Air-Broadening of H_2O as a function of Temperature: 696 – 2163 cm^{-1}

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Abstract

The temperature dependence of air-broadened halfwidths are reported for some 500 transitions in the (000)-(000) and (010)-(000) bands of $H_2^{16}O$ using gas sample temperatures ranging from 241 to 388 K. These observations were obtained from infrared laboratory spectra recorded at 0.006 to 0.011 cm^{-1} resolution with the McMath-Pierce Fourier transform spectrometer located at Kitt Peak. The experimental values of the temperature dependence exponents, η, were grouped into eight subsets and fitted to empirical functions in a semi-global procedure. Overall, the values of η were found to decrease with increasing rotational quantum number J. The number of measurements (over 2200) and transitions (586) involved exceeds by a large margin that of any other comparable reported study.

Key Words: water, air-broadened widths, temperature dependence

1. Introduction

The analysis of atmospheric spectra requires accurate characterization of the air broadened line shape parameters: halfwidths and pressure-induced frequency shifts and their temperature dependences [1]. The temperature dependence of widths is given by

$$b^0(T) = b^0(T_0) \times \left[\frac{T_0}{T}\right]^{\eta} \tag{1}$$

where $b^0(T)$ is the halfwidth coefficient at temperature T and $b^0(T_0)$ is the corresponding value at $T_0 = 296$ K. Empirical determination of these η exponents requires the use of gas samples through a range of temperatures.

In a recent study, Zou and Varanasi [1] measured the spectroscopic line parameters of water vapor transitions in the 610-2100 cm^{-1} and 3000-4050 cm^{-1} regions using gas samples at room and cold temperatures (252, 274 and 296 K). They compared their results at 296 K with Toth [2] for line positions and strengths; Toth et al. [3] for self-broadened width and shift coefficients; Toth [4] for air-broadened width and shift coefficients, and with the available parameters given in the HITRAN-2000 [5] and GEISA [6] databases. In addition, they also derived the temperature dependence of the air-broadening line widths (η) for 128 transitions.

Following that study, Wagner et al.[7] investigated temperature dependence exponents using H_2O+air spectra obtained by flowing gas samples at room and hot temperatures (296, 742 and 980 K) with total mixture pressures of 0.5 and 1.0 atm. They obtained air-broadening half-width coefficients in the ν_2 band and deduced 31 values of η for transitions for which K_a = 0,1, K_a = J and J=0 up to 16; some of these coefficients were found to be negative, in agreement with a theoretical prediction [8].

In the present study, we combined previous measurements [4] at room temperature with retrievals from new hot and cold sample spectra (with temperatures ranging from 241 K to 275 K and from 345 K to 388 K). With these data, values of η were derived for 512 rotational transitions in the ν_2 and pure rotational bands of $H_2^{16}O$ between 696 and 2200 cm^{-1}. The experimental values of η were grouped by rotational quantum number subsets and fitted to empirical expressions. These data can be used to guide and validate theoretical models [8] to predict halfwidth coefficients of air-broadened water.

2. Experiment

The laboratory spectra obtained in this study were recorded with the McMath-Pierce Fourier transform spectrometer (FTS) at the National Solar Observatory located on Kitt Peak in Arizona. Two absorption cells were used, one a heatable multiple-pass chamber for the hot sample spectra and another straight-pass cell for the cold sample scans. For both cells, the sample temperatures were inferred from readings of thermister probes attached to the exterior cell walls with estimated uncertainties in the temperature readings of ~1.0 K. The pressure readings were monitored with Datametrics or Baratron gauges. A 0-10 Torr head and a 0-100 Torr head were used to measure H_2O pressures and a 1000 Torr head was used to measure the total pressures of the water + air mixtures. Pressures

were recorded after sufficient time had passed (up to one hour) to permit the mixtures to come to equilibrium with outgassing from the cell walls.

The H_2O partial pressures were derived empirically by retrieving the intensities of known lines [2] which were converted to corresponding values at the sample temperature using the expression:

$$S(T) = C \frac{v}{Q} \frac{g}{T} \left[1 - \exp(-\frac{v}{kT}) \right] \times \exp \left[\frac{-E(L)}{kT} \right] |R(L,U)|^2 \qquad (2)$$

where $S(T) = S(296) \times F(T,296)$ and $Q = Q_V \times Q_R$.

C is a temperature independent constant, g represents the nuclear spin statistic of the lower state and R(L,U) is the vibration-rotation dipole moment matrix element . v is the transition's line center (in cm^{-1}), and E(L) is the lower state energy (in cm^{-1}). The temperature dependent function, F(T,296), is equal to the ratio of S(T)/S(296), derived from Eq. (2). For water, the partition functions Q_R and Q_V can be accurately expressed by:

$$Q_R(T) = Q_R(296) \left[\frac{T}{296} \right]^{3/2}, and \; Q_V(T) = Q_V(296). \qquad (3)$$

Using Eqs. (2) and (3), accurate values of uncertainties for the H_2O partial pressures of the various spectra were determined.

In Table 1, the experimental conditions of the present spectral data are listed, along with uncertainties in the H_2O partial pressures (in parentheses). Two sets of measurements are shown: one set with gas sample temperatures > 347 K, and the other with sample temperatures < 275 K. The spectral coverage for most of the data ranged from 1100 to 2300 cm^{-1}. The exceptions were three spectral runs with sample temperatures near 347.4 K covering the region from 600 to 1400 cm^{-1}. Due to the signal-to-noise-peak-to-peak-ratio (S/N) of about 100/1 for the hot sample runs, the spectral resolution for these observations was degraded to 0.01 cm^{-1} whereas the S/N ratio for the cold sample runs was about 300/1 with the spectral resolution of 0.006 cm^{-1}.

The low-temperature air-broadened H_2O spectra (T<296 K listed in Table 1) were all recorded using the 50-cm long cooled sample cell (described in detail by Smith et al. [9]).

The cell has double Pyrex walls through which refrigerated ethanol is circulated to maintain the desired temperature and is enclosed in an insulated metal chamber that is evacuated to prevent condensation or frost on the optical windows. Wedged KCl windows were used on both the cell and the vacuum chamber. Sample temperatures were monitored by six copper-constantan (T-type) thermocouples attached to the cell body. Total pressures in the cell were continuously monitored by a Datametrics Barocel 0-1000-Torr pressure sensor. While the cell was initially being filled with water vapor, a Datametrics 10-Torr sensor was used to monitor the H_2O pressure until the air was added into the cell. The entire optical path was evacuated except for two short segments: one between the IR glower source and the entrance window of the cell's vacuum chamber, and the other between the exit window of the vacuum chamber and the FTS entrance aperture. These two air paths totaled about 43 cm. The extra absorption arising from H_2O outside the absorption cell was reduced in the cold sample spectra by enclosing the air paths with plexiglass boxes and purging the paths with dry N_2 vapors.

The high-temperature, air-broadened H_2O spectra were all recorded using a Model OV-20M heatable White cell purchased from Infrared Analysis, Inc. in 1994. The cell has a glass body ~60 cm long and 15 cm in diameter and it is enclosed in a custom-built convection oven heated by two resistance heaters and squirrel-cage fans. To enhance temperature stability and uniformity, the cell body was wrapped in a heating blanket. Temperatures were measured by four iron-constantan (J-type) thermocouples mounted on the cell body, and the controller readouts of the resistance heaters and the heating blanket were also monitored. Wedged KCl windows were installed in this cell to minimize channel spectra. The base path of the cell is 0.5588 m, and there is an additional 3 cm path from each window to the plane of the field mirror. Most of the heated H_2O-air spectra were recorded with the number of passes set to 8 (4.53 m path), and three spectra with sample temperatures around 347 K were recorded with 20 passes (11.24 m path). For most of the hot-cell spectra the optical path from the exit window of the White cell to the FTS tank was always evacuated, but the path from the IR source to the entrance window of the cell contained some length (either 25 or 33 cm) that was mostly in the open air with some dry N_2 flowing into the source enclosure. One spectrum was recorded with the outside optical path entirely evacuated, and the three spectra with 11.24 m path were recorded with the entire 2.21 m path outside the cell and FTS purged by dry N_2.

As described above, much of the external optical path outside either cell was evacuated or purged with N_2-vapor while the tank that enclosed the FTS was evacuated to pressures of ~0.2 Torr. As a result, the spectra contained residual absorptions arising from outside the cell, and so a few spectra (not listed in Table 1) were also recorded with the absorption cells empty in order to characterize the extra absorption. The empirical values of H_2O partial pressures, the total H_2O+air sample pressures, and effective path lengths for the regions outside of the optical path are given in the lower portion of Table 1.

An example of a hot temperature (388 K) spectrum is shown in Fig. 1.   The narrow absorptions located on top of the broadened counterpart are due to the low pressure residual H_2O inside the FTS tank. Although these residual features added complexity to the analysis, these line centers [2] did provide absolute calibration of the wavenumber (cm^{-1}) scale for the spectra. Several of the air-broadened lines shown in the figure are saturated (100% peak absorption) yet they do not reach zero in transmission because of emission properties of the hot gas in the absorption cell. Only our spectra recorded with temperatures > 347 K showed this effect. This is illustrated further in Fig. 2 by showing the synthetic spectrum of a saturated line for a gas sample temperature of 388 K. The transmission function, $T(\omega)$, used to generate the broadened line is given as follows:

$$T(\omega) = \exp(-\alpha_1 - \alpha_2) + cg\left[1 - \exp(-\alpha_1)\right] \qquad (4)$$

where α_1 is the absorption coefficient for the gas in the sample cell and α_2 is the coefficient for the absorption contribution outside of the cell having no emission effects. cg is the transmission at ω=0 and labeled as "zero offset" in Fig. 2. The expression given in Eq. (4) was derived with the aid of the discussion on emission experiments given by Penner [10]. The zero offsets of saturated lines observed in the hot water vapor spectra were measured and were used as data in a smoothing function. The data were least-squares fitted with this function:

$$cg(v) = \exp\left\lfloor \Sigma a(i)v^i \right\rfloor \quad \text{i=0,1,} \rightarrow 5, \qquad (5)$$

where $a(i)$ are the various coefficients and v is the line position.

The calculated values of cg(ν) may diverge outside of the experimental data limits, cg(ν$_{min}$) and cg(ν$_{max}$), so the limits were extended by inserting appropriate "experimental" values of cg(ν) to cover the spectral range of the measured transitions. Plots of calculated cg(ν) vs. ν are shown in Fig. 3 for three sample temperatures where cg(ν) in the figure is labeled as the minimum transmission (zero offset). The upper trace in Fig. 3 covers the range from 600 to 1200 cm^{-1} where a 11.24 m path and sample temperatures of 348 K were used.

3. Spectral Analysis

A nonlinear least-squares (NLLS) curve-fitting technique [2-4] was used to retrieve the parameters from each spectrum individually. The algorithm adjusted the input values of positions [2], strengths [2], and widths [3,4] in the computed spectrum to minimize the differences between the observed and computed spectra. The self- and foreign-broadened width coefficients, b$_s$, and b$_f$, which are related to the measured width, b, are

$$b = b_f + b_s$$
$$b = b_f^0 p_f + b_s^0 p_s,$$

(6)

where b_f^0 and b_s^0 are the foreign- and self-broadening width coefficients, respectively, and p$_f$ and p$_s$ are the partial foreign and self-broadened pressures. The NLLS retrievals produce b from which b_f^0 is determined from Eq. (6). In this, the values of b_s^0 at 296 K from [3] were computed to corresponding values at the sample temperature T using Eq.(1) with η=0.5. Even if η is much different (±0.3) for a given line, the result for b_f^0 should be little affected due to the small contribution that self-broadening b$_s$ makes to the overall width b for most of the data. Also for the sample temperatures applied in this study (241 to 388 K) an uncertainty in η of ±0.3 results in an uncertainty of about 7% for b_s^0 for the extreme cases which has minimal effect on the outcome for b_f^0. b_f^0 is also denoted as b^0(air) in this study and represents the halfwidth coefficient of H$_2$O broadened by air in the absorption cell.

As shown in Fig. 1, the absorption features contain two components, one due to pressure broadening and the other due to the residual H_2O in the vacuum tank which encloses the FTS. The input line-list also contained a component representing the narrow feature. Figure 4 is a plot of observed and synthetic spectra overlaid for the rotational transition, 3 1 2 ← 3 2 1, located at 1560.2571 cm^{-1}. The sample temperature was 246.8 K and the air-broadening pressure was 517 Torr. The residuals (percent differences between the observed and computed spectra) are shown above the spectra. The two hash marks located above the spectra represent the center locations of the pressure broadened (shifted) and narrow (low pressure) absorptions. The 100% absorption level or 0 transmission is located at "0" in the figure as was the case for all the observations of the cold sample runs (T<296 K). This was not the case for runs with sample temperatures above 296 K in which the transmission function is given in Eq.(4). The NLLS software was programmed with the basic transmission function for a line:

$$T(\omega) = \exp(-\alpha), \qquad\qquad\qquad (7)$$

where the absorption parameter, α, contains line profile functions from Doppler to Voigt with algorithms for collision-narrowing and line mixing effects. The instrument (FTS) function was applied to $T(\omega)$ in the analysis using the NLLS program.

Our retrieval software is not currently programmed to treat the hot sample spectra based on the transmission function given in Eq. (4). To implement Eq.(4) into the NLLS program would involve a major (and costly) programming effort to determine and use correct values of cg. For this reason, an alternative method was explored in which the spectra were fitted in the usual manner and the retrieved results were subsequently corrected via another computer program. First of all, one could think that setting the zero at the zero offset position would solve the problem using the unmodified NLLS program. Without considering the instrument function, the transmission function in such a mode would take on the form:

$$T(\omega, \text{zero at zero offset}) = [T(\omega, \text{zero at zero}) - cg]/[1 - cg]$$

$$= \left[\frac{\exp(-\alpha_1 - \alpha_2) - cg \times \exp(-\alpha_1)}{1 - cg} \right] \tag{8}$$

Therefore, in the zero offset modes, the NLLS program would not give the true results. For the present work, we fitted the spectra from the true zero level using the unmodified NLLS program. The results for strengths and widths were then corrected using another program. This procedure will not work if the fitted spectrum does not agree with the observed. By this token, an additional computer program was created to test this method. The true transmission of a line was generated and from that contour, effective values were derived for the strength and width which would simulate the transmission function using the NLLS program or Eq. (7). The initial condition set in this program was that $T'(\omega=0) = T(\omega=0)$ where T' and T are the transmission functions given in the NLLS program, Eq. (7), and the true function, Eq. (4), respectively. Figure 5 shows three plots generated from this program. The true transmissions (solid curves) are of an absorption line with cg=0.3, b_f^0=0.046, p_f=485 Torr. The effective contours (dashed curves) were computed from Eq.(7). The optical densities vary in the three plots with the largest amount (saturated line) represented in the lowest plot. From top to bottom, $T(\omega=0)$-cg, goes from 0.14, 0.04, 0.0, respectively. The top plot shows very good agreement between the two curves which validates the use of the unmodified NLLS program for fitting this type of spectra with peak absorptions at least 20% from the saturation level. The middle plot shows the peak absorption of about 94% from the saturation limit and still a near fit. The bottom curves do not agree as one would expect for saturated absorptions.

In Fig. 6, a portion of a scan is plotted for a spectrum obtained with air and H_2O pressures equal to 485 and 9.7 Torr, respectively, at T=388.3 K; the path length is 4.53 m. The lower panel contains the observed spectrum overlaid with the synthetic spectrum with the computed spectrum derived from the NLLS program which includes inputs for the narrow features located on top of the pressure broadened absorptions. In general the fit is good except for the near or saturated line located at 1411.5056 cm^{-1} which shows deviations between the two spectra as predicted from the exercise described above and exemplified in Fig. 5.

The output from the fit of spectra using the NLLS program includes the measured line positions, strengths and air and self-broadened width coefficients. Results from the fit of

the hot sample spectra required further analysis as outlined above. This included corrections to the strength and width results. Calculations were made for the measured transitions which involved the true transmission function given in Eq. (4) from which effective values of strengths and widths were derived when the transmission function used in the NLLS program, given in Eq. (7), simulated the true or observed line profile. These effective values represent the output from the least-squares fit of the T > 347 K sample spectra. The line strength correction factors were applied in an iterative procedure to determine the H_2O partial pressures of the hot sample runs. The b^o(air) values obtained from the fits required correction factors ranging from about 0.3 (almost saturated) to almost 1.0 (weak absorption) depending on the absorption of the feature and cg (the zero offset level) where lines with peak absorptions of almost 100% required the most corrections. Since results for such lines may be in error by a large amount, lines with correction factors of 0.7 or greater were the only ones considered for further analyses.

The experimental air-broadened width coefficients were grouped together in terms of sample temperatures. For example, those with sample temperatures of 246.8 and 247.0 K, listed in Table 1, were put together and averaged and estimated uncertainties, Δb^o(air), were established for a temperature of 246.9 K for each measured transition. One run with a sample temperature of 241.2 K had no other runs to compare to so the average value was the value found and estimated uncertainty was given in terms of the observed condition of the absorption in the spectrum. The measurements for 296 K are given in Ref. [4] with uncertainties.

4. Temperature exponent, η, and fitting to empirical expressions

Experimental values of the exponent, η, involved in the relation expressed in Eq. (1) were derived from the measured b^0(T). For this work, η for each measured transition was derived from a least-squares fit of the experimental b^0(air) or b^0(T) using the expression:

$$\ln\left[b^0(T)\right] = a' + \eta \times \ln\left[\frac{T_0}{T}\right]$$

$$a' = \ln\left[b^0(T_0)\right] \tag{9}$$

where $T_0 = 296K$ and $a = \exp(a')$.

ln is the natural log, and this expression is the same as Eq.(1) given in another form. The constant, a' (thus a), was also found from the fit; the derived values of a do not necessarily equal the experimental values given in [4] for b^0 (at 296 K) except when only two temperature values are involved, one of which is for 296 K. The experimental parameters η and a found in this manner are labeled here as η(efit) and a(efit), respectively.

   The uncertainty in η, $\Delta\eta$, for each transition was derived from the following expressions:

$$\Delta\eta = \{\Sigma_i[\Delta\eta_i]^2/[N-1]\}^{\frac{1}{2}} \tag{10a}$$
$$\Delta\eta_i = \Delta b^0(T_i)/b^0(T_i) \times z(T_i) \tag{10b}$$
$$z(T_i) = \left| \, [\ln(296/T_i)]^{-1} \, \right|, T_i \neq 296 \text{ K}. \tag{10c}$$

$b^0(T_i)$ represents the measured air-broadened halfwidth coefficients at temperature T_i and $\Delta b^0(T_i)$ is the measured uncertainty in $b^0(T_i)$; N is the number of averaged $b^0(T_i)$ for each measured transition. When $T_i = 296$, $z(T_i)$ is not defined and was not used to derive $\Delta\eta_i$. The uncertainty of the derived constant, a, was obtained from the measurements using the following expression:

$$\Delta a = \{\Sigma_i[\Delta b^0(T_i)]^2/[N-1]\}^{\frac{1}{2}}. \tag{11}$$

   In prior studies [3,4,11,12], it was seen that subsets of self- and foreign-broadened water widths varied smoothly according to quantum numbers. Subsets of widths were formed according to the values of ΔJ, J, ΔK_a, K_a and $\Delta\tau$ and τ where $K_a + K_c - J = \tau$ (see Ref. 12). Widths were examined as a function of Jm (= $J'' + 1$ for R branch lines and J'' for P and Q branch lines) and Km (= $K_a'' + 1$ for R branch lines and K_a'' for P and Q branch lines). It was seen that pairs of transitions often had similar values of widths if Jm and Km were the same. We also noted that the asymmetry of the molecule affected the values of the width coefficients; widths of v_2 for which $\Delta\tau = 0$ and $\tau'' = 0$ were larger than those of v_2 transitions for which $\Delta\tau = 0$ and $\tau'' = 1$.

In an analysis of widths obtained at room temperature [11], "smoothed" values of the widths were obtained by fitting subsets of experimental values to

$$a(i) = \exp[\Sigma_i\, c(i)x(i)], \tag{12}$$

where $a(i)$ are the parameter values, $c(i)$ are the fitted coefficients and $x(i)$ are term elements, shown in the upper part of Table 2. In the present study, Eq. (12) was applied to the temperature dependence exponents $\eta(efit)$. The computed (smoothed) values of η obtained in this manner (semi-global fit) are labeled here as $\eta(gfit)$. The lower portion of Table 2 lists the quantum number group sets that were fitted together and the associated statistics. Such fits proved useful in identifying suspicious measurements and for estimating the temperature dependence coefficients of unmeasured transitions. Not all term elements were used in the final analysis (21-28) because these terms did not help the fits nevertheless they have been included in the table to show the extent of the analysis.

The results give values of $\sigma\%$ for each fitting condition and were derived from the expression which had been applied previously to halfwidths [11].

$$\sigma\% = \{(\Sigma\ ([\eta(gfit)\text{-}\eta(efit)]/\eta(efit))^2/N_c\}^{\frac{1}{2}} \times 100, \tag{13}$$

where N_c are the number fitted for the condition and the sum goes to N_c. The values obtained for $\sigma\%$ given in Table 2 are rather large and do not necessarily reflect inadequacy of the empirical model used to obtain $\eta(gfit)$ but rather the sensitivity of the uncertainties to the temperature ranges. For example, an uncertainty of 5% in the halfwidth coefficient reflects an uncertainty of about 24% in η for a temperature of 241 K and $T_0 = 296$ K as derived from Eq. (1). This value increases to 68% for T=275 K. On the other hand, Wagner et al. [7] obtained their measurements for high sample temperatures, and an uncertainty of 5% in their measured halfwidth coefficient results in uncertainties of only 5.4% (T=742 K) and 4.2% (T=980 K) in η. It should be noted that this analysis includes many more transitions than given in other studies for halfwidth temperature effects and with these extra measurements, the uncertainties, $\sigma\%$, could be lower than given in Table 2 if computed in a different way. However the present method was applied because the derived $\sigma\%$ is more realistic.

5. Results

In Table 3, the values of the temperature dependent exponents η(gfit), η(efit), and the air-broadened width coefficients *a*(efit) are listed along with experimental values of b^0(296 K) from Ref. [4] for $H_2^{16}O$ transitions in the (000)-(000) band (below 950 cm^{-1}) and the (010)-(000) band. Also included are the uncertainties, Δ η(efit), Δ *a*(efit), and Δ b^0(296 K). The rotational quantum assignments are given in terms of families (subgroups) of transitions, as described in previous studies [2-4, 11-12]. Values given within brackets are the number of different sample temperature measurements used to derive η(efit) and *a*(efit). An asterisk placed before the line position denotes a doubled absorption unresolved in the spectral data and the quantum assignment pertains to the stronger of the two comparable transitions. 10 transitions were not included in the fit to determine values of η(gfit), and they are given in the table with an asterisk placed just behind the line position. The values of the halfwidth coefficient measurements at various sample temperatures are not given in this study due to the length of the data. However, in Figs. 7-9, these measurements are shown with uncertainties for 15 rotational transitions which includes plots of η(efit) and η(gfit) and uncertainty traces for η(efit).

6. Discussion

In Table 4, the present temperature dependent exponents of air-broadened water transitions are compared to selected values reported by Zou and Varanasi [1] and Wagner et al. [7] for the transitions involving K_c=J in both the upper and lower states. The present values are the smoothed values, η(gfit), and those from the other studies include their values of uncertainties given within parenthesis. For each transition, Wagner et al. [7] reported coefficients obtained separately from the two high temperatures, and these are shown in the middle columns of Table 4. Otherwise, the results from the other two studies are grouped by P and R branch transitions involving the same quantum numbers under the assumption that these pairs have the same halfwidths and therefore the same temperature dependence exponents; this seems to be the case in the values reported by Zou and Varanasi [1] and the present values shown in Table 3.

One notes there is general agreement between this work and that of Wagner et al. [7], considering the rather large uncertainties related to the present values and the relatively accurate η's (due to analysis of high sample temperature absorptions) in their work. It is interesting that the sign of η changes from plus to minus at higher J in both studies. This was not observed by Zou and Varanasi [1] since their data included neither higher J transitions nor high temperature samples.

Another comparison with the other two studies can be made by comparing absolute differences, dif_i, in the exponent, η, using the following expression:

$$\text{dif}_i = |\, \eta(\text{gfit})_i - \eta(\text{other study})_i\, |, \qquad (14)$$

where i pertains to a common rotational transition. The average difference, χ, between this study and another is:

$$\chi = \Sigma_i \, \text{dif}_i \, / \text{num.}, \qquad (15)$$

where num. are the number of measured η's that are compared between the two studies and the sum extends to num. The values of χ were found to be as follows: (a) between this work and that of Wagner et al. [7] with num.=31 for sample temperatures of 742K and 980K are 0.072 and 0.054, respectively, and (b) between this work and that of Zou and Varanasi [1] with num.=128 was 0.091. Translating χ into Eq.(1) shows the following:

$$b^0(T) = b^0(296K)\{296/T\}^{\eta}_{\text{true}} \times \{296/T\}^{\pm\chi}, \qquad (16)$$

where η_{true} can be regarded as the correct value of η for a transition and χ as the uncertainty. Carrying this further, the percent uncertainty, δ%, in deriving $b^0(T)$ from $b^0(296K)$ using Eq. (16) can be expressed as:

$$\delta\% = |\, 1 - \{296/T\}^{\pm\chi}\, | \times 100. \qquad (17)$$

For applications to the Earth's atmosphere in which $b^0(\text{air})$ for water vapor is important in the upper troposphere (T~220 K) and near the Earth's surface (T<320 K), δ% is equal to

or less than 4% for $0.054 \leq \chi \leq 0.096$. In fact for T=220K, $\delta\%$ is 2.2%, 1.6% and 4.0% for χ equal to 0.072, 0.054, and 0.091, respectively.

7. **Conclusion**

The spectral data in the present study cover the region between 600 and 2200 cm^{-1} with sample temperatures from 241 to 388 K. Some 500 values of the temperature dependence exponent η of air-broadened water halfwidths were obtained for each measured transition in the analysis; these experimental values of η, η(efit), were grouped into eight subsets and fitted to an empirical model using a semi-global fitting procedure. The resulting computed values, η(gfit), provide an evaluation of the measurement precision and estimates for the temperature dependence coefficients of unmeasured transitions. Individual measurements of the broadening coefficients at each temperature are not given here, but a sampling of broadening coefficients is shown for 15 transitions in Figs. 7-9. Also shown are plots of η(efit), η(gfit) and uncertainties in η(efit). A comparison of the exponent, η, between this work and that of Zou and Varanasi [1] and Wagner et al. [7] is presented for transitions involving K_c=J for upper and lower states. The values given from this work are η(gfit) and compare satisfactorily with the relatively accurate results of Wagner et al. [7] even when η changes sign at higher J.

To obtain accurate values of the temperature dependence of widths, it is necessary to have spectral data covering a wide range of temperatures. Hot sample spectra are desired for water studies because the vapor freezes so readily. Unfortunately, the resulting emissions from heated gas samples complicate the retrieval process. In both the present and Wagner et al. [7] studies, the recorded spectra were not fully exploited because of limitations in the retrieval software for dealing with the emissions.

Future efforts should include an investigation to develop retrieval algorithms customized for this situation. Many more measurements could then be obtained by retrieving air-broadened halfwidths (and pressure-induced shifts) simultaneously from all three datasets (Present, Wagner et al. and Zou and Varanasi). Such investigations would then provide a thorough confirmation of the quantum mechanical prediction of broadening coefficients as a function of temperature [8] or, alternatively, a reliable set of empirical values for updating molecular compilations [5,6] in the event the theoretical models were not sufficiently accurate. On the other hand, since the emissions diminish

dramatically with decreasing wavelength, a similar study of air-broadened water using hot sample spectra at 2.7 μm could be performed to avoid this extra complexity.

8. Acknowledgments

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Table 1. Experimental conditions of the pressure-broadening measurements[†]

Partial pressure of H$_2$O in Torr	Partial pressure of air in Torr	Sample temperature in Kelvin	Absorption cell length in meters
0.162(2)	199.9	241.2	0.50
0.321(15)	517.0	246.8	0.50
0.328(7)	401.4	247.0	0.50
0.516(8)	149.6	251.0	0.50
0.530(10)	312.7	251.0	0.50
0.525(12)	312.7	251.2	0.50
0.536(20)	488.9	251.8	0.50
1.135(55)	597.0	257.8	0.50
1.116(47)	418.5	258.0	0.50
1.28(3)	99.0	265.0	0.50
1.99(6)	349.1	265.0	0.50
5.57(13)	584.9	275.0	0.50
5.74(20)	286.3	275.5	0.50
36.4(18)	466.2	347.2	11.24
23.8(12)	292.5	347.6	11.24
15.0(8)	143.8	347.6	11.24
2.70(10)	500.0	357.0	4.53
2.33(9)	348.0	358.0	4.53
2.69(10)	499.0	358.0	4.53
1.69(6)	250.2	362.0	4.53
1.59(5)	426.0	362.0	4.53
1.56(5)	426.0	362.0	4.53
1.39(5)	372.6	372.7	4.53
1.41(4)	374.0	372.7	4.53
1.50(5)	478.0	372.9	4.53
1.52(5)	478.0	372.7	4.53
2.63(8)	388.0	388.0	4.53
2.90(10)	539.0	388.0	4.53
1.45(6)	271.0	388.3	4.53
7.90(30)	348.0	388.3	4.53
9.70(40)	485.0	388.3	4.53

[†]Values given within parenthesis are uncertainties in the last digits. Analysis of empty absorption cell runs indicate the following results for effective path length, H$_2$O partial pressure and air pressure for the region external to the cell and in the optical path.

External optical density derived from spectral analysis of empty cell runs

Type of runs to apply	Partial H$_2$O pressure in Torr	Air pressure in Torr	Effective path length in m	Effective temp. In Kelvin
Runs with T < 275 K	0.008	600	0.43	296
Runs with T > 347 K	10.0	590	0.21	329

Table 2. Term elements used in the analysis of the H_2O experimentally determined values of the exponent, η, and fitting conditions[†].

no.	element	no.	element
1	1	15	$(K_a'^4 + K_a''^4) \times M$
2	M	16	$K_a'^6 + K_a''^6$
3	m^2	17	$(K_a'^6 + K_a''^6) \times M$
4	M^3	18	$(K_a' + K_a'') \times m$
5	m^4	19	$(K_a'^2 + K_a''^2) \times m$
6	M^5	20	$(K_a'^2 + K_a''^2) \times m^3$
7	m^6	21	$K_a'^2 - K_a''^2$
8	$K_a' + K_a''$	22	$K_a'^4 - K_a''^4$
9	$K_a'^2 + K_a''^2$	23	$(K_a'^2 - K_a''^2) \times M$
10	$K_a'^4 + K_a''^4$	24	$(K_a'^2 - K_a''^2) \times m^2$
11	$(K_a' + K_a'') \times M$	25	$(K_a'^4 - K_a''^4) \times M$
12	$(K_a' + K_a'') \times m^2$	26	$(K_a'^4 - K_a''^4) \times m^2$
13	$(K_a'^2 + K_a''^2) \times M$	27	$(K_a'^2 + K_a''^2) \times M \times (J' - J'') \times ((K_a' - K_a''))$
14	$(K_a'^2 + K_a''^2) \times m^2$	28	$(K_a'^4 + K_a''^4) \times M \times (J' - J'') \times ((K_a' - K_a''))$

[†]prime and double prime denote upper and lower states, respectively.
$M = |m|$, $m = -J''$ (P-branch), $m = J'$ (R-branch), and $m = J$ (Q-branch).

Fitting conditions and results

Branch	ΔK_a	τ''	Elements used	no. fitted	$\sigma\%$
P&R	1(R), −1(P)	0(R), 1(P)	1-20	183	55.9
P&R	1(R), −1(P)	0(R), 1(P)	1-20	151	36.8
P&R	1(R), −1(P)	0(R), 1(P)	1-20	83	34.8
P&R	1(R), −1(P)	0(R), 1(P)	1-20	107	36.5
P&R	1(R), −1(P)	0 and 1	1-17	32	37.5
Q	±1	0	1-17	133	33.3
Q	±1	1	1-17	108	34.8
Q	±3	0 and 1	1-11	11	7.4

$\tau'' = K_a + K_c - J$ for the lower state
$\Delta K_a = K_a' - K_a''$