

# **HALF-WIDTHS AND LINE SHIFTS OF WATER VAPOR FOR ATMOSPHERIC APPLICATIONS: MEASUREMENT AND THEORY**

SHORT TITLE: *HALF-WIDTHS AND LINE SHIFTS OF H<sub>2</sub>O*

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**Abstract.** Pressure-broadened half-widths are the principal source of error in the retrieval of concentration profiles for the Earth's atmosphere. The importance of the pressure-induced line shift is now becoming understood. In this work the current state of knowledge of the line shape parameters for water vapor transitions is discussed with respect to the experimental record and the theory. The measurement databases that have been compiled and the intercomparisons of measurements are discussed. The theoretical determination of the line shape parameters via the Complex Robert-Bonamy (CRB) formalism is presented. The dependence of the line shape parameters on rotational state, vibrational state, imaginary terms, temperature, intermolecular potential, collision dynamics, and method of calculation are discussed. Finally a comparison of the CRB line shape parameters with the measurement database is made and compared with the intercomparisons of the measurements.

**Keywords:** Complex Robert Bonamy formalism, half-width, line shift, spectral lines, H<sub>2</sub>O, temperature dependence of half-width, vibrational dependence of half-width

## **1. Introduction**

Water vapor is the strongest absorber of radiation and is therefore the most important gas controlling Earth's surface temperature. There are about 50 000

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spectral transitions for H<sub>2</sub>O ranging from microwave to the visible range of the spectrum. The interpretation of remote sensing measurements and study of the radiative property of atmosphere depends on the knowledge of spectral parameters for the gases present in the atmosphere. Of the parameters needed for inverting remotely sensed data, the air-broadened half-width is the least well known for atmospheric applications.<sup>1</sup> The effects of uncertainty in half-widths on the accuracy of retrieved parameters is well understood.<sup>2-5</sup> The spectroscopic and remote sensing communities<sup>6-8</sup> have determined that for accurate retrievals the half-width and its temperature dependence should be known with an uncertainty of **3%** for strong lines and **10%** for weak lines. The effect of the line shift on reducing data from remote sensing measurements is now known to be significant.<sup>9-11</sup>

In order for retrievals to be successful, spectral parameter data must be available for all transitions of absorbing molecules in the spectral channels of the measurement. Here the focus is on the collision broadened half-widths,  $\gamma$ , and pressure-induced line shifts,  $\delta$ , of water vapor transitions. Many measurements have been performed to determine  $\gamma$  for H<sub>2</sub>O in a bath of N<sub>2</sub>, O<sub>2</sub>, air, and H<sub>2</sub>O; a lesser number of measurements have been made for the line shifts. A question of prime importance is what are the uncertainties of the measurements? Because it is not practical to make observations in the laboratory for all transitions for all the conditions encountered in the Earth's atmosphere, an additional question should be is there a theory capable of computing the needed half-widths that meets the needs of the remote sensing community? In Section 2 the state of the measurements of collision-broadened half-widths of H<sub>2</sub>O is addressed. In section 3 the complex formulation of Robert-Bonamy is presented and the calculations of  $\gamma$  and  $\delta$  discussed. The measurements and calculations are compared in section 4 and the current state of affairs is discussed in section 5.

## 2. Measurements of collision broadened half-widths of water vapor

In 1994 Gamache *et al.* undertook a critical survey<sup>12</sup> of measured half-widths of water vapor perturbed by H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, air, CO<sub>2</sub>, and Ar. There were four goals identified in that work: (1) To use the available data to draw conclusions concerning the influence of vibration, relations between half-widths and their temperature dependence, ratios between broadening by different collision partners, etc. (2) To extract different broadening values for selected transitions in which one may be very confident by comparing measurements from different authors. Such accurate etalon lines should be of great use to experimentalist as tests of their measurement procedures, for remote sensing, and comparisons

with theoretical models. (3) To propose measurements that are crucially missing in order to complete the selected set in regard to the requirements of applications and testing of theoretical models. (4) To make a first test of theoretical results. Unfortunately, the disagreement among the data was much larger than the stated experimental uncertainty making it difficult to address the goals of the work. Goal 1 was addressed as well as could be done at the time with the available data; goal 2 yielded a very small number of transitions for which the confidence in the half-width was high; they were able to address goal 3 based on the measurements at the time, and goal 4 was not possible.

Over the past ten years there have been a number of newer measurements of pressure-broadened half-widths. The data sets have grown to 7 683, 598, 14 067, and 10 596 measurements of N<sub>2</sub>-, O<sub>2</sub>-, air-, and self-broadened half-widths. Gamache and Hartmann<sup>13</sup> have taken these newer data and added them to their databases and performed intercomparisons of the measurements with the aim of addressing the goals of their first study.

The vibrational dependence of the half-widths of water vapor was addressed in a number of studies,<sup>14-18</sup> in a survey paper<sup>12</sup> and in several workshops.<sup>1,6,8</sup> It was estimated that in general the effect of the vibrational states of the transition was smaller than experimental uncertainties and could change the half-width by ~3-5%. However, a recent theoretical work<sup>19</sup> on the vibrational dependence of the half-widths of water vapor lines found that the half-widths of certain transitions (doublet transitions where  $K_c=J$  or  $J-1$ ) exhibit a strong vibrational dependence. The difference in the half-widths can be up to a factor of 6 for high  $J$  transitions for bands involving 4 quanta of stretch modes. Using the database of measured half-widths the authors were able to confirm their prediction with experimental data. Because of this fact, intercomparisons can only be made between measurements made by different groups for transitions with the same quantum numbers;  $v_1'v_2'v_3'J'Ka'Kc' \leftarrow v_1''v_2''v_3''J''Ka''Kc''$ .

Grouping the data for a particular ro-vibrational transition gave groups of 2, 3, 4, ..., 8 points depending on the number of measurements made. The procedure yields 499, 19, 3514, and 440 ro-vibrational transitions for which intercomparisons of half-widths could be made for N<sub>2</sub>, O<sub>2</sub>, air, and self broadening, respectively. Table 1 lists the number of intercomparisons of half-widths made as a function of the number of points in the group, the number of the intercomparisons for which the estimated uncertainty is less than or equal to 3, 5, and 10%, the number with estimated uncertainty greater than 10%, and the maximum estimated uncertainty. It should be noted that most of the intercomparisons are for pairs of points, from 80% for air-broadening to 93% for self-broadening. Certainly at the same level of agreement more confidence is gained as the number of points compared increases. Unfortunately, the

number of intercomparisons with n greater than 3 is small; 6, 10, 2, and 0.9 percent for nitrogen-, oxygen-, air-, self-broadening, respectively.

Table 1 Half-width intercomparisons: Number of data in 2, 3, 4...8 point intercomparisons, number of intercomparisons with estimated uncertainties (U) in the given ranges, and maximum estimated uncertainty for the H<sub>2</sub>O-N<sub>2</sub>, H<sub>2</sub>O-O<sub>2</sub>, H<sub>2</sub>O-air, and H<sub>2</sub>O-self systems.

# data in intercomparison		2	3	4	5	6	7	8
H <sub>2</sub> O-N <sub>2</sub>	N <sup>†</sup>	420	48	30			1	
	U ≤ 3%	46						
	3% < U ≤ 5%	67	6	1				
	5% < U ≤ 10%	216	30	25				
	10% < U	91	12	4			1	
	U <sub>max</sub> = 140.%							
H <sub>2</sub> O-O <sub>2</sub>	N <sup>†</sup>	16	1	1		1		
	U ≤ 3%							
	3% < U ≤ 5%	1						
	5% < U ≤ 10%	4	1	1		1		
	10% < U	11						
	U <sub>max</sub> = 51.8%							
H <sub>2</sub> O-air	N <sup>†</sup>	2818	615	63	11	4	2	1
	U ≤ 3%	65	48					
	3% < U ≤ 5%	297	83	8	1	1		
	5% < U ≤ 10%	967	382	37	5	1	1	
	10% < U	1489	102	18	5	2	1	1
	U <sub>max</sub> = 137.%							
H <sub>2</sub> O-self	N <sup>†</sup>	409	27	3	1			
	U ≤ 3%	2						
	3% < U ≤ 5%	3						
	5% < U ≤ 10%	156	8					
	10% < U	248	19	3	1			
	U <sub>max</sub> = 186.%							

<sup>†</sup> number of intercomparisons

The intercomparisons for nitrogen broadening show no 3 point or larger data sets with estimated uncertainty less than or equal to 3%. Table 1 shows that most of the estimated uncertainties are in the range greater than 5% to less than or equal to 10% with a fair number greater than 10%. One ro-vibrational transition, the  $3_{12} \leftarrow 2_{20}$  of the rotational band or 183 GHz line, was studied by 7 groups and here the estimated uncertainty is greater than 10%. These data are shown in Fig. 1. This plot is typical of the intercomparisons. Often the data are separated by more than the uncertainty assigned to it. This fact leads to questions about the uncertainties reported in the literature. For the line shifts there are only intercomparisons of pairs of points.

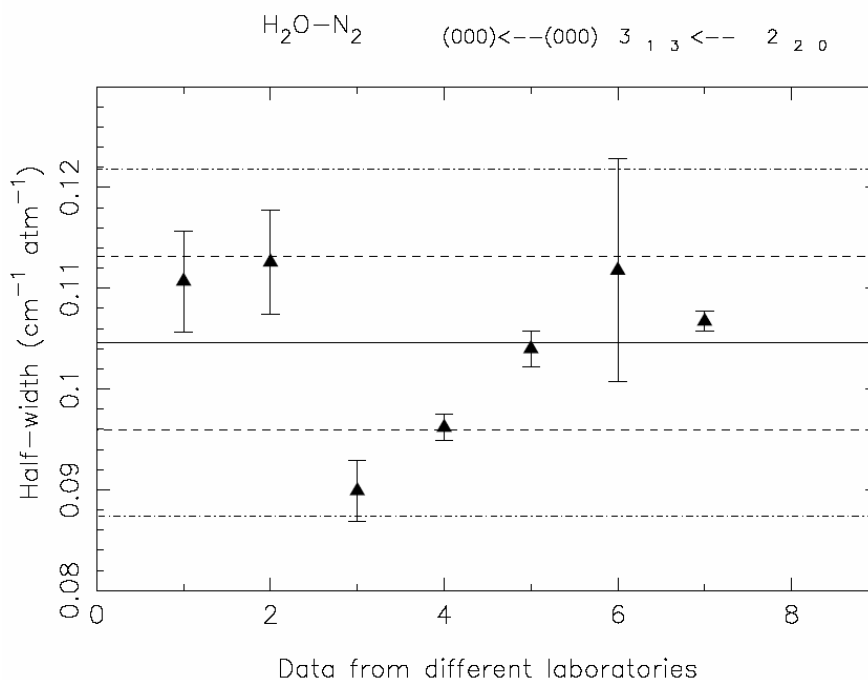


Figure 1. Measured half-widths ( $\text{cm}^{-1} \text{atm}^{-1}$ ) for nitrogen-broadening of the 183 GHz line of water vapor with reported uncertainties. Solid line is the average half-width, dashed lines are 1 and 2 standard deviations.

For oxygen-broadening of water vapor there are only 19 intercomparisons: mostly pairs of data. The estimated uncertainties are mostly greater than 10%. There are no shift measurements for intercomparison.

The largest data set is for air-broadening of  $\text{H}_2\text{O}$  which allows 3514 intercomparisons to be made. Unfortunately, only 81 of the intercomparisons have more than 3 data points. Of these intercomparisons none meet the 3% uncertainty criterion of the spectroscopic community. Most of the error estimates are in the 5-10 % range or above 10%. There are two transitions for which 7 measurements have been made. The first is typical of many of the air-broadening plots with the error bars of the data points not overlapping. While for the second the error bars do overlap, the overall 2 sigma uncertainty is almost 3 times that needed for remote sensing. The intercomparisons for the line shifts only occur as pairs of measurements.

The self-broadening data set allows 440 intercomparisons of half-widths to be made. There are no intercomparisons of the line shifts. For intercomparisons with more than 3 data points the estimated uncertainty is greater than 10%.

### 3. Complex Robert Bonamy formalism

The model chosen is the semiclassical complex formalism of Robert and Bonamy<sup>20</sup>, (CRB) for several reasons.

1. The formalism is complex valued, yielding half-widths and line shifts from a single calculation.
2. The cumulant expansion incorporated in the RB formalism allows for the inclusion of higher order terms in the S matrix, eliminating an awkward cutoff procedure that characterized earlier theories.
3. The intermolecular dynamics are treated more realistically than in earlier theories, i.e. using curved rather than straight line trajectories. This has important consequences in the description of close intermolecular collisions (small impact parameters).
4. Connected to item (3) is the incorporation in the RB theory of a short range (Lennard-Jones 6-12<sup>21</sup>) atom-atom component to the intermolecular potential. This component has been shown to be essential for a proper description of pressure broadening, especially in systems where electrostatic interactions are weak.<sup>22</sup> (Here, the notion of strong and weak collisions adopts the definition of Oka.<sup>23</sup>)

A detailed description of the theory may be found in Refs. 24-26 and references therein. Here only the salient features are discussed. In the CRB approach half-width and line shifts for a ro-vibrational transition  $f \leftarrow i$  are given by the real and imaginary part of the expression,

$$(\gamma - i\delta)_{f \leftarrow i} = \frac{n_2}{2\pi c} \left\langle v \times \left[ 1 - e^{-(S_2(f,i,J_2,v,b) + iS_1(f,i,J_2,v,b))} \right] \right\rangle_{v,b,J_2} \quad (1)$$

where,  $n_2$  is the number density of perturbers and  $\langle \rangle_{v,b,J_2}$  is the average over all trajectories, with impact parameter  $b$  and relative velocity  $v$ , and initial rotational state  $J_2$  of the collision partner. The real  $S_1$  and complex  $S_2$  terms are the first and second order terms in the successive expansion for the scattering matrix.  $S_1$  and  $S_2$  depend on the ro-vibrational states (and the associated collision induced transitions between these levels), the intermolecular potential and the collision dynamics involved. The expressions for these terms are explicitly defined in Refs. 24-26.

Most of the molecular parameters needed in the calculations are well known and the best available values from the literature are used. Many studies have

been carried out and the results allow the investigation of the dependencies of the line shape parameters.

### 3.1. EFFECTS OF THE EXPANSION OF THE ATOM-ATOM POTENTIAL

When expressed in spherical tensor form, the atom-atom potential can be understood as two simultaneous expansions. One is defined by the tensorial ranks  $\ell_1$  and  $\ell_2$ , which determine the symmetry of the interaction.<sup>27,28</sup> A second expansion is defined by the sum  $\ell_1+\ell_2+2w$ ,<sup>29,30</sup> which we call the order of the expansion. It hardly needs to be emphasized that any calculation of line width or shift should be converged with respect to both order and rank. All of our CRB calculations begin with testing the convergence of the atom-atom potential. The order of the expansion, ranging from 0 to high order, and the tensorial rank from  $\ell=0$  to 2 are investigated to ensure convergence. An order equal to zero corresponds using only the electrostatic parts of the anisotropic potential.

The studies have indicated that the order of the potential needed to ensure convergence is dependent on the interacting system. The results have shown that convergence is achieved with expansions of 8<sup>th</sup> order for the H<sub>2</sub>O-N<sub>2</sub>, H<sub>2</sub>O-O<sub>2</sub>, H<sub>2</sub>O-CO<sub>2</sub> systems, 12<sup>th</sup> order for H<sub>2</sub>O-Ar, and 0<sup>th</sup> order for H<sub>2</sub>O-H<sub>2</sub>O.

### 3.2. EFFECTS OF THE TRAJECTORIES

It is well known that the calculation of the line shape parameters is dependent on the trajectory model chosen. The trajectory model is studied for the system under consideration before routine calculations are made. The codes employed have the options to consider solutions of Hamilton's equations or the Robert and Bonamy parabolic model<sup>20</sup> both based on the isotropic potential yielding curved trajectories. We find that the RB model, which is correct to second order in time, yields results in agreement with the more exact and time consuming Hamilton's equations method. To simplify the trajectory calculations the isotropic part of the atom-atom expansion is fit to an isotropic Lennard-Jones 6-12 potential and the resulting parameters are used in the trajectory calculations. For H<sub>2</sub>O broadened by N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, or Ar the change from straight line to curved trajectories has a marked effect on the half-width. However, for self-broadening of H<sub>2</sub>O the trajectory model used has negligible influence.

Based on these observations the calculations presented here were made employing the RB parabolic model.

### 3.3. THE EFFECTS OF THE COMPLEX TERMS

As stated above, the complex Robert-Bonamy formalism leads to the imaginary components of the expanded S matrix appearing in the formula for the half-width. The contribution of these components to the half-width has remained a relatively unexplored facet of the theory because some of the imaginary resonance function integrals were only derived in the mid-nineties.<sup>24</sup>

Our studies on water vapor<sup>24-26,31-33</sup> have demonstrated the importance of the inclusion of imaginary components of the  $S_2$  terms in the calculation of half-widths. Differences in the half-width from calculations with and without the imaginary terms can be as large as 25%.<sup>33</sup> For the H<sub>2</sub>O-N<sub>2</sub> system, the difference between the real and complex calculations of  $\gamma$  are generally small with exceptions up to 10-15% observed. For the H<sub>2</sub>O-O<sub>2</sub> system, the imaginary terms are more pronounced, accounting for up to 25% difference in the calculated half-width. For all the systems studied the imaginary components affect the half-width by more than the uncertainty criterion set by the remote sensing community hence they must be retained in the calculations if reliable results are to be obtained.

### 3.4. TEMPERATURE DEPENDENCE OF THE HALF-WIDTH

In order to reduce atmospheric remote sensing measurements the temperature dependence of the spectral parameters must be known. Here the temperature dependence of the collision broadened half-width is discussed. The standard model for temperature dependence of the half-width is the power law expression

$$\gamma(T) = \gamma(T_0) \left[ \frac{T_0}{T} \right]^n \quad (2)$$

where  $\gamma(T_0)$  is the half-width at the reference temperature  $T_0$ , and  $n$  is called the temperature exponent. The model works quite well over small temperature ranges, i.e.  $\Delta T=50-100$  K. The model becomes less valid for large temperature ranges, thus one must be cautious in applying Eq. (2) in combustion studies for example. Recently, Wagner *et al.*<sup>34</sup> discovered that for certain types of transitions for N<sub>2</sub>-, O<sub>2</sub>-, and air-broadening of H<sub>2</sub>O the power law formula is not valid. This occurs when the energy jumps for collisionally induced transitions for the active and bath molecule do not match yielding large energy gaps. These collisions are said to be “off resonance” and the result is the rotational contributions to the half-width become small and the process is dominated by the vibrational terms. At large  $J''$  values the resulting temperature exponents



are negative and the power law, while giving a reasonable fit, is not theoretically correct. At intermediate  $J''$  values ( $\sim 8-10$ ) the contributions to the half-width are a mix of rotational and vibrational terms and the power law does not fit to the data.

Chu *et al.*<sup>4</sup> have studied the effect of changing the temperature exponent on retrieved mixing ratios. They found that changing  $n$  from 0.5 to 0.7 results in roughly a 4 percent change in the mixing ratio at 10 km. Given these results it is clear that the use of the temperature exponent for the ro-vibrational transition in question will yield the best results. Gamache and Rothman<sup>35</sup> have also shown that temperature exponents averaged as a function of  $J''$  or fit by polynomials in the rotational quantum numbers do not give reliable predictions for all transitions.

The temperature exponents for 2029 transitions in the  $\nu_2$  band of the H<sub>2</sub>O-N<sub>2</sub> system are plotted in Fig. 2 versus  $(J''+J')/2$ . What is clear from the figure is that fitting the data with a polynomial will not yield reliable results. Also the use of a constant value, which is the default on HITRAN<sup>36</sup>, will not give good results either. As  $J$  increases the range of the temperature exponents increases. For example at  $(J''+J')/2$  equal to 14.5,  $n$  varies from 0.5 to -0.75. As shown by Chu *et al.* a deviation of a default or polynomial value from the true value will lead to large error in the mixing ratio at 10 km.

### 3.5. VIBRATIONAL DEPENDENCE

There have been a number of studies into the dependence of the half-width on vibration. Mandin *et al.*<sup>14, 15</sup> took ratios of their measured half-widths to those of the HITRAN database<sup>36</sup> in the 8500-9300 and 9500-11500 cm<sup>-1</sup> regions. From this they concluded that there was a small ( $\pm 3\%$ ) vibrational dependence of the half-width. Grossman and Browell<sup>16</sup>, reported a 5% difference between transitions in the  $3\nu_1+\nu_3$  and  $2\nu_1+2\nu_2+\nu_3$  bands with the  $3\nu_1+\nu_3$  lines having the larger broadening values. This study compared average broadening values, not  $J$  dependent half-widths. In a 1996 study by Brown and Plymate<sup>17</sup> on H<sub>2</sub>O broadened by hydrogen, the ratios of half-widths for the same set of rotational quantum numbers were formed for the rotation and  $\nu_1$  bands divided by the  $\nu_2$  band. For rotational/ $\nu_2$  transitions the rms ratio is 1.016 ( $\pm 2.6\%$ ) and is 1.08 ( $\pm 4\%$ ) for  $\nu_1/\nu_2$  transitions. Brown and Plymate concluded that these differences are too large to be caused by experimental error and that there is a small vibrational dependence in the half-width.

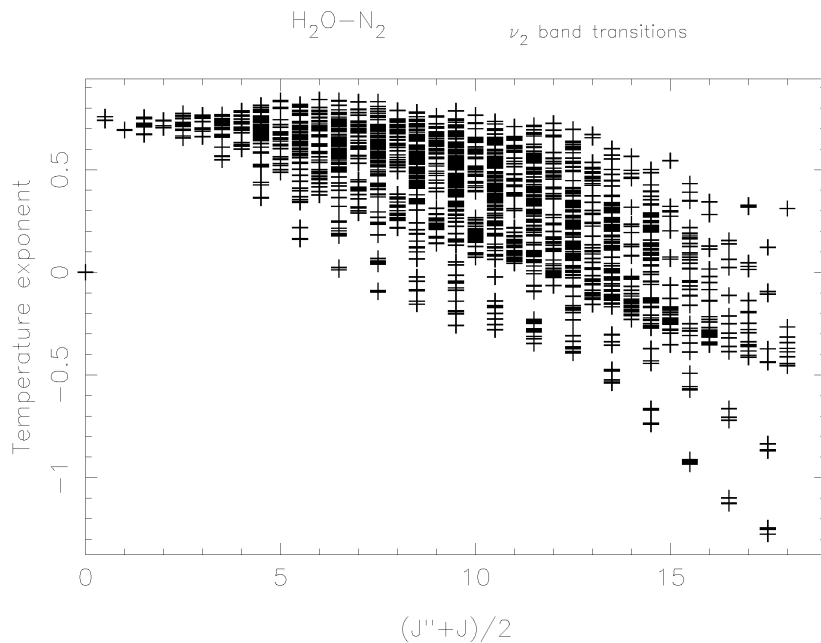


Figure 2. Temperature dependence of the half-width versus  $(J''+J')$  for  $\nu_2$  transitions of H<sub>2</sub>O perturbed by nitrogen.

Zou and Varanasi, in a 2003 study<sup>18</sup>, investigated the vibrational dependence of self- and air-broadening of water vapor in the 950-2100 and 3000-4050 cm<sup>-1</sup> regions. They considered ratios of the half-widths for the same rotational transition for the  $2\nu_2$  and the  $\nu_2$  bands, the  $\nu_1$  and the  $\nu_2$  bands, and the  $2\nu_2$  and the  $\nu_1$  bands for both self- and air-broadening. From the analysis of the self-broadening data they concluded that the half-widths in the  $2\nu_2$  band are smaller than their counterparts in the  $\nu_2$  band by about 10%. The differences in the ratios for the  $\nu_1$  and the  $\nu_2$  bands, and the  $2\nu_2$  and the  $\nu_1$  bands contained too much scatter to state conclusively if there was a definite vibrational dependence. Their analysis of the air-broadening data indicated that the half-widths in the  $\nu_1$  band are larger than the corresponding half-widths in the  $\nu_2$  band by about 5%. This is in rough agreement with the work of Brown and Plymate<sup>17</sup>. There were too few ratios for the  $2\nu_2$  and the  $\nu_2$  bands and the  $2\nu_2$  and the  $\nu_1$  bands to draw any solid conclusions.

The vibrational dependence of the half-widths of water vapor was addressed in a survey paper<sup>12</sup> and several workshops.<sup>1, 6, 8</sup> It was estimated that in general

the effect of the vibrational states of the transition was smaller than experimental uncertainties and could change the half-width by ~3-5%. However, a recent theoretical study<sup>19</sup> on the vibrational dependence of the half-widths of water vapor lines found that the half-widths of certain transitions (doublet transitions where  $K_c=J$  or  $J-1$ ) exhibit a strong vibrational dependence. The calculations show up to a factor of 8 at  $J=16$  for a change of 6 stretch quanta. This fact was sought in the measurement database and is shown in Fig. 3 where the half-width, in mk/atm, is plotted on a log scale versus  $m$  ( $m=-J$  for P-type transitions and  $m=J+1$  for R-type transitions). The lines with error bars are the measurements, the circles are the CRB calculations for a change of 3 stretch quanta, and the triangles are calculations for the  $\nu_2$  band. Comparison of the measurements with the three quanta calculations shows good agreement. The comparison of the  $\nu_2$  band calculations to the  $3\nu_1$  band calculations shows the difference in the half-widths to be a **factor** of 2 for the  $J=15$  transitions. Similar results are found for transitions with a change of 4 stretch quanta.

### 3.6. EFFECTS OF EXPLICIT VELOCITY AVERAGING

Most of the calculations presented here were made using the mean relative thermal velocity (mrtv) approximation to Eq. (1). In this approximation the integral over velocity is replaced by the mean relative thermal velocity for the temperature under consideration. Gamache and Rosenman<sup>37</sup> have shown that for water vapor transitions this approximation is within ~5% of the results obtained by doing the velocity integral at 296K. They found that the agreement was due to a fortuitous cancellation of errors. In a study of the 500.4 GHz line ( $34_2 32 \leftarrow 34_1 35$  transition) of ozone with nitrogen as the bath molecule Gamache<sup>38</sup> compared results from a mrtv calculation and a velocity integral calculation with the measurements of Priem *et al.*<sup>39</sup> made at three temperatures. For all temperatures the velocity integrated results agree with measurement better than the mrtv results.

Recently Gamache<sup>40</sup> has compared velocity integrated (VI) calculations, mrtv calculations, and measurements for H<sub>2</sub>O in a bath of nitrogen. In most cases the VI results agree with measurement much better than the mrtv results. Also, the very narrow lines that are observed, which have been a problem for the mrtv calculations, are better modeled by the VI-CRB calculations. Figure 4 shows two measured values for the pure rotation band  $18_{216} \leftarrow 17_{117}$  transition and the corresponding VI and mrtv calculations. The VI result is a factor of ~1.6 smaller than the mrtv result and is in excellent agreement with experiment.

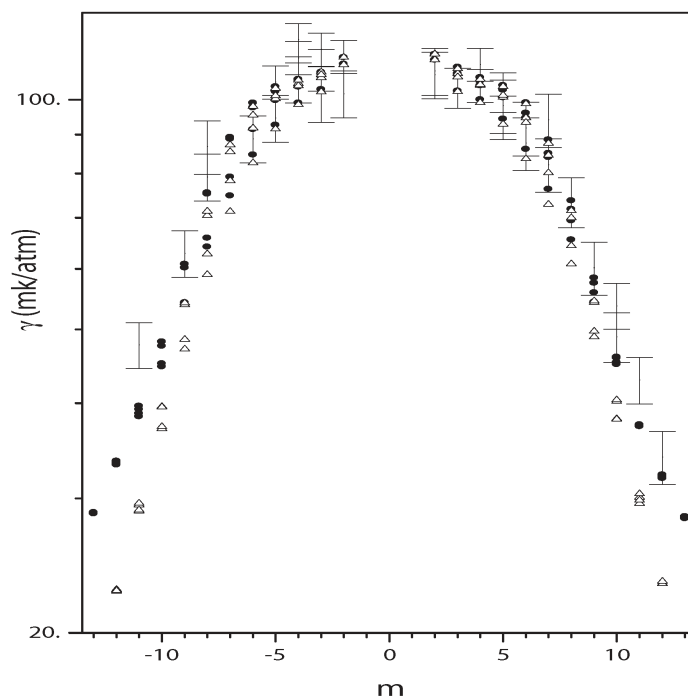


Figure 3.  $\text{H}_2\text{O-N}_2$  half-widths for transitions with  $K_c=J$  in bands involving three quanta of stretching vibration.  $|$  are experimental values whereas  $\bullet$  and  $\Delta$  are values calculated in the  $3\nu_1$  band and in the  $\nu_2$  band, respectively. Units are in  $\text{mk/atm}$ , ( $1000 \text{ mk}=1 \text{ cm}^{-1}$ )

#### 4. Comparison of measurement with measurement and calculations

The ultimate test of the theory is the comparison with measurement. The intercomparison of the experimental results<sup>13</sup> has brought into question the uncertainty of the measurements. Here the CRB calculations are compared with the measurements and related to the intercomparison of measurements. A good number of comparisons of CRB calculated half-widths and a lesser number of comparisons of the pressure-induced line shift have been made. A subset of these comparisons are presented in Table 2.

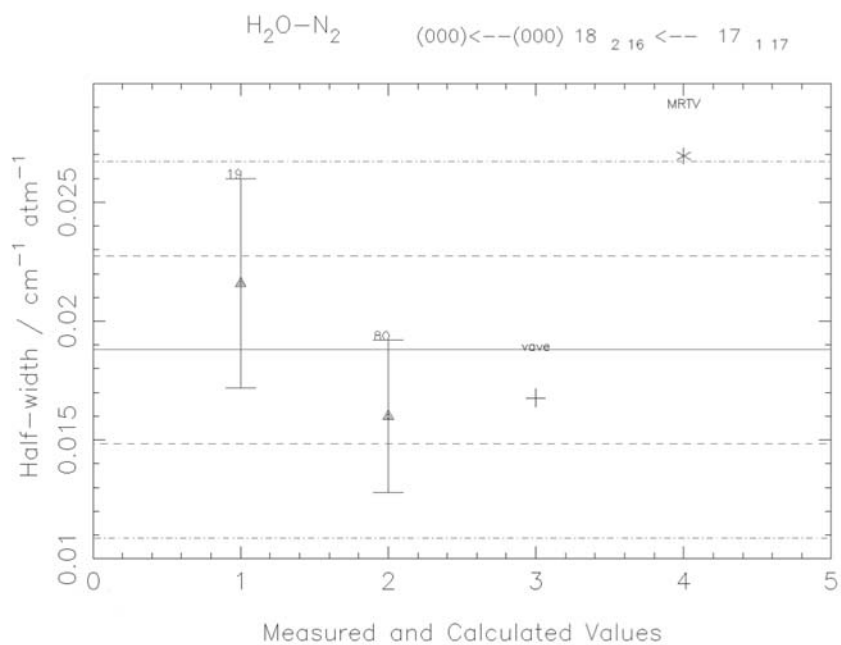


Figure 4. Measured N<sub>2</sub>-broadened half-widths for the rotation band 18<sub>2 16</sub> ← 17<sub>1 17</sub> H<sub>2</sub>O transition (triangle with error bars) and the corresponding VI (+ symbol) and mrtv (\* symbol) calculations.

We have also considered the agreement of the measured values with the average of the measurements and the agreement of the CRB calculations with the average measured value. Here the results for the H<sub>2</sub>O-N<sub>2</sub> system are presented. These results are typical for other perturber gases. The intercomparison and comparison are made for cases where there are 2 or more measured data for a specific ro-vibrational transition. Table 3 presents the results for the comparison of measurement with measurement and measurement with calculations.

Table 2 Comparison of measurements with CRB calculations for a number of systems

	Band	Parameter	# lines	Ave % diff	SD	Ref.
H <sub>2</sub> O-air	3 $v_1+v_3$	$\gamma$	49	-2.00	3.54	16
		$\delta$	78	0.43	6.37	
	2 $v_1+2v_2+v_3$	$\gamma$	22	-3.71	-3.71	
		$\delta$	29	-0.98	-0.98	
H <sub>2</sub> O-N <sub>2</sub>	203.4 GHz line	$\gamma$	1	-3.6		41
		n	1	22		
H <sub>2</sub> O-N <sub>2</sub>	325.2 GHz line	$\gamma$	1	-3.2		41
		n	1	58		
H <sub>2</sub> O-O <sub>2</sub>	203.4 GHz line	$\gamma$	1	-1.5		41
		n	1	2.3		
H <sub>2</sub> O-O <sub>2</sub>	325.2 GHz line	$\gamma$	1	-1.6		41
		n	1	-3.9		
H <sub>2</sub> O-N <sub>2</sub>	3.2 to 17.76 $\mu$ m region	$\gamma$	1251	-1.97		42
H <sub>2</sub> O-O <sub>2</sub>	3.2 to 17.76 $\mu$ m region	$\gamma$	377	-2.60		42
H <sub>2</sub> O-air	3.2 to 17.76 $\mu$ m region	$\gamma$	2139	-1.55		42
H <sub>2</sub> O-CO <sub>2</sub>	$v_1$	$\gamma$	8	0.4		33
	2 $v_2$		1	-0.8		
	$v_3$		22	1.8		
H <sub>2</sub> O-H <sub>2</sub>	Rotation	$\gamma$	64	-1.9	4.2	17
	$v_1$	$\gamma$	92	2.7	4.6	
	$v_2$	$\gamma$	273	-2.8	5.4	
	$v_3$	$\gamma$	137	3.9	4.2	
H <sub>2</sub> O-Ar	3 $v_1+v_3$	$\gamma$	80	-5.8	7.3	16
	2 $v_1+2v_2+v_3$	$\gamma$	30	-10.8	-20.	
H <sub>2</sub> O- H <sub>2</sub> O	Many	$\gamma$	119	0.28		43
	Many		100	-4.65		44
	Many		132	0.70		45

Table 3. Intercomparison of measurements and comparison of calculations with measurement for the H<sub>2</sub>O-N<sub>2</sub> system.

	Exp-Exp	Exp-CRB
Standard deviation	7.35	8.42
Average absolute percent error	4.95	6.03
Number of points	672	322

As can be seen by the table the agreement among the measurements is roughly the same as the agreement of the calculations with the measurements. It should also be noted that the comparisons are biased toward the measurements. Tables 2 and 3 indicate that in general there is very good agreement between the CRB calculations and the measurements.

## 5. Discussion

Measurements of pressure-broadened half-widths have been made for a great number of transitions of water vapor in a bath of N<sub>2</sub>, O<sub>2</sub>, air, and H<sub>2</sub>O and to a lesser extent for the line shifts. The results of the intercomparisons show that the current databases of measured parameters do not demonstrate good agreement with each other, certainly not of the quality needed to meet the needs of remote sensing. Trends in line shift parameters are now becoming evident, however more measurements are needed. The study of the temperature dependence of the half-width needs more measurements to identify trends, and the study of temperature dependence of the line shift is still in its infancy. There is much to be learned for both properties.

From the point of view of theory, measurements are needed for nitrogen-, oxygen-, and self-broadening. In particular, measurements for high J lines of bands such as the rotation and  $\nu_2$  band and the doublet transitions for high vibrational bands would be useful for adjusting the interaction potential. Temperature dependence of the half-width and line shift for these transitions would also be useful given the results of Refs. 19 and 34.

The following comments are made with respect to calculations of pressure-broadened half-widths and pressure-induced line shifts for ro-vibrational transitions of the systems discussed here. The effects of the imaginary components, the choice of potential, and the order of expansion of the potential vary from transition to transition and from system to system. To ensure reliable calculations, the potential in the CRB formalism must include the leading electrostatic terms, the atom-atom potential expanded to reach convergence, and the isotropic induction and dispersion potentials. The results of the studies

discussed above demonstrate a profound dependence of the half-width on the imaginary terms in the calculation for all perturbing species. It has been observed that as the imaginary components and the atom-atom potential expanded to high order are included in the calculations, the results almost always move in the direction of measurement. Recent results also indicate that the line shifts calculated by the CRB method agree very well with experiment.

One advantage of the theory is that many aspects of the broadening and shifting mechanisms can be elucidated. The vibrational dependence of the H<sub>2</sub>O-N<sub>2</sub> system is now well understood. Temperature dependence studies of the half-width have revealed some interesting results. In addition, the need to explicitly velocity average the optical cross-sections is becoming more clear. The authors are testing the CRB formulation on other radiator-perturbing systems and investigating the temperature dependence of the half-width and line shift.

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