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# Self-broadening of water vapor transitions via the complex Robert–Bonamy theory

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#### Abstract

Calculations of self-broadened half-widths and self-induced pressure shifts are made using the complex Robert–Bonamy formalism. The results of calculations using different approximations of the intermolecular potential indicate that this is a strong collision system. The effects of the imaginary components on the half-widths are studied. The temperature, vibrational, and rotational state dependence of the half-width are investigated. Results are compared with measurements from the database of self-broadening of water vapor [Gamache RR, Hartmann J-M. An intercomparison of measured pressure-broadening and pressure-shifting parameters of water vapor. Can J Chem 2004; 82: 1013–27]. © 2006 Elsevier Ltd. All rights reserved.

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## 1. Introduction

Water vapor is the strongest atmospheric absorber of infrared radiation and is therefore the most important gas controlling Earth's surface temperature. There are about 50 000 significant atmospheric spectral transitions for  $H_2O$  ranging from microwave to the visible range of the spectrum. The transitions can be described in terms of spectral parameters, which are cataloged in databases such as HITRAN [1] or GEISA [2]. The interpretation of remote sensing measurements and study of the radiative properties of atmosphere depends on knowledge of these spectral parameters. Of the parameters needed for inverting remotely sensed data, the air-broadened half-width is the least well known for atmospheric applications [3]. The effect of uncertainty in half-widths on the accuracy of retrieved concentration profiles depends on molecule and altitude [4–7] and is a major source of the uncertainty on 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 [8–10]. The spectroscopic and remote sensing communities [3,11–13] have

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determined that for accurate retrievals the half-width and its temperature dependence should be known with an uncertainty of 3% for strong lines and 10% for weak lines. However, the self-broadening contribution in typical air-broadened spectra can be as large as 5% and if omitted will result in values with uncertainty greater than that desired for the inversion process. Thus, the self-broadening correction must be accounted for in retrievals.

There have been a fair number of measurements of self-broadening of water vapor transitions from the microwave to visible region of the spectrum [14–63] and a lesser number of measurements of the self-induced line shift [26,34,42,47,50,56,58]. Together these studies yield data for 10 596 self-broadened half-widths and 1543 self-induced line shifts. An intercomparison of these data, i.e. comparing measured values for the same ro-vibrational transition, has recently been done [64]. From this data set it is possible to make 440 intercomparisons of half-widths. Only four intercomparisons are possible for more than three measured data points; three 4-point and one 5-point intercomparisons. The estimated uncertainty (see Ref. [64] for details) for these intercomparisons is greater than 10%. The 5-point intercomparison for the  $3_{13} \leftarrow 2_{20}$  transition of the rotational band is shown in Fig. 1 demonstrating typical spread in the measurements. The intercomparison of pairs of points contains 92% of the self-broadening intercomparisons of which 61% have estimated uncertainties greater than 10%. There are no intercomparisons of the line shifts.

Theory can contribute to the spectroscopic picture in uniquely useful ways. Although laboratory measurements can and do supply pressure-broadened half-widths and line shifts, it is difficult to exhaustively cover the vast spectral range and diversity of environmental conditions encountered in the actual atmosphere. Theoretical calculations are in principle an attractive alternative, depending on the accuracy requirements of the radiative transfer application one has in mind, and of course the credibility of the theory. Even when laboratory measurements are available, however, certain effects (such as line mixing [65]) may still require a sophisticated theoretical model in order to unravel observed spectra.

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. With the increased computational capacity over the past decade, there have been many improvements in the potential and wavefunctions yielding more accurate results. In this article, we report the self-broadening of water vapor transitions using the CRB formalism. The effects of the expansion of the atom–atom potential and the imaginary components were studied. Dependence of the half-width on temperature, vibrational state, and rotational state was also investigated. The results were compared with measurements from the self-broadening of water vapor database [64].



Fig. 1. The 5-point intercomparison of measured half-widths for the  $3_{13} \leftarrow 2_{20}$  transition of the rotational band demonstrating typical spread in the measurements.

#### 2. CRB formalism

#### 2.1. The general theory

The present calculations were based on the CRB formalism [66]. A detailed description of the theory may be found in [67–69] and references therein. Here only the salient features are discussed. In the present approach, the half-width and line shifts for a ro-vibrational transition  $f \leftarrow i$  are given by the real and imaginary part of the expression,

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

where  $n_2$  is the number density of perturbers and  $\langle \rangle_{v,b,J2}$  specifies an average over impact parameter *b*, initial relative velocity *v*, and initial rotational state  $J_2$  of the collision partner. Real-valued  ${}^{I}S_1$  and complex-valued  $S_2 = {}^{R}S_2 + i^{I}S_2$  are the 1st- and 2nd-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. Explicit expressions for these terms are given in Refs. [67–69].

In the CRB formalism, two important features have been incorporated, (i) the elimination of the cut-off procedure and (ii) more correct treatment of close collisions. The cut off procedure adopted by earlier theories [70,71] was eliminated by the use of linked-cluster techniques [72]. The close intermolecular collisions (small *b*) in CRB theory are now well defined by (a) the dynamics, which is 2nd order in time producing curved trajectories based on the isotropic part of the intermolecular potential, and the short-range (Lennard–Jones) atom–atom potential, which has been shown to play an important role in pressure broadening when long-range intermolecular forces are weak.

The present calculations for the line shape parameters used the mean relative thermal velocity  $(\bar{v})$  approximation (mrtv). Most previous calculations used this method. The reason for using the approximation is due to the time taken to perform the averaging over the Boltzmann distribution of velocities. It is estimated that mrtv approximation gives results 30–50 times faster with a difference of a few percent from the velocity averaged results at ~300 K for the systems considered here [73].

### 2.2. The potential

The  $S_1$  term (real-valued; appears as imaginary-valued  $i^I S_1$ ) of Eq. (1), in the absence of any vibrational dependence of the anisotropic intermolecular forces, is determined by isotropic parts of the intermolecular potential. It is called the vibrational dephasing term and arises in CRB theory 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:

$$V_{\rm iso}^{\rm induction} = -\frac{\mu_1^2 \alpha_2}{R^6} \tag{2}$$

and

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

where  $\mu_1$  is the dipole moment of the radiator molecule and  $\alpha_k$  and  $I_k$  are the polarizability and ionization potential (IP) of the radiator (k = 1) and perturber (k = 2). For water vapor, the vibrational dependence of Eqs. (2) and (3) is contained in  $\mu_1$  (by Shostak and Muenter [74] in Debyes) and  $\alpha_1$  (by Luo et al. [75] in au) given respectively as

$$\mu = 1.855 + 0.0051(v_1 + \frac{1}{2}) - 0.0317(v_2 + \frac{1}{2}) + 0.0225(v_3 + \frac{1}{2})$$
(4)

and

$$\alpha = 9.86 + 0.29(v_1 + \frac{1}{2}) - 0.03(v_2 + \frac{1}{2}) + 0.28(v_3 + \frac{1}{2}), \tag{5}$$

with  $v_n$  the number of quanta in the *n*th normal mode.

In this work, the vibrational dependence of the short-range part of the isotropic potential has been neglected because there is no convenient means of determining the parameters, short of fitting. The result is that the line shifts for high rotational quantum number may be in question.

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 [76] interactions between atoms of the radiating and perturbing molecules given by

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

where *n* and *m* are the number of atoms in molecules 1 and 2 and the subscripts 1*i* and 2*j* stands for the *i*th atom of molecule 1 and *j*th atom of molecule 2, respectively. The  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are the Lennard–Jones parameters for the atomic pairs. Heteronuclear atom–atom parameters can be constructed from homonuclear atom–atom parameters ( $\varepsilon_i$  and  $\sigma_j$ ) by the combination rules of Hirschfelder et al. [77] or Good and Hope [78]. Here the method of Hirschfelder et al. was used. The atom–atom distance  $r_{ij}$  is expressed as an expansion of the inverse of center of mass separation, *R* given by Sack [79]. This yields an atom–atom potential that can be understood as two simultaneous expansions. One is defined by the tensorial ranks  $\ell_1$  and  $\ell_2$ , which determine the symmetry of the interaction [77,80]. A second expansion is defined by the sum  $\ell_1 + \ell_2 + 2w$ , [79,81] which we call the order of the expansion. It hardly needs to be emphasized that any calculation of line width or shift should be converged with respect to both order and rank. In the present case, we have tested the results up to 8th order. The values for the atom–atom parameters ( $\varepsilon_{ij}$  and  $\sigma_{ij}$ ) are tabulated in Table 1.

#### 2.3. The wavefunctions

The reduced matrix elements were evaluated using the wavefunctions determined by diagonalizing the Watson Hamiltonian [82] in a symmetric top basis for the vibrational states involved in the transition for the radiator H<sub>2</sub>O. The Watson constants are from Matsushima et al. [83] for the ground state, from Flaud and Camy-Peyret [84] for the  $v_2$ , and  $v_3$  states, from Grossmann et al. [85] for the  $2v_1 + 2v_3$ ,  $2v_1 + 2v_2 + v_3$ , and  $3v_1 + v_3$  states. For the  $v_1 + v_3$ ,  $v_1 + 2v_2 + v_3$ , and  $2v_1 + v_2 + v_3$  states, the wavefunctions of the  $v_3$  state were used.

Table 1 The atom-atom Lennard-Jones (6-12) parameters for the H<sub>2</sub>O-H<sub>2</sub>O collision pairs

Atomic pair	H–H	H–O	0–0
$\sigma$ (Å)	2.683	2.565	3.010
$\epsilon/k_{\rm B}$ (K)	11.25	24.13	51.73

Table 2 Molecular parameters of H<sub>2</sub>O, references in brackets

Moments (10 <sup>-26</sup> esu)	IP (eV)
$\mu = 1.8549 \times 10^{8} [74]$ $Q_{xx} = -0.13 [86]$ $Q_{yy} = -2.5 [86]$ $Q_{zz} = 2.63 [86]$	12.6 [87]

Most of the molecular parameters used here for the water vapor system are well known and we have used the best available values from the literature. The multipole moments, rotational constants, polarizability and IP employed and their references are tabulated in Table 2.

# 3. Calculations

Calculations were made for the transitions from the intercomparison of measured self-broadened halfwidths discussed above. This selection results in 440 transitions belonging to 16 vibrational bands. Calculations were performed for the  $H_2O-H_2O$  system for these 440 transitions using the CRB formalism at 296 K to determine the half-widths and line shifts. The intermolecular potential used in the calculations was varied with the atom-atom components ranging from the 0th order expansion (i.e. electrostatic potential) to 8th order. The imaginary components of the potential were also turned on and off to study their effects. The parabolic trajectory model of Robert and Bonamy [66] was compared with calculations employing exact trajectories. The half-widths were calculated at five temperatures, 200, 250, 296, 350 and 500 K, for the 440 transitions and their dependence on temperature was studied.

In order to assess the vibrational dependence of the half-width, transitions must be chosen that sample a range of vibrational bands and rotational states that go from the prolate  $(K_a = J)$  to oblate  $(K_c = J)$  limit of H<sub>2</sub>O. The vibrational dependence of the half-width and line shift were investigated for 71 rotational transitions which include some of the doublet lines  $(J \pm 1_{0,J\pm 1} \leftarrow J_{0,J})$  which have been shown to have strong vibrational dependence [88] as well as unusual temperature dependence [89]. Calculations were made for four vibrational bands, the rotational band,  $2v_3$ ,  $4v_3$ , and  $6v_3$ , for a total of 284 transitions.

# 4. Results and discussion

The CRB method was used to calculate half-width and line shift for the  $H_2O-H_2O$  system. As described in Section 1, the effects of the expansion of the atom-atom potential and importance of the imaginary components were studied and the importance of each of these terms is discussed. The temperature, vibrational state, and rotational state dependence of the half-width were also studied. The results of the CRB calculations are compared with the intercomparison data from the measurement database [64].

## 4.1. Effects of the expansion of the atom-atom potential

As discussed above, the atom-atom potential is expressed as two simultaneous expansions; one in terms of the tensorial ranks  $\ell_1$  and  $\ell_2$ , which determine the symmetry of the interaction [80,90] and a second expansion defined by the sum  $\ell_1 + \ell_2 + 2w$ , [80,90] which is called the order of the expansion. In the calculation of line width or shift the atom-atom potential should be converged with respect to both order and rank. In our calculations, the tensorial rank ranged from  $\ell = 0$  to 2. The convergence of the atom-atom potential was investigated with the order of the expansion ranging from 0 to 8. Note, the order equal to zero corresponds to using only the electrostatic parts of the anisotropic potential.

In the prevailing view of the self-broadening of water, broadening is dominated by strong dipole–dipole forces; the atom–atom potential is expected to play only a small part in determining the half-width or line shift. To test the merits of this view, calculations were made for atom–atom expansion orders equal to 0, 2, 4, 6, and 8 and the results compared. In most cases, the differences in the half-width calculations of different orders differ by much less than 1%. However, there are a few transitions where the difference from 0th to 8th order is ~1%. Fig. 2 shows such a plot for the self-broadened half-width of the  $8_{81} \leftarrow 7_{70}$  transition of the  $v_2$  band versus the order of the atom–atom potential. The half-width for this transition changes about 1% in going from 0th (electrostatic) to an 8th order expansion of the atom–atom potential. In this case, most of this change takes place in going from 0th to 2nd order. Fig. 3 shows the line shift for the  $16_{016} \leftarrow 15_{115}$  transition of the  $v_2$  band changes by ~9% as the order of the atom–atom potential is varied from 0 to 8. In this case, convergence appears to require all eight orders. In Fig. 4 the percent difference between the 0th order (electrostatic) and 8th order atom–atom potential calculation of the half-width is plotted for the transitions studied versus the half-width. Note, only for the small half-widths does the percent error reach ~1%.



Fig. 2. The calculated self-broadened half-width of the  $8_{81} \leftarrow 7_{70}$  transition of the  $v_2$  band versus the order of the atom-atom potential.



Fig. 3. The calculated line shift for the  $16_{016} \leftarrow 15_{115}$  transition of the  $v_2$  band versus the order of the atom-atom potential.



Fig. 4. The percent difference between the 8th order and 0th order (electrostatic) atom-atom potential calculation of the half-width for the 440 transitions studied versus the half-width.

In general, the pattern suggests failure to include higher order terms will result in an overestimation of the half-widths.

For the line shifts, there are some comparisons of the 8th and 0th order calculations that exhibit large percent differences; however, this fact can be expected given the small magnitude of the line shifts. This trend is shown in Fig. 5 where the percent difference between the 8th order and 0th order calculation of the line shift versus the absolute line shift is plotted. It is for small values of the line shift where appreciable percent differences are found. For such transitions the uncertainty in the calculations may also contribute to the differences between the two calculations.

These results indicate that the effect of the atom-atom potential is small in computing the half-width (up to 1 %) and more noticeable for computing the line shift for the  $H_2O-H_2O$  system. However, given the uncertainty criterion set forth by the spectroscopic and remote sensing communities for the half-width, the calculations below employ the atom-atom potential expanded to 8th order.

## 4.2. Effects of the trajectories

It is known that for certain collision systems the effects of the trajectories can be important [91,92]. The current model uses the Robert and Bonamy parabolic model [66], which is correct to 2nd order in time. The method uses the isotropic part ( $\ell_1 = \ell_2 = 0$ ) of the atom-atom potential to determine the distance, effective velocity, and force at closest approach. To simplify the trajectory calculations the isotropic part of the atom-atom expansion is fit to an isotropic Lennard-Jones 6–12 potential and the resulting parameters are used in the trajectory calculations. As the order of the expansion changes so do the resulting Lennard-Jones 6–12 potential parameters that define the trajectories. For a number of systems the change in the trajectories has a marked effect on the half-width [92–97].

Calculations were made using the isotropic part of the 8th order expansion of the atom-atom potential and solving Hamilton's equations for the exact trajectories. There are no significant differences in the half-width or line shift computed from the two models. These results imply the R-B trajectory model works well for this system. However, the above results for calculations for different orders of expansion of the atom-atom potential imply that the trajectory model has little or no effect on the line shape parameters for the  $H_2O-H_2O$  system. To test this hypothesis, calculations for five randomly chosen transitions were made using epsilon and sigma values for the Lennard-Jones 6-12 potential that are 20% higher and lower than the 8th order fitted values and the half-widths and line shifts from the three calculations compared. The average absolute percent differences in the half-width are 0.65 and 0.08 and in the line shifts are 3.4 and 4.5, respectively, for raised and lowered Lennard-Jones 6-12 parameters. These values can be compared to those obtained for



Fig. 5. The percent difference between the 8th order and 0th order calculation of the line shift for the 440 transitions studied versus the absolute line shift.

oxygen-broadening of the same transitions giving 28% and 9%, respectively for the half-width and 140% and 67%, respectively, for the line shifts.

To understand these results the effect of the isotropic part of the potential on the trajectories must be considered. At large internuclear separation, the effect of the isotropic potential is negligible and the trajectories are essentially straight lines. As the molecules come closer together, the effects of the potential lead to bent trajectories. The results above suggest that for self-broadening of water vapor, the interaction is strong enough so that the real part of  $S_2$  is large and the  $exp(-S_2)$  term in Eq. (1) is zero before the trajectories start to bend. Thus, for this system, a straight line trajectory model will yield results that equal those made using a more sophisticated trajectory model. In our calculations, we have used the Robert–Bonamy parabolic model.

### 4.3. The effects of the complex terms

Previous studies on water vapor [67,69,98–100] have demonstrated the importance of the inclusion of the imaginary components of the  $S_2$  terms in the calculation of the half-width. Differences in the half-width determined from calculations with and without the imaginary terms can be as large as 25%. Here, the role of the imaginary terms in determining the self-broadened half-widths of water vapor is investigated. Calculations were made employing the imaginary part of  $S_2$  and the  $S_1$  term and are compared with calculations made using only the real terms of Eq. (1). The calculations were done for orders equal to 0, 2, 4, 6, and 8. Fig. 6 shows the half-width for the  $3_{31} \leftarrow 3_{12}$  transition of the  $2v_1 + 2v_2 + v_3$  band determined from the real Robert–Bonamy (RRB) calculation (dashed line with squares) and from the CRB calculation (solid line with circles) versus the order of the atom–atom potential used in the calculation. At all orders of the atom–atom potential the difference between the two calculations is ~9%. In Fig. 7, the percent difference between the 8th order CRB and RRB calculations have differences from 0 to 12 percent, with an average percentage difference of 4.8 and standard deviation of 2.2. It seems noteworthy to mention that a systematic error is evident, with RRB predicting half-widths that are too small. It is evident that in order to address the accuracy needs of the remote sensing and spectroscopic communities the imaginary terms must be included in the calculations.

### 4.4. Temperature dependence of the half-width

Knowledge of the temporal and spatial variations of the distributions of  $H_2O$  is essential, due to its major role in thermo-physical processes in our atmosphere and combustion media. Hence, many experimental studies on the spectroscopic parameters of  $H_2O$  lines have been carried out. However, most of these



Fig. 6. The half-width for the  $3_{31} \leftarrow 3_{12}$  transition of the  $2v_1 + 2v_2 + v_3$  band determined from the real Robert–Bonamy calculation (dashed line with squares) and from the complex Robert–Bonamy calculation (solid line with circles) versus the order of the atom–atom potential.



Fig. 7. The percent difference between the 8th order complex Robert–Bonamy and real Robert–Bonamy calculations versus the half-width for the 440 transitions studied.

investigations restricted to the measurements at the room temperature for the Lorentz widths and shifts. In fact, less than 10% of the measurements made of the pressure-broadened half-width consider the variation with temperature. The difficulty in experimental setup for variable temperature may be the prime reason for this.

The standard model for the temperature dependence of the half-width is the power law expression:

$$\gamma(T) = \gamma(T_0) \left[ \frac{T_0}{T} \right]^n,\tag{7}$$

where  $\gamma(T_0)$  is the half-width at the reference temperature  $T_0$ , and *n* is called the temperature exponent. A "rule-of-thumb" expression for the temperature exponent has been given by Birnbaum [101]. For a "dipole–dipole" system, such as H<sub>2</sub>O–H<sub>2</sub>O, the temperature exponent is 1.0. Eq. (7) works quite well over temperature ranges of 50–100 K and where the major contributions to the half-widths are from the  $Re(S_2)$  terms. The model becomes less valid for large temperature ranges, so one must be cautious in applying Eq. (7) in combustion studies for example. Recently, Wagner et al. [89] discovered that for certain types of transitions for N<sub>2</sub>-, O<sub>2</sub>-, and air-broadening of H<sub>2</sub>O the power law formula is not valid. This occurs when the energy jumps for collisionally induced transitions for the active and bath molecule do not match, yielding large energy defects. These collisions are said to be "off resonance" and the result is that, at 300 K, the rotational contributions to the half-width become small and the process is dominated by the vibrational terms. At large *J*" values, the resulting temperature exponents are negative and the power law, while not theoretically the correct model, gives a reasonable fit. Hartmann et al. [32] have shown that as the temperature increases there are kinetic and resonance terms that contribute to the temperature dependence of the half-width and a "resonance overtaking" mechanism which can lead to small and even negative values for *n*.

Chu et al. [6] have studied the effect of changing the temperature exponent on retrieved mixing ratios of water vapor. They find that changing n from 0.5 to 0.7 results in roughly a 4% change in the mixing ratio at 10 km. It has also been demonstrated that temperature exponents averaged as a function of J" or fit by polynomials in the rotational quantum numbers do not give reliable predictions for all transitions [102,103]. Given the results of Chu et al. it is clear that the use of the specific measured or calculated temperature exponent for the ro-vibrational transition in question will yield the best results.

In this study, five temperatures were considered, 200, 250, 296, 350 and 500 K. Calculations were done for 440 rotational transitions in sixteen vibrational bands. Some of the transitions match those of the Wagner et al. [89] study and hence test the validity of the power law expression. The resulting half-widths at the five temperatures are then least-squares fit to Eq. (7) and the slope, intercept, and correlation coefficient of the fit



Fig. 8.  $\ln\{g(T)/g(T_0)\}$  versus  $\ln\{T_0/T\}$  for the  $7_1 \neq 8_{0.8}$  transition of the  $v_2$  band from CRB calculations, the straight line is the power law fit to the data, the slope of the fit is the temperature exponent.



Fig. 9. The calculated temperature exponents for the 440 transitions studied here versus J'' of the transition, the solid line is the average temperature exponent,  $n_{ave} = 0.66$ .

determined. Fig. 8 is a typical example of the fit for the  $7_{17} \leftarrow 8_{08}$  transition of the  $v_2$  band. The power law, while not working perfectly, does provide a good model of the temperature dependence.

Fig. 9 is a plot of the temperature exponents for the 440 transitions studied here versus J' of the transition. The average value of *n* is 0.66. The range of the temperature exponent is from about 0.15 to 1.0 giving a large spread around the average value. Unlike that for N<sub>2</sub>-broadening [104], negative temperature exponents are not observed for self-broadening. As will be discussed below, this is due to resonant collisions being present for self-broadening of water vapor. See Ref. [89] for more details.

# 4.5. Vibrational dependence

Influence of vibration on the half-width and line shift of water vapor has been the subject of several experimental studies [47,105–108]. The results showed that the difference for the half-width is in the range of  $\pm 3-5\%$ . The vibrational dependence arises due to spectroscopic and purely vibrational effects. In the first case, it is due to the slightly different rotational wavefunctions, energy gaps and transition probabilities for

different vibrational bands. The reason for the second effect is the change in the vibrational part of the intermolecular potential with the change in vibrational bands, i.e. the vibrational dephasing terms [88].

Seventy one ro-vibrational transitions were investigated for the pure rotation,  $2v_3$ ,  $4v_3$  and  $6v_3$  vibrational bands. Two sets of calculations were performed: (i) with  $K_c = J$  and  $K_a = 0$  (36 transitions), and (ii) with  $K_c = J$  and  $K_a = 1$  (35 transitions). These transitions were chosen since they have been shown to have strong vibrational dependence for water vapor broadened by nitrogen [88]. For nitrogen broadening of H<sub>2</sub>O, low J transitions show only a small sensitivity to the vibrational states in the transition. By intermediate J the effects of vibration are noticeable and by large J they can result in a factor of 2–4 difference in the half-width. The reason for this change in vibrational dependence with J was found to be related to the terms in the potential that affect the half-width [88]. At low J, the collisions are on resonance leading to the rotational contributions dominating the half-width. At large J, the collisional energy transfer is off resonance leading to the vibrational dephasing term being dominant. At intermediate J, the half-width is determined by a mixture of the two terms.

For self-broadening of  $H_2O$ , a different picture emerges. For this collision system (the perturbing molecule is the same as the radiating molecule), there are always some collisions that are on resonance thus the half-width always has a substantial contribution from the rotational terms. Fig. 10 shows the half-width for the



Fig. 10. The calculated half-width for the pure rotation,  $2v_3$ ,  $4v_3$ , and  $6v_3$  doublet transitions with  $K_a = 0$  versus the average of (J'' + J').



Fig. 11. The calculated line shift for the pure rotation,  $2v_3$ ,  $4v_3$ , and  $6v_3$  doublet transitions with  $K_a = 0$  versus the average of (J'' + J').

pure rotation,  $2v_3$ ,  $4v_3$ , and  $6v_3$  doublet transitions with  $K_a = 0$  versus the average of (J'' + J'). In the figure, the differences between the vibrational bands is small (the spread is 0.1-3.3% with 3.3% for high J's) indicating only a small vibrational dependence.

The line shifts follow the usual vibrational dependence. In Fig. 11, the line shift for all the transitions versus the average of (J'' + J') is plotted. It can be seen that the line shifts for higher J transitions of  $6v_3$ , compared with the pure rotational transitions, are shifted to the red (more negative) by as much as  $0.01 \text{ cm}^{-1} \text{ atm}^{-1}$ , an amount comparable to the line shift values themselves.

## 4.6. Rotational dependence

The dependence of the half-width on the rotational quantum numbers for water, being an asymmetric rotor, is rather complicated. Brown and Plymate [108] have shown that for transitions with fixed  $K_a$ ,  $\Delta J$ ,  $\Delta K_a$ , and  $\Delta K_c$  there is often structure as a function of J''. With such structure half-widths for transitions not studied can be estimated by the curves. In order to see if this procedure is useful for many combinations of  $K_a$ ,  $\Delta J$ ,  $\Delta K_a$ , and  $\Delta K_c$ , we took the calculated half-widths in the  $v_2$  band (238 transitions) and made plots for combinations with  $\Delta J = 0, \pm 1, \Delta K_a = 1, \Delta K_c = -1$  with  $K_a'' = 1, 2$ , and 3. Several of the figures do show structure however for many the structure does not allow predicting half-widths for missing transitions. These plots are also complicated by multiple points for a given J' value that obey the selection rules.

## 4.7. Comparison with measurement

Calculations were performed for half-width and line shift for  $H_2O-H_2O$  for 440 ro-vibrational transitions belonging to sixteen vibrational bands for which measurement intercomparisons are available for comparison. Table 3 presents the comparison of the CRB calculations with the measured intercomparison average values. The table gives the vibrational band, the number of rotational transitions studied, and the average % difference between measurement and calculation. For the 440 transitions studied in this work the overall average percent difference between measurement and theory is 1.3 with a standard deviation of 8.9%.

# 5. Summary

CRB calculations were done for 440 transitions belonging to 16 vibrational bands. The effects of the expansion of the atom-atom potential, the complex terms, the trajectory model, the dependence of  $\gamma$  on

Table 3

Vibrational band, number of rotational transition studied, the average percent difference between the measured half-widths and the C	RB
calculated value and the absolute average percent difference from measurement intercomparisons for H <sub>2</sub> O-H <sub>2</sub> O	

$v'_1 v'_2 v'_3$	$v_1''v_2''v_3''$	No of lines	Ave. % diff.	Explave % diff.
000	000	7	6.15	7.67
010	000	238	0.68	7.30
020	010	1	1.33	6.90
101	000	3	0.34	8.55
122	000	1	-9.12	7.75
141	000	1	-9.98	3.80
201	000	2	9.19	26.86
202	000	20	0.78	6.38
203	000	1	-14.11	18.63
211	000	2	-0.25	0.82
221	000	63	0.04	3.94
231	000	1	-8.86	3.88
300	000	1	15.16	0.43
301	000	97	2.80	4.43
320	000	1	3.18	0.37
500	000	1	63.16	93.2

temperature, vibrational and rotational states were investigated. It was found that the  $H_2O-H_2O$  system is a strong collision system. The effect of the atom-atom potential on the half-width tends to be small. There is a more pronounced effect on the line shift of transitions. Although the effects are small for determining the half-width, there are a number of transitions where the effect should be taken into consideration if the results are to address the concerns of the spectroscopic and remote sensing communities. Because of this fact it is recommended that the calculations are done using the 8th order expansion of the atom-atom potential.

The effects of the complex terms on the half-widths are too large to be ignored and the recommendation is that calculations of the self-broadened half-width be done via the CRB formalism.

The temperature dependence of the half-width can be adequately modeled by the standard power law formula. It was found that there are always a number of on resonance rotational contributions to the half-width that dominate and the unusual temperature dependence found for nitrogen-broadening of some doublet transitions of water vapor are not observed for self-broadening. It is cautioned that the temperature range used in the determination of the temperature exponent not be too great. In cases when the range is large the power law model may not be exact.

Because there are always a number of collisional transitions that are on resonance for  $H_2O-H_2O$  this system does not exhibit a strong dependence on vibrational state. While there are some trends associated with the rotational state dependence of the half-width these are difficult to model and cannot be predicted a priori.

Finally, the comparison of the CRB calculations run with the 8th order expansion of the atom-atom potential and the RB parabolic trajectory model agree well with a database of 440 measurement intercomparisons.

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#### References

- Rothman LS, Jacquemart D, Barbe A, Benner DC, Birk M, Brown LR, et al. The HITRAN 2004 molecular spectroscopic database. J Quant Spectrosc Radiat Transfer 2005;96:139–204.
- [2] Jacquinet-Husson N, Scott NA, Chedin A, Bonnet B, Barbe A, Tyuterev VG, et al. The GEISA system in 1996: towards an operational tool for the second generation vertical sounders radiance simulation, J. Quant Spectrosc Radiat Transfer 1998;59:511–27.
- [3] Barbe A. In: Proceedings of the atmospheric spectroscopy applications workshop, ASA REIMS 96, Université de Reims, Champagne Ardenne, September 4–6, 1996.
- [4] Smith MAH, Gordley LL. Sensitivity of ozone retrievals in limb-viewing experiments to errors in line-width parameters. J Quant Spectrosc Radiat Transfer 1983;29:413–8.
- [5] Traub W, Chance K. BIC-2 Campaign, private communication, 1985.
- [6] Chu WP, Chiou EW, Larsen JC, Thomason LW, Rind D, Buglia JJ, et al. Algorithms and sensitivity analyses for stratospheric aerosol and gas experiment II water vapor retrieval. J Geophys Res 1993;98:4857–66.
- [7] Liljegren JC, Boukabara S-A, Cady-Pereira K, Clough SA. The effect of the half-width of the 22-GHz water vapor line on retrievals of temperature and water vapor profiles with a 12-channel microwave radiometer. IEEE Trans Geosci Remote Sens 2005;43:1102–8.
- [8] Bosenberg J. Measurements of the pressure shift of water vapor absorption lines by simultaneous photoacoustic spectroscopy. Appl Opt 1985;24:3531–4.
- [9] Pumphrey HC, Buehler S. Instrumental and spectral parameters: their effect on and measurement by microwave limb sounding of the atmosphere. J Quant Spectrosc Radiat Transfer 2000;64:421–37.
- [10] Margolis J. Jet Propulsion Laboratory, private communication 1997.
- [11] Smith MAH. NASA conference publication 2396. NASA, Scientific and Technical Information Branch; 1985.
- [12] Smith MAH. Third langley spectroscopic parameters workshop. Hampton, VA: NASA Langley Research Center; 1992.
- [13] Reber CA. NASA Goddard space flight center publication 430-1003-001, 1985.
- [14] Grossmann BE, Browell EV. Spectroscopy of water vapor in the 720-nm wavelength region: line strengths, self-induced pressure broadenings and shifts, and temperature dependence of linewidths and shift, J. Mol Spectrosc 1989;136:264–94.

- [15] Giver LP, Gentry B, Schwemmer G, Wilkerson TD. Water absorption lines, 931–961 µm: selected intensities, N<sub>2</sub>-collisionbroadening coefficients, self-broadening coefficients, and pressure shifts in air. J Quant Spectrosc Radiat Transfer 1982;27:423–36.
- [16] Mandin JY, Flaud J-M, Camy-Peyret C. Measurements and calculations of self broadening coefficients of lines belonging to the  $v_2$  band of  $H_2^{16}O$ . J Quant Spectrosc Radiat Transfer 1980;23:351–70.
- [17] Mandin JY, Flaud J-M, Camy-Peyret C. New measurements and improved calculations of self-broadening coefficients of lines in the v<sub>2</sub> band of H<sub>2</sub><sup>16</sup>O. J Quant Spectrosc Radiat Transfer 1981;26:483–94.
- [18] Nicolaisen FM, Workshop paper 5.8. In: Atmospheric spectroscopy applications workshop, Moscow, USSR, June 6-8, 1990.
- [19] Devi VM, Fridovich B, Jones GD, Snyder DGS. Intensities and half-widths for several H<sub>2</sub>O v<sub>2</sub> lines in the region 1500–1523 cm<sup>-1</sup>. J Mol Spectrosc 1985;111:114–8.
- [20] Eng RS, Kelley PL, Mooradian A, Calawa AR, Harman TC. Tunable laser measurements of water vapor transitions in the vicinity of 5 μm. Chem Phys Lett 1973;19:524–8.
- [21] Eng RS, Mantz AW. Tunable diode laser measurement of water vapor line parameters in the 10- to 15-µu spectral region. J Mol Spectrosc 1979;74:388–99.
- [22] Ben Aryeh Y. Line widths and intensities in the wings of the  $v_2$  water vapor band at 400 K and 540 K. J Quant Spectrosc Radiat Transfer 1967;7:211–24.
- [23] Izatt JR, Sakai H, Benedict WS. Positions, intensities, and widths of water-vapor lines between 475 and 692 cm<sup>-1</sup>. J Opt Soc Am 1969;59:19–26.
- [24] Guerra MA, Ketabi M, Sanchez A, Feld MS, Javan A. Water vapor spectroscopy at 5 µm using a tunable SFR laser. J Chem Phys 1975;63:1317–9.
- [25] Bauer A, Godon M, Duterage B. Self- and air-broadened linewidth of the 183 GHz absorption in water vapour. J Quant Spectrosc Radiat Transfer 1985;33:167–75.
- [26] Mrowinski D. Refraction and absorption in atmospheric gases near the 22 GHz water vapour rotational line. Z Angew Phys 1970;29:323–30.
- [27] Mucha JA. Tunable diode laser measurements of water vapor line parameters in the 6-μm spectral region. Appl Spectrosc 1982;36:141-7.
- [28] Eng RS, Kelley PL, Calawa AR, Harman TC, Nill KW. Tunable diode laser measurements of water vapour absorption line parameters. Mol Phys 1974;28:653–64.
- [29] Mandin JY, Camy-Peyret C, Flaud JM, Guelachvili G. Measurements and calculations of self-broadening coefficients of lines belonging to the 2v<sub>2</sub>, v<sub>1</sub>, and v<sub>3</sub> bands of H<sup>16</sup><sub>2</sub>O. Can J Phys 1982;60:94–101.
- [30] Frenkel L, Woods D. The microwave absorption by H<sub>2</sub>O vapor and its mixtures with other gases between 100 and 300-Gc/s. Proc IEEE 1966;54:498–505.
- [31] Markov VN. Temperature dependence of self-induced pressure broadening and shift of the 643–550 line of the water molecule. J Molec Spectrosc 1994;164:233–8.
- [32] Hartmann JM, Taine J, Bonamy J, Labani B, Robert D. Collisional broadening of rotation-vibration lines for asymmetric-top molecules II. H<sub>2</sub>O diode laser measurements in the 400–900 K range; calculations in the 300–2000 K range. J Chem Phys 1987;86:144–56.
- [33] Bauer A, Godon M, Kheddar M, Hartmann J-M, Bonamy J, Robert D. Temperature and perturber dependences of water-vapor 380 GHz-line broadening. J Quant Spectrosc Radiat Transfer 1987;37:531–9.
- [34] Liebe HJ, Thompson MC, Dillon TA. Dispersion studies of the 22 GHz water vapor line shape I. The Lorentzian behavior. J Quant Spectrosc Radiat Transfer 1969;9:31–47.
- [35] Rusk JR. Line-breadth study of the 1.64-mm absorption in water vapor. J Chem Phys 1965;42:493-500.
- [36] Bauer A, Godon M, Kheddar M, Hartmann J-M. Temperature and perturber dependences of water vapor line-broadening. Experiments at 183 GHz\* calculations below 1000 GHz. J Quant Spectrosc Radiat Transfer 1989;41:49–54.
- [37] Kasuga T, Kuze H, Shimizu T. Determinations of relaxation rate constants on the 22 GHz rotational transition of H<sub>2</sub>O by coherent transient spectroscopy. J Chem Phys 1978;69(11):5195–8.
- [38] Emery R. Atmospheric absorption measurements in the region of 1 mm wavelength. Infrared Phys 1972;12:65–79.
- [39] Sanderson RB, Ginsburg N. Line widths and line strengths in the rotational spectrum of water vapor. J Quant Spectrosc Radiat Transfer 1963;3:435–44.
- [40] Aushev AF, Borisova NF, Bykova ES, Osipov VM, Tsukanov VV. On the temperature dependence of the half-widths of the spectral lines of CO<sub>2</sub> and H<sub>2</sub>O. Opt Spectrosc 1990;68:700–1.
- [41] Adler-Golden S, Lee J, Goldstein N. Diode laser measurements of temperature dependent line parameters for water vapor near 820 nm. J Quant Spectrosc Radiat Transfer 1992;48:527–35.
- [42] Avetisov VG, Nadezhdinskii AI, Khusnutdinov AN, Omarova PM, Zyrianov MV. Diode laser spectroscopy of water vapor in 1.8 μM: line profile measurements. J Mol Spectrosc 1993;160:326–34.
- [43] Godlevskii AP, Kapitanov VA. Changes in the line shapes of water vapor due to broadening by foreign gases. J Appl Spectros 1978;28:142–6.
- [44] Remedios JJ. PhD thesis, University of Oxford, 1990.
- [45] Townes CH, Merritt FR. Water spectrum near one-centimeter wave-length. Phys Rev 1946;70:558-9.
- [46] Arroyo MP, Hanson RK. Absorption measurements of water-vapor concentration, temperature, and line-shape parameters using a tunable InGaAsP diode laser. Appl Opt 1993;32:6104–16.
- [47] Zou Q, Varanasi P. Laboratory measurement of the spectroscopic line parameters of water vapor in the 610–2100 and 3000–4050 cm<sup>-1</sup> regions at lower-tropospheric temperatures. J Quant Spectrosc Radiat Transfer 2003;82:45–98.

- [48] Toth RA. Air- and N<sub>2</sub>-broadening parameters of water vapor: 604 to 2271 cm<sup>-1</sup>. J Mol Spectrosc 2000;201:218–43.
- [49] 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. J Quant Spectrosc Radiat Transfer 2002;72:775–82.
- [50] Coheur PF, Fally S, Carleer M, Clerbaux C, Colin R, Jenouvrier A, et al. New water vapor line parameters in the 26000–13000 cm<sup>-1</sup> region. J Quant Spectrosc Radiat Transfer 2002;74:493–510.
- [51] Singh K, O'Brien JJ. Intensities and self-broadening coefficients of weak water vapor lines in the 720-nm region determined by intracavity laser absorption spectroscopy. J Mol Spectrosc 1994;167:99–108.
- [52] Upschulte BL, Allen MG. Diode laser measurements of line strengths and self-broadening parameters of water vapor between 300 and 1000 K near 1.31 μm. J Quant Spectrosc Radiat Transfer 1998;59:653–70.
- [53] Langlois S, Birbeck TP, Hanson RK. Diode laser measurements of H<sub>2</sub>O line intensities and self-broadening coefficients in the 1.4μm region. J Mol Spectrosc 1994;163:27–42.
- [54] Nagali V, Chou SI, Baer DS, Hanson RK. Diode laser measurements of temperature dependent half-widths of H<sub>2</sub>O transitions in the 1.4 μm region. J Quant Spectrosc Radiat Transfer 1997;57:795–809.
- [55] Chance KV, Park K, Evenson KM. Pressure broadening of far infrared rotational transitions: 88.65 cm<sup>-1</sup> H<sub>2</sub>O and 114.47 cm<sup>-1</sup> O<sub>3</sub>. J Quant Spectrosc Radiat Transfer 1998;59:687–8.
- [56] Podobedov VB, Plusquellic DF, Fraser GT. THz laser study of self-pressure and temperature broadening and shifts of water vapor lines for pressures up to 1:4 kPa. J Quant Spectrosc Radiat Transfer 2004;87:377–85.
- [57] Davis SJ, Kessler WJ, Bachmann M. Collisional broadening of absorption lines in water vapor and atomic iodine relevant to COIL diagnostics. In: Proceedings of the SPIE—The International Society for Optical Engineering; 1999.
- [58] Toth RA, Brown LR, Plymate C. Self-broadened widths and frequency shifts of water vapor lines between 590 and 2400 cm<sup>-1</sup>. J Quant Spectrosc Radiat Transfer 1998;59:529–62.
- [59] Merienne M-F, Jenouvrier A, Hermans C, Vandaele AC, Carleer M, Clerbaux C, et al. Water vapor line parameters in the 13000–9250 cm<sup>-1</sup> region. J Quant Spectrosc Radiat Transfer 2003;82:99–117.
- [60] Fally S, Coleur P-F, Carleer M, Clerbaux C, Colin R, Jenouvrier A, et al. Water vapor line broadening and shifting by air in the 26000–13000 cm<sup>-1</sup> region. J Quant Spectrosc Radiat Transfer 2003;82:119–31.
- [61] Lepere M, Henry A, Valentin A, Camy-Peyret C. Diode-laser spectroscopy: line profiles of H<sub>2</sub>O in the region of 1.39 μm. J Mol Spectrosc 2001;208:25–31.
- [62] Moretti L, Sasso A, Gianfrani L, Ciurylo R. Collisional-broadened and dicke-narrowed lineshapes of H<sup>16</sup><sub>2</sub>O and H<sup>18</sup><sub>2</sub>O transitions at 1.39 μm. J Mol Spectrosc 2001;205:20–7.
- [63] Toth R. Linelists of water vapor parameters from 500 to 8000 cm<sup>-1</sup>, see < http://mark4sun.jpl.nasa.gov.data/spec/H2O>, private communication, 2005.
- [64] Gamache RR, Hartmann J-M. An intercomparison of measured pressure-broadening and pressure-shifting parameters of water vapor. Can J Chem 2004;82:1013–27.
- [65] Levy A, Lacome N, Chackerian Jr. C. Collisional line mixing. In: Narahari Rao K, Weber A, editors. Spectroscopy of the Earth's atmosphere and interstellar medium. Boston: Academic Press Inc.; 1992. p. 261–337.
- [66] Robert D, Bonamy J. Short range force effects in semiclassical molecular line broadening calculations. J Phys 1979;20:923-43.
- [67] Lynch R. Half-widths and line shifts of water vapor perturbed by both nitrogen and oxygen. PhD dissertation, University of Massachusetts Lowell, June 1995.
- [68] Gamache RR, Lynch R, Neshyba SP. New developments in the theory of pressure-broadening and pressure-shifting of spectral lines of H<sub>2</sub>O: the complex Robert–Bonamy formalism. J Quant Spectrosc Radiat Transfer 1998;59:319–35.
- [69] Lynch R, Gamache RR, Neshyba SP. N<sub>2</sub> and O<sub>2</sub> induced halfwidths and line shifts of water vapor transitions in the (301)  $\leftarrow$  (000) and (221)  $\leftarrow$  (000) Bands. J Quant Spectrosc Radiat Transfer 1998;59:595.
- [70] Anderson PW. Pressure broadening in the microwave and infra-red regions. Phys Rev 1949;76:647-61.
- [71] Tsao CJ, Curnutte B. Line-widths of pressure-broadened spectral lines. J Quant Spectrosc Radiat Transfer 1962;2:41-91.
- [72] Kubo R. Generalized cumulant expansion method. J Phys Soc Japan 1962;17:1100-20.
- [73] Gamache RR, Rosenmann L. The effects of velocity averaging in broadening coefficient calculations. J Mol Spectrosc 1994;164:489–99.
- [74] 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.
- [75] Luo Y, Agren H, Vahtras O, Jorgensen P, Spirko V, Hettema H. Frequency-dependent polarizabilities and first hyperpolarizabilities of H<sub>2</sub>O. J Chem Phys 1993;98:7159–64.
- [76] Jones JE. On the determination of molecular fields. II. From the equation of state of a gas. Proc R Soc A 1924;106:463-77.
- [77] Hirschfelder JO, Curtiss CF, Bird RB. Molecular theory of gases and liquids. New York: Wiley; 1964.
- [78] 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.
- [79] Sack RA. Two-center expansion for the powers of the distance between two points. J Math Phys 1964;5:260-8.
- [80] Gray CG, Gubbins KE. Theory of molecular fluids. Oxford: Clarendon Press; 1984.
- [81] Downs J, Gray CG, Gubbins KE, Murad S. Spherical harmonic expansion of the intermolecular site-site potential. Mol Phys 1979;37:129.
- [82] Watson JKG. Determination of centrifugal distortion coefficients of asymmetric- top molecules. J Chem Phys 1967;46:1935-49.
- [83] Matsushima F, Odashima H, Iwaskai T, Tsunekawa S. Frequency measurement of pure rotational transitions of H<sub>2</sub>O from 0.5 to 5 THz. J Mol Struct 1995;352–353:371–8.

- [84] Flaud J-M, Camy-Peyret C. Watson Hamiltonian constants for low lying vibrational states of H<sub>2</sub>O. Private communication, 2005.
- [85] Grossmann BE, Browell EV, Bykov AD, Kapitanov VA, Lazarev VV, Ponomarev YN, et al. Investigation of H<sub>2</sub>O absorption line shifts caused by air pressure in the visible. Atm Opt 1990;3:617–30.
- [86] Flygare WH, Benson RC. The 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.
- [87] Lide DR, editor. CRC handbook of physics and chemistry. 83rd ed. Clevland, OH: The Chemical Rubber Company; 2003.
- [88] Gamache RR, Hartmann J-M. Collisional parameters of H<sub>2</sub>O lines: effects of vibration. J Quant Spectrosc Radiat Transfer 2004;83:119–47.
- [89] Wagner G, Birk M, Gamache RR, Hartmann J-M. Collisional parameters of H2O lines: effects of temperature. J Quant Spectrosc Radiat Transfer 2005;92:211–30.
- [90] Gray CG. On the theory of multipole interactions. Can J Phys 1968;46:135-9.
- [91] Neshyba SP, Lynch R, Gamache RR, Gabard T, Champion J-P. Pressure induced widths and shifts for the v<sub>3</sub> band of methane. J Chem Phys 1994;101:9412–21.
- [92] Buldyreva J, Benec'h S, Chrysos M. Infrared nitrogen-perturbed NO linewidths in a temperature range of atmospheric interest: an extension of the exact trajectory model. Phys Rev A 2000;63:012708.
- [93] Tipping RH, Herman RM. Impact theory for the noble gas pressure-induced HCl vibration-rotation and pure rotation line widths—I. J Quant Spectros Radiat Transfer 1970;10:881–96.
- [94] Herman RM, Tipping RH. Impact theory for the noble gas pressure-induced HCl vibration-rotation and pure rotation line shifts-II. J Quant Spectros Radiat Transfer 1970;10:897–908.
- [95] Berard M, Lallemand P. Influence of the use of approximate trajectories for binary collision calculations. J Quant Spectros Radiat Transfer 1978;19:387–96.
- [96] Buldyreva J, Bonamy J, Robert D. Semiclassical calculations with exact trajectory for N2 rovibrational Raman linewidths at temperatures below 300 K. J Quant Spectros Radiat Transfer 1999;62:321–43.
- [97] Buldyreva J, Benec'h S, Chrysos M. Oxygen-broadened and air-broadened linewidths for the NO infrared absorption bands by means of the exact-trajectory approach. Phys Rev A 2001;63:032705.
- [98] Lynch R, Gamache RR, Neshyba SP. Pressure broadening of H<sub>2</sub>O in the (301) ← (000) band: effects of angular momentum and close intermolecular interactions. J Quant Spectrosc Radiat Transfer 1998;59:615–26.
- [99] Lynch R, Gamache RR, Neshyba SP. Fully complex implementation of the Robert–Bonamy formalism: halfwidths and line shifts of H<sub>2</sub>O broadened by N<sub>2</sub>. J Chem Phys 1996;105:5711–21.
- [100] Gamache RR, Lynch R, Plateaux JJ, Barbe A. Halfwidths and line shifts of water vapor broadened by CO<sub>2</sub>: measurements and complex Robert–Bonamy formalism calculations. J Quant Spectros Radiat Transfer 1997;57:485–96.
- [101] Birnbaum G. Microwave pressure broadening and its application to intermolecular forces. Adv Chem Phys 1967;12:487-548.
- [102] Gamache RR, Neshyba SP, Plateaux JJ, Barbe A, Régalia L, Pollack JB. CO<sub>2</sub>-broadening of water-vapor lines. J Mol Spectrosc 1995;170:131–51.
- [103] Gamache RR, Lynch R, Brown LR. Theoretical calculations of pressure broadening coefficients for H<sub>2</sub>O perturbed by hydrogen or helium gas. J Quant Spectros Radiat Transfer 1996;56:471–87.
- [104] Wagner G, Birk M, Gamache RR, Hartmann J-M. Collisional parameters of H<sub>2</sub>O lines: effects of temperature. J Quant Spectrosc Radiat Transfer 2004;92:211–30.
- [105] Mandin J-Y, Chevillard JP, Flaud J-M, Camy-Peyret C. N<sub>2</sub> broadening coefficients of H<sub>2</sub><sup>16</sup>O lines between 8500 and 9300 cm<sup>-1</sup>. J Mol Spectrosc 1988;132:352–60.
- [106] Mandin J-Y, Chevillard JP, Camy-Peyret C, Flaud J-M. N<sub>2</sub>-broadening coefficients of H<sub>2</sub><sup>16</sup>O lines between 9500 and 11 500 cm<sup>-1</sup>. J Mol Spectrosc 1989;138:272–81.
- [107] Grossmann BE, Browell EV. Water-vapor line broadening and shifting by air, nitrogen, oxygen, and argon in the 720-nm wavelength region. J Mol Spectrosc 1989;138:562–95.
- [108] Brown LR, Plymate C. H<sub>2</sub>-broadened H<sub>2</sub><sup>16</sup>O in four infrared bands between 55 and 4045 cm<sup>-1</sup>. J Quant Spectrosc Radiat Transfer 1996;56:263–82.