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Reduced matrix elements in semi-classical line shape calculations: Application to H₂O-H₂

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Abstract. Making reliable semi-classical calculations using the Modified Complex Robert and Bonamy formalism require an intermolecular potential expanded to a high order. Reduced matrix elements (RMEs) need to be computed for each component of the intermolecular potential using the wavefunctions of the states involved in the transition. Calculations for a number of transitions of 13 vibrational bands were performed using the vibrational dependent RMEs and using the ground state RMEs for both upper and lower states. The calculations show that for transitions that obey the sum rules the spectroscopic effect is small.

1. Introduction

It is now possible to make semi-classical calculations for the collisional broadened half-width and line shift that do not utilize scaling factors or arbitrary adjustable parameters. The theory was developed by Robert and Bonamy [1] and later modified by Ma *et al.* [2] and is called the Modified Complex Robert and Bonamy formalism (MCRB). Reliable calculations can be made if the calculations employ the best-known intermolecular potentials, with the atom-atom component expanded to high order as recommended by Ma *et al.* [3], include the imaginary components of the collisional cross-sections, and the velocity integral is explicitly computed; all of these factors have been shown to be necessary to yield accurate results [4-8]. It was shown that the potential should be expanded up to 20th order and rank = 4 to ensure the convergence of the calculations [3, 9]. The resulting intermolecular potential can contain hundreds to thousands of terms.

To make a complete calculation using the MCRB formalism, one must compute the reduced matrix elements (RMEs) that correspond to each term of the intermolecular potential. The RMEs squared give the probability of a collisionally induced transition between a lower and an upper state. When calculations are performed for vibrational bands, the vibrationally dependent reduced matrix elements must be used.

In the calculations, all collisional connections $i' \leftarrow i$ must be included. A convenient check that all connected states have been included can be accomplished using the sum rules developed by Lamouroux *et al.* [10]. These sums rules states that, for a given state i , the sum of the reduced matrix elements squared for all possible connected states i' equals 1. The sums rules are applied for each term in the intermolecular potential (see Ref. [10] for details).

2. Calculation for the H₂O-H₂ system

Calculations were performed on the H₂O-H₂ collision system using the MCRB formalism for the rotational band, 1-4 quanta of exchange for the 3 fundamental bands, as well as the 301-000 band,



allowing a study of the vibrational dependence of the half-width and the line shift (all parameters used in the calculations can be found in Ref. [11]). The calculation used *ab initio* reduced matrix elements from Lamouroux *et al.* [10]. The H₂O energy levels were taken from the MARVEL list [12].

For a number of transitions, the vibrational dependence showed unphysical behavior, with half-widths too low by as much as ~40%. By looking more closely at the problematic transitions, it was found that the sum rules were not obeyed either for the upper or lower states (or both). In their study of vibrational dependence of H₂O, Gamache and Hartmann [13] showed that the spectroscopic effects, resulting from the modification of the wavefunction and the energy levels (giving different energy gaps) when the vibrational band changes are small. Given this information, test calculations were made using the ground state RMEs for both the upper and lower states. Note, the H₂O energy levels were fixed from MARVEL, making the spectroscopic effect even smaller.

Figure 1 presents the percent difference between the calculated half-width using the ground state RMEs and the vibrational dependent RMEs, for some water vapor transitions perturbed by hydrogen. The selected transitions are taken from the ν_1 , $2\nu_1$, ν_2 , $2\nu_2$, $3\nu_2$, ν_3 , $2\nu_3$, $3\nu_3$, $4\nu_3$ and $3\nu_1+\nu_3$ bands. In Figure 1, transitions for which the upper and lower states obey the sum rules are shown as blue solid circles. The transitions for which the sum rules are not obeyed for all states are shown as red solid triangles. This figure demonstrates that using ground state RMEs does not introduce significant error to the calculations. Thus, calculations made in the future will employ the ground state RMEs.

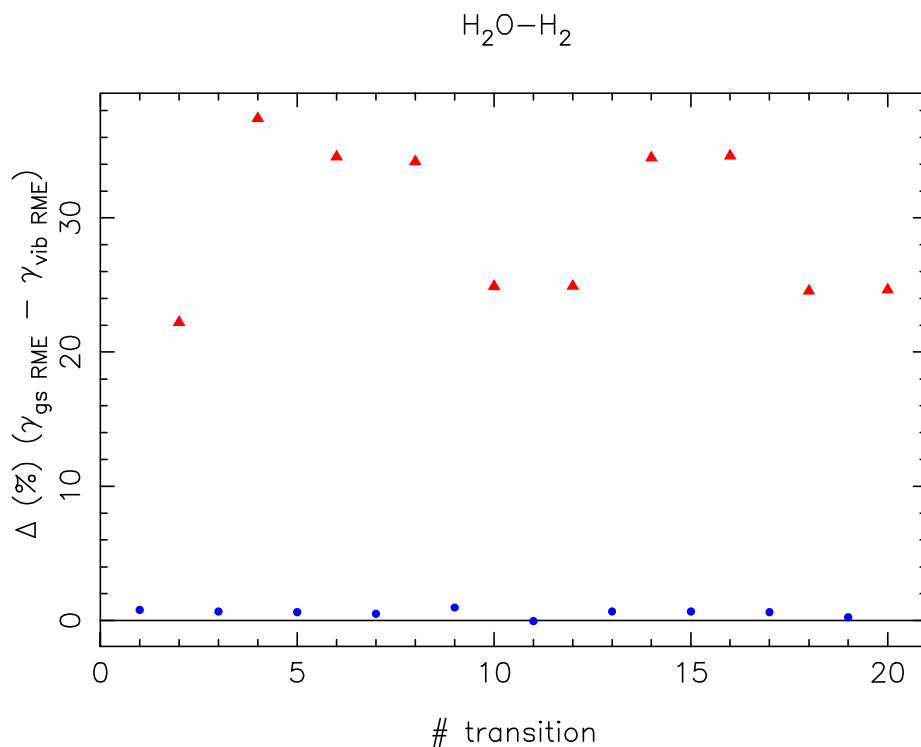


Figure 1. Percent difference between the calculated half-width using the ground state RMEs and the vibrational dependent RMEs for some transitions of the H₂O-H₂. The transitions that obey the sum rules are the blue solid circles, the transitions that does not obey the sum rules are the red solid triangles.

3. Conclusion

Calculations were performed for water vapor transitions broadened by hydrogen using the vibrational dependent RMEs and using the ground state RMEs for both upper and lower states. The percent difference between the calculated half-width using the ground state RMEs and the vibrational RMEs was computed for a large number of transitions. Small differences were observed for the transitions that obey the sum rules, showing a small spectroscopic effect of the reduced matrix elements.

The effects of using vibrationally dependent RMEs is undergoing further investigation. Until the study is finalized ground-state RMEs will be utilized in the MCRB calculations.

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