PERGAMON

Journal of Quantitative Spectroscopy &
Radiative Transfer 78 (2003) 305–318

Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

www.elsevier.com/locate/jqsrt

Half-widths of $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$: II. Comparison with measurement

Robert R. Gamache*, Jonathan Fischer

Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell,
1 University Avenue, Lowell, MA 01854, USA

Received 29 May 2002; accepted 3 September 2002

Abstract

Pressure-broadened half-widths of ν_2 transitions are determined using the complex Robert–Bonamy formalism for four isotopomers of water vapor: $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$. The calculations are made with nitrogen and oxygen as the perturbing gases. A survey of the literature revealed N_2-broadened measurements of 365, 61, 990, and 545 ν_2 transitions of the $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$ isotopomers, respectively, and O_2-broadened measurements of 266 and 134 ν_2 transitions of the $HD^{16}O$, and $D_2^{16}O$ isotopomers, respectively. The calculated and measured half-widths are compared. In general, good agreement is observed when the most recent atom–atom constants are employed.

Keywords: Half-width; $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$; Water vapor isotopomers

1. Introduction

In a previous study [1], hereafter called part I, the collision-broadened half-widths of five isotopomers of water vapor, $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$, broadened by N_2, and O_2 were calculated via the complex Robert–Bonamy formalism. The half-widths of the lesser abundant isotopomers were compared with the values for the principal species. It was observed that for $H_2^{18}O$ and $H_2^{17}O$ the differences are small, a few percent maximum, whereas for $HD^{16}O$ and $D_2^{16}O$ the differences can be quite large, up to 43%. These differences will have large effects if one is relying on the current databases [2,3] to interpret spectra since these databases use the half-widths of the principal species for all isotopomers. Half-widths determined from algorithms based on an average ratio between different isotopomers will have large errors because the ratios change greatly as a function of the transition considered with little dependence on the rotational quantum numbers.

---

[*] Corresponding author. Tel.: +1-978-934-3904; fax: +1-978-934-3069.
E-mail address: robert_gamache@uml.edu (R.R. Gamache).

PII: S0022-4073(02)00218-2

Many questions must be asked of the results of part I before algorithms are developed to predict half-widths of one isotopomer of water vapor from another isotopomer. It was observed that a relatively small change in the atom–atom parameters of D resulted in noticeable changes in the calculated half-widths. The change in the parameters came from a study [4] where the atom–atom parameters for H_2 and D_2 were determined via ab initio calculation. The new values were then used to determine the atom–atom parameters for the interactions N-D and O-D using conventional combination rules [5]. There are a number of different methods that have been proposed to determine heteronuclear potential parameters from homonuclear parameters [6 (and references therein),7,8]. Thus, the resulting parameters have an uncertainty which depends on the method chosen to go from the homonuclear to the heteronuclear parameters. For some methods the uncertainty is quite large. Hence adjustment of the atom–atom parameters within ∼15% around the values given by the combination formula of Hirchfelder et al. is not unreasonable provided there are reliable experimental data. For water vapor the confidence in the measured database in 1994 was not high [9]. However, the situation is improving with multiple newer measurements available for the principle isotopic species. Toth [10] has studied the region from 604 to 2271 cm^{-1}, the measurements of Zou and Varanasi [11] consider the regions 950–2100 and 3000–4050 cm^{-1}. Schermaul et al. [12,13] have investigated the region 8600–15 000 cm^{-1}, Coheur et al. [14] have looked at the 13 000–25 000 cm^{-1} region, and Steyert et al. [15] measured rotational transitions in the 380–600 cm^{-1} range.

There are now a number of measurements of the half-widths for the lesser isotopomers of water vapor [10,15–20] to which the calculations can be compared. Devi et al. [16,17] made measurements of air- and N_2-broadening of v_2 transitions for D_2O, and for HDO, $H_2^{16}O$ and $H_2^{18}O$. Rinsland et al. [18] later studied pressure-broadening and pressure-induced line shifts for more than 100 transitions in the v_2 band of D_2O in air, nitrogen, and oxygen. This work was later extended [19] to consider air-, nitrogen-, and oxygen-pressure broadening and pressure-induced line shifts for more than 200 transitions in the v_2 band of $HD^{16}O$. More recently, Toth has measured a large number of air- and N_2-broadened half-widths and pressure-induced frequency shifts for transitions of HDO and D_2O from 709 to 1936 cm^{-1} [20] and $H_2^{16}O$, $H_2^{18}O$, and $H_2^{17}O$, from 604 to 2271 cm^{-1} [10].

In this work, the intermolecular potentials of the isotopomers of H_2O are refined by fitting to several transitions that have been measured for $H_2^{16}O$ by a number of investigators. This is done for nitrogen and oxygen broadening of water vapor. Next, using the ratios between H and D and the results of part I, values are predicted for the other isotopomers. Calculations are then made for N_2- and O_2-broadened transitions of H_2O that have been measured and the calculations compared with the measurements.

2. Complex Robert–Bonamy formalism

All calculations made employ the complex Robert–Bonamy formalism [21], which was described in part I; here only salient features are described. The CRB formalism is a complex valued semi-classical method which yields the half-width and line shift from a single calculation. The collision dynamics are correct to second order in time, which has important consequences in the description of close intermolecular collisions (small impact parameters). Also important for close collision systems is the incorporation in the CRB theory of a short range (Lennard-Jones 6–12 [22]) 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 [23]. (Here, the notion of strong and weak collisions adopts the definition of Oka [24].)

The half-width, γ of a ro-vibrational transition $f \leftarrow i$ is given in the complex Robert–Bonamy (CRB) formalism by minus the imaginary part of the diagonal elements of the complex relaxation matrix. In computational form, the half-width is usually expressed in terms of the Liouville scattering matrices, S_1 and S_2 [25,26] which depend on the intermolecular potential.

The potential employed in the calculations consists of the leading electrostatic components for the H_2O–X pair (the dipole and quadrupole moments of H_2O with the quadrupole moment of N_2 or O_2), and an atom–atom component [27,28] and isotropic induction and dispersion components. The isotropic component of the atom–atom potential is used to define the trajectory of the collision within the semi-classical model of Robert and Bonamy [21].

The atom–atom potential is defined as the sum of pair-wise Lennard-Jones 6–12 interactions [22] between atoms of the radiating molecule and the perturbing molecule, N_2 or O_2 and is given in terms of the Lennard-Jones parameters for the atomic pairs, the ε_{ij} and σ_{ij}. The heteronuclear atom–atom parameters are usually constructed from homonuclear-atom–atom parameters (ε_i and σ_i) by “combination rules” [29], however as described above the resulting parameters may have some error.

The atom–atom potential must be expanded in terms of the center-of-mass internuclear separation, R. The order of the expansion has been discussed by Labani et al. [30] and by Gamache et al. [27,28,31]. Here the formulation of Neshyba and Gamache [28] expanded to eighth order is used.

2.1. Details of CRB theory

The expressions for the S_1 and S_2 terms in the CRB formalism are described in detail in Refs. [31,32]. Note that the first-order (imaginary) term, S_1, depends only on the difference in the isotropic part of the interaction potential between the initial and final vibrational states of the radiator and is accounted for by the vibrational dependence of the dipole moment and polarizability of H_2O, the ionization potentials of the collision molecules, and the polarizability of the perturbing molecule. The second-order terms are comprised of two basic parts; one describing the internal states of the radiating and perturbing molecules and another describing the interaction and dynamics of the collision. These are calculable in terms of a number of molecular constants describing the colliding pair: electrostatic moments, atom–atom potential constants, isotropic potential constants.

Many of the molecular parameters are well known and the calculations use the best available values from the literature. The dipole and quadrupole moments of water vapor are taken from Refs. [33,34], respectively. The quadrupole moment of nitrogen is from Mulder et al. [35] and that for oxygen is from Stogryn and Stogryn [36]. The numerical values are listed in Table 1.

The ionization potential of water is taken to be a vibrationally independent 12.6 eV [37]. The polarizability of nitrogen and oxygen are taken from Ref. [38] and are $17.4 \times 10^{-25}\ \text{cm}^3$ and $15.8 \times 10^{-25}\ \text{cm}^3$, respectively. The ionization potential of nitrogen is 15.576 eV [39] and the value for oxygen is 12.063 eV [37].

The reduced matrix elements for the internal states of the radiator and perturber must be determined. For water vapor, these are evaluated using wave functions determined by diagonalizing the Watson Hamiltonian [40] in a symmetric top basis for the vibrational states involved in the transition. For the ground state of $H_2^{16}O$ the Watson constants derived by Flaud and Camy-Peyret [41] are used. For $H_2^{18}O$ and $H_2^{17}O$ the Watson constants of Toth [42] are used. For HDO and D_2O the

Table 1
Values of electrostatic moments for the water vapor, N_2, and O_2

Molecule	Multipole moment (esu)	Reference
H_2O	$\mu = 1.8549 \times 10^{-18}$	[33]
	$Q_{xx} = -0.13 \times 10^{-26}$	[34]
	$Q_{yy} = -2.5 \times 10^{-26}$	[34]
	$Q_{zz} = 2.63 \times 10^{-26}$	[34]
N_2	$Q_{zz} = -1.4 \times 10^{-26}$	[35]
O_2	$Q_{zz} = -0.4 \times 10^{-26}$	[36]

Watson constants are those of Toth [43]. The rotational constants for N_2 and O_2 are 2.0069 and 1.4377 cm^{-1}, respectively [44].

In the parabolic approximation, the isotropic part of the interaction potential is taken into account in determining the distance, effective velocity, and force at closest approach [21]. To simplify the trajectory calculations, the isotropic part of the atom–atom expansion is fit to an isotropic Lennard-Jones 6–12 potential.

Part I showed marked improvement in the comparison of theory and experiment for HDO and D_2O by utilizing homonuclear-atom–atom parameters for deuterium derived by Wang [4] in the standard combination rules. The difference in the constants is only ~10% for ε and 0.5% for σ yet this change leads to improved theoretical values. Good and Hope [8] showed that different combination rules lead to variations in ε of ~15% and σ of ~3%. It would not seem unreasonable to adjust the atom–atom potential coefficients if sufficient experimental data exist. This is the case for the principal species of water vapor for which many measurements exist [45].

For nitrogen broadening of $H_2^{16}O$ six transitions were chosen for which there are multiple measurements [10,14,46–52] and for which the calculations were too high for two lines, too low for two lines, and in agreement for the last two transitions. The potential parameters were adjusted to give a good fit of all the lines. The parameters are ε_{HN}, σ_{HN}, ε_{ON}, and σ_{ON}. For the starting values the heteronuclear atom–atom parameters used are derived from homonuclear-atom–atom parameters obtained by Bouanich [53] using the combination rules [29]. The final values 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}. Note, a full least-squares minimization was not thought worthwhile until the work of Ref. [45] is completed. For oxygen broadening of $H_2^{16}O$, there are not multiple measurements to allow fitting to an average. A similar procedure to that used for H_2O-N_2 with some of the data from Ref. [54] was done. The best fit was obtained by lowering σ_{HO} by 10% of the combination rule value. The other atom–atom parameters (ε_{HO}, ε_{OO}, σ_{OO}) are the combination rule values.

The atom–atom parameters for the deuterated species of water were derived by taking the combination rule values for are $\varepsilon_{HN}, \sigma_{HN}$, ε_{ON}, σ_{ON} and ε_{HO}, σ_{HO}, ε_{OO}, σ_{OO} derived by taking the homonuclear-atom–atom parameters obtained by Bouanich [53] and the D_2 parameters given by Wang [4], forming the D to H ratio of the parameters, and then scaling the best fit parameters by the same ratios to get ε_{DN}, σ_{DN}, ε_{DO}, σ_{DO}. Since homonuclear-atom–atom parameters are not available for the lesser isotopomers of H_2O, the $H_2^{18}O$ and $H_2^{17}O$ atom–atom constants are those of the principal species. The values used in the calculations are given in Table 2.

Table 2
Values of the heteronuclear atom–atom Lennard-Jones (6–12) parameters for the collision pairs considered in this work

Atomic pair	σ/Å	ε/k_B (°K)
H-N	2.7807	22.506
H-O	2.565	24.13
D-N	2.7704	20.339
D-O	2.5524	21.81
O-N	3.148	39.51
O-O	3.010	51.73

Table 3
Statistics of the comparison of measured half-widths for isotopomers of water vapor. APD ≡ average percent difference, AAPD ≡ average absolute percent difference, SD ≡ standard deviation

Comparison	# Points	PD/APD	Max difference	SD
$H_2^{18}O$-N_2				
Refs. [17–10]	5	13/36	55	34
HDO-N_2				
Refs. [17–19]	21	−2.6/4.4	11	5.0
Refs. [17–20]	29	−2.4/5.0	16	6.1
Refs. [17–10]	2	29/29	43	20
Refs. [19–20]	261	0.32/1.8	16	2.7
Refs. [19–10]	32	20/20	62	16
Refs. [20–10]	53	19/20	68	18
D_2O-N_2				
Refs. [18–20]	125	−1.0/2.5	12	3.2

3. Calculations

The measured data for $H_2^{18}O$ [10,17], $H_2^{17}O$ [10], $HD^{16}O$ [10,17,19,20], and $D_2^{16}O$ [16,18,20] were taken and the N_2- and O_2-broadened values extracted. This yielded 365, 61, 990, and 545 N_2-broadened measurements of ν_2 transitions of the $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$ isotopomers, respectively, and 266 and 134 O_2-broadened measurements of ν_2 transitions of the $HD^{16}O$, and $D_2^{16}O$ isotopomers, respectively. The rotational quantum numbers were taken and used as input to the CRB codes. Calculations were made at a temperature of 296 K with nitrogen and oxygen as the perturbing gases.

4. Results

Tables of the results for each isotopomer and perturber have been prepared. Electronic copies of the complete tables can be obtained from one of the authors (RRG).

Table 4
Statistics of the comparison of multiple measurements compared with measurement average for half-widths for isotopomers of water vapor. AAPD ≡ average absolute percent difference

Common measurements	# Compared	$H_2^{18}O$ AAPD	# Compared	HDO AAPD	# Compared	D_2O AAPD
2	5	20	239	2.1	125	1.2
3	0		49	6.6	0	
4	0		2	13	0	

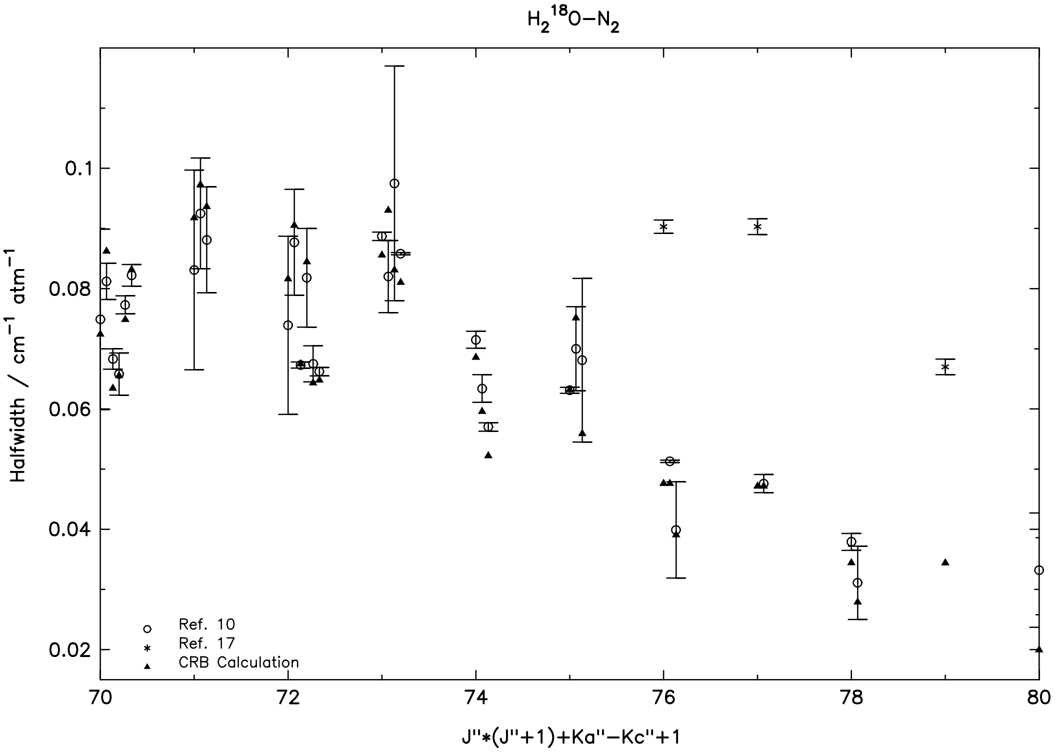

Fig. 1. Measured [10,17] and CRB calculated half-widths for the $H_2^{18}O$-N_2 system versus an energy-ordered index, J*(J+1)+Ka-Kc+1. The range of the x-axis was chosen to demonstrate the comparison of the data.

The comparison of the calculated half-widths with the measurements is complicated by the fact that multiple measurements have been made for a number of transitions. Before comparing the calculations with the measurements, it is useful to first ask how well the measurements compare with each other. This is possible for nitrogen broadening of $H_2^{18}O$, HDO and D_2O for which there are 2, 4, and 2 independent measurements. The data were taken and the transitions for which there were multiple measurements were found and the average percent difference (APD), average absolute percent difference (AAPD), maximum percent difference between the measurements and the standard deviation (SD) of the percent differenced determined. These data are presented in Table 3 along with

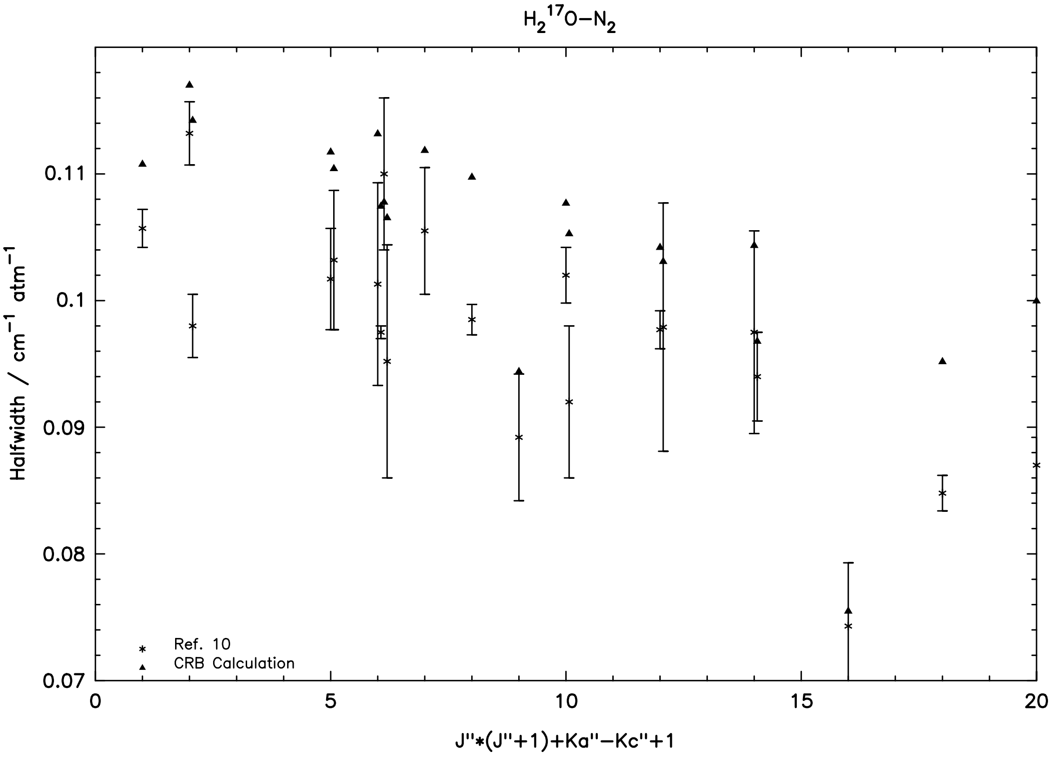

Fig. 2. Measured [10] and CRB calculated half-widths for the $H_2^{17}O$-N_2system versus an energy-ordered index, J*(J+1)+Ka-Kc+1. The range of the *x*-axis was chosen to demonstrate the comparison of the data.

the number of comparisons made. The first column of the table gives the reference numbers for the data being compared. For $H_2^{18}O$-N_2 there are only five lines that can be compared. The AAPD is about 36% between the measurements with a maximum difference of ∼55%.

For HDO-N_2 there are four independent measurements allowing six intercomparisons to be made. The number of transitions compared in the table are 21, 29, 2, 261, 32, and 53. Of particular interest is the comparison of Refs. [19,20]. These are measurements by two different groups that compare 261 transitions. The AAPD is 2%, the SD is 3%, and the maximum difference is 16%. Several of the other comparisons show an AAPD ∼4% and SD ∼5%. Three of the intercomparisons show AAPD of 20%, 20%, and 29%, however the 29% is based on a comparison of two transitions. The maximum deviations range from ∼11% to 68%. The comparison of Refs. [10,20] based on 53 transitions shows a slightly larger maximum difference of 68%. However it should be noted that for high J transitions the values of the half-width can be rather small which can exaggerate small differences in the reported values.

For D_2O-N_2 only two measurements were made allowing the single comparison. One hundred and twenty five transitions were measured in common and the AAPD is 2.5% with an SD of 3.2 and a maximum difference of 12%.

Unfortunately there are only single measurements for $H_2^{17}O$-N_2, HDO-O_2, and D_2O-O_2 and no measurements for $H_2^{18}O$-O_2 or $H_2^{17}O$-O_2 making comparisons between measurements impossible.

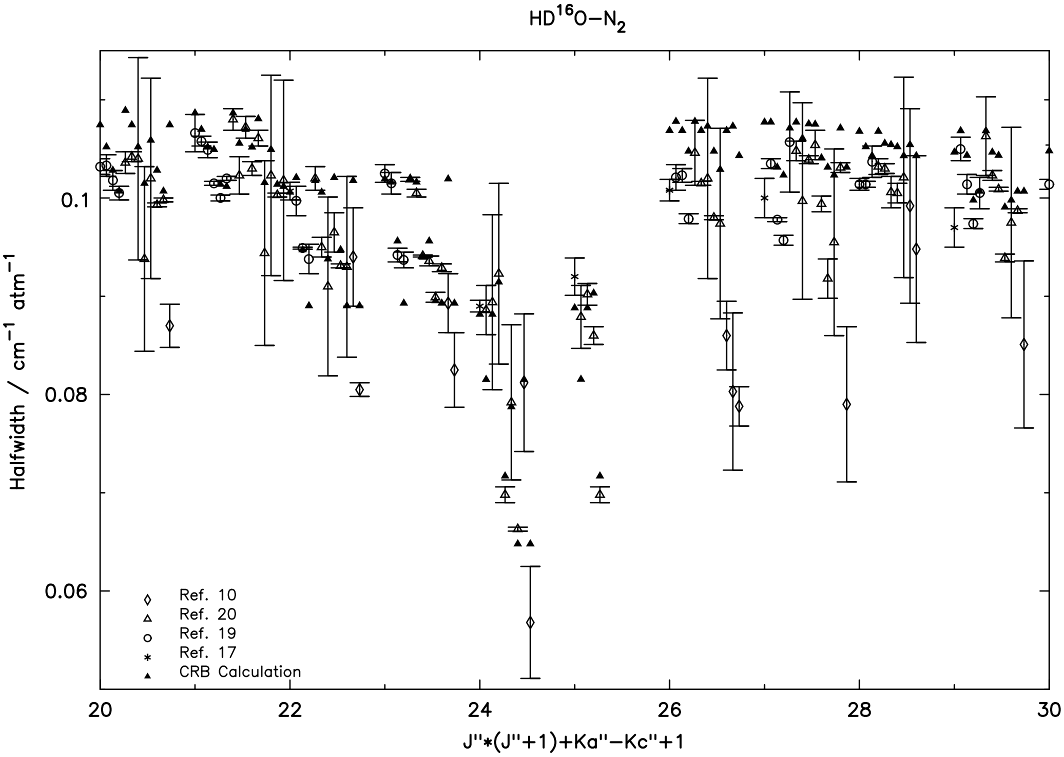

Fig. 3. Measured [10,17,19,20] and CRB calculated half-widths for the HDO-N_2 system versus an energy-ordered index, J*(J+1)+Ka-Kc+1. The range of the *x*-axis was chosen to demonstrate the comparison of the data.

In some cases there are two, three, or four measurements for a given transition. In such cases the calculations will be compared with the measurement average. One would expect to have more confidence for such cases if the measurements agree. In Table 4, the measurements are compared to the measurement average when multiple data are available for a transition. Listed are the number of common measurements, the number of comparisons, and the average absolute percent differences (AAPD) for the systems where multiple measurements were made: $H_2^{18}O$-N_2, HDO-N_2, and D_2O-N_2. For $H_2^{18}O$-N_2 and D_2O-N_2 only pairs of data are possible. For $H_2^{18}O$-N_2 there are five pairs and the APD is 20%, for D_2O-N_2 there are 125 pairs with an AAPD of 1.24. HDO-N_2 has 239 pairs, 49 3-data comparisons, and two 4-data comparisons with AAPDs of 2.1%, 6.6%, and 12.8%, respectively. These results indicate that having multiple data for a transition does not necessarily improve the data to compare with the calculations. For example, for HDO-N_2 comparing 2-data points for 239 transitions gives an AAPD of 2.1%, comparing 3-data points for 49 transitions yields an AAPD of 6.6%, and when 4-data points are compared for two transitions the AAPD is 13%.

Figs. 1–6 present portions of the comparisons of the measurements with the calculated values for $H_2^{18}O$-N_2, $H_2^{17}O$-N_2, HDO-N_2, D_2O-N_2, HDO-O_2, and D_2O-O_2, respectively. Because of the number of data, plots of the entire data sets are too confusing and not as useful as regions where the comparisons can be better seen. The regions were chosen to give a good number of comparisons and multiple measurements for a single transition when possible. The plots are the measured half-widths

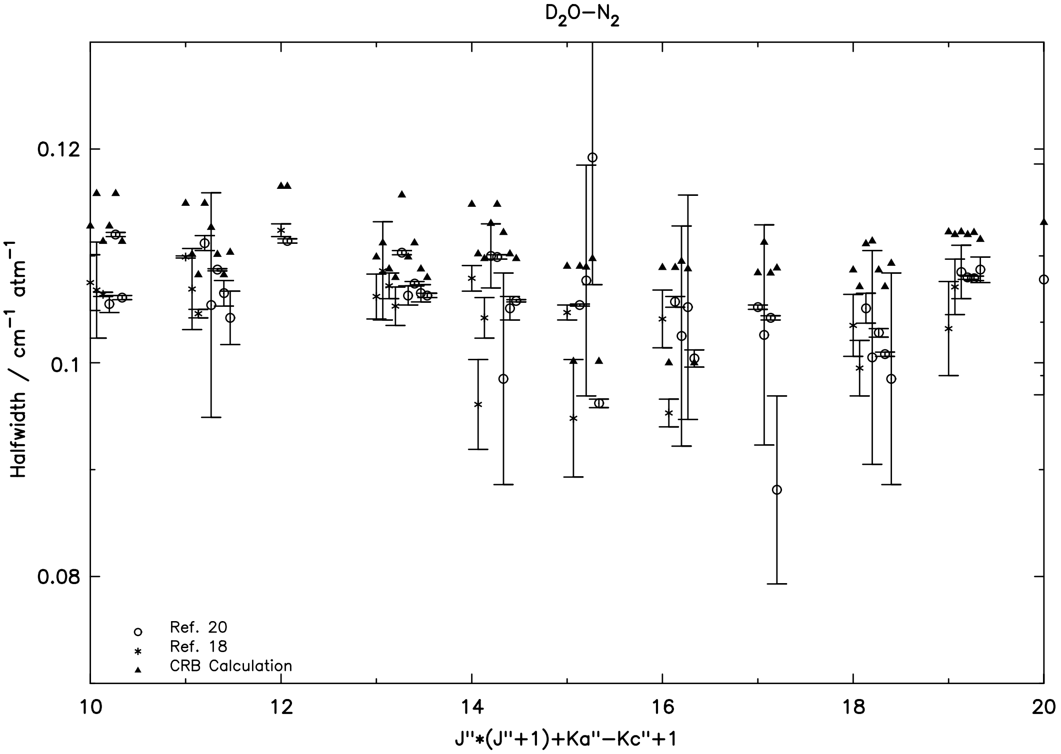

Fig. 4. Measured [18,20] and CRB calculated half-widths for the D_2O-N_2 system versus an energy-ordered index, J*(J+1)+Ka-Kc+1. The range of the *x*-axis was chosen to demonstrate the comparison of the data.

with error bars and the calculated half-widths (solid triangle symbols) versus a unique lower state rotational quantum number index, J*(J+1)+Ka-Kc+1. Because there can be multiple transitions from a lower rotational state to a number of upper rotational states, the points are shifted for each new transition with a given lower state index. This was done to allow better interpretation of the figures.

In Table 5, the calculations are compared with the measurement average for the systems studied. Presented are the number of measurements per transition, the number of transitions compared, the APD and AAPD for $H_2^{18}O$-N_2, HDO-N_2, and D_2O-N_2. This is of a similar format as Table 4 except that in Table 4 the APDs were necessarily zero. For the comparison with the average of pairs for $H_2^{18}O$-N_2 there are five transitions and the result shows an AAPD of 24%, roughly the same as the comparison of experiment with experiment. This is clear from Fig. 1 which shows three points from Ref. [17] which do not agree with the measurements of Ref. [10] or the calculations. The comparison with the average of pairs of measurements for 125 transitions for D_2O-N_2 gives an APD of −4.9% and an AAPD of 5.2%. These numbers are higher than the corresponding values in Table 4 indicating that the calculations are at least a few percent high. This is evident in Fig. 4.

For HDO-N_2 comparisons can be made with averages of 2, 3, and 4 measured points. There are 239 pair transitions for which the measurements were averaged. The comparison with the calculations shows −3.1 for the APD and 4.7 for the AAPD. There are 49 transitions for which three measured values are averaged to compare with the calculations. The APD and AAPD for this comparison

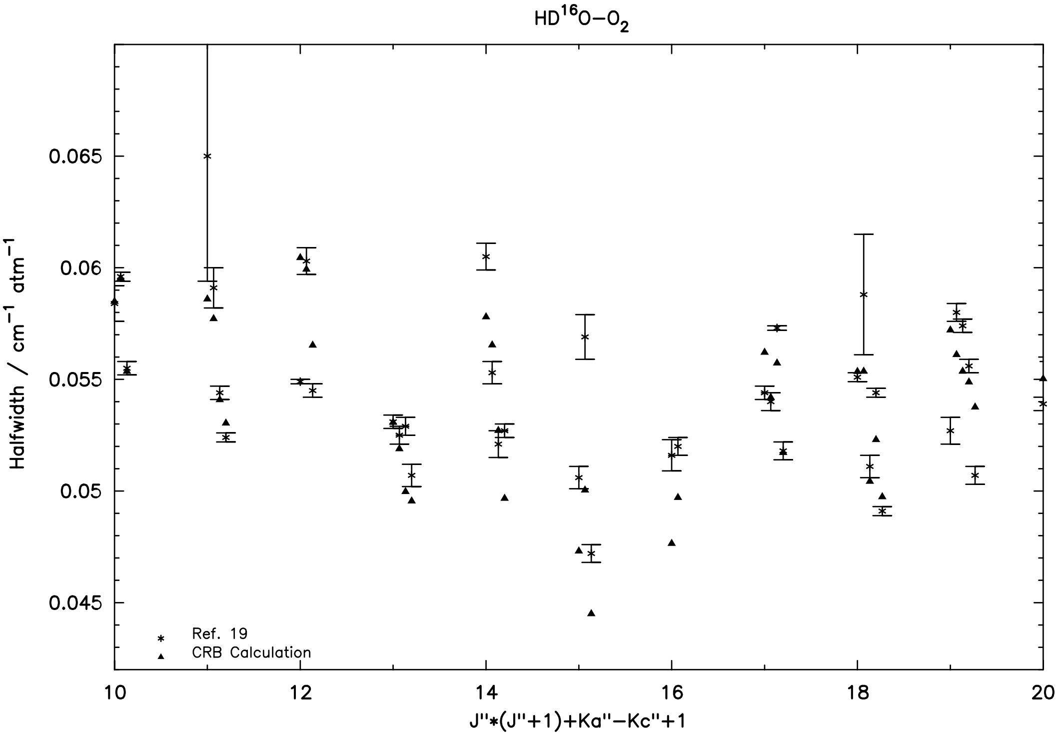

Fig. 5. Measured [19] and CRB calculated half-widths for the HDO-O$_2$ system versus an energy-ordered index, J*(J+1)+Ka-Kc+1. The range of the *x*-axis was chosen to demonstrate the comparison of the data.

are −7.5% and 7.9%, respectively. For the two 4-measurement averages the APD is −15 and the AAPD is 15. These values are comparable to those for the measurement–measurement comparisons, possibly indicating that the calculated half-widths are ∼1% too large on average.

Finally, in Table 6 the comparisons for the single measurement with the calculation are made for the systems considered here. For $H_2^{18}O$-N_2 the results are quite good, 355 transitions compared, APD equal to 0.74%, AAPD 6.4%. What is difficult to explain is that for $H_2^{17}O$-N_2 the results are not as good. There are only 61 transitions that are compared. The APD between measurement and calculation is −7.0 and the AAPD is 9.3. The measurements are mostly those of Toth [10] for which there are 21 transitions that he reports half-widths for both isotopomers, $H_2^{18}O$-N_2 and $H_2^{17}O$-N_2. Comparing Toth's measurements for the two isotopomers gives an APD of 0.03% and an AAPD of 4.6%. Thus, similar agreement is expected for the comparison of the $H_2^{18}O$-N_2 and $H_2^{17}O$-N_2 results. Perhaps the particular 61 transitions for $H_2^{17}O$-N_2 system are not as well calculated compared with the 355 transitions for $H_2^{18}O$-N_2 system.

For HDO the comparisons for N_2- and O_2-broadening are quite good, APD = −3.4% and 2.2%, respectively. For D_2O the comparisons give larger APDs, −6.8% and −7.8% for N_2- and O_2-broadening, respectively, indicating the calculations are too high. However, for nitrogen broadening the comparison with the 125 transitions that were measured by two groups [16,20] the AAPD drops to ∼5%. This fact is observed in Figs. 4 and 6.

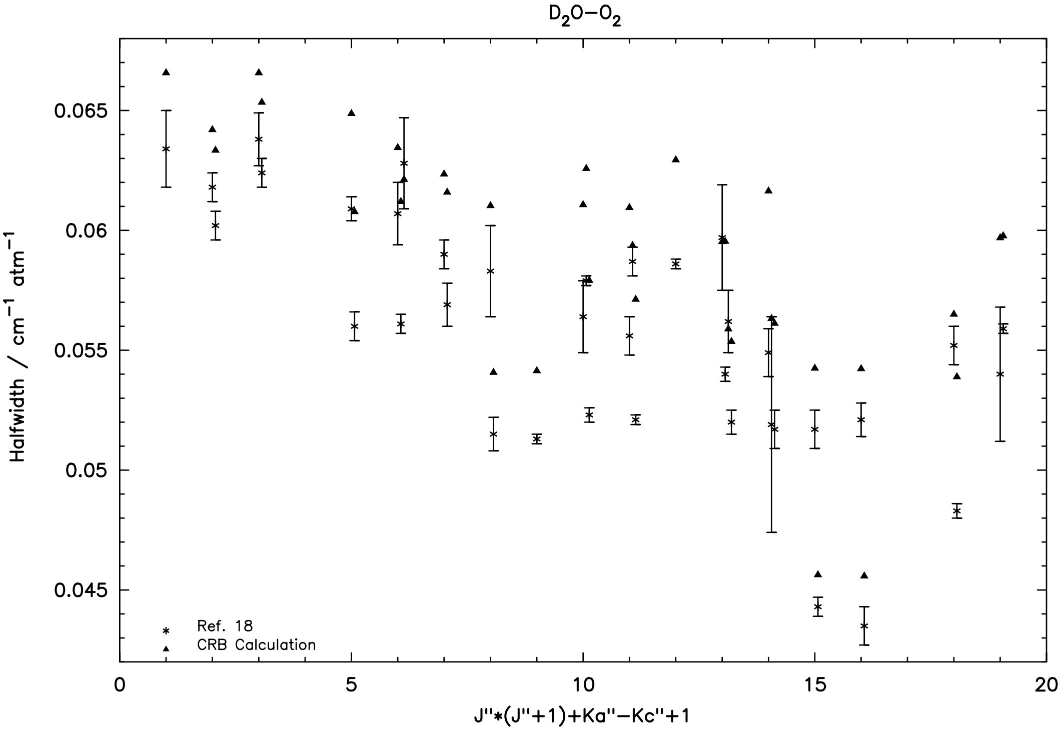

Fig. 6. Measured [18] and CRB calculated half-widths for the D_2O-O_2 system versus an energy-ordered index, J*(J+1)+Ka-Kc+1. The range of the *x*-axis was chosen to demonstrate the comparison of the data.

Table 5
Statistics for the comparison of CRB calculated values compared with multiple measurement average for half-widths for isotopomers of water vapor. AAPD ≡ average absolute percent difference, AAPD ≡ average absolute percent difference

# Measurements per transition	# Compared	$H_2^{18}O$-N_2 APD/AAPD	# Compared	HDO-N_2 APD/AAPD	# Compared	D_2O-N_2 APD/AAPD
2	5	12/24	239	−3.1/4.7	125	−4.9/5.2
3	0	—	49	−7.5/7.9	0	—
4	0	—	2	−15/15	0	—

5. Summary

CRB calculations of the pressure-broadened half-width were made for some two thousand v_2 band transitions of the lesser isotopomers of water vapor for which measured values are available. Comparisons were made for 365 transitions for the $H_2^{18}O$-N_2 system, 61 transitions for the $H_2^{17}O$-N_2 system, 990 and 266 transitions for the $HD^{16}O$-N_2 and -O_2 systems, respectively, and 545 and 134 transitions for the $D_2^{16}O$-N_2 and -O_2 systems, respectively. The atom–atom part of the intermolecular potential was adjusted for the principal isotopomers of water vapor from which the parameters for the lesser isotopomers species were determined by scaling by the H/D ratio. The authors feel that for

Table 6
Statistics for the comparison of CRB calculated values compared with a single measurement for half-widths for isotopomers of water vapor. AAPD ≡ average absolute percent difference, AAPD ≡ average absolute percent difference

System	# Compared	APD	AAPD
$H_2^{18}O$-N_2	355	0.74	6.4
$H_2^{17}O$-N_2	61	−7.0	9.3
HDO-N_2	375	−3.4	6.9
D_2O-N_2	295	−6.8	7.5
HDO-O_2	266	2.2	3.5
D_2O-O_2	134	−7.8	8.0

the lesser isotopomers there are not enough measurements by different groups to make adjustments to the atom–atom parameters at this time. The $H_2^{18}O$-N_2 and $H_2^{17}O$-N_2 systems employed the parameters of the $H_2^{16}O$-N_2 system.

The agreement of the calculations with the measurements was good, roughly on par with the agreement between different measurements. The figures and statistics suggest that the calculations for $H_2^{17}O$ broadened by N_2 may be ∼5% too high. The calculations for D_2O broadened by N_2 and O_2 appear to be ∼5% higher on average than measurement. The calculations for $HD^{16}O$-N_2 may be ∼1% too high compared with the measured values.

Before calculations of the half-width are made for many transitions of the isotopomers of water vapor to generate a database, a refinement of the atom–atom potential should be made. However, this will require that more measurements are made. Currently, only the $HD^{16}O$-N_2 system has had many measurements by several groups. The authors suggest that measurements of ν_2 band transitions be made for N_2- and O_2-broadening of transitions of $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$. For atmospheric applications D_2O can be left off the list; however, from the point of view of the theory it is interesting to compare calculations for HDO and D_2O.

Acknowledgements

The authors would like to thank Ms. Caroline Claude for preparing many of the files of measured half-widths. The authors are pleased to acknowledge support of this research by the National Science Foundation through Grant No. ATM-9415454. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

References

[1] Gamache RR, Fischer J. Half-widths of $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, and $D_2^{16}O$: I Comparison between isotopomers. JQSRT 2003; this issue.

[2] Rothman LS, Rinsland CP, Goldman A, Massie ST, Edwards DP, Flaud J-M, Perrin A, Dana V, Mandin J-Y, Schroeder J, McCann A, Gamache RR, Wattson RB, Yoshino K, Chance KV, Jucks KW, Brown LR, Nemtchinov V, Varanasi P. The HITRAN molecular spectroscopic database and hawks (HITRAN atmospheric workstation): 1996 ed. JQSRT 1998;60:665–710.

[3] Jacquinet-Husson N, Arié E, Ballard J, Barbe A, Bjoraker G, Bonnet B, Brown LR, Camy-Peyret C, Champion J-P, Chédin A, Chursin A, C1erbaux C, Duxbury G, Flaud J-M, Fourrié N, Fayt A, Graner G, Gamache RR, Goldman A, Go1ovko Vl, Guelachvili G, Hartmann J-M, Hilico JC, Hillman J, Lefèvre G, Lellouch E, Mikhailenko SN, Naumenko OV, Nemtchinov V, Newnham DA, Nikitin A, Orphal J, Perrin A, Reuter DC, Rinsland CP, Rosenmann L, Rothman LS, Scott NA, Selby J, Sinitsa LN, Sirota JM, Smith MAH, Smith KM, Tyuterev VlG, Tipping RH, Urban S, Varanasi P, Weber M. The 1997 spectroscopic GEISA databank. JQSRT 1999;62:205–54.

[4] Wang WF. Atomic-potential parameters for H_2 and D_2: quantum corrections in the calculation of second virial coefficients. JQSRT; in press, 2003.

[5] Hirschfelder JO, Curtiss CF, Bird RB. Molecular theory of gases and liquids. New York: Wiley, 1964.

[6] Diaz Pena M, Pando C, Renuncio JAR. Combination rules for intermolecular potential parameters. I. Rules based on approximations for the long-range dispersion energy. J Chem Phys 1982;76:325–32.

[7] Diaz Pena M, Pando C, Renuncio JAR. Combination rules for intermolecular potential parameters. II. Rules based on approximations for the long-range dispersion energy and an atomic distortion model for the repulsive interactions. J Chem Phys 1982;76:333–9.

[8] Good RJ, Hope CJ. Test of combining rules for intermolecular distances, potential function constants from second virial coefficients. J Chem Phys 1971;55:111–6.

[9] Gamache RR, Hartmann JM, Rosenmann L. Collisional broadening of water-vapor lines: I. A survey of experimental results. JQSRT 1994;52:481–99.

[10] Toth RA. Air- and N_2-broadening parameters of water vapor: 604 to 2271 cm^{-1}. J Mol Spec 2000;201:218–43.

[11] Zou Q, Varanasi P. Laboratory measurement of the spectroscopic line parameters of water vapor in the 950–2100 and 3000–4050 cm^{-1} regions at lower-tropospheric temperatures. JQSRT, 2002; in press.

[12] Schermaul R, Learner RCM, Newnham DA, Williams RG, Ballard J, Zobov NF, Belmiloud D, Tennyson J. The water vapor spectrum in the region 8600–15 000 cm^{-1}: experimental and theoretical studies for a new spectral line database I. Laboratory measurements. J Mol Spec 2001;208:32–42.

[13] Schermaul R, Learner RCM, Newnham DA, Ballard J, Zobov NF, Belmiloud D, Tennyson J. The water vapor spectrum in the region 8600–15 000 cm^{-1}: experimental and theoretical studies for a new spectral line database II. Linelist construction. J Mol Spec 2001;208:43–50.

[14] Coheur PF, Fally S, Carleer M, Clerbaux C, Colin R, Jenouvrier A, Mérienne MF, Hermans C, Vandaele AC. New water vapor line parameters in the 26 000–13 000 cm^{-1} region. JQSRT 2001;74:493–510.

[15] Steyert DW, Wang WF, Sirota JM, Donahue NM, Reuter DC. Pressure broadening coefficients for rotational transitions of water in the 380–600 cm^{-1} range. JQSRT 2002;72:775–82.

[16] Devi V Malathy, Rinsland CP, Benner DC, Smith MAH. Tunable diode laser measurements of air and N2 broadened half-widths in the v_2 band of D_2O. Applied Optics 1986;25:336–38.

[17] Devi VM, Benner DC, Rinsland CP, Smith MAH, Barry DS. Diode laser measurements of air and nitrogen broadening in the nu2 bands of HDO, $H_2^{16}O$ and $H_2^{18}O$. J Mol Spec 1986;117:403–7.

[18] Rinsland CP, Smith MAH, Devi VM, Benner DC. Measurements of Lorentz-broadening coefficients and pressure-induced line shift coefficients in the nu2 band of D216O. J Mol Spec 1991;150:173–83.

[19] Smith MAH, Rinsland CP, Devi VM, Benner DC. Measurements of Lorentz-broadening coefficients and pressure induced line shift coefficients in the nu2 band of HD16O. J Mol Spec 1991;150:640–6.

[20] Toth RA. Air and N2 broadening parameters of HDO and D2O; 709 to 1936 cm^{-1}. J Mol Spec 1999;198:358–70.

[21] Robert D, Bonamy J. Short range force effects in semiclassical molecular line broadening calculations. J Phys 1979;40:923–43.

[22] Lennard-Jones JE. On the determination of molecular fields.-II From the equation of state of a gas. Proc Roy Soc 1924;A106:463–77.

[23] Neshyba SP, Lynch R, Gamache RR, Gabard T, Champion J-P. Pressure-induced widths and shifts for the $v3$ band of methane. J Chem Phys 1994;101:9412–21.

[24] Oka T. In: Bates DR, editor. Advances in atomic and molecular physics. New York: Academic Press, 1973.

[25] Baranger M. General impact theory of pressure broadening. Phys Rev 1958;112:855–65.

[26] Ben-Reuven A. Spectral line shapes in gases in the binary-collision approximation. In: Prigogine I, Rice SA, editors. Advances in Chemical Physics, vol. 20. New York: Academic Press, 1975. p. 235.

[27] Gamache RR, Lynch R, Neshyba SP. New developments in the theory of pressure-broadening and pressure-shifting of spectral lines of H_2O: the complex Robert–Bonamy formalism. JQSRT 1998;59:319–35.

[28] Neshyba SP, Gamache RR. Improved line-broadening coefficients for asymmetric rotor molecules with application to ozone lines broadened by nitrogen. JQSRT 1993;50:443–53.

[29] While there are a number of forms for the "combination" rules, see Refs. [5–8] for details, we have chosen the method of Ref. [5].

[30] Labani B, Bonamy J, Robert D, Hartmann J-M, Taine J. Collisional broadening of rotation-vibration lines for asymmetric top molecules. I. Theoretical model for both distant and close collisions. J Chem Phys 1986;84: 4256–67.

[31] Lynch R, Gamache RR, Neshyba SP. N_2 and O_2 induced halfwidths and line shifts of water vapor transitions in the $(301) \leftarrow (000)$ and $(221) \leftarrow (000)$ bands. JQSRT 1998;59:595–613.

[32] Lynch R, Ph.D. Dissertation, Physics Department, University of Massachusetts, Lowell, June 1995.

[33] Shostak SL, Muenter JS. The dipole moment of water. II. Analysis of the vibrational dependence of the dipole moment in terms of a dipole moment function. J Chem Phys 1991;94:5883–90.

[34] Flygare WH, Benson RC. Molecular Zeeman effect in diamagnetic molecules and the determination of molecular magnetic moments (g values), magnetic susceptibilities, and molecular quadrupole moments. Mol Phys 1971;20: 225–50.

[35] Mulder F, Van Dijk G, Van der Avoird A. Multipole moments, polarizabilities, and anisotropic long range interaction coefficients for nitrogen. Mol Phys 1980;39:407–25.

[36] Stogryn DE, Stogryn AP. Molecular multipole moments. Mol Phys 1966;11:371–93.

[37] Lide DR, editor. CRC handbook of physics and chemistry, 77th ed. Cleveland, OH: The Chemical Rubber Company, 1996.

[38] Bogaard MP, Orr BJ. MPT international review of science, physical chemistry, series two. In: Buckingham AD, editor. Molecular structure and properties, vol. 2. London: Butterworths, 1975 [chapter 5].

[39] Lofthus A. The molecular spectrum of nitrogen. Department of Physics, University of Oslo, Blindern, Norway, Spectroscopic Report No. 2, 1960.

[40] Watson JKG. Determination of centrifugal distortion coefficients of asymmetric-top molecules. J Chem Phys 1967;46:1935–49.

[41] Flaud J-M, Camy-Peyret C. Private communication. University of Pierre and Marie Curie, Paris, France, 1994.

[42] Toth RA. $HD^{16}O$, $HD^{18}O$, $HD^{17}O$ transition frequencies and strengths in the nu2 bands. J Mol Spec 1993;162: 20–40.

[43] Toth RA. $D_2^{16}O$ and $D_2^{18}O$ transition frequencies and strengths in the nu2 Bands. J Mol Spec 1993;162:41–54.

[44] Huber KP, Herzberg G. Molecular spectra and molecular structure constants of diatomic molecules. New York: Van Nostrand, 1979.

[45] Hartmann J-M, Gamache RR. A survey of measured half-widths and line shifts of water vapor, manuscript in preparation, 2002.

[46] Grossmann BE, Browell EV. J Mol Spec 1989;138:562–95.

[47] Mandin J-Y, Chevillard JP, Flaud JM, Camy-Peyret C. J Mol Spec 1989;138:430–9.

[48] Mandin J-Y, Chevillard JP, Camy-Peyret C, Flaud J-M. J Mol Spec 1989;138:272–81.

[49] Mandin J-Y, Chevillard JP, Flaud J-M, Camy-Peyret C. J Mol Spec 1988;132:352–60.

[50] Devi VM, Benner DC, Smith MAH, Rinsland C. J Mol Spec 1992;155:333–42.

[51] Lepere M, Henry A, Valentin A, Camy-Peyret C. J Mol Spec 2001;208:25–31.

[52] Claveau C, Henry A, Hurtmans D, Valentin A. Narrowing and broadening parameters of H_2O lines perturbed by He, Ne, Ar, Kr and nitrogen in the spectral range 1850–2140 cm^{-1}. JQSRT 2001;68:273–98.

[53] Bouanich J-P. Site-site Lennard–Jones potential parameters for nitrogen, oxygen, hydrogen, carbon monoxide and carbon dioxide. JQSRT 1992;47:243–50.

[54] Brown L, Toth RL. Jet Propulsion Laboratory, Pasadena, CA, private communication, 1999.