

# Modified complex Robert–Bonamy formalism calculations for strong to weak interacting systems

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In 1979 Robert and Bonamy published a complex formalism (CRB) for the calculations of the pressure broadened half-width and collision-induced line shifts [J. Phys. Paris **40**, 923 (1979)]. Application of the linked cluster theorem produced expressions that no longer needed the cut-off procedure that plagued earlier line shape theories. Recently, Ma, Tipping and Boulet (MTB) suggested that the application of the linked cluster theorem in their derivation of Robert and Bonamy was based on an invalid assumption. In their work MTB gave the modified expressions and state that the effect of the modification is more important for strong interaction systems. Here the effect of the MTB modification on the formalism of Robert and Bonamy is studied for systems which range in interaction strength from strong to weak. In particular, complex Robert–Bonamy calculations and calculations based on the modified formalism are made in the mean-relative thermal velocity approximation for the systems H<sub>2</sub>O–H<sub>2</sub>O, H<sub>2</sub>O–N<sub>2</sub>, H<sub>2</sub>O–O<sub>2</sub>, O<sub>3</sub>–N<sub>2</sub>, O<sub>3</sub>–O<sub>2</sub>, and CH<sub>4</sub>–N<sub>2</sub> and the results from the formalisms compared for both the pressure-broadened half-width and pressure-induced line shift. The results of the two methods of computation are compared with the measurement database. It is shown that the difference between the two methods of computation is proportional to the strength of the radiator–perturber interaction and for some systems is larger than the uncertainty desired by the spectroscopy and remote sensing communities. Comparison with the measurement database shows better agreement with the CRB calculations.

## 1. Introduction

Even though enormous scientific and technological developments have been achieved in space research, the knowledge of our own atmosphere is far from complete. Remote spectroscopic observation of Earth's atmosphere can yield information such as concentration, temperature and pressure profiles and can help in unravelling the chemistry and dynamics of the atmosphere. However, to extract this information from the measurements requires that the basic spectroscopic parameters (namely line position, intensities, half-widths, and line shifts [1]) of the gases present in the atmosphere be known. While the line parameters are correlated in the retrieval process, the line positions and intensities have small uncertainties compared with the half-width and line shift. This work focuses on the half-width and line shift.

The spectroscopic and remote sensing communities [2–5] have determined that for accurate retrievals of concentration profiles the half-width and its temperature dependence should be known with uncertainty less than 3% for strong lines and 10% for weak lines. The effect of uncertainty in half-widths on the accuracy of retrieved concentration profiles depends on the molecule and altitude [6–9] and is a major source of uncertainty in the resulting concentration profile, especially in the lower atmosphere. It is now known that the effect of the line shift on reducing data from remote sensing measurements can be significant [10–12].

For many years, the Complex Robert–Bonamy (CRB) formalism has been successful in predicting the half-width and line shift for self- and foreign-broadened spectral lines of many molecular systems. A series of improvements in the potential, trajectory models, and wave functions used in this method have been realized, however, the basic theory has remained unchanged. Recently Ma *et al.* (MTB) [13] suggested that there was a subtle error in the original CRB theoretical formulation.

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According to the authors, the modification to the existing theory will show deviations compared with CRB formalism proportional to the strength of the interaction between the colliding molecules. Thus two questions arise: (1) what are the effects of the modification proposed by MTB on the pressure-broadened half-width? and (2) does the proposed formalism agree better with measurement?

The error results from Robert and Bonamy's application of the cumulant expansion (a core part of the Linked-Cluster expansion) to evaluate the Liouville matrix element  $\langle\langle j_2 i_2 | S | j_2 i_2 \rangle\rangle$ . While the matrix elements appear to be diagonal, a requirement to be a proper average in applying the cumulant expansion, MTB found by decomposing the Liouville matrix element into its two Hilbert matrix elements that the matrix elements are not diagonal in Hilbert space. Therefore, the cumulant expansion is not applicable to  $\langle\langle j_2 i_2 | S | j_2 i_2 \rangle\rangle$ . They found that by choosing an average over the internal degrees of the bath molecule as the average in the cumulant expansion, one is able to apply this expansion correctly. The new formulas for half-width ( $\gamma$ ) and line shift ( $\delta$ ) are given in [13] and below.

In this article a variety of strong to weak (here, the notion of strong and weak interaction systems adopts the definition of Oka [14]) interacting molecular systems have been studied ( $\text{H}_2\text{O}-\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}-\text{N}_2$ ,  $\text{H}_2\text{O}-\text{O}_2$ ,  $\text{O}_3-\text{N}_2$ ,  $\text{O}_3-\text{O}_2$  and  $\text{CH}_4-\text{N}_2$ ). The deviations between the CRB formalism and that of Ma *et al.* [13], hereafter called the modified-CRB (MCRB) formalism, are studied. Finally, a comparison with measurements is presented.

## 2. Complex Robert–Bonamy formalism

### 2.1. The general theory

The present calculations are based on the CRB formalism [15] and the new modification due to Ma *et al.* [13]. Here we discuss the salient features of the CRB theory and briefly introduce the modification proposed by MTB. In the CRB approach the half-width and line shifts for a ro-vibrational transition  $f \leftarrow i$  are calculated by the real and imaginary part of the expression,

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

where,  $n_2$  is the number density of perturbers and  $\langle \cdots \rangle_{v, b, J_2}$  is the average over all trajectories (with impact

parameter  $b$  and initial relative velocity  $v$ ) and initial rotational state  $J_2$  of the collision partner. The real  $S_1$  and complex  $S_2 = {}^R S_2 + i {}^I S_2$  are the first- and second-order terms in the expression 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 [16–18].

In the CRB formalism two important features have been incorporated; elimination of the cut-off procedure and better modelling of close collisions. The cut-off procedure adopted by earlier theories [19] was eliminated by the use of linked-cluster techniques [20]. The close intermolecular collisions (small  $b$ ) are now very well defined by (a) the dynamics, which is second order in time, produce curved trajectories based on the isotropic part of the intermolecular potential, and (b) the short range (Lennard–Jones) atom–atom potential, which is an important component for a proper description of pressure broadening, especially in the case of weakly interacting molecules.

The present calculation for the line shape parameters uses the mean relative thermal velocity ( $\bar{v}$ ) approximation (mrtv). Most previous calculations used this method. The reason for using this approximation is the long time taken to perform the averaging over the Boltzmann distribution of velocities. It is estimated that the mrtv approximation gives results 30–50 times faster at  $\sim 300$  K with a difference of a few percent in the velocity averaged results for the systems considered here [21].

### 2.2. The potential

The  $S_1$  term (a purely imaginary part) of equation (1) is isotropic in the absence of any vibrational dependence of the anisotropic intermolecular forces. It is called the vibrational dephasing term and arises only for transitions where there is a change in the vibrational state. The potential leading to  $S_1$  is given in terms of the isotropic induction and London dispersion interactions:

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

and

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

where  $\mu_1$  is the dipole moment of the radiator molecule and  $\alpha_k$  and  $I_k$  are the polarizability and ionization

potential of the radiator ( $k=1$ ) and perturber ( $k=2$ ). For water vapour the vibrational dependence of equations (2) and (3) is contained in  $\mu_1$  (by Shostak and Muentner [22] in Debyes) and  $\alpha_k$  (by Luo *et al.* [23] in au) given respectively as

$$\mu = 1.855 + 0.0051 \left( \nu_1 + \frac{1}{2} \right) - 0.0317 \left( \nu_2 + \frac{1}{2} \right) + 0.0225 \left( \nu_3 + \frac{1}{2} \right) \quad (4)$$

and

$$\alpha = 9.89 + 0.29 \left( \nu_1 + \frac{1}{2} \right) - 0.03 \left( \nu_2 + \frac{1}{2} \right) + 0.28 \left( \nu_3 + \frac{1}{2} \right) \quad (5)$$

with  $\nu_n$  the number of quanta in the  $n$ th normal mode. Similar expressions are obtained for CH<sub>4</sub> from Raynes *et al.* [24].

The complex valued  $S_2 = {}^R S_2 + i {}^I S_2$  results from the anisotropic interaction potential with leading electrostatic components and atom–atom terms. The atom–atom potential is defined as the sum of pair-wise Lennard–Jones 6–12 [25] interactions between atoms of the radiating and perturbing molecules given by

$$V^{at-at} = \sum_{i=1}^n \sum_{j=1}^m 4\varepsilon_{ij} \left\{ \frac{\sigma_{ij}^{12}}{r_{1i2j}^{12}} - \frac{\sigma_{ij}^6}{r_{1i2j}^6} \right\} \quad (6)$$

where  $n$  and  $m$  are the number of atoms in molecules 1 and 2 and the subscripts  $1i$  and  $2j$  stands for the  $i$ th atom of molecule 1 and  $j$ th atom of molecule 2, respectively.  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are the Lennard–Jones parameters for the atomic pairs. The heteronuclear atom–atom parameters are constructed from the homonuclear atom–atom parameters ( $\varepsilon_i$  and  $\sigma_j$ ) by the combination rules of Hirschfelder *et al.* [26] or Good and Hope [27]. The atom–atom distance  $r_{ij}$  is expressed as an expansion of the inverse of centre of mass separation,  $R$  given by Sack [28]. As this expansion is truncated, sufficient order must be taken to ensure the convergence of calculated half-widths and line shifts [29]. In the present case we find that  $\gamma$  and  $\delta$  are converged using an 8th-order expansion of the atom–atom potential. The values for the homonuclear atom–atom parameters ( $\varepsilon_i$  and  $\sigma_j$ ) are shown in table 1.

### 2.3. The wavefunctions

For water vapour and ozone, the reduced matrix elements are evaluated using the wavefunctions determined

by diagonalizing the Watson Hamiltonian [30] in a symmetric top basis for the vibrational states involved in the transition. For water vapour the Watson constants for the ground vibrational state are from Matsushima *et al.* [31], those for  $\nu_1, \nu_2, \nu_3$  are from Flaud and Camy-Peyret [32] and those for  $3\nu_2$  from Camy-Peyret and Flaud [33]. The Watson constants for ozone are from the University of Reims database [34]. In the case of CH<sub>4</sub> the wavefunction from Gabard and Champion [35] has been employed.

Most of the molecular parameters used here for the radiator–perturber pairs are well known and incorporate the best available values from the literature. The multipole moments, rotational constants, polarizability and ionization potential (IP) employed here with their references are given in table 2 for the radiating molecules and in table 3 for the perturbing molecules.

Table 1. Atom–atom parameters.

Atomic pair	H–H	H–O	O–O	H–N	N–O	C–N
$\sigma$ (Å)	2.683	2.565	3.010	2.990	3.148	3.45
$\varepsilon/k_B$ (K)	11.25	24.13	51.73	20.46	43.90	34.3

Table 2. Molecular parameters of the radiating molecules; references in square brackets.

Molecule	Moments <sup>†</sup> ( $10^{-26}$ esu)	IP (eV)
H <sub>2</sub> O	$\mu = 1.8549 \times 10^8$ [22] $Q_{xx} = -0.13$ [36] $Q_{yy} = -2.5$ [36] $Q_{zz} = 2.63$ [36]	12.612 [37]
O <sub>3</sub>	$\mu = 0.532 \times 10^8$ [38] $Q_{xx} = -1.4$ [38] $Q_{yy} = -0.7$ [38] $Q_{zz} = 2.1$ [38]	12.430 [37]
CH <sub>4</sub>	$\Omega = 2.6 \times 10^{-8}$ [39] $\Phi = 4.8 \times 10^{-16}$ [40]	12.598 [37]

<sup>†</sup>Dipole ( $\mu$ ), quadrupole ( $Q$ ), octupole ( $\Omega$ ), and hexadecapole ( $\Phi$ ).

Table 3. Molecular parameters of the perturbing molecules; references in square brackets.

Molecule	Quadrupole moments ( $10^{-26}$ esu)	Rotational constant ( $\text{cm}^{-1}$ )	Polarizability ( $10^{-26}$ cm <sup>3</sup> )	IP (eV)
N <sub>2</sub>	$Q_{zz} = -1.4$ [41]	2.0069 [42]	17.4 [43]	15.576 [44]
O <sub>2</sub>	$Q_{zz} = -0.4$ [45]	1.4377 [42]	15.8 [43]	12.063 [37]

#### 2.4. Modification to the CRB formalism

The basic theory as described above remains the same for the modified version of CRB. The difference arises in the averaging over  $J_2$  states. In their paper, MTB have shown that the application of the linked cluster theorem in their derivation of Robert and Bonamy was based on the invalid assumption that the cumulant expansion can be used to evaluate the Liouville matrix element  $\langle\langle j_2 i_2 | \hat{S} | j_2 i_2 \rangle\rangle$  and can be equated to  $\exp\{-iS_1^{(C)} - S_2^{(C)}\}$ . The assumption seems valid as this matrix element appears to be diagonal, satisfying the requirement to be a proper average in applying the cumulant expansion. However, a closer look at the matrix elements shows that they are not diagonal in Hilbert space. This problem is corrected by choosing an average over the internal degrees of the perturbing molecule as the average in the cumulant expansion. In the MTB formulation for the half-widths and line shifts, the averages over the perturber angular momentum quantum number,  $J_2$ , are carried out on the functions  $S_1$  and  $S_2$ , instead of over the exponential function  $\exp\{-iS_1 - S_2\}$ . MTB state that the effect of this correction is more important for strong interaction systems.

To compare the differences between these two formulations, the real and imaginary part of the CRB equation (1) give  $\gamma$  and  $\delta$  in the mrtv approximation as,

$$\gamma = \frac{n_2 \bar{v}}{2\pi c} \int_0^{+\infty} 2\pi b db \langle 1 - \cos\{S_1 + \text{Im}S_2\} \exp\{-\text{Re}S_2\} \rangle_{J_2} \quad (7)$$

and

$$\delta = \frac{n_2 \bar{v}}{2\pi c} \int_0^{+\infty} 2\pi b db \langle \sin\{S_1 + \text{Im}S_2\} \exp\{-\text{Re}S_2\} \rangle_{J_2} \quad (8)$$

The formulation suggested by MTB gives the half-widths and line shifts as,

$$\gamma_m = \frac{n_2 \bar{v}}{2\pi c} \int_0^{+\infty} 2\pi b db [1 - \cos\{\langle S_1 \rangle_{J_2} + \text{Im}\langle S_2 \rangle_{J_2}\} \times \exp\{-\text{Re}\langle S_2 \rangle_{J_2}\}] \quad (9)$$

and

$$\delta_m = \frac{n_2 \bar{v}}{2\pi c} \int_0^{+\infty} 2\pi b db [\sin\{\langle S_1 \rangle_{J_2} + \text{Im}\langle S_2 \rangle_{J_2}\} \times \exp\{-\text{Re}\langle S_2 \rangle_{J_2}\}] \quad (10)$$

where the averaging over  $J_2$  is done individually for  $S_1$  and  $S_2$  rather than for the exponential function as in equations (7) and (8).

#### 3. Calculations

Calculations were performed using the CRB formalism and the MCRB formalism for a number of vibrational bands for several systems at 296 K to determine the half-widths and line shifts using the equations (7) and (8) and equations (9) and (10), respectively. For self-broadening of water vapour, calculations have been performed for 499 rotational transitions in eight vibrational bands. In the case of  $\text{H}_2\text{O}-\text{N}_2$  and  $\text{H}_2\text{O}-\text{O}_2$  systems, half-widths and line shifts for 5442 rotational transitions were calculated in 11 vibrational bands. Calculations for 254 transitions in two vibrational bands for both  $\text{O}_3-\text{N}_2$  and  $\text{O}_3-\text{O}_2$  and finally 352 transitions in the  $\nu_3$  band for  $\text{CH}_4-\text{N}_2$  system were carried out.

#### 4. Results and discussion

The CRB formalism and that of MTB are used to calculate half-width and line shift for  $\text{H}_2\text{O}-\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}-\text{N}_2$ ,  $\text{H}_2\text{O}-\text{O}_2$ ,  $\text{O}_3-\text{N}_2$ ,  $\text{O}_3-\text{O}_2$  and  $\text{CH}_4-\text{N}_2$  systems. All computations were made using the mean relative thermal velocity approximation. The results are compared and the differences discussed. The calculations are also compared with the available measurements for these systems.

##### 4.1. $\text{H}_2\text{O}-\text{H}_2\text{O}$

The leading electrostatic interaction of the  $\text{H}_2\text{O}-\text{H}_2\text{O}$  collision pair is the dipole-dipole. The dipole moment of  $\text{H}_2\text{O}$  is  $\sim 1.85$  D [22] making the  $\text{H}_2\text{O}-\text{H}_2\text{O}$  collision pair a classic strong interaction system. Calculations of the half-width and line shift for the  $\text{H}_2\text{O}-\text{H}_2\text{O}$  system were made for 499 transitions belonging to eight different vibrational bands. The number of transitions for each vibrational band and the average percentage difference for half-width observed are detailed in table 4. The last column of this table shows the average percentage difference for half-widths determined by the CRB and MCRB formulations. The maximum deviation is seen in the case of pure rotational and the  $\nu_2$  vibrational band. In figure 1 the percentage difference is plotted versus the half-width. Most of the points lie close to or less than  $\pm 5\%$  with a number of points reaching  $\sim 15\%$ . The MCRB results are generally larger than the CRB results. For the 499 transitions studied the average absolute percent difference between the methods is 3.53 and the standard deviation is 3.86.

For the line shifts the percentage differences and the ratios were studied. The reason for considering the two comparisons is that the small values of the shifts give percent differences that are often very large.



Table 4. Upper and lower vibrational states, number of rotational transitions studied, average percentage difference between CRB and MCRB half-width for H<sub>2</sub>O–H<sub>2</sub>O.

$\nu'_1\nu'_2\nu'_3$	$\nu''_1\nu''_2\nu''_3$	No. of lines	Ave.% diff.
000	000	8	1.25
010	000	277	1.75
101	000	3	9.17
121	000	29	4.09
202	000	20	2.61
211	000	2	4.39
221	000	63	3.79
301	000	97	3.98
Total		499	2.66
Standard deviation			3.87

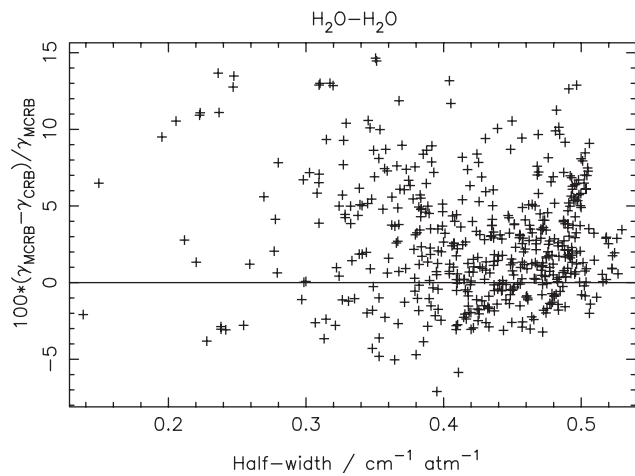


Figure 1. Percentage difference between self-broadened half-widths determined by the modified CRB and CRB formulations versus the half-width in cm<sup>-1</sup> atm<sup>-1</sup> units.

For such cases the ratios give a better view of the comparison. The average percentage difference is  $-2.3$ , however, the average absolute percentage difference is 197 and the standard deviation is 854. When the ratios are considered the average ratio is 2.79 and the standard deviation is 69.2. Most of the ratios are between  $\pm 5$  with a maximum value of 148 and a minimum value of  $-40.5$ .

#### 4.2. H<sub>2</sub>O–N<sub>2</sub> and H<sub>2</sub>O–O<sub>2</sub>

In the terrestrial atmosphere H<sub>2</sub>O is the principal absorber of infrared radiation and N<sub>2</sub> and O<sub>2</sub> are the most abundance gases. Hence, the study of these systems is very important for atmospheric applications. In terms of the electrostatic interaction, these are dipole-quadrupole systems. In the present work H<sub>2</sub>O–N<sub>2</sub> then H<sub>2</sub>O–O<sub>2</sub> follows H<sub>2</sub>O–H<sub>2</sub>O in terms of the strength of

Table 5. Upper and lower vibrational states, number of rotational transitions studied, average percentage difference between CRB and MCRB half-width for H<sub>2</sub>O–N<sub>2</sub> and H<sub>2</sub>O–O<sub>2</sub> systems.

$\nu'_1\nu'_2\nu'_3$	$\nu''_1\nu''_2\nu''_3$	No. of lines	Ave.% diff.	
			H <sub>2</sub> O–N <sub>2</sub>	H <sub>2</sub> O–O <sub>2</sub>
000	000	506	2.13	0.097
010	000	1885	3.12	0.181
010	010	144	1.95	0.093
020	000	326	3.85	0.243
020	010	872	3.24	0.199
100	000	90	1.45	0.134
100	010	532	3.67	0.251
001	000	75	2.00	0.109
001	010	484	4.17	0.284
030	010	146	3.96	0.273
030	020	382	3.08	0.198
Total		5442	3.18	0.195
Standard deviation			4.20	0.276

interaction. There are also reliable measurements for the half-width and line shift for H<sub>2</sub>O broadened by N<sub>2</sub> to compare with.

A total of 5442 ro-vibrational transitions were studied for both H<sub>2</sub>O–N<sub>2</sub> and H<sub>2</sub>O–O<sub>2</sub> systems. Table 5 lists the particular vibrational bands, the number of transitions studied in each band, and the average percentage difference between the two methods of calculation. The average percentage difference for the half-width for the 5442 transitions studied is around 3% for the H<sub>2</sub>O–N<sub>2</sub> system and  $\sim 0.2\%$  for the H<sub>2</sub>O–O<sub>2</sub> system. Figure 2 shows the percentage difference versus half-width for H<sub>2</sub>O–N<sub>2</sub>.

The ratio of the line shifts for the H<sub>2</sub>O–N<sub>2</sub> system give an average of 0.69 with a standard deviation of 4.14. For O<sub>2</sub>-broadening of water vapour the average line shift ratio is 0.994 with a SD of 0.260. In figure 3 the percentage difference between the O<sub>2</sub>-induced pressure shifts calculated by the two methods is plotted versus the magnitude of the line shift. Only for very small shifts, where both calculations are suspect, are the percentage differences appreciable.

#### 4.3. O<sub>3</sub>–N<sub>2</sub> and O<sub>3</sub>–O<sub>2</sub>

Next on the decreasing interaction scale is O<sub>3</sub> broadened by N<sub>2</sub>: 254 transitions were studied, 62  $\nu_1$  and 192  $3\nu_3$  transitions, by the CRB and MCRB formalisms. For the half-widths the average percentage difference between the two methods of calculation is 0.47 with a standard

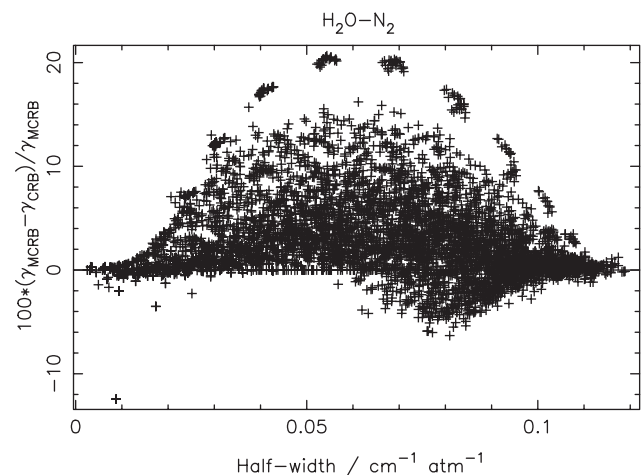


Figure 2. Percentage difference between  $\text{N}_2$ -broadened half-widths determined by the modified CRB and CRB formulations versus the half-width in  $\text{cm}^{-1} \text{atm}^{-1}$  units.

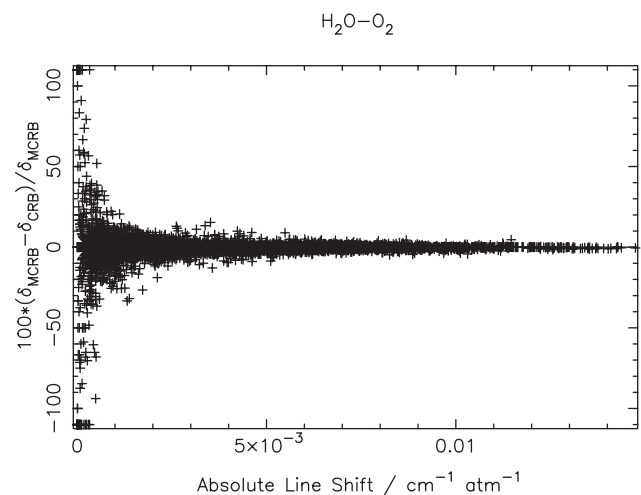


Figure 3. Percentage difference between  $\text{O}_2$ -induced pressure shifts determined by the modified CRB and CRB formulations versus the magnitude of the pressure shift in  $\text{cm}^{-1} \text{atm}^{-1}$  units.

considered an octupole–quadrupole system, however, Neshyba *et al.* [29] showed that the atom–atom interaction is the dominant term in the intermolecular potential. Calculations were made for 352  $\nu_3$  transitions using the CRB and the MCRB methods. The average percent difference between the half-widths from the two methods of calculation is  $-0.0056$  ( $\text{SD} = 0.018$ ) and the average ratio of the line shifts is  $0.9999$  ( $\text{SD} = 0.0027$ )

## 5. Comparison with measurement

The ultimate test of any theory is comparison with observation. For most of the systems studied here there are databases of measured values [46, 47] available to compare with the calculations. Here the CRB calculations and the MCRB calculations are compared with measurement for  $\text{H}_2\text{O}-\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{N}_2$ . For oxygen-broadening of  $\text{H}_2\text{O}$  there are only twelve half-width measurements for which comparisons can be made. For  $\text{N}_2$ - and  $\text{O}_2$ -broadening of ozone the statistics of the comparisons with measurement are essentially identical. Given the close agreement of the two methods of calculation for ozone this is not a surprise. The same is true for methane broadened by nitrogen.

The uncertainty in the measurement of the half-width and line shift is large and often the reported uncertainties are underestimated [46, 47]. In the discussion of self- and nitrogen-broadened half-widths comparisons are made only for transitions that have been measured by more than one experimental group. For the line shifts we report a comparison with all the measurements and when possible a separate comparison where two groups have measured the shift ( $\text{H}_2\text{O}-\text{N}_2$ ). The conclusions are drawn from the comparing the theoretical calculations with the measurement intercomparison results. One should be cautious of reading too much into the comparisons since the uncertainties of the intercomparison data are still large; however, it is all one can go by at this time.

Table 6 gives the statistics for the comparison of the CRB and MCRB calculated half-widths for  $\text{H}_2\text{O}-\text{H}_2\text{O}$  (322 transitions) and  $\text{H}_2\text{O}-\text{N}_2$  (182 transitions) for transitions for which two or more measurements exist. The CRB results agree slightly better with measurement than the results determined by the modification to the CRB formalism (MCRB) suggested by MTB. However, the small differences make it difficult to judge which method is better. The line shifts, on the other hand, demonstrated large differences between the two methods of calculation for these radiator-perturber systems.

For self-induced pressure shifts of  $\text{H}_2\text{O}$  there are only single measurements to compare with, i.e. no transition has been measured by more than one group.

340 deviation of 0.097. The line shift comparison gave an average ratio of 0.986 with a SD of 0.078.

Oxygen-broadening of ozone shows closer agreement between the two methods; an average percentage difference between the half-widths of 0.075 ( $\text{SD} = 0.04$ ) and an average ratio of line shifts equal to 0.999 ( $\text{SD} = 0.002$ ).

### 4.4. $\text{CH}_4-\text{N}_2$

350 The weakest interaction system considered in this work is  $\text{CH}_4$  broadened by  $\text{N}_2$ . The electrostatic interaction for methane, due to its high symmetry, starts with the octupole moment. At one time the system was

There are 225 transitions for which line shift measurements have been made and CRB and MCRB calculations done. The average percentage difference between the CRB calculations and measurement and the MCRB calculations and measurement are  $-4.76$  and  $-115.3$  respectively. The standard deviation of the MCRB comparison with experiment is more than a factor of 2 larger than that of the CRB comparison, 1741 versus 853.

For nitrogen broadening of  $\text{H}_2\text{O}$  the situation is somewhat better in that there are a number of transitions for which the line shifts have been measured by two groups giving more confidence in the results. Overall there are 438 comparisons of measurement with the calculations, 66 of these are for transitions for which two measurements exist. For the single measurements, the MCRB method gives an average percentage difference of 42 compared with experiment ( $\text{SD} = 380$ ) and the CRB method gives 27% ( $\text{SD} = 279$ ). Comparing with the pairs of measurements for each transition, the CRB method has an average percentage difference of 31 ( $\text{SD} = 37$ ) and the MCRB method has an average percentage difference of 56 ( $\text{SD} = 50$ ). In fact, of the 66 comparisons with pairs of measurements only two

transitions have the MCRB result in better agreement with measurement than the CRB result. Figure 4(a), (b), (c) shows typical comparisons of the line shift measurements [48, 49] and the CRB (square) and MCRB (star) calculations of the line shift for three transitions in the  $\nu_2$  band of  $\text{H}_2\text{O}$ .

For both systems that exhibit large differences between the pressure-induced line shift determined by the CRB and MCRB methods,  $\text{H}_2\text{O}-\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{N}_2$ , the CRB results agree much better with the measurement database, especially when pairs of measurements exist for a transition.

In the study by Ma *et al.* [13] calculations were made for the system  $\text{HF}-\text{HF}$ . It was noted that for this interaction system large differences in the line shift exist between the two methods of calculation. However, no comparison with measured values was presented. Comparing Ma *et al.*'s CRB and MCRB calculations of the line shift for self-broadening of  $\text{HF}$  with the measurements of Pine and Fried [50] shows that calculations using the CRB formalism demonstrate quite good agreement with the measured line shifts. The calculations made using MTB modification to the CRB formalism do not agree with Pine and Fried's measurements. In fact, the MCRB shifts are often the opposite sign of the measured values.

Table 6. Comparison of CRB and MCRB half-widths with measurement for  $\text{H}_2\text{O}-\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{N}_2$ .

	$\text{H}_2\text{O}-\text{H}_2\text{O}$		$\text{H}_2\text{O}-\text{N}_2$	
	322 transitions		182 transitions	
	CRB	MCRB	CRB	MCRB
Percentage difference	1.4	-1.7	0.66	-2.5
Percentage difference	6.0	6.6	5.4	6.4
Standard deviation	8.4	9.0	9.3	10.4

## 6. Summary and conclusions

Calculations employing the CRB formalism and the modification to the CRB formalism suggested by MTB were made for the collision systems  $\text{H}_2\text{O}-\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}-\text{N}_2$ ,  $\text{H}_2\text{O}-\text{O}_2$ ,  $\text{O}_3-\text{N}_2$ ,  $\text{O}_3-\text{O}_2$  and  $\text{CH}_4-\text{N}_2$ . As suggested by MTB the differences between the two methods of calculation are proportional to the strength of the interaction

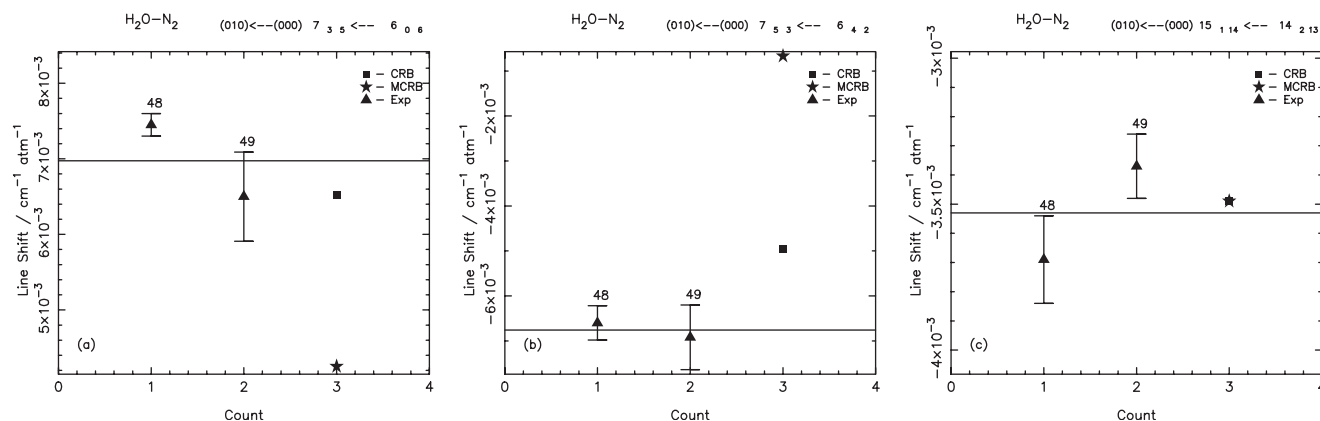


Figure 4. Comparisons of the line shift measurements of [48] and [49] with the CRB (square) and MCRB (star) calculations of the line shift for three transition in the  $\nu_2$  band of  $\text{H}_2\text{O}$  in a bath of  $\text{N}_2$ : (a)  $7_{3,5} \downarrow 6_{0,6}$  transition; (b)  $7_{5,3} \downarrow 6_{4,2}$  transition; (c)  $15_{1,14} \downarrow 14_{2,13}$  transition.

460 between the radiating molecule and the perturbing  
molecule. For the systems considered here, large differ-  
ences are observed for the H<sub>2</sub>O–H<sub>2</sub>O system and  
noticeable differences are observed for the H<sub>2</sub>O–N<sub>2</sub>  
465 system. For the H<sub>2</sub>O–O<sub>2</sub> and O<sub>3</sub>–N<sub>2</sub> systems the differ-  
ences are small, for O<sub>3</sub>–O<sub>2</sub> system the differences  
are very small, and for the CH<sub>4</sub>–N<sub>2</sub> system the differences  
are negligible.

Comparisons with half-width and line shift measure-  
ment were made for self- and N<sub>2</sub>-broadening of water  
vapour. In all cases the CRB calculations agreed with  
470 measurement better, on average, than the MCRB  
calculations. Particular attention was paid to the line  
shift since the differences between the two methods  
of calculation are greater than the differences in the  
half-widths. For the line shift the CRB calculations  
475 give better agreement with the measurements. This fact  
is especially evident for N<sub>2</sub>-broadening of H<sub>2</sub>O where  
there are pairs of measurements for a number of  
transitions. The CRB calculations agree better with the  
shift measurement for 64 of the 66 transitions measured  
480 by two groups.

The results of the MTB paper were compared with the  
measurements of Pine for HF–HF and it was found that  
the MCRB method often gave shifts with the wrong sign  
and demonstrated poor agreement with measurement.  
485 The CRB results, however, gave good agreement with  
the measurements of Pine.

Given the results of this study, it is clear that the  
differences between the CRB and MCRB formalisms  
is significant with respect to the uncertainty criterion  
set forth by the remote sensing and spectroscopic  
490 communities. Comparisons with measurement indicate  
that the CRB formalism gives better agreement with  
measurement.

This study raises an interesting question about the  
proposed modification to the CRB formalism. Why does  
a more correct formalism give worse results? It would be  
useful to know what the contributions of the S<sub>3</sub> term in  
the MCRB formalism is. It would also be interesting to  
see if Robert and Bonamy's approximate expressions  
500 include higher order terms due to their derivation. These  
are interesting problems that must be answered before  
theoretical calculations change to the method suggested  
by Ma *et al.*

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