Theoretical Studies of Spectroscopic Line Mixing in Remote Sensing Applications

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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 contained in the relaxation matrix whose diagonal elements give half-widths and shifts, and off-diagonal elements correspond to line interferences. For simple systems, accurate fully quantum calculations are feasible. However, full quantum calculations become unrealistic for more complex systems. On the other hand, the semi-classical Robert-Bonamy (RB) formalism, 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 fitting or scaling laws such as the ECS and IOS models are commonly used. Recently, we have found that in developing the RB formalism, without justification these authors had applied the isolated line approximation in evaluating the scattering operator given in exponential form. Furthermore, 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 capable formalism. With this new formalism, we are now able not only to 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 $\exp(iS_1 - S_2)$ 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 $iS_1 - S_2$ is not correct. The difference between their expression and the correct one is

$$S_{1or2, new} = \sum_{j_b}(2j_b + 1)\rho_{j_b}S_{1or2,RB}$$

It turns out that this subtle difference results in profound consequences. Within the RB formalism, $iS_1 - S_2$ depends on states of the bath molecule and its matrix dimension equals to (# of lines) times (# 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 a **much smaller size matrix** for each of trajectories. As an example, the computational burdens for the $N_2 - N_2$ system could differ by 68,900 times. Mainly due to this difficulty, Robert and Bonamy had to apply the isolated line approximation to evaluate $\exp(iS_1 - S_2)$. Unfortunately, it is this simplifying assumption that blocks the 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

$$\ll if|\, e^{-iS_1 - S_2}\, |if \gg\, = e^{\ll if|-iS_1-S_2|if \gg}$$

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

$$\ll if|W|if \gg = \frac{n_b \bar{v}}{2\pi c}\int_{r_{c,min}}^{+\infty} 2\pi\left(b\frac{db}{dr_c}\right)dr_c[1 - e^{\ll if|-iS_1-S_2|if \gg}].$$

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

$$\ll if\left|\frac{1}{\omega - L_a - in_b W}\right| if \gg\, = \frac{1}{\omega - \omega_{if} - in_b \ll if|W|if \gg}.$$

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 $iS_1 - S_2$ is small, one can diagonalize this matrix and accurately evaluate all matrix elements of $\ll i'f'|\, e^{-iS_1 - S_2}\, |if \gg$. Then, the whole matrix elements of W can be calculated from the expression of

$$\ll i'f'|W|if \gg = \frac{n_b \bar{v}}{2\pi c}\int_{r_{c,min}}^{+\infty} 2\pi\left(b\frac{db}{dr_c}\right)dr_c[\delta_{i'i}\delta_{f'f} - \ll i'f'|\, e^{-iS_1 - S_2}\, |if \gg].$$

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

$$Y_k = 2\sum_{l\neq k}\frac{d_l}{d_k}\times\frac{W_{lk}}{\omega_k - \omega_l},$$

where d_i are reduced dipole matrix elements and ω_i are line frequencies.

Applications for linear molecules

A. Raman Q lines of N_2 lines broadened by N_2

We have considered Raman Q lines of N_2 in N_2 bath. For the Raman Q transitions, lines can be simply labeled by a number of Q(j) (i.e., $j = j_i = j_f$). Due to the symmetry, the line mixing occurs only among lines with the same evenness or the oddness of Q(j). As a result, the whole W matrix is divided into two sub-matrices constructed by even Q(j) and odd Q(j), respectively. Based on an accurate potential model, we have calculated these matrices.

Fig. 1 Calculated half-widths of Raman Q lines from the RB and new theories are given by + and Δ. Values from the close coupling method are given by ○ and two measured results are plotted by □ and ×.

In Fig. 1, we present a comparison between calculated half-widths (i.e., real parts of the diagonal elements of W) from the RB formalism and the new theory. In general, new calculated results are reduced by 15 % and become closer to measured data and results obtained from the full quantum close coupling (CC) method.

Furthermore, a re-normalization procedure can be applied to improve the accuracy of calculated off-diagonal elements. we present comparisons between our renormalized results and that obtained from CC method for some selected elements of W(j', j) (in units of 10^{-3} cm^{-1} atm^{-1}) with j = 4, 6, and 8 in Fig. 2. As shown in the figure, the agreements are very good.

Fig. 2 (a)-(c). Comparison of our renormalized results and the CC values for some selected off-diagonal elements

B. Infrared P and R lines of C_2H_2 broadened by N_2

For infrared lines where initial and final rotational quantum numbers are not identical, to calculate off-diagonal elements of $iS_1 - S_2$ requires more resonance 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 $C_2H_2 - N_2$ 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_1 of the potential must be even, lines with even j values don't mixed with lines with odd j. In Matrix 1, we present a calculated W matrix in the line space constricted by R(0), P(2), R(2), ..., R(40), and P(42). The diagonal elements of this matrix are calculated half-widths. In comparison with the RB results, the new values are significantly reduced and closer to measured data.

Matrix 1. A 42 × 42 sub-matrix of relaxation operator (10^{-3} cm^{-1} atm^{-1}) in the P and R line space

	R(0)	P(2)	R(2)	P(4)	R(4)	P(6)	R(6)	P(8)	R(8)	P(10)	R(10)	P(12)			P(40)	R(40)	P(42)
1 R(0)	122.06	7.27	−10.25	2.98	−3.74	2.07	−2.45	1.58	−1.79	1.23	−1.34	0.99	.	.	−0.00	.	0.00
2 P(2)	7.22	115.90	4.53	−12.93	2.88	−5.12	2.21	−3.39	1.75	−2.45	1.42	−1.84	.	−0.01	0.00	.	−0.00
3 R(2)	−10.08	4.48	112.36	3.53	−13.94	2.65	−5.97	2.13	−3.99	1.74	−2.88	1.46	.	−0.01	−0.01	.	0.00
4 P(4)	2.90	−12.61	3.48	109.02	2.98	−14.05	2.40	−6.47	2.00	−4.36	1.69	−3.17	.	−0.01	−0.01	.	0.00
5 R(4)	−3.56	2.77	−13.45	2.94	105.60	2.61	−13.94	2.19	−6.76	1.88	−4.61	1.63	.	0.01	−0.01	.	0.00
6 P(6)	1.95	−4.80	2.54	−13.36	2.57	102.42	2.32	−13.93	2.02	−6.97	1.78	−4.80	.	−0.02	0.00	.	−0.01
7 R(6)	−2.25	2.07	−5.49	2.31	−13.00	2.29	99.80	2.10	−14.19	1.88	−7.17	1.68	.	0.01	−0.01	.	0.01
8 P(8)	1.44	−3.04	1.99	−5.82	2.10	−12.69	2.07	97.90	1.93	−14.72	1.76	−7.43	.	−0.02	0.00	.	−0.01
9 R(8)	−1.58	1.60	−3.49	1.87	−5.93	1.94	−12.61	1.91	96.60	1.80	−15.33	1.65	.	0.01	−0.02	.	0.00
10 P(10)	1.09	−2.11	1.59	−3.73	1.76	−5.96	1.81	−12.76	1.77	95.79	1.68	−15.96	.	−0.03	0.00	.	−0.01
11 R(10)	−1.16	1.27	−2.43	1.56	−3.86	1.67	−5.98	1.70	−13.01	1.66	95.26	1.56	.	0.01	−0.02	.	0.00
12 P(12)	0.87	−1.56	1.32	−2.64	1.50	−3.93	1.58	−6.03	1.59	−13.31	1.54	94.83	.	−0.04	0.00	.	−0.02
13	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
14 P(40)	0.00	−0.00	0.00	−0.00	0.00	−0.01	0.00	−0.01	0.00	−0.03	0.00	−0.02	.	45.94	0.05	.	−12.26
15 R(40)	−0.00	0.00	−0.00	0.00	−0.01	0.00	−0.01	0.00	−0.01	0.00	−0.01	0.00	.	0.05	46.97	.	0.04
16 P(42)	0.00	−0.00	0.00	−0.00	0.00	−0.00	0.00	−0.00	0.00	−0.01	0.00	−0.00	.	−8.09	0.03	.	44.76

C. Parallel and perpendicular Bands of CO_2 broadened by N_2

For the CO_2 molecule whose rotational constant is small (i.e., 0.4 cm^{-1}), one must consider the line mixing and sizes of the W matrices would be pretty large. For the $\Sigma\to\Sigma$ and the $\Sigma\to\Pi$ bands, we have calculated a 122 × 122 and a 183 × 183 of matrices of W, respectively. Some results are presented in Figs. 3 and 4.

Fig. 3. Comparison between ECS and our results of off-diagonal elements of W coupling R(16) to other R(J') lines.

Fig. 4. Comparison of the ECS line mixing coefficients and the present results with measured data in $\Sigma\to\Sigma$ band.

Applications for symmetric-top molecules

We have considered the ν_1 band of NH_3 and calculated the W matrices in NH_3 bath based on a potential model consisting of the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. The ν_1 transitions occur between two NH_3 states that have 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 j_i are less than 9. With this cut-off, there are 9 sub-matrices associated with k = 0, 1, …, 8 and their corresponding dimensions are 17, 46, 40, 34, 28, 22, 16, 10, and 4.

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 Pine et al. (JQRST **50**, 337 (1093)) for some lines with k = 3. The agreement between the new values and the data is very good. 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 obtain all information about the line mixing. For example, one can conclude that the doublets are strongly mixed.

Table 1. Self-broadened half-widths (10^{-3} cm^{-1} atm^{-1}) of NH_3 lines in the ν_1 band

Lines	33a ← 33s	33s ← 33a	43a ← 33s	43s ← 43a	43a ← 43s	43s ← 43a	53a ← 53s	53s ← 53a	63a ← 63s	63s ← 63a
Exp.	656.18	644.83	630.95	627.51	543.61	539.76	483.12	476.02	422.73	448.77
New	660.48	660.07	616.06	616.00	562.61	561.87	498.64	498.45	445.38	445.38
RB	747.90	747.58	687.96	687.89	621.70	621.10	541.38	541.22	479.06	479.06

Matrix 2. A real part of 16 × 16 sub-matrix of relaxation operator (10^{-3} cm^{-1} atm^{-1}) with k = 6

	66a ← 66s	66s ← 66a	76a ← 66s	76s ← 66a	66a ← 76s	66s ← 76a	76a ← 76s	76s ← 76a	86a ← 76s	86s ← 76a	76a ← 86s	76s ← 86a	86a ← 86s	86s ← 86a	96a ← 86s	96s ← 86a
1 66a ← 66s	660.6	−358.4	0.0	0.0	0.0	0.0	−10.9	−13.2	0.0	0.0	0.0	0.0	−1.8	−1.7	0.0	0.0
2 66s ← 66a	−358.4	660.3	0.0	0.0	0.0	0.0	−14.5	−10.9	0.0	0.0	0.0	0.0	−1.8	−1.8	0.0	0.0
3 76a ← 66s	0.0	0.0	631.9	−332.1	0.0	0.0	0.0	0.0	−4.4	−5.2	0.0	0.0	0.0	0.0	−0.4	−0.4
4 76s ← 66a	0.0	0.0	−332.1	631.8	0.0	0.0	0.0	0.0	−4.2	−4.4	0.0	0.0	0.0	0.0	−0.4	−0.4
5 66a ← 76s	0.0	0.0	0.0	0.0	630.8	−336.2	0.0	0.0	0.0	0.0	−3.4	−3.3	0.0	0.0	0.0	0.0
6 66s ← 76a	0.0	0.0	0.0	0.0	−336.2	630.6	0.0	0.0	0.0	0.0	−3.9	−3.4	0.0	0.0	0.0	0.0
7 76a ← 76s	−10.9	−14.5	0.0	0.0	0.0	0.0	594.6	−311.9	0.0	0.0	0.0	0.0	−12.0	−15.3	0.0	0.0
8 76s ← 76a	−13.2	−10.9	0.0	0.0	0.0	0.0	−311.9	594.6	0.0	0.0	0.0	0.0	−16.7	−12.0	0.0	0.0
9 86a ← 76s	0.0	0.0	−4.4	−4.2	0.0	0.0	0.0	0.0	569.6	−289.6	0.0	0.0	0.0	0.0	−4.2	−5.2
10 86s ← 76a	0.0	0.0	−5.2	−4.4	0.0	0.0	0.0	0.0	−289.6	569.8	0.0	0.0	0.0	0.0	−4.1	−4.3
11 76a ← 86s	0.0	0.0	0.0	0.0	−3.4	−3.9	0.0	0.0	0.0	0.0	567.7	−296.0	0.0	0.0	0.0	0.0
12 76s ← 86a	0.0	0.0	0.0	0.0	−3.3	−3.4	0.0	0.0	0.0	0.0	−296.0	567.7	0.0	0.0	0.0	0.0
13 86a ← 86s	−1.8	−1.8	0.0	0.0	0.0	0.0	−12.0	−16.7	0.0	0.0	0.0	0.0	536.0	−276.7	0.0	0.0
14 86s ← 86a	−1.7	−1.8	0.0	0.0	0.0	0.0	−15.3	−12.0	0.0	0.0	0.0	0.0	−276.7	536.2	0.0	0.0
15 96a ← 86s	0.0	0.0	−0.4	−0.4	0.0	0.0	0.0	0.0	−4.2	−4.1	0.0	0.0	0.0	0.0	515.1	−255.3
16 96s ← 86a	0.0	0.0	−0.4	−0.4	0.0	0.0	0.0	0.0	−5.2	−4.3	0.0	0.0	0.0	0.0	−255.3	515.2

Matrix 3. An imaginary part of 16 × 16 sub-matrix of relaxation operator (10^{-3} cm^{-1} atm^{-1}) with k = 6

	66a ← 66s	66s ← 66a	76a ← 66s	76s ← 66a	66a ← 76s	66s ← 76a	76a ← 76s	76s ← 76a	86a ← 76s	86s ← 76a	76a ← 86s	76s ← 86a	86a ← 86s	86s ← 86a	96a ← 86s	96s ← 86a
1 66a ← 66s	23.23	−0.34	0.0	0.0	0.0	0.0	−0.04	−0.03	0.0	0.0	0.0	0.0	−0.01	−0.01	0.0	0.0
2 66s ← 66a	−0.34	−23.70	0.0	0.0	0.0	0.0	−0.06	−0.05	0.0	0.0	0.0	0.0	−0.01	−0.01	0.0	0.0
3 76a ← 66s	0.0	0.0	22.98	1.67	0.0	0.0	0.0	0.0	0.29	0.01	0.0	0.0	0.05	0.06	0.0	0.0
4 76s ← 66a	0.0	0.0	1.67	−18.74	0.0	0.0	0.0	0.0	0.27	0.28	0.0	0.0	0.04	0.05	0.0	0.0
5 66a ← 76s	0.0	0.0	0.0	0.0	18.14	−2.11	0.0	0.0	0.0	0.0	−0.25	−0.23	0.0	0.0	0.0	0.0
6 66s ← 76a	0.0	0.0	0.0	0.0	−2.11	−23.10	0.0	0.0	0.0	0.0	−0.25	−0.23	0.0	0.0	0.0	0.0
7 76a ← 76s	−0.04	−0.06	0.0	0.0	0.0	0.0	17.70	−0.13	0.0	0.0	0.0	0.0	−0.03	0.04	0.0	0.0
8 76s ← 76a	−0.03	−0.05	0.0	0.0	0.0	0.0	−0.13	−18.01	0.0	0.0	0.0	0.0	0.04	−0.03	0.0	0.0
9 86a ← 76s	0.0	0.0	0.27	0.27	0.0	0.0	0.0	0.0	19.83	2.46	0.0	0.0	0.29	0.32	0.0	0.0
10 86s ← 76a	0.0	0.0	0.29	0.28	0.0	0.0	0.0	0.0	2.46	−13.77	0.0	0.0	0.29	0.32	0.0	0.0
11 76a ← 86s	0.0	0.0	0.0	0.0	−0.25	−0.25	0.0	0.0	0.0	0.0	12.66	−2.51	0.0	0.0	0.0	0.0
12 76s ← 86a	0.0	0.0	0.0	0.0	−0.23	−0.23	0.0	0.0	0.0	0.0	−2.51	−19.05	0.0	0.0	0.0	0.0
13 86a ← 86s	−0.01	−0.01	0.0	0.0	0.0	0.0	−0.03	0.04	0.0	0.0	0.0	0.0	14.69	0.05	0.0	0.0
14 86s ← 86a	−0.01	−0.01	0.0	0.0	0.0	0.0	0.04	−0.03	0.0	0.0	0.0	0.0	0.05	14.76	0.0	0.0
15 96a ← 86s	0.0	0.0	0.06	0.05	0.0	0.0	0.0	0.0	0.29	0.29	0.0	0.0	0.0	0.0	18.81	2.36
16 96s ← 86a	0.0	0.0	0.06	0.06	0.0	0.0	0.0	0.0	0.32	0.32	0.0	0.0	0.0	0.0	2.36	−12.71

Applications for asymmetric-top molecules

The new formalism is also applicable for asymmetric-top molecules. Many papers have been devoted to the line mixing for molecules important in atmospheric applications. But, few of them explicitly carry out numerical calculations for the H_2O lines. In general, because energy gaps between different H_2O states are pretty large, one expects that effects from the line mixing are negligible. This conclusion was supported by a paper by K. S. Lam in 1977. He calculated the line mixing for 11 lines in the microwave region and found that the line mixing is weak. With the new method, we have verified his calculations and confirmed his works, regarding either the mixing selection rules or the weakness of the off-diagonal elements mixing some of these lines. However, among all 11 lines considered by him, none of them are in favor of the line mixing. As a result, the group considered by him is not a candidate to have significant effects. His conclusions are correct, but the applicability is limited. One should not apply it everywhere without exception. In fact, we have found that there are dozens of strongly coupled lines. For example, for a pair of $15_{69}\leftarrow 15_{510}$ and $15_{510}\leftarrow 15_{411}$, in comparison with results obtained from the RB formalism, calculated half-widths could be reduced by 5 % and meanwhile, variations of calculated shifts could be as large as 25 %. In summary, one can conclude that for most of the H_2O lines, it is unnecessary to consider the line mixing. But, there could be exceptions in vibrational bands.

Conclusions

With the new formalism and accurate potential models, we have studied the line mixing for linear , symmetric-top, and asymmetric-top molecules perturbed by molecules. So far, for such complex systems, there are no "first principle" calculations existing and one has to rely on the semi-empirical ECS and IOS models. In comparison with the latter, the present formalism does not neglect the internal degrees of freedom of the perturbing molecules and enables one to obtain the whole relaxation matrix starting from the potential energy surface. Thus, the calculated results are more physics sound. Thus, the present work opens a door to provide information of the line mixing for molecules important in remote sensing applications.

All these W matrices are available to readers by their requesting

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