**Theoretical Studies of Spectroscopic Line Mixing in Remote Sensing Applications**

Q. Ma¹, C. Boulet², and R. H. Tipping¹

NASA/GISS and Columbia University, New York NY¹, Institut des Sciences Moléculaires, CNRS and Université Paris-Sud Bât 350, Campus d'Orsay, France², University of Alabama, Tuscaloosa AL³

**Introduction**

The phenomenon of collisional transfer of intensity due to line mixing has an increasing importance for atmospheric monitoring. From a theoretical point of view, all relevant information of the line mixing is determined by the rotational constants and the transition dipole moment. The diagonal elements correspond to line interferences. For simple systems, accurate fully quantum calculations are feasible. However, fully quantum calculations become unrealistic for more complex systems. On the other hand, the semi-empirical approaches (for example, ECS and ICS models) have found that in developing the spectroscopic line mixing, without justification these authors had applied the isolated line approximation in evaluating the scattering cross sections. Thus, it is this assumption that blocks the possibility to calculate the whole relaxation matrix at all. By eliminating this unjustified application, and accurately evaluating matrix elements of the exponential operators, we have developed a more complete formalism. In this formalism, we are now able to systematically reduce uncertainties for calculated half-widths and shifts, but also to remove a once insurmountable obstacle to calculate the whole relaxation matrix.

**New Formalism**

A. A derivation error in developing the RB formalism

The error occurs in a process to apply the cumulant expansion for the operator of exp(S(S̃ − S̃)) in developing the RB formalism. Because Robert and Bonamy adopted a wrong definition of the average of the cumulant expansion, their expression for the operator of S̃ − S̃ is not correct. The difference between the expression and the correct one is

\[ \langle e^{iS(S̃ − S̃)} \rangle = \sum_{n=0}^{\infty} \frac{\theta_n(S(S̃ − S̃))^n}{n!} \]

It turns out that this subtle difference results in profound consequences. Within the RB formalism, (S̃ − S̃) depends on states of the bath molecule and its matrix dimension equals to (K lines) times (K lines) (of bath states). In contrast, within the new formalism, this operator is independent of the bath states and its matrix dimension equals to # of lines.

As a result, within the RB formalism, one has to diagonalize a huge size matrix for each of collisional trajectories. On the other hand, one only needs to diagonalize this much smaller size matrix for each trajectory. And therefore, the total number of Ñ_Ñ_S̃_S̃ systems will be reduced by 68,000 times. Mainly due to this difficulty, Robert and Bonamy had to apply the isolated line approximation to evaluate the relaxation matrix whose diagonal elements give half-widths and shifts, and off-diagonal elements. This assumption that ability of their formalism to calculate off-diagonal elements of the relaxation matrix W at all. This is the intrinsic reason why the RB formalism fails in studying the line mixing.

B. The isolated line approximation adopted by Robert and Bonamy

Based on the isolated line approximation, Robert and Bonamy assumed that

\[ \langle i f | e^{-iS(S̃ − S̃)} | f \rangle = \delta_{if} \delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\zeta} \]

and only calculated the diagonal elements of W from the expression of

\[ \langle i f | W | f \rangle = 2 \pi \int_{0}^{\infty} \frac{dk}{k} k \cdot \frac{dk}{dk} \langle i f | e^{-iS(S̃ − S̃)} | f \rangle \delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\zeta} \]

Unfortunately, this assumption is not valid in many cases and due to this unjustified assumption, several theoretical problems, half-widths and shifts contain errors. Furthermore, because only diagonal elements of W are available, they had to assume that matrix elements of the resolved operator is given by

\[ \langle i f | W | f \rangle \approx \frac{1}{2 \pi} \int_{0}^{\infty} \frac{dk}{k} k \cdot \frac{dk}{dk} \langle i f | e^{-iS(S̃ − S̃)} | f \rangle \delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\zeta} \]

Thus, they can’t consider the line mixing at all.

C. The new formalism capable to consider the line mixing

Within the new formalism, because the size of S̃ − S̃ is small, one can diagonalize this matrix and accurately evaluate all matrix elements of i f | e^{-iS(S̃ − S̃)} | f \rangle \approx \frac{1}{2 \pi} \int_{0}^{\infty} \frac{dk}{k} k \cdot \frac{dk}{dk} \langle i f | e^{-iS(S̃ − S̃)} | f \rangle \delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\zeta} \]

The method is applicable for all trajectory models and for complicated accurate potentials. After the matrix is available, one can easily obtain line mixing and line splitting mixing parameters with

\[ \Delta \nu_a = \sum_{\beta \neq \alpha} \delta \nu_{a\beta} = \sum_{\beta \neq \alpha} \Delta \nu_{a\beta} \]

where \( \delta \nu_{a\beta} \) are reduced dipole matrix elements and \( \Delta \nu_a \) are line frequencies.

**Applications for linear molecules**

A. Raman Q lines of NH₃ in NH₃ bath

We have considered Raman Q lines of NH₃ in NH₃ bath. For the Raman Q transitions, lines can be simply labeled by a number of Q(i) (i = 1, 2, ...). Due to the symmetry, the line mixing occurs only among lines with the same evenness or the oddness of Q(i). As a result, the whole matrix is divided into two sub-matrices constructed by even Q(i) and odd Q(i), respectively. Based on an accurate potential model, we have calculated these matrices.

**Applications for symmetric-top molecules**

C. Parallel and perpendicular Bands of CO₂ broadened by N₂

For infrared lines where both rotational and vibrational quantum numbers are the same, the calculated W matrix for two NH₃ states with the same k, but different vibrational inversion symmetries. Because the potential does not cause line coupling between two lines with different k values, the relaxation matrix is divided by sub-matrices associated with different k values. In the present study, we have considered 217 lines whose initial angular quantum number k is less than 9. With this cut-off, there are 9 sub-matrices associated with k = 0, 1, ..., 8 and their corresponding dimensions are 17, 40, 34, 28, 22, 16, 10, and 4.