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 bestowed in the 2D-Rotational Raman (2DR) or 2D-Vibrational Raman (2DV) spectra. 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. One of the most promising approaches used in recent years is the mixing approximation, which has been widely used to calculate half-widths and shifts for decades, fails in calculating the off-diagonal matrix elements. As a result, in order to understand the line mixing, semi-empirical or fitting laws such as the ECS and IOS models have been developed. We have found that in developing a new theoretical approach, without justification these authors had applied the isolated line approximation in evaluating the scattering cross-section of a Raman band, this is its 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 careful formalism. Finally, we are now able not only to reduce uncertainties for calculated half-widths and shifts, but also to remove a once inescapable obstacle to calculate the whole relaxation matrix.

**New formalism**

### 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_{i} − S_{j}) 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 S_{i} − S_{j} is not correct. The difference between the expression and the correct one is

\[ \bar{S}_{i,j} \approx \frac{1}{2} \left( \frac{\partial^{2} \rho}{\partial S_{i} \partial S_{j}} + \frac{\partial^{2} \rho}{\partial S_{j} \partial S_{i}} \right) \]

It turns out that this subtle difference results in profound consequences. Within the RB formalism, S_{i,j} depends on states of the bath molecule and its matrix dimension equals to (k of lines) times (k 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 colossal trajectories. On the other hand, only one trajectory is needed to be diagonalized in the new formalism. Also, the size of diagonalization of the N_{2} Ny system could be slight by 68,000 times. Mainly due to this difficulty, Robert and Bonamy had to apply the isolated line approximation to evaluate the reduced matrix whose diagonal elements give half-widths and shifts, and off-diagonal matrix elements cannot be evaluated by 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

\[ \left\langle f \right| \rho \left| f \right\rangle \approx \sum_{n=1}^{k} \left( \frac{\partial^{2} \rho}{\partial S_{i} \partial S_{j}} + \frac{\partial^{2} \rho}{\partial S_{j} \partial S_{i}} \right) \]

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

\[ \left\langle \left\langle \frac{1}{2} \right| W | \frac{1}{2} \right\rangle \approx \sum_{n=1}^{k} \left( \frac{\partial^{2} \rho}{\partial S_{i} \partial S_{j}} + \frac{\partial^{2} \rho}{\partial S_{j} \partial S_{i}} \right) \]

Unfortunately, this assumption is not valid in many cases and due to this unjustified assumption, half-widths and shifts can be erroneous. Therefore, because only diagonal elements of W are available, they had to assume that matrix elements of the resolved operator is given by

\[ \left\langle \left\langle f \right| \rho \left| f \right\rangle \approx \sum_{n=1}^{k} \left( \frac{\partial^{2} \rho}{\partial S_{i} \partial S_{j}} + \frac{\partial^{2} \rho}{\partial S_{j} \partial S_{i}} \right) \]

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 S_{i,j} is small, one can diagonalize this matrix and accurately evaluate all matrix elements of \[ \left\langle f \right| \rho \left| f \right\rangle \]. Then, the whole matrix elements of W can be calculated from the expression of

\[ \left\langle \left\langle \frac{1}{2} \right| W | \frac{1}{2} \right\rangle \approx \sum_{n=1}^{k} \left( \frac{\partial^{2} \rho}{\partial S_{i} \partial S_{j}} + \frac{\partial^{2} \rho}{\partial S_{j} \partial S_{i}} \right) \]

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

\[ \frac{\partial^{2} \rho}{\partial S_{i} \partial S_{j}} \frac{\partial^{2} \rho}{\partial S_{j} \partial S_{i}} \]

### Applications for linear systems

#### A. Raman Q lines in N_{2} in N_{2} bath

We have considered Raman Q lines of N

\[ \text{in N}_{2} \text{ bath. For the Raman Q transitions, lines can be simply labeled by a number of Q only.} \]

Due to the symmetry, the line mixing occurs only among lines with the same evenness or oddness of Q). As a result, the whole W matrix is divided into two sub-matrices constructed by even Q of Q) and odd Q), respectively. Based on an accurate potential model, we have calculated these matrices.

#### B. Infrared P and R lines of CH_{2} broadened by N_{2}

For infrared lines with l > 1, the wave numbers are not identical, to calculate off-diagonal elements of \( S_{i,j} \), requires more resonances functions than Raman Q lines. However, by introducing symmetric two dimensional Fourier and Hilbert transforms, we have developed a tool to solve this difficulty. By applying this method to the CH_{2} – N_{2} system, we have successfully calculated the W matrices based on a new updated potential model. Similar to the N_{2} – N_{2} system, the tensor rank L of the potential must be even, lines with even values of l does not mix with lines with odd l. In Matrix 1, we present a calculated W matrix in the line space constituted by P(R) + R(P). In contrast, in the RB formalism, we have obtained the results that the new formalism is significantly reduced and closer to measured data.

#### Conclusion

In comparison with the RB formalism, half-widths obtained from the new formalism are significantly reduced and become closer to measured data. In Table 1, we present calculated half-widths together with measured data by Fine et al. (JCP 99, 537 (1993)) for some lines with k = 3. The agreement between our results and measured data is very poor. In Table 2, we also present the calculated complex relaxation sub-matrix with k = 6 whose real and imaginary parts are given in Matrix 2 and Matrix 3. From these W matrices, one can find a satisfying description about the line mixing. For example, one can conclude that the doublets are strongly mixed.