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2 Lineshape parameters for water vapor in the 3.2–17.76 μm region 3 for atmospheric applications

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8 Abstract

9 Several NASA EOS instruments, the atmospheric infrared sounder (AIRS) on Aqua, and the tropospheric emission spectrometer
10 (TES) and the high-resolution dynamics limb sounder (HIRDLS) on AURA, will be measuring water vapor in the Earth's atmo-
11 sphere in the 3.2–17.76 μm spectral region. In order to do retrievals of temperature and concentration profiles, the spectral param-
12 eters for many thousands of water vapor transitions must be known. Currently the largest uncertainty in these data is associated
13 with the pressure-broadened half-width. To help ameliorate this situation, complex Robert–Bonamy calculations were made to
14 determine N_2 -, O_2 -, and air-broadened half-widths and line shifts for 5442 transitions of the principal isotopologue of water vapor
15 for the 11 vibrational bands in this region. The intermolecular potential is a sum of electrostatic terms (dipole–quadrupole and quad-
16 rupole–quadrupole), isotropic induction and London dispersion terms, and the atom–atom potential expanded to eighth order. The
17 parameters are adjusted as described in Gamache and Hartmann [J. Quant. Spectrosc. Radiat. Transfer 83 (2004) 119]. Calculations
18 were made at 225 and 296 K in order to determine the temperature dependence of the half-widths. When possible the data are com-
19 pared with measurements. The average percent difference between the measured and calculated half-widths is -1.97 , 2.6 , and -1.55
20 for N_2 -, O_2 -, and air-broadening of water vapor, respectively. The agreement for the line shifts is less satisfactory. It is clear from this
21 work that the calculations will benefit from a comprehensive adjustment of the intermolecular potential.

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23 *Keywords:* Half-widths; Line shifts; Water vapor; H_2O ; Nitrogen-, oxygen-, air-broadening; Temperature dependence of the half-width

25 1. Introduction

26 The scientific evidence that human activities are
27 increasing the rates of global changes is growing [1].
28 For example, carbon dioxide levels have risen 25% since
29 the industrial revolution and continue to rise. The Earth
30 system is complex and the cause-and-effect relationships
31 among lands, oceans, and atmosphere are not known
32 well enough to predict accurately the impacts these
33 anthropogenic forcings will have on future climate. To
34 help address these questions, measurements must be
35 made over the entire globe for long periods of time.

These data can then be used to construct accurate com- 36
puter models that will enable a forecast of the causes 37
and effects of climate change. The only feasible way to 38
measure such data is from satellites with “remote” sen- 39
sors. This approach is one of the principal components 40
of NASA’s Earth Observing System. A number of satel- 41
lites with a variety of instrumentation are either in orbit 42
or will be launched into orbit to collect remote sensed 43
data to use as input to climate models. 44

The translation of remotely measured data (including 45
ground based, balloon-borne, rocket, and satellite 46
observations) to an understanding of the Earth system 47
is based on the use of physical models. The reduction 48
of these remote sensed data into concentration or tem- 49
perature profiles, wind velocities, pollutant concentra- 50

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160 Within the CRB formalism the half-width, γ , and line
161 shift, δ , of a ro-vibrational transition $f \leftarrow i$ are given by
162 minus the imaginary part and the real part, respectively,
163 of the diagonal elements of the complex relaxation ma-
164 trix. In computational form the half-width and line shift
165 are usually expressed in terms of the scattering matrix
166 [22,23]

$$(\gamma - i\delta)_{f \leftarrow i} = \frac{n_2}{2\pi c} \langle v \times [1 - e^{-R S_2(f,i,J_2,v,b)} \\ \times e^{-i[S_1(f,i,J_2,v,b) + I S_2(f,i,J_2,v,b)]}] \rangle_{v,b,J_2}, \quad (1)$$

168 where n_2 is the number density of perturbers and
169 $\langle \dots \rangle_{v,b,J_2}$ represents an average over all trajectories (im-
170 pact parameter b and initial relative velocity v) and ini-
171 tial rotational state J_2 of the collision partner. S_1 (real)
172 and $S_2 = {}^R S_2 + i I S_2$ are the first- and second-order terms
173 in the expansion of the scattering matrix; they depend
174 on the ro-vibrational states involved and associated col-
175 lision-induced jumps from these levels, on the intermo-
176 lecular potential and characteristics of the collision
177 dynamics. The exact forms of the S_2 and S_1 terms are giv-
178 en in [12–14].

180 The S_1 term, which makes a purely imaginary contri-
181 bution, is isotropic in the absence of any vibrational
182 dependence of the anisotropic intermolecular forces. It
183 then has the appellation of the vibrational dephasing
184 term and arises only for transitions where there is a
185 change in the vibrational state. The potential leading
186 to S_1 is written in terms of the isotropic induction and
187 London dispersion interactions:

$$V_{\text{iso}}^{\text{induction}} = -\frac{\mu_1^2 \alpha_2}{R^6}, \quad (2)$$

$$V_{\text{iso}}^{\text{dispersion}} = -\frac{3}{2} \frac{I_1 I_2}{I_1 + I_2} \frac{\alpha_1 \alpha_2}{R^6},$$

189 where μ_1 is the dipole moment of water vapor and α_k
190 and I_k are the polarizability and ionization potential
191 for water vapor ($k = 1$) and collision partner ($k = 2$).
192 The vibrational dependence of these terms is contained
193 in the dipole moment, μ_1 , and polarizability, α_1 , of water
194 vapor. The first was investigated by Shostak and Muen-
195 ter [24] and is given in Debyes by

$$\mu = 1.855 + 0.0051(v_1 + \frac{1}{2}) - 0.0317(v_2 + \frac{1}{2}) \\ + 0.0225(v_3 + \frac{1}{2}), \quad (3)$$

200 where v_n is the number of quanta in the n th normal
201 mode. The polarizability of water vapor was obtained
202 by Luo et al. [25] and is, in atomic units, [26],

$$\alpha = 9.86 + 0.29(v_1 + \frac{1}{2}) + 0.03(v_2 + \frac{1}{2}) \\ + 0.28(v_3 + \frac{1}{2}). \quad (4)$$

206 The $S_2 = {}^R S_2 + i I S_2$ term is complex valued and results
207 from the anisotropic interactions. The potential em-
208 ployed in the calculations consists of the leading electro-
209 static components for the $\text{H}_2\text{O}-\text{X}$ pair (the dipole and

quadrupole moments of H_2O with the quadrupole mo-
moment of N_2 or O_2) and atom–atom interactions [12,27].
The latter are defined as the sum of pair-wise Len-
nard-Jones 6-12 interactions [19] between atoms of the
radiating (1) and the perturbing (2) molecules,

$$V^{\text{at-at}} = \sum_{i=1}^n \sum_{j=1}^m 4\epsilon_{ij} \left\{ \frac{\sigma_{ij}^{12}}{r_{1i,2j}^{12}} - \frac{\sigma_{ij}^6}{r_{1i,2j}^6} \right\}. \quad (5)$$

216 The subscripts $1i$ and $2j$ refer to the i th atom of mol-
217 ecule 1 and the j th atom of molecule 2, respectively, n
218 and m are the number of atoms in molecules 1 and 2,
219 respectively, and ϵ_{ij} and σ_{ij} are the Lennard-Jones
220 parameters for the atomic pairs. The heteronuclear
221 atom–atom parameters can be constructed from homo-
222 nuclear atom–atom parameters (ϵ_i and σ_i) by the “com-
223 bination rules” of Hirschfelder et al. [28] or Good and
224 Hope [29]. The atom–atom distance, r_{ij} , is expressed in
225 terms of the center of mass separation, R , via the expan-
226 sion in $1/R$ of Sack [30]. This development being trun-
227 cated, sufficient order must be chosen to insure the
228 convergence of calculated half-widths and line shifts,
229 as has been discussed by Labani et al. [31] and by Gam-
230 ache et al. [12,13,27]. Here the formulation of Neshya
231 and Gamache [27] expanded to eighth order is used.

232 Finally, recall that the isotropic component of the
233 atom–atom potential is used to define the trajectory of
234 the collisions within the semiclassical model of Robert
235 and Bonamy [11].

236 For water vapor, the reduced matrix elements are
237 evaluated using wavefunctions determined by diagonal-
238 izing the Watson Hamiltonian [32] in a symmetric top
239 basis for the vibrational states involved in the transition.
240 For the ground state the Watson constants of Matsu-
241 shima et al. [33] were used. For the v_1 , v_2 , v_3 , and $2v_2$
242 bands, Watson constants are from Flaud and Camy-
243 Peyret [34], and for the $3v_2$ band the Watson constants
244 from [35] are used so that the wavefunctions would have
245 proper symmetry properties. The rotational constants
246 for N_2 and O_2 are 2.0069 and 1.4377 cm^{-1} , respectively
247 [36].

248 Many of the molecular parameters for the $\text{H}_2\text{O}-\text{N}_2$
249 or $\text{H}_2\text{O}-\text{O}_2$ systems are well known and the present cal-
250 culations use the best available values from the litera-
251 ture. The dipole and quadrupole moments of water
252 vapor are taken from [24,37], respectively. The quadru-
253 pole moment of nitrogen is from Mulder et al. [38], that
254 for oxygen is from Stogryn and Stogryn [39]. The
255 numerical values are listed in Table 1. The ionization po-
256 tential of water is taken to be a vibrationally indepen-
257 dent value of 12.6 eV [40]. For nitrogen the
258 polarizability, $17.4 \times 10^{-25} \text{ cm}^3$, is taken from [41] and
259 the ionization potential, 15.576 eV , from [42]. For oxy-
260 gen the polarizability, $15.80 \times 10^{-25} \text{ cm}^3$, is taken from
261 [41] and the ionization potential, $12.063(\pm 0.001) \text{ eV}$,
262 from [40]. In the parabolic approximation, the isotropic
263

Table 1

Values of the electrostatic moments for the water vapor, N₂, O₂, and heteronuclear atom–atom Lennard-Jones (6-12) parameters for the collision pairs considered in this work

Molecule	Multipole moment	Reference
H ₂ O	$\mu = 1.8549 \times 10^{-18}$ esu	[24]
	$Q_{xx} = -0.13 \times 10^{-26}$ esu	[37]
	$Q_{yy} = -2.5 \times 10^{-26}$ esu	[37]
	$Q_{zz} = 2.63 \times 10^{-26}$ esu	[37]
N ₂	$Q_{zz} = -1.4 \times 10^{-26}$ esu	[38]
O ₂	$Q_{zz} = -0.4 \times 10^{-26}$ esu	[39]
Atomic pair	σ (Å)	ϵ/k_B (K)
<i>Atom–atom parameters</i>		
H–N	2.990	20.46
O–N	3.148	43.90
H–O	2.565	24.13
O–O	3.010	51.73

part of the interaction potential is taken into account in determining distance, effective velocity, and force at closest approach [11]. To simplify the trajectory calculations, the isotropic part of the atom–atom expansion is fit to an isotropic Lennard-Jones 6-12 potential.

Generally the atom–atom parameters are determined by taking the homonuclear atom–atom parameters, for example, see Bouanich [43], and using combination rules [28] to produce the heteronuclear atom–atom parameters. Calculations made using these parameters for some transitions in the ν_2 band showed some structured discrepancies when compared with measurements of both the shifts and widths. In a recent study of the lesser isotopologues of water vapor [44] it was observed that a relatively small change in the atom–atom parameters for the N–D and O–D interactions resulted in much improved agreement with measurement. The atom–atom parameters for the interactions N–D and O–D were obtained using D₂ atom–atom parameters determined via ab initio calculation [45] and combination rules. Furthermore, there are a number of different methods which have been proposed to determine heteronuclear potential parameters from homonuclear parameters [46 (and references therein), 47]. Good and Hope [29] showed that different combination rules used to determine ϵ cause variations of up to 15% in the final values. Thus the resulting parameters have an increased uncertainty (besides that resulting from the imprecision of the homonuclear data) which depends on the method chosen to go from the homonuclear to the heteronuclear parameters. From these facts, we conclude that adjustment of the atom–atom parameters within $\sim 15\%$ around the values given by the combination formula of Hirschfelder et al. is not unreasonable provided there are reliable experimental data on collisional parameters for adjustment.

In order to improve the quality of calculations for nitrogen broadening of H₂¹⁶O, six transitions of the ν_2

band were chosen for which there are multiple measurements and for which the calculated widths using unadjusted atom–atom parameters were too high for two lines, too low for two lines, and in agreement for the last two transitions. The potential parameters ϵ_{HN} , σ_{HN} , ϵ_{ON} , and σ_{ON} were adjusted to give a good fit of all these lines. With respect to the starting values (from combination rules of [28] and the homonuclear data by Bouanich [43]), the final parameters correspond to a 10% lowering of ϵ_{ON} , a 10% increase in ϵ_{HN} , a 3.9% decrease in σ_{HN} , and no change in σ_{ON} . These potential parameters were then further refined for transitions in the ν_2 band. The final values are presented in Table 1. Note, a full least-squares minimization was not thought worthwhile until a detailed study of velocity averaging effects (see below) are completed. The final adjustment of the potential parameters was made by comparing calculated line shifts to measurement. For transitions involving changes in a number of quanta in ν_1 and ν_3 the calculations made using the coefficients in Eq. (4) give sufficiently good agreement with the measurements [13]. Comparing calculations for the ν_2 band with the measurements of Toth [48] indicated that the ab initio value of 0.03 in Eq. (4) should be changed to 0.07 [49]. Currently, there are not enough data for oxygen-broadening of water vapor to make similar adjustments of the potential.

In the present calculations, the lineshape parameters have been calculated without performing the averaging over the Boltzmann distribution of velocities. Only the mean thermal value \bar{v} was used as has been done in most previous calculations, i.e., the mrtv approximation. The reason is that the velocity averaged calculations take 30–50 times more time than the mrtv approximation calculations and for half-widths of H₂O at ~ 300 K the mrtv calculation and the velocity averaged calculation give results within a few percent of one another [50].

3. Calculations

In the spectral region covered by the instruments, 3.2–17.76 μm (3124.2–563.2 cm^{-1}), the 2001 HITRAN database [2] contains 13622 water vapor transitions for all isotopologues of water. Here we focus on the range 563–3125 cm^{-1} for the principal isotopologue of water vapor and transitions with $J \leq 18$ (5442 transitions). Table 2 lists the vibrational bands of H₂¹⁶O in the wavenumber region and the number of lines considered in this work. These data were taken and sorted into files according to the 11 vibrational bands shown in Table 2. From these files the rotational quantum numbers were extracted to create lists to use in the CRB calculations.

For each vibrational band calculations were made at 225 and 296 K for the H₂O–N₂ and H₂O–O₂ systems. The half-width and line shift for air as the perturbing

Table 2
Number of H₂¹⁶O transitions in the 3.2–17.76 μm region as a function of vibrational band

$v'_1 v'_2 v'_3$	$v''_1 v''_2 v''_3$	Number of lines
000	000	506
010	010	144
010	000	1885
020	010	872
100	010	532
030	020	382
001	010	484
020	000	326
030	010	146
100	000	90
001	000	75

355 gas were obtained assuming binary collisions and Dal-
356 ton's law

$$357 \quad \gamma_{\text{air}} = 0.79 \gamma_{\text{N}_2} + 0.21 \gamma_{\text{O}_2} \quad \text{and}$$

$$359 \quad \delta_{\text{air}} = 0.79 \delta_{\text{N}_2} + 0.21 \delta_{\text{O}_2}. \quad (6)$$

360 This was done at both temperatures of the study.

361 From the calculations made at the two temperatures,
362 the temperature dependence of the half-widths can be
363 determined assuming the usual power law form

$$365 \quad \gamma(T) = \gamma(T_0) \left\{ \frac{T_0}{T} \right\}^n, \quad (7)$$

366 where the reference temperature T_0 is usually taken as
367 296 K but is not restricted to that value.

368 The data files for each band for nitrogen or oxygen as
369 the perturbing gas were taken at each temperature and
370 Eq. (6) applied to determine the air-broadened half-width
371 and line shift at 225 and 296 K. These data were then used
372 to determine the temperature dependence of the air-
373 broadened half-widths. The results of these calculations
374 are available as [Supplementary Material](#) to this article
375 and at http://faculty.uml.edu/Robert_Gamache.

376 4. Discussion

377 The CRB half-width data were compared to the
378 water vapor databases of lineshape parameters [51].

379 Comparisons were made between measurement and cal-
380 culation for cases where multiple measurements and sin-
381 gle measurements exist for the same ro-vibrational
382 transition. The results of the comparisons are given in
383 [Tables 3–5](#) for each vibrational band studied and for
384 N₂-, O₂-, and air broadening of water vapor. The tables
385 are divided into columns where the CRB values are
386 compared with a single measurement ($N_{\text{Exp}} = 1$) and
387 with multiple measurements of the same transition
388 ($N_{\text{Exp}} > 1$). Note that for many of the bands there are
389 no measured data. In general the agreement between
390 measurement and calculation is quite good especially
391 considering the results of an intercomparison of mea-
392 sured half-widths published recently [51]. The average
393 percent difference between the measured and calculated
394 half-widths is -1.97, 2.6, and -1.55 for N₂-, O₂-, and
395 air-broadening of water vapor, respectively. While these
396 numbers are good it should be realized that when there
397 are a large number of comparisons the standard devia-
398 tions are in general between 10 and 20%.

399 In addition, plots were made to compare the CRB cal-
400 culated value of the half-width with measurements for
401 each ro-vibrational transition where two or more mea-
402 surements were made. A note here to explain some fea-
403 tures of the databases. Often there are pairs of
404 measured data for a particular ro-vibrational transition;
405 however, one datum will be for the principal isotopo-
406 logue and the other datum for one of the other isotopo-
407 logues. Thus, there are a number of plots with only one
408 measured point and the CRB point. [Fig. 1](#) shows the
409 air-broadened half-width data for the $7_{53} \leftarrow 6_{42}$ transi-
410 tion of the ν_2 band, for which there are seven measure-
411 ments. The CRB calculated value is 2.45% from the
412 average of the measurements. Note: the number above
413 each measurement refers to a reference number in the
414 bibliography of the measurement database [51], the solid
415 line is the average of the measurements and the dashed
416 lines are 1 and 2 standard deviations of the comparison
417 of the measurements. [Fig. 2](#) shows the air-broadened
418 half-width data for a high J line ($13_{112} \leftarrow 12_{211}$) of the
419 rotation band. Again there are seven measurements,
420 however, the CRB calculated value is ~20% from the
421 average of the measurements. Note that the half-width

Table 3
Comparison of the CRB calculations with measurement for N₂-broadened half-widths of water vapor transitions in the 3.2–17.76 μm region at 296 K

$v'_1 v'_2 v'_3$	$v''_1 v''_2 v''_3$	H ₂ O–N ₂			
		$N_{\text{Exp}} = 1$		$N_{\text{Exp}} > 1$	
		Number of lines	% error	Number of lines	% error
000	000	160	7.04	10	5.97
010	010	2	17.93		
010	000	570	-1.76	371	-5.31
020	010	90	-5.24	6	-15.82
100	010	15	-8.15		
001	010	27	-0.70		

Table 4

Comparison of the CRB calculations with measurement for O₂-broadened half-widths of water vapor transitions in the 3.2–17.76 μm region at 296 K

$v'_1 v'_2 v'_3$	$v''_1 v''_2 v''_3$	H ₂ O–O ₂			
		$N_{\text{Exp}} = 1$		$N_{\text{Exp}} > 1$	
		Number of lines	% error	Number of lines	% error
000	000	1	6.59		
010	000	349	1.82	24	15.75
020	010	3	–12.92		

Table 5

Comparison of the CRB calculations with measurement for air-broadened half-widths of water vapor transitions in the 3.2–17.76 μm region at 296 K

$v'_1 v'_2 v'_3$	$v''_1 v''_2 v''_3$	H ₂ O–air			
		$N_{\text{Exp}} = 1$		$N_{\text{Exp}} > 1$	
		Number of lines	% error	Number of lines	% error
000	000	124	8.84	117	8.86
010	010	1	31.32		
010	000	285	1.04	1441	–3.57
020	010	111	–3.85	8	–15.21
100	010	13	–1.52		
001	010	27	–2.36		
020	000	9	1.09	2	–1.42
100	000	1	–0.37		

422 is roughly a factor of 4 smaller than that of Fig. 1 so per-
 423 centage difference does not tell the entire story. Fig. 3
 424 shows air-broadened half-width data for a high J line
 425 ($17_{215} \leftarrow 16_{116}$) of the ν_2 band where there is excellent
 426 agreement with measurement. Fig. 4 demonstrates a situ-
 427 ation where scatter in the measurements can lead to
 428 what appears to be poor agreement between the CRB va-
 429 lue and the average measurement. Here what is reported

430 as approximately an 11% difference between measurement
 431 and the calculation is in reality good agreement.
 432 Eliminating the stray point gives –0.42% difference.
 433 Plots for all transitions of each perturbing gas and the
 434 measurement database with bibliography are available
 435 at http://faculty.uml.edu/Robert_Gamache.

436 Comparisons between measurement and CRB calcu-
 437 lations for line shifts are fewer due to the number of

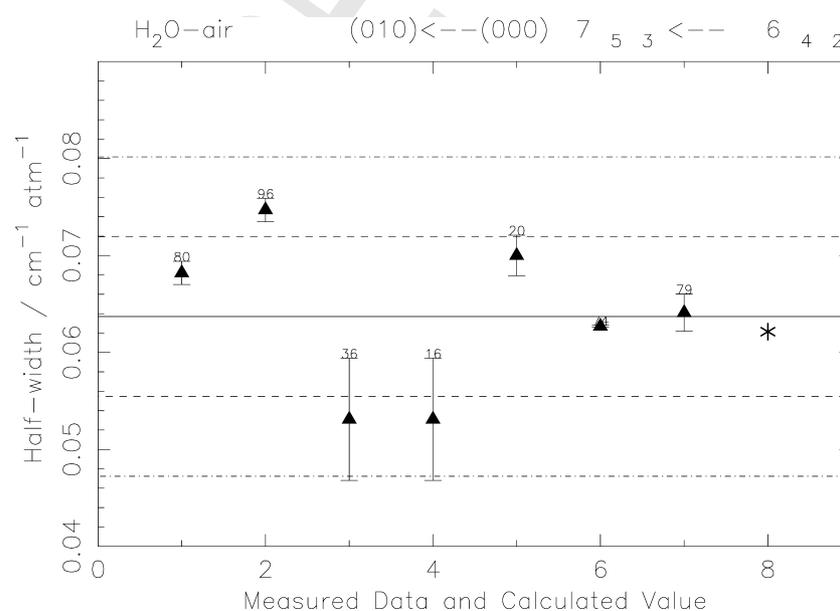


Fig. 1. Measured air-broadened half-widths (triangle symbol with error bars) and CRB value (asterisk) for the $7_{53} \leftarrow 6_{42}$ transition of the ν_2 band of water vapor.

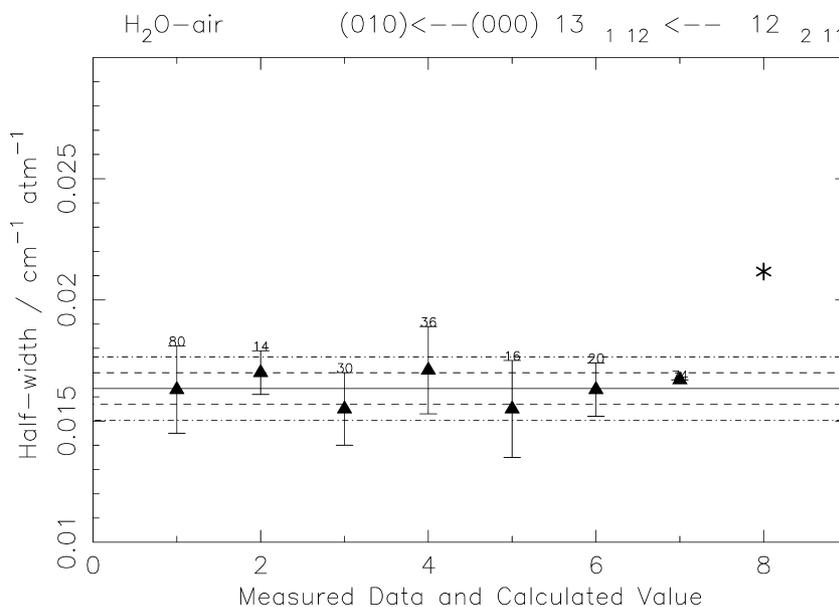


Fig. 2. Measured air-broadened half-widths (triangle symbol with error bars) and CRB value (asterisk) for the $13_{1,12} \leftarrow 12_{2,11}$ transition of the ν_2 band of water vapor.

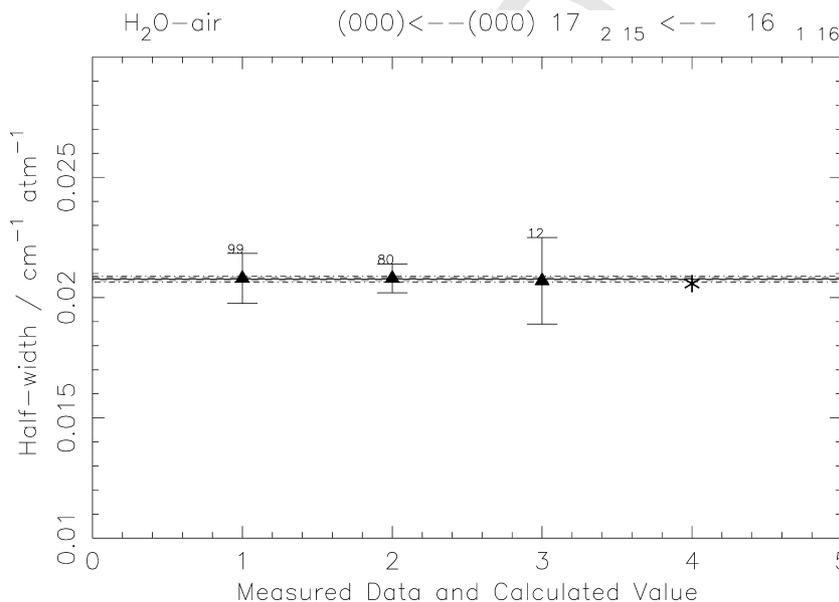


Fig. 3. Measured air-broadened half-widths (triangle symbol with error bars) and CRB value (asterisk) for the $17_{2,15} \leftarrow 16_{1,16}$ transition of the rotation band water vapor.

438 measurements reporting line shifts. Table 6 gives the
 439 comparisons possible for the bands and wavenumber re-
 440 gion of this study. Reported in the table are the number
 441 of comparisons and the average absolute difference
 442 (AAD) in cm^{-1} between measurement and theory
 443 (Exp - CRB). This is thought to be a better way to com-
 444 pare the data since percent difference for comparison of
 445 line shifts is generally large. In fact there are transitions
 446 where the uncertainty of the line shift is more than 100%
 447 of the shift value. Hence the absolute difference between

the measured and calculated line shifts was considered. 448
 Of the 5442 transitions in this region shifts have been 449
 studied experimentally for 2894 transitions: 1100, 342, 450
 and 1452 for N_2 -, O_2 -, and air broadening, respectively. 451
 Seven hundred and sixty-five transitions have been measured 452
 by more than one group, 132 and 633 for N_2 - and 453
 and air-broadening, respectively. Of these transitions five 454
 air-broadened transitions have been measured by three 455
 groups; all other multiple measurements are pairs of 456
 data. 457

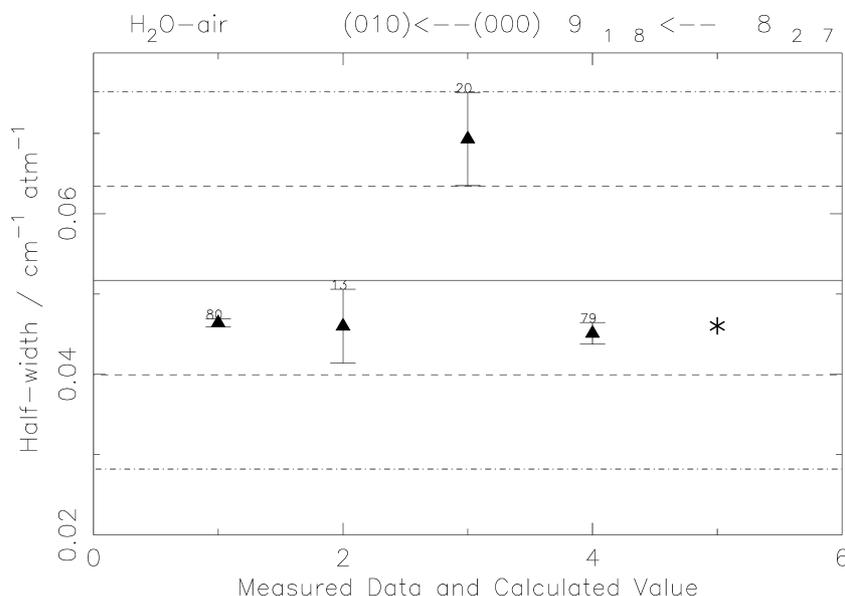


Fig. 4. Measured air-broadened half-widths (triangle symbol with error bars) and CRB value (asterisk) for the $9_{18} \leftarrow 8_{27}$ transition of the ν_2 band of water vapor.

Table 6

Comparison of the CRB calculations with measurement for N_2 , O_2 , and air-induced line shifts of water vapor transitions in the 3.2–17.76 μm region at 296 K

$\nu'_1 \nu'_2 \nu'_3$	$\nu''_1 \nu''_2 \nu''_3$	Number of lines	Average deviation ^a
$\text{H}_2\text{O}-\text{N}_2$			
000	000	162	0.0082
010	000	679	0.0054
		132 ^b	0.0041
010	010	1	0.0051
020	010	82	0.0039
100	010	16	0.0058
001	010	28	0.0049
$\text{H}_2\text{O}-\text{O}_2$			
010	000	342	0.0026
$\text{H}_2\text{O}-\text{air}$			
000	000	152	0.0073
010	000	507	0.0059
		633 ^b	0.0019
010	010	1	0.0017
020	000	3	0.0038
020	010	111	0.0040
100	000	1	0.0010
100	010	16	0.0067
001	010	28	0.0052

^a In $\text{cm}^{-1} \text{atm}^{-1}$.

^b Multiple measurements of the same transition.

458 For nitrogen and air broadening of H_2^{16}O the multi-
 459 ple measurements are for transitions in the ν_2 band.
 460 Comparing the multiple measurement comparisons with
 461 the single measurement comparisons shows that the
 462 average absolute difference between measurement and
 463 calculation is lower for comparison with multiple points.
 464 For the pairs of data the AAD between the measure-
 465 ments and the AAD between the CRB value and the

average of the measurements can be compared. For
 466 nitrogen broadening there are 132 pair comparisons.
 467 The AAD between the CRB value and the average of
 468 the measured values is 0.00411 cm^{-1} compared with
 469 the AAD between the pairs of measurements of
 470 0.00050 cm^{-1} . For air broadening there are 628 pairs
 471 of measurements with an average absolute difference
 472 of 0.00046 cm^{-1} compared with the AAD between mea-
 473 surement and theory of 0.00186 cm^{-1} (note this contains
 474 the five transitions for which there are three measure-
 475 ments each). Thus in both cases the agreement between
 476 measurement is better than the agreement between the-
 477 ory and measurement.

478 From the results in Table 6, it is obvious that the
 479 overall agreement is not as good as that described in
 480 [49]. One reason is that the adjustment of the coefficient
 481 of the vibrational dependence of the polarizability for
 482 the ν_2 bending mode made in [49] was done for the dou-
 483 ble transitions studied in that work. Here there are very
 484 few double transitions, hence the adjustment of the
 485 vibrational dephasing terms is not optimum for these
 486 transitions. This clearly indicates that the adjustment
 487 of the intermolecular potential must be revisited. This
 488 is underway and the results will be presented in a future
 489 publication.
 490

5. Conclusion

491 Calculations of the pressure-broadened half-width
 492 and pressure-induced line shift have been made for
 493 nitrogen-, oxygen-, and air-broadening of H_2^{16}O transi-
 494 tions for the 11 vibrational bands in the 563–3125 cm^{-1}
 495 region of the spectrum. The calculations were made at
 496

497 two temperatures, 225 and 296 K, and for rotational
498 states with $J \leq 18$. In total 5442 transitions were studied.
499 From the calculations the temperature dependence of
500 the nitrogen-, oxygen-, and air-broadened half-widths
501 was determined. The CRB results for the half-widths
502 compared very well with measurement. The compari-
503 sons for the line shifts were not as good in part due to
504 the use of parameters from [49]. The final air-broadened
505 data file was given to Dr. Larry Rothman to be merged
506 with the measured half-widths for addition to the HI-
507 TRAN database.

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517 Appendix A. Supplementary material

518 Supplementary data associated with this article can
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