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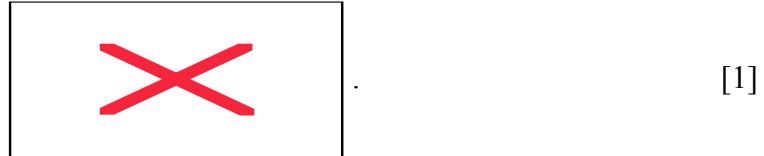
Line-Shape Parameters for Water Vapor in the 3.2-17.76 μm Region.

The focus of this theoretical study is to update the molecular line shape parameters in the HITRAN compilation for water and methane in the spectral regions important for AIRS, TES and HIRDLS. In the second year, we continued the calculations of the collision-broadened half-width and collision-induced line shift of water vapor lines in the 3.2-17.76 μm region. The water vapor transitions in the region 563-3125 cm^{-1} for the principal isotopologue of water vapor and transitions with $J \leq 18$ (5442 transitions) were extracted from the HITRAN database. The data were separated into the different vibrational bands, which are listed in Table 1 along with the number of transitions for the band in the selected wavenumber region. From these files the rotational quantum numbers were extracted to create lists to use in the CRB calculations.

The calculations for nitrogen-broadening of water vapor were redone using an improved intermolecular potential. Six transitions were chosen for which there are multiple measurements [1-9] 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 [10] using the combination rules [11]. 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} . These potential parameters were then further refined for transitions in the v_2 band the final values are

presented in Table 2. Note, a full least-squares minimization was not thought worthwhile until the work of Ref. 12 is completed. For oxygen broadening of H₂¹⁶O there are not multiple measurements to allow fitting to an average. A similar procedure to that used for H₂O-N₂ with some of the data from Ref. 13 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.

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 gas were obtained assuming binary collisions and Dalton's law



This was done for both temperatures of the study.

The data files for each band for nitrogen and oxygen as the perturbing gas were taken at each temperature and Eq. (1) applied to determine the air-broadened half-width and line shift at 225 K and 296 K. These data were then used to determine the temperature dependence of the air-broadened half-widths via the usual power law form

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

where the reference temperature T₀ is usually taken as 296K but is not restricted to that value.

The CRB half-width data were compared to the water vapor databases of line shape parameters (12). Comparisons were made between measurement and calculation

for cases where multiple measurements and single measurements exist for the same ro-vibrational transition. The results of the comparisons are given in Tables 3-5 for each vibrational band studied and for N₂-, O₂-, and air broadening of water vapor, respectively. Note that for many of the bands there are no measured data. In general the agreement between measurement and calculation is quite good especially considering the results of an intercomparison of measured half-widths recently published (12). The average percent difference between the measured and calculated half-widths is -1.97, 2.6, and -1.55 for N₂-, O₂-, and air-broadening of water vapor, respectively. While these numbers are good it should be realized they contain cancellation, when there are a large number of comparisons the standard deviations are in general between 5 and 10 percent.

In addition, plots were made comparing the CRB calculated value of the half-width with measurements for each ro-vibrational transition where two or more measurements were made. A note here about the databases, often there are pairs of measured data for a particular ro-vibrational transition however one will be for the principal isotopologue and the other for one of the other isotopologues. Thus, there are a number of plots with only one measured point and the CRB point.

Self-broadening calculations have been made employing the real components of the Robert-Bonamy formalism. This in effect neglects the vibrational dephasing terms. Hence the calculations neglect vibrational dependence at this stage. The list of transitions in this region was used to extract the set of unique rotational transitions. This yielded 3096 transitions for which calculations were made for self-broadening of water vapor in the (000)↔(000) and (010)↔(000) bands. Note, these calculations only employed the real terms of the intermolecular potential and the atom-atom potential expanded to 4th

order via the method of Labani et al. [14] The calculations were made at 296 K for the transitions for both bands.

These data have been collected into data files and given to Dr. Larry Rothman to be merged later with the measured half-widths for addition to the HITRAN database. These data are also available on the web site of the author (www.uml.edu/faculty/Robert_Gamache).

The calculations of nitrogen-broadened half-widths of methane have begun. Test calculations were made for a number of transitions and the results confirmed the codes work properly. We are currently getting better wavefunctions to start making the necessary calculations. We are also working on the codes to make complex Robert-Bonamy calculations for self-broadening of water vapor.

A manuscript of the work on N₂-, O₂-, and air-broadening of water vapor in the 3.2-17.76 μm region is in progress and a paper on this work will be delivered at the 2004 HITRAN meeting in June.

References

- [1] Grossmann BE and Browell EV, J Mol Spec 1989;138: 562-95.
- [2] Mandin, J-Y, Chevillard JP, Flaud JM, and Camy-Peyret C, J Mol Spec 1989;138: 430-39.
- [3] Mandin J-Y, Chevillard JP, Camy-Peyret C, and Flaud J-M, J Mol Spec 1989;138: 272-81.

- [4] Mandin J-Y, Chevillard JP, Flaud J-M, and Camy-Peyret C, *J Mol Spec* 1988;132: 352-60.
- [5] Devi V Malathy, Benner DC, Smith MAH, and Rinsland C, *J Mol Spec* 1992;155: 333-42.
- [6] Lepere M, Henry A, Valentin A, and Camy-Peyret C, *J Mol Spec* 2001;208: 25-31.
- [7] Toth RA, Air- and N₂-Broadening Parameters of Water Vapor: 604 to 2271 cm⁻¹. *J Mol Spec* 2000;201: 218-43.
- [8] Coheur, P. F., Fally, S., Carleer, M., Clerbaux, C., Colin, R., Jenouvrier, A., Mérienne, M. F., Hermans, C., Vandaele, A. C., New water vapor line parameters in the 26000–13000 cm⁻¹ region, *JQSRT* 2001;74: 493-510.
- [9] Claveau C, Henry A, Hurtmans D, and Valentin A, Narrowing and broadening parameters of H₂O lines perturbed by He, Ne, Ar, Kr and nitrogen in the spectral range 1850-2140 cm⁻¹, *JQSRT* 2001;68: 273-98.
- [10] Bouanich J-P. Site-site Lennard-Jones potential parameters for nitrogen, oxygen, hydrogen, carbon monoxide and carbon dioxide. *JQSRT* 1992;47: 243-50.
- [11] Hirschfelder JO, Curtiss CF, and Bird RB, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1964.
- [12] Robert R. Gamache and Jean-Michel Hartmann, An intercomparison of measured pressure-broadening and pressure-shifting parameters of water vapor, *J. Can. Chem.*, in press 2004.
- [13] Brown L and Toth RL, Jet Propulsion Laboratory, Pasadena, CA, private communication, 1999.

- [14] Labani B, Bonamy J, Robert D, Hartmann J-M, and 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.

Table 1. Number of H₂¹⁶O transitions in the 3.2 to 17.76 μm region

v ₁ 'v ₂ 'v ₃ '	v ₁ ''v ₂ ''v ₃ ''	# 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

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

Atomic pair	$\sigma/\text{Angstrom}$	$\varepsilon/k_B \text{ (}^{\circ}\text{K)}$
H-N	2.99	20.46
O-N	3.148	43.9
H-O	2.565	24.13
O-O	3.010	51.73

Table 3. Comparison of the CRB calculations with measurement for N₂-broadening of water vapor transitions in the 3.2 to 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 _{Exp} =1		N _{Exp} >1	
		# lines	% error	# 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		
030	020				
001	010	27	-0.70		
020	000				
030	010				
100	000				
001	000				

Table 4. Comparison of the CRB calculations with measurement for O₂-broadening of water vapor transitions in the 3.2 to 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 _{Exp} =1		N _{Exp} >1	
		# lines	% error	# lines	% error
000	000	1	6.59		
010	010				
010	000	349	1.82	24	15.75
020	010	3	-12.92		
100	010				
030	020				
001	010				
020	000				
030	010				
100	000				
001	000				

Table 5 Comparison of the CRB calculations with measurement for air broadening of water vapor transitions in the 3.2 to 17.76 μm region at 296 K.

$v_1'v_2'v_3'$	$v_1''v_2''v_3''$	H ₂ O-air			
		$N_{\text{Exp}}=1$		$N_{\text{Exp}}>1$	
		# lines	% error	# 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		
030	020				
001	010	27	-2.36		
020	000	9	1.09	2	-1.42
030	010				
100	000	1	-0.37		
001	000				