)
002-000	10 5 6-9 4 5	7733.98820(10)	8.0783 ^a	(0.20)										
002-000	982-871	7737.89300(7) ^b	4.0317	(0.20)	54.09	(0.3)	-2.66	(34)	3.34	(7)	0.0969	(3)	-0.252	(30)
002-000	981-872	Blended ^b												
002-000	964-853	7738.55053(7)	6.1638	(0.20)	93.23	(0.3)	-6.81	(13)	5.83	(5)	0.0824	(3)	-0.982	(7)
101-000	12 5 8-11 3 9	7740.49272(7) ^b	3.7444	(0.23)	107.73	(0.4)	6.54	(2)	10.7	(8)	0.0282	(17)	1.49	(17)
101-000	853-716	Blended ^b												
002-000	10 7 4-9 6 3	7745.69507(7)	0.9378	(0.20)	78.14	(0.5)	-3.55	(17)	4.38	(22)	0.0872	(9)	Fixed to 0	
002-000	1073-964	7745.86616(15)	0.3078	(0.23)	71.81	(1)			13.7	(8)	Fixed to 0		Fixed to 0	
101-000	844-707	7748.60876(9)	1.8131	(0.20)	121.40	(0.2)	-7.10	(29)	9.44	(4)	0.0773	(2)	0.757	(9)
002-000	945-836	7751.66707(10)	10.679 ^a	(0.30)		. ,		. ,		. ,		. ,		
002-000	835-726	7755.91596(10)	11.569 ^a	(0.35)										
002-000	10 6 5-9 5 4	7757.376814(10)	7.4566 ^a	(0.20)										
002-000	10 6 4–9 5 5	7760.47054(7)	2.5131	(0.22)	86.63	(0.2)	5.03	(18)	6.45	(5)	0.0934	(2)	-0.538	(16)
101-000	13 6 8-12 4 9	7761.14369(11)	0.6780	(0.23)	87.49	(0.9)	10.4	(37)	3.79	(56)	0.0973	(15)	Fixed to 0	. ,
120-000	11 5 7-10 0 10	7761.66635(15)	0.7470	(0.23)	78.38	(0.7)	7.69	(62)	9.17	(23)	0.0499	(29)	Fixed to 0	
200-000	14 5 10-13 2 11	7761.90620(11)	0.1798	(0.57)	80.83	(2.3)	6.51	(50)	18.9	(15)	Fixed to 0	. ,	Fixed to 0	
101-000	12 3 9-11 1 10	7763.54931(7)	5.2068	(0.20)	91.75	(0.3)	-4.14	(15)	7.63	(5)	0.0843	(3)	-0.358	(17)
200-000	12 3 10-11 0 11	7763,77931(10)	0.6926	(0.20)	77.19 ^c	(1)			30.5 [°]	(5)		(-)		
200-000	945-818	7769.38335(15)	0.9057	(0.20)	122.99	(0.4)			8.43	(14)	0.0832	(7)	Fixed to 0	
050-000	423-414	7770.37320(7)	0.11886	(0.20)	121.49	(1.4)	16.0	(6)	23.9	(12)	Fixed to 0	()	Fixed to 0	
101-000	12 4 9-11 2 10	7770.51204(7)	1.8887	(0.23)	89.71	(0.3)	4.59	(4)	7.19	(8)	0.0632	(6)	1.72	(8)
002-000	11 6 6-10 5 5	7773.27444(15)	0.8677	(0.23)	105.27	(0.5)		. ,	8.19	(17)	0.0769	(11)	Fixed to 0	
101-000	10 10 0-9 8 1	7773.43616(15)	0.1835	(0.33)	46.60	(2.8)			9.08	(16)	Fixed to 0	. ,	Fixed to 0	
200-000	770-643	7773.68215(15)	0.8572	(0.20)	95.80	(0.4)			1.51	(26)	0.1366	(2)	Fixed to 0	
101-000	13 5 9-12 3 10	7774.89002(7)	1.2796	(0.20)	85.86	(0.3)	5.83	(1)	5.47	(9)	0.0751	(5)	0.541	(11)
101-000	954-817	7777.49110(15)	0.4515	(0.25)	121.54 ^c	(0.4)		(-)	39.1°	(2)		(-)		()
002-000	11 6 5-10 5 6	7781.49700(10)	2.6613	(0.21)	99.77	(0.3)			6.15	(6)	0.0893	(3)	-0.962	(9)
200-000	10 5 5 - 9 2 8	7781.86369(10)	0.2453	(0.31)	112.40	(0.8)			5.59	(48)	0.0863	(15)	Fixed to 0	
002-000	11 8 4-10 7 3	7781.97215(10)	0.17849	(0.20)	60.77	(1.7)			13.1	(9)	Fixed to 0	()	Fixed to 0	
002-000	11 8 3-10 7 4	7782.00031(10)	0.5428	(0.27)	67.07	(0.6)			2.63	(32)	0.1065	(8)	Fixed to 0	
002-000	735-606	7784 32831(10)	9 0778 ^a	(0.20)		()				()		(-)		
002000	, , , , , , , , , , , , , , , , , , , ,	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	010770	(0120)										
002-000	12 6 7-11 5 6	7785.02003(15)	0.7803	(0.21)	114.06	(0.4)			8.79	(10)	0.0626	(8)	Fixed to 0	
021-000	991-872	7785.13612(15)	0.13456	(0.20)	51.87	(2.1)			8.73	(13)	Fixed to 0		Fixed to 0	
002-000	744-615	7786.98549(7)	5.4951	(0.20)	130.60	(0.2)	7.40	(16)	9.76	(3)	0.0755	(2)	1.12	(5)
200-000	872-743	7789.89955(9)	1.1711	(0.20)	103.79	(0.2)	11.8	(18)	8.14	(4)	0.0668	(3)	1.53	(5)
101-000	11 8 4-10 6 5	7792.06736(7)	1.1659	(0.20)	77.58	(0.5)	- 11.5	(8)	5.03	(9)	0.0936	(5)	0.787	(12)
002-000	541-414	7793.13112(7)	1.5539	(0.21)	134.56	(0.5)	18.6	(5)	7.22	(17)	0.0979	(7)	2.61	(11)
002-000	10 4 6-9 3 7	7799.99696(7)	2.5806	(0.20)	123.29	(0.2)	-4.14	(15)	8.55	(3)	0.0775	(2)	-1.64	(3)

002-000	12 8 5–11 7 4	7801.57752(7)	0.1931	(0.33)	67.55 ^c	(1.3)	-4.73	(13)	23.8 ^c	(7)				
002-000	12 8 4–11 7 5	7801.68999(15)	0.0677	(0.44)	76.75 ^c	(2)			16.2 ^c	(16)				
200-000	973-844	7803.49591(11)	0.3082	(0.50)	108.47	(0.9)	6.81	(52)	5.59	(14)	0.1103	(6)	Fixed to 0)
101-000	13 3 10-12 1 11	7803.78179(9) ^b	0.6122	(0.35)	93.97	(0.5)	-6.81	(31)	8.52	(17)	0.0302	(23)	Fixed to 0)
002-000	12 6 6-11 5 7	Blended ^b												
200-000	14 4 11-13 1 12	7803.90416(8)	0.1203	(0.37)	68.70	(2)	- 11.5	(13)	9.29	(37)	0.0839	(27)	Fixed to 0)
021-000	12 4 8-11 0 11	7804.60928(15)	0.6872	(0.20)	100.45	(0.5)			7.46	(16)	0.0802	(10)	Fixed to 0)
200-000	10 7 4-9 4 5	7812.43179(8)	0.5120	(0.24)	108.61	(0.5)	7.99	(23)	5.33	(23)	0.0945	(8)	Fixed to 0)
101-000	13 4 10-12 2 11	7812.55554(7)	1.6095	(1.47)	72.58	(1)	0.858	(35)	4.47	(17)	0.1258	(12)	4.53	(15)
200-000	972-845	7812.57606(8)	0.9682	(2.46)	92.16	(0.6)	3.55	(42)	8.58	(14)	0.1203	(7)	0.577	(29)
002-000	826-717	7812.97055(7)	6.0294	(0.20)	129.12	(0.2)	-2.51	(36)	8.91	(3)	0.0813	(2)	0.846	(6)
101-000	12 3 10-11 1 11	7814.25471(8)	1.5353	(0.20)	74.03	(0.5)	-4.14	(29)	9.29	(11)	0.0512	(16)	-0.867	(27)
101-000	12 2 10-11 0 11	7814.48627(8)	3.8631	(0.20)	78.91	(0.3)	-3.55	(34)	6.54	(7)	0.0937	(4)	-2.11	(6)
200-000	854-707	7818.26003(8)	0.6969	(0.20)	107.79	(0.4)	4.73	(3)	11.2	(7)	0.0604	(8)	0.802	(15)
002-000	6 5 2-5 2 3	7830.86720(9)	1.1320	(0.22)	119.12	(0.27)	17.2	(14)	12.6	(6)	0.0771	(5)	2.93	(6)
002-000	753-624	7843.31577(11)	0.6928	(0.20)	128.14	(0.33)	13.0	(32)	12.4	(8)	0.0647	(8)	1.45	(15)
002-000	11 4 7-10 3 8	7846.56971(9)	2.4453	(0.20)	120.51	(0.25)	-8.28	(25)	9.11	(6)	0.0764	(4)	1.04	(11)
200-000	863-716	7848.49465(7)	0.8777	(0.21)	106.28	(0.29)	14.8	(4)	6.57	(9)	0.0850	(4)	Fixed to 0)
101-000	14 3 11-13 1 12	7851.27781(15)	0.4126	(0.29)	70.80	(1.09)			2.46	(43)	0.121	(9)	Fixed to 0)
002-000	946-817	7851.32214(9)	2.7316	(0.20)	114.41	(0.23)	11.8	(23)	7.75	(5)	0.0758	(3)	1.65	(7)
002-000	8 5 4–7 2 5	7856.29301(8)	2.7390	(0.20)	125.45	(0.25)	6.81	(13)	8.88	(2)	0.0828	(1)	1.39	(4)
101-000	13 3 11-12 1 12	7859.10405(9)	1.4395	(0.22)	68.26	(0.27)	- 10.9	(22)	4.50	(8)	0.0881	(4)	0.290	(19)
002-000	10 3 7-9 2 8	7860.20748(15)	1.8952	(0.20)	116.66	(0.23)			9.91	(5)	0.0743	(4)	-0.577	(12)
002-000	937-808	7870.27748(15)	1.1406	(0.20)	108.26	(0.32)			8.25	(9)	0.0727	(6)	-0.722	(14)
002-000	9 5 5-8 2 6	7872.00995(15)	0.8865	(0.22)	102.21	(0.3)			9.64	(8)	0.0767	(5)	Fixed to 0)
200-000	9 5 5-8 0 8	7880.78613(15)	1.8429	(0.20)	107.31	(0.21)			7.54	(5)	0.0822	(3)	1.16	(8)
002-000	743-616	7887.70287(15)	0.9947	(0.21)	127.87	(0.29)			8.58	(10)	0.0763	(6)	-0.473	(38)
002-000	10 4 7-9 1 8	7889.57427(7)	4.0406	(0.20)	102.28	(0.26)	8.88	(10)	7.57	(4)	0.0769	(2)	0.444	(14)
002-000	10 5 6-9 2 7	7892.30195(8)	1.8915	(0.20)	112.14	(0.28)	2.34	(7)	9.85	(2)	0.0714	(2)	1.45	(4)
002-000	7 5 2–6 2 5	7893.49941(15)	0.8566	(0.22)	114.50	(0.34)			8.49	(17)	0.0845	(9)	2.75	(12)
002-000	11 3 8-10 2 9	7912.11895(15)	2.1342	(0.20)	105.36	(0.28)			8.40	(4)	0.0709	(3)	-1.39	(6)
002-000	10 2 8-9 1 9	7916.64679(7)	1.4395	(0.22)	104.44	(0.42)	-8.88	(7)	8.05	(8)	0.0645	(7)	-1.94	(11)
0 0 2-0 0 0	10 3 8-9 0 9	7919.87689(15)	3.2820	(0.20)	97.67	(0.25)			7.28	(4)	0.0766	(3)	1.11	(7)

^a Single pressure measurement. ^b Overlapped lines.

^c Fit with a GP, the signal to noise ratio is not sufficient for these lines to go beyond this profile.

were corrected to the reference temperature T_r =296 K using the formula $S(T_r) = S(T)[Q(T)/Q(T_r)]e^{-E^r/k_B(1/T_r - 1/T)}$ where Q(T) is the total partition function calculated based on the coefficients found in Ref. [21], and E^r is the lower state energy from HITRAN 2012 [21].

In the multispectrum analysis, the spectral area *A* at each pressure was treated as a fitted parameter, which then was used to calculate line intensity by the relation $S(T) = A_{fit}(T, p)/n(p, T)$. As an illustration of the measurement precision, in Fig. 3 we show the fitted spectrum areas for three transitions investigated over the pressure range 0.15–0.8 kPa. The results show that the measured peak area precisely scales in proportion to gas density. For these data the normalized (relative to the peak area) residuals of the regression and the spread in fitted line intensities are less than 0.1%. Finally, the reported line intensities are obtained by averaging the temperature-corrected values obtained at each pressure.

We quantified the accuracy of the measured intensities by considering the dominant Type A (statistical) and Type B (systematic) uncertainties that occur when evaluating the relevant terms in Eq. (11). A summary of the standard (1σ) uncertainties for the line intensity measurements is given in Table 2. As illustrated in Fig. 3, the relative uncertainty in determining the fitted area from a given spectrum is typically about 0.07% for the strongest lines. However, the Type A (statistical) measurement uncertainty was dominated by long-term reproducibility of the fitted areas, which had a standard deviation ranging from 0.18% (strong lines) to 0.23% (weakest lines). Systematic uncertainty in the temperature correction of the line intensity was negligible because the average laboratory temperature was generally within 0.02 K of the reference temperature. In order to estimate the sensitivity to choice



Fig. 3. Pressure-dependent spectrum areas (symbols) determined from multispectrum fits of the pCqSDNGP for three specified transitions and the corresponding linear regressions (lines). The lower panel represents the residuals of each linear regression. The rightmost values in the legend are the relative standard deviations of the temperature-corrected line intensities for each transition.

Table 2

Relative standard uncertainty (1σ) components u_r , of the measured line intensities. The Type A terms (which are representative of the strongest lines) are statistical and can be reduced by signal averaging, whereas the Type B components are systematic. The combined result is obtained by quadrature addition of all component uncertainties.

Туре	A
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51		
Reproducibility (%)	0.180	Long-term relative standard deviation of intensities
Fit uncertainty (%)	0.070	Relative uncertainty reported by multispectrum fit
Type B		
$u_r(\rho)$ (%)	0.034	Sample density
$u_r(x_{\rm H218O})$ (%)	0.020	Isotopic abundance
$u_r(A)$ (%)	0.020	Spectrum area uncertainty caused by choice of line shape ^a
<i>u_r</i> (FSR) (%)	0.0015	Cavity free spectral range
$u_r(x_{O_2})$ (%)	0.010	Residual oxygen
$u_r(x_{CO_2})$ (%)	0.002	Residual carbon dioxide
(%)	0.20	Type A and B relative combined standard uncertainty

^a Estimated to scale inversely with QF.

of line profile, spectrum areas also were determined by fits with the GP. We found that for nearly all cases, the fitted areas differed from those obtained using the pCqSDNGP by less than 0.1%. We take this value as a conservative upper bound for the contribution of line shape to Type B uncertainty in our measured spectrum area, with a more realistic upper bound of 0.02% related to the quality of fit parameter defined below. Other sources of uncertainty include the measurements of *p* and *T* (which enter into the calculated water vapor number density through the nonideal equation of state), residual gas impurities, deviations from natural isotopic abundance, and the cavity freespectral range (which effectively defines the detuning axis in the spectrum). Adding all of these uncertainty contributions in quadrature, gives a relative combined standard uncertainty of the measured line intensity equal to $\approx 0.20\%$ for the strongest lines.

In Fig. 4 the measured intensity values reported in the literature are compared to our measurements. The intensity results labeled HITRAN 2012 [21], Mikhailenko et al. [17], Régalia et al. [9] and Tolchenov and Tennyson [12] differ relative to our values by 4.8%, -4.4%, -0.6%, and -3.2% respectively. With the exception of the CRDS data of Mikahailenko et al. [17], all of these prior results were based on FTS measurements. Excluding one large outlier at $\tilde{\nu} = 7851.278 \text{ cm}^{-1}$, the intensities of Régalia et al. [9] differ by -2% from our measurements. These results confirm the previously noted systematic deviation of about -5% between the measurements of Mikhailenko et al. and the SP (see below) intensities, which was attributed to inaccuracy in the CRDS cell pressure gauge [17]. We also note that Mikhailenko et al. fit the VP to their measured spectra at a single pressure and obtained residuals that did not reproduce all spectral features at the noise level (see Fig. 3 of Ref. [17]). However as discussed above, systematic deviations caused by fitting the VP should lead to a bias of only about -0.5%.



Fig. 4. Relative difference in intensities between literature values [9,12,17,21] and those measured in this work. The horizontal lines correspond to the color-coded, indicated mean values for each of the four sets. Our results are based on the retrieved area obtained by multispectrum fitting of the pCqSDNGP to the measured spectra. All but 10 of the HITRAN 2012 [21] data points are from Fourier transform spectroscopy measurements, with the remaining values taken from the *ab initio* BT2 line list of Barber et al. [3]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We also compared the theoretical line intensity values of the so-called Schwenke-Partridge (SP) and Barber-Tennyson-2 (BT2) [3] water line lists to our measurements. These results, are summarized in Fig. 5 and are sorted by three vibrational bands which have the upper states given by $(\nu_1, \nu_2, \nu_3) = (1, 0, 1), (0, 0, 2)$ and (2, 0, 0), respectively. The SP line list (the relevant portion of which can be found in Supplementary data 1 of Ref. [17]) was generated by S.A. Tashkun (Tomsk, Russia) using the VTET computer code of Schwenke [61] and the *ab initio* potential energy and dipole moment surfaces of Schwenke and Partridge [19,20]. The agreement between these calculations and our measurements is best for the (1, 0, 1) band, where the average relative differences for the BT2 and SP cases are -0.36% and 0.54%, respectively. Moreover, for the (1, 0, 1) band BT2 case, the mean absolute relative difference normalized by the BT2 relative uncertainty is approximately unity. This result confirms the estimated theoretical uncertainties (of the order of 1%) in line intensity for this band. Compared to our measured intensities, the SP calculations differ on average by nominally 0.5% for both the (1, 0, 1) and (0, 0, 2) bands, whereas the BT2 shows a relatively large -5.3% bias for the (0, 0, 2) band. Considering the (2, 0, 0) band, the average deviations for the SP and BT2 intensities are nearly equal in magnitude ($\approx 2\%$) but of opposite sign.

It is also instructive to compare the standard deviations of the fractional intensity differences summarized in Figs. 4 and 5. The largest spread occurs for the measured intensities given by HITRAN 2012 [13,21] (17%), Régalia et al. [9] (13%) and Tolchenov and Tennyson [12,62] (12%). Notably, the smallest standard deviation (3%) for the experimental results occurs when comparing the CRDSbased measurements of Mikhailenko et al. [17] with our



Fig. 5. Relative difference in intensities between theoretical values and those measured in this work, sorted by vibrational band. The horizontal lines correspond to the color-coded, indicated mean values for each set. The results labeled BT2 are from the *ab initio* calculations of Barber et al. [3], and those labeled SP (Schwenke and Partridge) come from *ab initio* calculations of S.A. Tashkun (Tomsk, Russia) as described in Ref. [17] and are based on the potential energy and dipole moment surfaces in Refs. [19,20]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

results. Although this standard deviation is smaller than those of the other literature values, it remains substantially larger than our nominally 0.2%-level measurement precision. Therefore, we conclude that these statistical variations likely are dominated by imprecision in the measurements of Mikhailenko et al. [17]. We attribute our improved precision to the length stabilization of the ring-down spectrometer and to the high thermal stability of the sample gas in our experiment.

We find that the scatter in both the BT2 and SP theoretical intensities is between 1% and 2% when considering either the (1, 0, 1) or (0, 0, 2) band. This spread, which is smaller than for all the prior measurements discussed above, quantifies deviations between the theoretical and measured (in this study), *J*-dependent intensities within these bands. In contrast, the (2, 0, 0) band calculations exhibit two to three times more scatter by comparison to the other two bands, although this spread is smaller than obtained with the FTS measurements shown in Fig. 4. In summary, these comparisons underscore the importance of validating theoretical line intensity calculations over a wide range of cases, while at the same time revealing that theoretical results with %-level uncertainties are possible.

4.4. Measured line shape parameters

In Figs. 6 and 7 we illustrate our measurement precision for the line shape parameters, Γ_0 and Δ_0 as well as



Fig. 6. Collisional width (HWHM) (top), and measured line centers (third from top) vs. pressure for the self-broadened [(0,0,2)–(0,0,0)] (10,4,6)–(9,3,7) H₂¹⁶ O transition at $\tilde{\nu}_0$ =7799.99696 cm⁻¹ based on single-spectrum fits of the pCqSDNGP. For each case, the measurements (symbols) and linear regression (line) are shown above the fit residuals.



Fig. 7. Upper two panels. Real and imaginary parts of the optical frequency of velocity-changing collisions obtained from single-spectrum fits of the pCqSDNGP (symbols) and linear regressions (lines). The diffusion-based value (red curve) was calculated using Eq. (4) and the self-diffusion coefficient of $D = 121.8 \text{ cm}^2 \text{ s}^{-1}$ calculated by Hellman et al. [62]. The bottom panel gives the broadening speed-dependence parameter a_w . The dashed lines in the upper and lower panels are the corresponding values of $Re\{\omega_{opt}/(2\pi)\}$ and a_w obtained from the multi-spectrum fit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 ω_{opt} and a_w . These results are for pCqSDNGP fits to single spectra. They were obtained over a range of pressures and are representative of the results for most of the transitions investigated here. In Fig. 6 the collisional width $\Gamma_0/(2\pi)$

exhibits extremely exceptional linearity with pressure and is relatively uncorrelated with other parameters in the single-spectrum fits. Its slope is equal to the selfbroadening parameter γ_{self} , and can be determined with a precision of about 0.1 kHz Pa⁻¹ with fit residuals of approximately 70 kHz. The frequency shift, whose slope is the self-frequency-shifting parameter δ_{self} , exhibits more scatter about the expected linear pressure dependence and exhibits a precision of nominally 250 kHz. The fitted values of a_w and ω_{opt} shown in Fig. 7 also show substantially more scatter about their respective expected pressure dependences than the collisional width. However, as previously discussed, this scatter arises from correlation effects in the fitting procedure and is eliminated by constraining $\omega_{opt}/(2\pi)$ to be proportional to pressure and a_w to be independent of pressure in the multispectrum analysis (see dashed lines in upper and lower panels of Fig. 7).

We also compare our measurement of $Re\{\omega_{opt}\}/(2\pi p)$ (≈ 9 kHz/Pa) with the collisional narrowing parameter ($\omega_{diff}/(2\pi p)$ =13.4 kHz/Pa) based on Eq. (4) and the selfdiffusion coefficient of water vapor (D=121.8 cm² s⁻¹ [62]). This result shown in Fig. 7 is consistent with an expected reduction in the effective optical frequency of velocity changing collisions (relative to the diffusion-based value) caused by partial correlation between velocitychanging and dephasing collisions.

The self-broadening parameters range from 135 kHz/Pa to 50 kHz/Pa and as usually observed tend to decrease with increasing J'', although the values also depend on vibrational band and rotational quantum number, K''_a and K''_c . Close inspection of the measured self-broadening parameters for the (0,0,2)–(0,0,0) vibrational band reveals that there is a relatively smooth dependence on J'' within a particular sub-branch determined by a fixed value of K_a'' . Although the largest number of observed transitions belong to this vibrational band, the range of J'' is relatively small (ranging from 4 to 11) and consequently large scale trends within each sub-branch are not revealed. The pressure shifting coefficients start out positive for



Fig. 8. Relative differences between previously reported line widths [9,21] and those measured in this work. The horizontal lines correspond to the color-coded, indicated mean values for each of the two sets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the smallest J'' considered here and tend to decrease with increasing J'', and for J'' > 6, both positive and negative values are observed.

In Fig. 8 we compare previously measured selfbroadening parameters reported in HITRAN 2012 [21] and Régalia et al. [9] to our measurements. The HITRAN values differ on average by -0.5% and have a standard deviation of 21%, whereas the Régalia et al. values show a larger bias of -5.5% and similar standard deviation of 22%. Unlike our measurements, these literature values are based upon fits of the Voigt profile. The negative bias in self-broadening parameter obtained by these fits is consistent with the occurrence of collisional and speeddependent narrowing effects, although the large amount of scatter is probably caused by relatively low signal-tonoise ratio in these previous line shape measurements.

4.5. Measured line positions

For the lines recorded at different pressures, the line position was corrected to the zero pressure value with the self, pressure-shifting coefficients determined here (see Table 1). For the lines recorded only at one pressure (133 Pa) or for the lines for which we were unable to measure the pressure shifting (due to the small pressure range available and the limited precision of our beat note measurement), we report the measured position as directly determined by the fit recorded at the lowest pressure. In general, the measurement uncertainty includes the quadrature sum of a 2 MHz component arising from the imprecision in the cavity lock and beat note, and uncertainty in the pressure shifting correction. The latter quantity was based on the uncertainty in the fit intercept resulting from the linear regression of measured frequency vs. pressure. When the line positions were based on measurements at a single pressure, we estimated the uncertainty due to pressure shifting assuming that the pressure shifting magnitude was nominally 10 kHz/Pa. After combining all of these components, our average combined uncertainty for the zero pressure position was approximately 3 MHz.

In Fig. 9 we present the differences between five previously reported sets of positions and our measurements. These data include the FTS-based results in HITRAN 2012 [21], Tolchenov and Tennyson [12] and Régalia et al. [9], the CRDS measurements of Mikhailenko et al. [17] and the MARVEL calculations of Tennyson et al. [11]. Relative to our values, the positions of Mikhailenko et al. range from 0 to 35 MHz with a standard deviation of 7.5 MHz and an average value of about 14 MHz. These differences are generally well within the combined uncertainty of the two sets of measurements, which is dominated by the uncertainty of their wavelength meter. There is a larger amount of scatter in the other data sets shown in Fig. 9, all of which have standard deviations of approximately 20 MHz. In the case of the HITRAN 2012 data, although half of the lines differ from our values by less than 5 MHz, there are differences as large as 100 MHz. Absolute deviations ranging from 50 to 100 MHz also occur for several transitions reported by Tolechenov and Tennyson and MARVEL. Nevertheless, the average differences between



Fig. 9. Differences in previously reported line positions [9,11,12,17,21] relative to our measurements. For each comparison we show the mean difference (horizontal line and indicated numerical value) and the standard deviation 1σ . For comparison, we illustrate our standard uncertainty (3 MHz) by the error bar on the open symbol labeled "NIST uncertainty".

the HITRAN 2012, Régalia et al. and MARVEL results and our measurements are only -2.5 MHz, -0.56 MHz and -0.7 MHz, respectively. These absolute differences are within the combined uncertainty of our measurements, and suggest that accuracy of these previously reported values was limited by measurement precision.

5. Conclusions

We have made high signal-to-noise ratio measurements of isolated, self-broadened $H_2^{16}O$ transitions in the 1.28 µm region with the frequency-stabilized cavity ringdown spectroscopy technique. This work substantially reduces the uncertainty of spectroscopic parameters for about 70 water transitions in this spectral region, providing benchmark data for future measurements and theoretical calculations. System improvements relative to previous spectroscopic studies of this band were realized by incorporating an optical frequency comb for absolute referencing of line positions to a Cs clock and by stabilizing our water samples at known temperature and pressure. The high spectral fidelity, absolute spectrum frequency axes, advanced line shape analysis and sample preparation resulted in spectrum signal-to-noise ratios up to 20,000, line position uncertainties of about 3 MHz, and intensities measured with a relative combined standard uncertainty of 0.20%.

Despite the recent update from HITRAN 2009 to HITRAN 2012 for water vapor in this region, there remain important discrepancies with our results. Moreover, we note that the HITRAN 2012 line list is incomplete for the other stable water isotopologues in this region. Indeed during our measurements and those made by Mikhailenko et al. [17] most of the HDO and H₂¹⁸O lines that we observed are not present in HITRAN 2012. We also suggest that the most comprehensive line list for the water vapor in this region easily could be realized by multiplying the

reported intensities of Mikhailenko et al. [17] (which encompass many more transitions than those considered here, albeit with larger uncertainties) by a factor of 1.044.

Our analysis level showed that the partially correlated quadratic-speed-dependent Nelkin–Ghatak profile (pCqSDNGP) captures the pressure dependence of selfbroadened water line shapes and can provide quality-of-fit parameters approaching 20,000. This work is consistent with the recent study of Tran et al. [43] in which mechanisms of collisional narrowing, speed-dependent effects and partial correlation between velocity-changing and dephasing collisions were found to contribute to water line shapes. Finally, the high quality-of-fit for our pCqSDNGP fits supports proposals that the pCqSDHCP (which is equivalent to the pCqSDNGP) be adopted as a next-generation, standardized profile to go beyond the VP [24,47].

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