Line interference effects using a refined Robert-Bonamy formalism: The test case of the isotropic Raman spectra of autoperturbed N_2

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A symmetrized version of the recently developed refined Robert-Bonamy formalism [Q. Ma, C. Boulet, and R. H. Tipping, J. Chem. Phys. 139, 034305 (2013)] is proposed. This model takes into account line coupling effects and hence allows the calculation of the off-diagonal elements of the relaxation matrix, without neglecting the rotational structure of the perturbing molecule. The formalism is applied to the isotropic Raman spectra of autoperturbed N_2 for which a benchmark quantum relaxation matrix has recently been proposed. The consequences of the classical path approximation are carefully analyzed. Methods correcting for effects of inelasticity are considered. While in the right direction, these corrections appear to be too crude to provide off diagonal elements which would yield, via the sum rule, diagonal elements in good agreement with the quantum results. In order to overcome this difficulty, a re-normalization procedure is applied, which ensures that the off-diagonal elements do lead to the exact quantum diagonal elements. The agreement between the (re-normalized) semi-classical and quantum relaxation matrices is excellent, at least for the Raman spectra of N_2, opening the way to the analysis of more complex molecular systems.

I. INTRODUCTION

As is well known, within the binary collision and impact approximations, the spectral density may be written in terms of a relaxation matrix W, which contains all the dynamics of the active molecule-bath interactions and which is generally not diagonal within the line space. At low perturber pressures, when the isolated line approximation is applicable, only the diagonal elements are important; these define the Lorentzian line widths (γ_k) and shifts. At higher pressures (depending on the distance between adjacent components), the lines overlap and the off-diagonal elements of the W matrix can no longer be neglected since they lead to line mixing effects, i.e., transfer of intensity among the various lines.

Therefore, determination of the whole relaxation matrix W (i.e., including its non-diagonal elements) is essential. Most of the theoretical analyses have been based on fitting or scaling laws, and calculations from first principles starting from a given potential energy surface appeared only recently, thanks to progress in computing power. Of course, a full quantum theory, at the Close Coupling (CC) level is the most accurate approach. However, the very large number of coupled channels involved renders CC calculations unfeasible for complex molecular systems except for those consisting of two diatomic molecules (in limited situations) or even simpler ones.

In an attempt to overcome this difficulty, alternative approximate theories have been developed, either purely classical or semi-classical. However, it can be reasonably claimed that the calculation of the whole relaxation matrix for complex molecular systems, starting from the knowledge of the intermolecular potential remains an open problem.

If one considers only the diagonal elements of W, until recently, it was believed that the ultimate refinement of the Anderson-Tsao-Curnutte theory, known as the Robert-Bonamy formalism, can treat molecule-molecule systems reasonably well. However, a recent series of papers have shown that this can be achieved only if the intermolecular potential is adjusted, when there is no room to adjust the potential (as in those cases where the potentials are accurately known), the RB formalism significantly overestimates the halfwidths, at least for the systems investigated in these works. In a recent paper, we have shown that part of that deficiency was due to an oversimplification of the RB formalism: the neglect of the non-diagonality (within the line space) of the matrix elements of the cumulant expansion of the Liouville scattering operator. By removing this approximation, i.e., by including line coupling into the formalism one obtains better results, at least for the calculated halfwidths of the Raman Q lines of the N_2-N_2 pair, for which benchmarking CC results were available. Moreover it becomes possible, with this new formalism to calculate not only the diagonal elements of W but also its off-diagonal elements as well, giving us an opportunity to propose a method allowing line mixing effects to be considered for complex molecular systems (like a mixture of polyatomic molecules). In the present paper, we will still test the new formalism on the Raman isotropic

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spectra of N$_2$ which is now possible after recent fully quantum calculations of W.$^{16}$

Section II gives a brief summary of the symmetrized refined RB formalism which is then applied to the N$_2$-N$_2$ system with a particular emphasis on the various rules that must be verified by the non-diagonal elements. As will be shown, the semi-classical frame leads to some deficiencies in the formalism. Sections III and IV propose a number of correction schemes in order to obtain a very reasonable agreement with the quantum data.

II. THEORY

A. General expressions

As is well known, within the binary collision and impact approximations, the spectral density can be written as

$$F(\omega) = \frac{1}{\pi} \text{Im} \sum_{k,l} d_l |l| \frac{1}{\omega - L_0 - iW} |k\rangle d_k \rho_k,$$  \hspace{1cm} (1)

where $\rho_k = \frac{(2j_i + 1)}{Z} e^{-\beta E_i}$ is the population of the initial level of the transition $k \equiv i \rightarrow f$, $d_k$ is the reduced matrix element of the tensor coupling matter and light (assumed to be real), and $L_0$ is the diagonal matrix of transition frequencies. Equation (1) which was used in the quantum study presented in Ref. 16 is based on the Gordon’s convention since the population $\rho_k$ appears in that equation. Conversely, the formalism developed in Ref. 14 is based on the Ben-Reuven’s convention and uses, for example, the matrix element of the density operator, exclusive of the degeneracy factor $\tilde{\rho}_k = e^{-\beta E_i}/Z$. Moreover, in the following, we will consider a symmetrized version of the formalism previously developed in Ref. 14. With a symmetrization of the density matrix,$^{18}$ Eq. (1) can also be written as

$$F(\omega) = \frac{1}{\pi} \text{Im} \sum_{k,l} d_l \sqrt{\tilde{\rho}_l |l| \frac{1}{\omega - L_0 - iW} |k\rangle \sqrt{\tilde{\rho}_k} d_k}.$$  \hspace{1cm} (2)

The correspondence between the two conventions may be quickly retrieved as shown in Appendix A. In the following, numerical calculations will be made starting from Eq. (2), $\tilde{W}_{l,k}$ matrix elements will be then transformed into $W_{l,k}$ elements in order to compare with the quantum results of Ref. 16.

We have shown in Ref. 14 that a correct way of applying the cumulant expansion, based on a new choice of the implied average, allows line coupling effects to be taken into account. Following Ben-Reuven,$^{17}$ we define a basic vector of the line space by

$$|k\rangle = |fi, JM_J\rangle = \sum_{m_f, m_l} (-1)^{m_l} C(j_f, j_i, m_f - m_l, M_J) |fm_f i m_l\rangle.$$  \hspace{1cm} (3)

Then, a matrix element of the relaxation matrix $\tilde{W}$ may be expressed in terms of the average of the Liouville scattering operator $\hat{S}$ over the internal degrees of the bath molecule:

$$\tilde{W}_{f', f; i, j} \equiv \tilde{W}_{l,k} = \frac{n_h \tilde{v}}{2\pi c (k_B T)} \int_0^\infty dE_{\text{kin}} e^{-\beta E_{\text{kin}}}$$

$$\times \int_\infty^{+\infty} 2\pi \left(\frac{db}{dr_c}\right) \times dr_c \delta_{f'f} \delta_{f'f} - \langle \langle f', J M_J | \langle \hat{S} | f i, J M_J \rangle \rangle).$$  \hspace{1cm} (4)

As detailed in Appendices A and B of Ref. 14, $\langle \hat{S} \rangle$ is expressed via a second order cumulant expansion and a refined definition of the average $\langle \ldots \rangle$. This definition must be adapted to the symmetrized version of the formalism. We give this in Appendix B together with some elements allowing to build the symmetrized formalism by following the procedures detailed in Ref. 14.

B. Application to the autoperturbed N$_2$ isotropic Raman Q branch

Recently, we have reported a quantum calculation of the corresponding W matrix based on the potential energy surface (PES) of Ref. 19. Using the same potential, we can check the accuracy of the new formalism by comparing our results with those of Ref. 16. Since the PES of Ref. 19 does not contain any vibrational dependences, $S_2$ disappears. Moreover for isotropic Raman Q branches (labelled here by a single quantum number since $j_i = j_f = j$), within the rigid rotor approximation, $S_2$ is purely real, so that a matrix element of $\tilde{W}$ may be simply written as

$$\tilde{W}(j_i', j_1; T) = \langle Q(j_f') | \tilde{W} | Q(j_i) \rangle = \langle j_1 | \tilde{W} | j_1 \rangle$$

$$\equiv \frac{n_h \tilde{v}}{2\pi c} \tilde{\sigma}(j_1, j_i; T),$$  \hspace{1cm} (5)

where the cross-section $\tilde{\sigma}(j_1, j_i; T)$ includes a Boltzmann average over the initial relative kinetic energy:

$$\tilde{\sigma}(j_1, j_i; T) = \frac{1}{(k_B T)^2} \int_0^\infty \sigma(j_1, j_i; E_{\text{kin}}) \exp(-E_{\text{kin}}/k_B T) E_{\text{kin}} dE_{\text{kin}}.$$  \hspace{1cm} (6)

Cross-sections were calculated over a large grid of kinetic energies, $E_{\text{kin}}/k_B : 50, 100, 150, 200, 250, 296, 300, 350, 400, 450, 500, 600, 800, 1000, 1200, 2080, and 2400 K.

For a given kinetic energy, the cross-section contains an average over all collisional trajectories labelled by the distances of closest approach $r_c$ :

$$\tilde{\sigma}(j_1, j_i; E_{\text{kin}}) = 2\pi \int_{r_{c_{\text{min}}}^{\infty}} dr_c \left(\frac{db}{dr_c}\right)$$

$$\times \left\{ \tilde{S}_{f'f} - \langle j_1 | e^{-\tilde{S}_2(r_c, E_{\text{kin}})} | j_i \rangle \right\}.  \hspace{1cm} (7)$$

As detailed in the previous paper, after all the matrix elements of $e^{-\tilde{S}_2}$ within the line space are available, it is easy
to calculate the whole relaxation matrix. The intermolecular potential, and consequently $e^{-S_2}$, do not allow interconversion between ortho and para species. As a result one can divide the whole line space into two independent subspaces corresponding, respectively, to even and odd $j_1$ lines. By setting their limits, respectively, to $j_1 = 30$ and $j_1 = 31$ we have calculated two $16 \times 16$ sub-matrices of $\tilde{W}$. Here we only present matrices corresponding to ortho-N$_2$. Table I gives the matrix elements $\tilde{\sigma}(j_j^1, j_1; E_{kin})$ for a given kinetic energy.

As expected the matrix is symmetric. Consequently, after averaging over the kinetic energy (cf. Eq. (6)), the non-diagonal elements will verify the detailed balance relation (Eq. (A10) in the symmetrized form). As may be shown by comparing with the initial (unsymmetrized) version of the model, this is a consequence of the use of a symmetrized formalism, which automatically provides a matrix verifying the detailed balance principle.

We present in Fig. 1 a comparison between some semi-classical off-diagonal cross-sections and the CC/CS results of Ref. 16 for some given values of $j_1$. Note here that Eq. (A7) which gives the correspondence between the conventions of Gordon and Ben Reuven has to be written within the semi-classical approximation. Indeed, our semi-classical formalism is a “classical path” formalism where the rotational degrees of freedom are treated quantum mechanically as long as translation is treated classically, neglecting any exchange of energy between translation and rotation, by assuming that

$$|E_{j_1} - E_{j_1'}| \ll k_BT \Rightarrow \frac{\tilde{\rho}(j_1')}{\tilde{\rho}(j_1)} \approx 1. \quad (8)$$

Inserting Eq. (8) into Eq. (A7) gives

$$\sigma_{SC}(j_j^1, j_1; T) = \sqrt{\frac{(2j_j^1 + 1)}{(2j_1 + 1)}} \alpha(j_j^1, j_1; T). \quad (9)$$

From Fig. 1, it appears that even if the rotational distribution is reproduced reasonably well, the agreement is not so good, particularly for upward cross-sections ($j_j^1 > j_1$), which correspond precisely to the greater inelasticity. They contribute mainly to the overestimation of the linewidths. For such upward transitions, the cross-sections must vanish if the inelasticity is greater than the available kinetic energy, and as is known, an obvious failure of the semi-classical scheme is the prediction of non-zero value for such processes. Moreover, as recalled above, the semi-classical formalism neglects any exchange of energy between translation and rotation. As expected, such an approximation fails for high inelasticity, leading to important deviations in the calculation of the corresponding cross-sections.

We now consider the sum rule (Eqs. (A9) or (A12)). In the particular case of isotropic Raman spectra and when the collision dynamics do not depend on vibrational motion, this rule holds.16 Starting from Table I, one can easily establish that the semi-classical cross-sections verify the following sum rule:

$$\tilde{\sigma}(j_1, j_1; E_{kin}) = - \sum_{j_1 \neq j_1^1} \frac{(2j_1 + 1)}{(2j_1^1 + 1)} \tilde{\sigma}(j_1^1, j_1; E_{kin})$$

$$\equiv - \sum_{j_1 \neq j_1^1} \sigma_{SC}(j_1^1, j_1; E_{kin}), \quad (10)$$

After averaging over $E_{kin}$, one obtains

$$\tilde{\sigma}(j_1, j_1; T) = - \sum_{j_1 \neq j_1^1} \frac{(2j_1 + 1)}{(2j_1^1 + 1)} \tilde{\sigma}(j_1^1, j_1; T), \quad (11)$$

which must be compared to Eq. (A12). This result was not unexpected since it is also a consequence of the semi-classical approximation (Eq. (8)). In other words, the semi-classical $W$ matrix elements verify the semi-classical approximation of the exact quantum sum rule, since instead of Eq. (A12) one has

$$\tilde{W}_{kk} \equiv \gamma_k = - \sum_{l \neq k} \frac{(2j_l + 1)}{(2j_k + 1)} \tilde{W}_{lk}. \quad (12)$$

This is also a clear indication of one of the weaknesses remaining in our refined formalism, even after including line coupling effects. Indeed, our semi-classical formalism still overestimates the halfwidths, although by a smaller amount than the former Robert-Bonamy formalism. Our results (black squares) are plotted in Fig. 2 and compared with the CC/CS results (blue triangles).

From the present analysis, it appears that part of the remaining differences may be a consequence of the semi-classical approximation. Indeed, since the half-width is con-
FIG. 1. Comparison of the present semi-classical calculations with the quantum data of Ref. 16 for selected off-diagonal matrix elements (in $10^{-3}$ cm$^{-1}$ at T = 298 K; j$_1$ = 4 (a), 6 (b), and 8 (c). (J stands for j$_1$ and J$'$ stands for j$'$).

FIG. 2. Comparison between calculated halfwidths (in $10^{-3}$ cm$^{-1}$ atm$^{-1}$) for N$_2$-N$_2$ at T = 298 K; semi-classical diagonal elements of Table I (black squares), SC diagonal elements making use of Eqs. (15) and (A12) (red disks) and CC/CS results (blue triangles).

FIG. 3. Comparison of the present semi-classical calculations with the quantum data of Ref. 16 for selected off-diagonal matrix elements (in $10^{-3}$ cm$^{-1}$ at T = 298 K; j$_1$ = 4 (a), 6 (b), and 8 (c). (J stands for j$_1$ and J$'$ stands for j$'$).

III. HOW TO IMPROVE THE SEMI-CLASSICAL FORMALISM

In the semi-classical scheme of the RB formalism, the single classical trajectory is driven by the isotropic part of the potential, and consequently the kinetic energy is conserved (and not the total energy). Therefore, following Billing, we will consider that the constant kinetic energy $U$ which drives the trajectory is some average kinetic energy and not the initial one. We assume that it can be defined in terms of an effective velocity $v_{eff} = \frac{v + v'}{2}$ equal to the arithmetic mean of the relative velocities before (v) and after (v') the inelastic collision:

$$E_{kin} + E(j_1) = \frac{1}{2} \mu v^2 + E(j'_1), \quad (13a)$$

so that

$$U \equiv \frac{1}{2} \mu v_{eff}^2 = \frac{1}{2} \left\{ \sqrt{E_{kin} + E(j_1)} + \sqrt{E_{kin} + E(j'_1) - E(j_1)} \right\}^2 \quad (13b)$$

($\mu$ is the reduced mass of the colliding pair). Equation (7) then becomes

$$\tilde{\sigma}(j'_1, j_1; E_{kin}) = 2\pi \int_{r_{c,min}} \int \frac{b}{dr_c} \left\{ \delta_{j_1j_1} - (j'_1 e^{-S_{j_1}(r_c, U)} | j_1) \right\}, \quad (14a)$$

and, in order to work within the Gordon’s convention, one also introduces

$$\sigma(j'_1, j_1; E_{kin}) = \sqrt{\frac{2j'_1 + 1}{(2j_1 + 1)}} \tilde{\sigma}(j'_1, j_1; E_{kin}). \quad (14b)$$
As is known,\textsuperscript{20} this has the advantage of forcing $\sigma(j_1', j_1; E_{\text{kin}})$ to zero below the threshold of excitation. But it is therefore necessary to re-establish the microscopic reversibility (and consequently the detailed balance after averaging over the kinetic energy). Following Davis and Boggs\textsuperscript{21} and McCann and Flannery,\textsuperscript{22} an additional correction has been added, interpreted in Ref. 22 as a “counting of trajectories”. Instead of Eq. (14a), we use therefore

$$\tilde{\sigma}(j_1', j_1; E_{\text{kin}}) = \frac{2\pi}{E_{\text{kin}}} \int_{r_c,\text{min}}^{\infty} dr_c \left( \frac{db}{dr_c} \delta_{j_1', j_1} - \langle j_1'|e^{-S_{L,U}(r_c)}|j_1 \rangle \right).$$

Finally, the $T$ dependent cross-sections are obtained from the average over the Boltzmann distribution of kinetic energies. Some results are given in Fig. 3 and compared with the CC/CS results of Ref. 16.

Comparing Figs. 1 and 3, it appears that these new results are, on the average, in better agreement with the fully quantum results, particularly for the upward transitions ($j_1' > j_1$) but not for the downward ones at low $j_1$ (see for instance $j_1 = 4$). As a consequence the sum rule, when evaluated with the new off-diagonal elements leads to halfwidths which still strongly differ both from the (unchanged) semi-classical diagonal elements and from the CC/CS data, as seen in Fig. 2 (red dots). If the agreement with the benchmark data is better for high $j_1$, the halfwidths are conversely smaller than the CC/CS references at low $j_1$.

At this stage, it appears that the semi-classical scheme, while leading to a reasonable description of the relaxation matrix elements with off diagonal elements verifying the detailed balance, still fails to provide, via the sum rule, diagonal elements in good agreement with the CC/CS references. It is clear that further work is needed in order to introduce exchange of translation and rotation energies and angular momentum in a more accurate way in the formalism since the very simple method introduced here, while going into the right direction, appears to be too crude.

In some sense, this situation is similar to that encountered in the application of the ECS formalism to the calculation of the relaxation matrix.\textsuperscript{1,23} In this method, any non-diagonal element of $W$ may be expressed in terms of a set of “fundamental” basic cross-sections $\sigma(L, 0; T)$ and an adjustable scaling length $l_s$. This set and $l_s$ are then obtained from the observed line widths by a least square fit based on the sum rule. Of course, with such a procedure, residuals subsist between observed and ECS optimized widths (generally around 15%), which may lead to important errors in the calculation of the spectral line shape in regions extremely sensitive to the accuracy of the sum rule (for instance the wings; see Ref. 23). To overcome this difficulty, Niro \textit{et al.}\textsuperscript{23} have proposed a renormalization procedure, forcing the off-diagonal elements to reproduce exactly the observed widths via the sum rule, while still satisfying the detailed balance. Such a method can be also applied here.

\begin{figure}
\centering
\includegraphics{fig3}
\caption{Comparison of room temperature selected off-diagonal elements (in 10^{-3} cm^{-1} atm^{-1}) corrected from both inelasticity and microscopic reversibility with the quantum data of Ref. 16; $j_1 = 4$ (a), 6 (b), and 8 (c). ($J$ stands for $j_1$, and $J'$ stands for $j_1'$.)}
\end{figure}

\section*{IV. Renormalization Procedure}

The reader will find in Ref. 23 a detailed description of the renormalization procedure. Here we impose the diagonal elements to be equal to the CC/CS data. Then we renormalize results of Sec. III according to the method of Ref. 23.
Comparisons between “renormalized” and CC/CS off-diagonal elements are illustrated in Fig. 4, showing that, in most cases, differences are now small.

Although empirical, this procedure offers the possibility of applying the improved Robert-Bonamy formalism to practical situations encountered in various fields (atmospheric physics, combustion diagnostic, etc.) where one has to calculate a “realistic” relaxation matrix for complex molecular systems. By “realistic” we mean here that the $W$ relaxation matrix, as calculated by the refined RB method, can be normalized to observed widths as given for instance in spectroscopic data bank.

V. CONCLUSION

This study has demonstrated that the refined RB formalism can provide semi-quantitative information on the relaxation matrix for complex molecular systems. The approach includes rotational levels of the perturber (which we do not assume to be an effective atomic perturber), and consequently resonance effects that may modify the intensity of the coupling.

Of course, the refined RB method remains a semi-classical formalism in which energy exchange between translation and rotation is neglected. Consequently the relaxation matrix elements cannot verify at the same time both detailed balance and the sum rule. Following Davis and Boggs, we have tried to introduce such exchanges into the formalism in a very simple way. However, these corrections, while going in the right direction, were too approximate to provide linewidths via the sum rule in good agreement with the CC/CS references. In our opinion, attention should now focus on the development of techniques for taking into account more accurately the exchange of rotational and translational energies and angular momentum during the collisions.

Meanwhile, we have proposed a method to circumvent this difficulty, forcing the off-diagonal elements of the RB-refined formalism to exactly reproduce a given set of line widths. This procedure, when applied to the isotropic Raman spectra of $N_2$, gives good results. It may be also applied to more complex molecular systems encountered in various fields of applications. Some such systems were discussed in the conclusion of Ref. 14. In a forthcoming paper, we will consider another test case: the infrared spectra of $C_2H_2$ perturbed by $N_2$ for which a new model potential has recently become available. One could apply the present method to calculate the relaxation matrix $W$ of this system and to analyze the intrabranch (R-R; P-P) as well as interbranch (R-P) coupling.

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APPENDIX A: COMPARISON BETWEEN DIFFERENT CONVENTIONS

In Gordon’s convention, which is used by Thibault et al., the spectral density is written as

$$F(\omega) = \frac{1}{\pi} \text{Im} \sum_{k,l} \rho_k d_k d_l |l| \frac{1}{\omega - L_0 - iW} |k|$$

(A1)
where
\[ \rho_k = \frac{(2j_k^i + 1)}{Z} e^{-\beta E_k^i} = (2j_k^i + 1) \tilde{\rho}_k, \] (A2)
with
\[ \tilde{\rho}_k = \frac{1}{Z} e^{-\beta E_k^i}. \] (A3)

\( \rho_k \) is the population of the initial level of the \( k \)th transition, while \( \tilde{\rho}_k \) is the population exclusive of the degeneracy factor (for simplicity, we omit here all spin factors).

Here, however, we use a different convention derived from Ben Reuven's one writing the spectral density in a while \( \tilde{\rho}_k \) vs. \( \tilde{\rho}_k \).

Identifying term by term and using the previous results, one obtains
\[ \sum_{k,l} \rho_k \tilde{\rho}_l \rho_{kl} = \langle \hat{\rho} \rangle = \langle \rho_1 \rangle \] (B1)
In terms of this vector, the average \( \langle \hat{\rho} \rangle \) defined in applying the cumulant expansion is now defined as
\[ \langle \hat{\rho} \rangle \] (B2)
where \( \hat{\rho} \) is a Liouville operator of interest. It is obvious that the normalization condition \( \langle \hat{\rho} \rangle = 1 \) is satisfied. Then, using Eq. (B2) a matrix element of \( \langle \hat{\rho} \rangle \) can be explicitly written as
\[ \langle \hat{\rho} \rangle \] (B3)
where a summary notation \( (m) \) means summations over all magnetic quantum numbers associated with the absorber molecule and a summation over \( M_f \) as well. Then, by following the procedures of Ref. 14, one is able to obtain all corresponding formulas in the current symmetrized version. For example, expressions for the diagonal and off-diagonal matrix elements of \( S_{2,middle} \) are

With our convention, Eq. (A8) becomes
\[ \tilde{W}_{kl} = \tilde{W}_{lk}, \] (A10)
and the sum rule becomes
\[ \sum_l d_l \sqrt{\rho_l} \tilde{W}_{lk} = 0, \] (A11)
which can be also written as
\[ \sum_l d_l \sqrt{\rho_l} \tilde{W}_{kl} = 0. \] (A11)

Equation (A11) corresponds, within that convention, to the double sum rule defined by Filippov and Tonkov 24 or Kouzov.

2. Case of isotropic Raman spectra
In that case, \( d_k \) is constant and Eq. (A11) may be also written as
\[ \tilde{W}_{kl} \equiv \gamma_k = -\sum_{l \neq k} \sqrt{\rho_l} \tilde{W}_{lk} = -\sum_{l \neq k} \frac{(2j_k^i + 1)}{(2j_k^i + 1)} \sqrt{\rho_l} \tilde{W}_{lk}. \] (A12)
It should be remembered that \( \tilde{W}_{lk} \) means \( \tilde{W}_{lk}(T) \) and contains an average over a Boltzmann distribution of kinetic energy (cf. Eq. (4)).
given by
\[
S_{2\text{middle}}^{fi}(r_c) = \sqrt{2\pi} (2j_i + 1)(2j_f + 1) \\
\times \sum_{L_{iL_2}} \{ (-1)^{j_i+j_f+L_i} W(j_i,j_f,j_i;j_f,L_1) C(L_1,j_iL_1,000) C(j_f,j_fL_2,000) \} \\
\times \sum_{ii'j'j''} (2i' + 1)(2i'' + 1) \sqrt{\rho_{i'i}} \sqrt{\rho_{i''j''}} C^2(i'i'j'i'j'i'L_2,000) H_{L_1L_2}(\omega_{i'i'}),
\] (B4)

and
\[
S_{2\text{middle}}^{fi'}(r_c) = \sqrt{2\pi} (-1)^{j_i+j_f'} \sqrt{(2j_i' + 1)(2j_f' + 1)(2j_i + 1)(2j_f + 1)} \\
\times \sum_{L_{iL_2}} \{ (-1)^{j_i+j_f+L_i} W(j_i',j_f',j_i;j_f,L_1) C(L_1,j_iL_1,000) C(j_f',j_fL_2,000) \} \\
\times \sum_{ii'j'j''} (2i' + 1)(2i'' + 1) \sqrt{\rho_{i'i}} \sqrt{\rho_{i''j''}} C^2(i'i'j'i'j'i'L_2,000) H_{L_1L_2}(\omega_{i'i'} + \omega_{i''j''}),
\] (B5)

respectively. Recall that Eq. (B5) is applicable only for Q lines since one has used the relation \( \omega_{ij} = \omega_{ff} \) to simplify the expression.

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