

Modification of the Robert–Bonamy formalism in calculating Lorentzian half-widths and shifts

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Abstract

We have found an invalid assumption in the Robert–Bonamy formalism that has been widely used for calculating Lorentzian spectral line half-widths and shifts for decades. The problem results in their derivation where they assumed the cumulant expansion can be used to evaluate the Liouville matrix element $\langle\langle j2i2|\hat{S}|j2i2\rangle\rangle$. At first sight, their assumption appears to be correct because this matrix element is diagonal in the Liouville space and as a result, it looks like that a basic requirement in applying the cumulant expansion is satisfied. However, by decomposing it into two Hilbert matrix elements associated with S_I and S_F ($\hat{S} = S_I S_F^*$), respectively, we have found that neither of these is diagonal in Hilbert space. Therefore, their assumption is not valid and their expressions for the half-widths and shifts are incorrect. We have found by choosing an average over the internal degrees of the bath molecule as the average in the cumulant expansion, one is able to apply this expansion properly and obtain the correct expressions. Numerical calculations show new half-width and shift values differ from previous ones, and the stronger the interaction between two molecules is, the larger these differences are. © 2006 Elsevier Ltd. All rights reserved.

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1. The Robert–Bonamy formalism for Lorentzian widths and shifts

The Robert–Bonamy (RB) formalism [1] was developed more than two decades ago and has been widely used in calculating the Lorentzian half-widths and shifts for spectral lines for many molecular systems of importance. This theory has been previously developed for linear molecules, extended to other molecules [2–4] and successfully applied to infrared and Raman spectra [5–7]. As claimed by one of these authors [7], the main features of this theory are the non-perturbative treatment of the S -scattering matrix through the use of the

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linked cluster theorem, and a convenient description of classical trajectories for large impact parameters as well as for the closest approach. Some progress has been made recently to improve the RB original results [8,9], but most of these efforts have been related to the extension to more complicated interaction potentials, vibrational dependences, more accurate trajectories, etc. None has focused on making further improvements to the basic theory itself. As a result, the calculations of half-widths and shifts using the RB results have become routine, and the results widely applied to the self- and foreign-broadened widths and shifts for atmospheric molecular systems, such as those compiled in the HITRAN database [10]. In cases where the calculated values did not match the experimental data well, the strategy used for improvements was to use more complicated potential models and higher potential expansion cut-offs, to take into account more sophisticated vibrational dependences, and to consider the translational motion moving along “exact” trajectories rather than to scrutinize the RB theory in detail. Recently, we have checked these authors’ early papers and found there was an invalid assumption made in their derivation of the starting formulas. More specifically, the problem occurred when Robert and Bonamy used Bloch’s Linked-Cluster theorem [11]

$$\begin{aligned} U(t) &= U_L(t)\langle 0|U(t)|0\rangle \\ &= U_L(t)e^{(0|U(t)|0)^{(C)}}, \end{aligned} \quad (1)$$

where $|0\rangle$ is the non-degenerate ground state of the unperturbed Hamiltonian and $U(t)$ is the time evolution operator, to evaluate the matrix elements $\langle j2'i2'|\hat{S}|j2i2\rangle$. Here j and i are simple notations to represent states of the absorber molecule and 2 and 2' for the states of the bath molecule. As can be seen from Eq. (6) of their paper¹

$$\begin{aligned} \langle j2'i2'|\hat{S}|j2i2\rangle &= \left[\delta_{2'2} - i\hbar^{-1} \int_{-\infty}^{+\infty} dt \langle j2'i2'|\hat{V}(t)|j2i2\rangle_{(L)} \right. \\ &\quad \left. - \hbar^{-2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^t dt' \langle j2'i2'|\hat{V}(t)\hat{V}(t')|j2i2\rangle_{(L)} \right] \\ &\quad \times \exp \left[-i\hbar^{-1} \int_{-\infty}^{+\infty} dt \langle j2i2|\hat{V}(t)|j2i2\rangle_{(C)} \right. \\ &\quad \left. - \hbar^{-2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^t dt' \langle j2i2|\hat{V}(t)\hat{V}(t')|j2i2\rangle_{(C)} \right] \\ &= \left[\delta_{2'2} - S_2^{(L)} \right] e^{-iS_1^{(C)} - S_2^{(C)}}, \end{aligned} \quad (2)$$

they have assumed that analogous to $\langle 0|U(t)|0\rangle = \exp\{\langle 0|U(t)|0\rangle^{(C)}\}$, the matrix element $\langle j2i2|\hat{S}|j2i2\rangle$ is equal to $\exp\{-iS_1^{(C)} - S_2^{(C)}\}$, where i in the exponentials denotes $\sqrt{-1}$. At first sight, their assumption appears to be correct because this matrix element is diagonal in the Liouville space and as a result, it appears that a basic requirement in applying the cumulant expansion [12,13] (i.e., equivalent to the Bloch’s connected diagram method that is the core part of the Linked-Cluster theorem) is satisfied. Some authors [14] have made comments on their later treatment for the off-diagonal terms, which they also put this into an exponential form, and combined the latter with the exponential associated with the connected terms in an ad hoc way; viz.

$$\langle j2'i2'|\hat{S}|j2i2\rangle = \left[\delta_{2'2} - S_2^{(L)} \right] e^{-iS_1^{(C)} - S_2^{(C)}} \approx e^{-iS_1 - S_2}, \quad (3)$$

where $S_1 = S_1^{(C)}$ and $S_2 = S_2^{(C)} + S_2^{(L)}$. Robert et al. [5] claimed in their paper that this latter procedure is based on an approximation, and they have shown that this approximation is valid for cases of interest. Heretofore, no one has questioned their treatment for the diagonal matrix element $\langle j2i2|\hat{S}|j2i2\rangle$. In this paper, we present our analysis of their assumption that $\langle j2i2|\hat{S}|j2i2\rangle = \exp\{-iS_1^{(C)} - S_2^{(C)}\}$.

¹Note: there is a typing error in the original expression.

It is worth mentioning first that the Liouville formalism was introduced in order to simplify notations given in Hilbert space. Some rules have been established for carrying out manipulations in the Liouville space, but one has to keep in mind that one cannot simply assume that rules applicable in Hilbert space are also applicable in the Liouville space or vice versa. A straightforward way to check whether an extension is correct or not is to rewrite everything back in Hilbert space and to check whether the same rule works or not. In our present study, the rules of interest are the cumulant expansion and the Bloch's Linked-Cluster theorem. It is well known these were developed in Hilbert space. Therefore, one cannot simply extend these methods into the Liouville space without verification. In fact, what Robert and Bonamy did in their derivation of the RB formalism is to assume that a similar cumulant expansion is also applicable for $\langle\langle j2i2|S|j2i2\rangle\rangle$ in the Liouville space just like that in Hilbert space. In order to check whether their assumption is correct or not, we rewrite $\langle\langle j2i2|S|j2i2\rangle\rangle$ in terms of Hilbert operators and states and to see whether the basic requirement in applying the cumulant expansion is satisfied or not.

It is well known that the RB formalism is applicable only for well-separated lines because it is based on the assumption that with respect to the line space of the absorber molecule, labeled by pairs of j and i , the Liouville resolvent operator is diagonal. In Fano's notation [15], this resolvent operator is denoted by $\langle m(0)\rangle_{\text{bath}} = i/2\pi\langle 1 - \hat{S}\rangle_{\text{bath}}$ where $\hat{S} = S_1 S_F^*$ and $\langle \dots \rangle_{\text{bath}}$ denotes averages over the internal degrees of the bath molecule as well as averages over the translational degrees of the interacting pair. For simplicity, we will suppress the vibrational quantum numbers in the following. In addition, because $\langle m(0)\rangle_{\text{bath}}$ is diagonal with respect to pairs of j and i , we will not present its explicit dependence on these absorber molecule quantum numbers. According to Eq. (5) of their paper [1], a comprehensive expression for $|22\rangle\rangle$, the bath component of the Liouville vector $|j2i2\rangle\rangle$, is given by

$$|22\rangle\rangle = \frac{(-1)^{j_2}}{\sqrt{2j_2 + 1}} \sum_{m_2} |j_2 m_2\rangle |j_2 m_2\rangle^\dagger. \quad (4)$$

Then, one can express the Liouville matrix element $\langle\langle j2i2|\hat{S}|j2i2\rangle\rangle$ in terms of products of two matrix elements of S_1 and S_F^* , respectively, that act on two Hilbert spaces constructed by the initial and final states of the interacting pair as

$$\langle\langle j2i2|\hat{S}|j2i2\rangle\rangle = \frac{1}{2j_2 + 1} \sum_{m_2, m_2'} \langle i; j_2 m_2' | S_1 | i; j_2 m_2 \rangle \langle j; j_2 m_2 | S_F^* | j; j_2 m_2' \rangle, \quad (5)$$

where only the explicit expression for the bath internal degrees is given. As shown by the above expression, none of these matrix elements of S_1 and S_F^* are diagonal. As a result, one cannot apply the cumulant expansion independently to S_1 and S_F^* and, thus, one cannot apply it to the Liouville operator \hat{S} at all. It is just this subtlety that introduced an error in their derivation.

There is an alternative way [16] developed to derive the RB formulas. In this work, the average $\langle \dots \rangle$ used in the cumulant expansion [12,13] is basically defined as a summation of \hat{S} over $2'$ and has been expressed as

$$\langle \hat{S} \rangle = \sum_{2'} \langle\langle j2'i2'|S|j2i2\rangle\rangle. \quad (6)$$

This also looks like it satisfies the condition for applying the cumulant expansion because the normalization condition of $\langle 1 \rangle = 1$ is satisfied. In addition, with this definition one is able to consider contributions from the off-diagonal matrix elements $\langle\langle j2'i2'|S|j2i2\rangle\rangle$ as well as the diagonal ones $\langle\langle j2i2|S|j2i2\rangle\rangle$, and derive formulas for the half-widths and shifts directly without relying on any ad hoc assumptions. The latter treatment gives results that are exactly the same as the RB ones obtained with the ad hoc treatment for the off-diagonal terms mentioned above. However, by carefully analyzing this derivation, we have found that there is an error in the expression for $\langle \hat{S} \rangle$. There is no problem to choose such average $\langle \dots \rangle$ because the averages could be numbers as well as operators [13]. The problem results from a misunderstanding between an operator and its matrix elements. The essential point here is that after taking the average that is defined as a summation over $2'$, the remaining $\langle \hat{S} \rangle$ is still a Liouville vector (i.e., a Hilbert operator) spanning the space constructed by the initial states 2 and the final states 2 , where these two running indices 2 and 2 are identical because the bath molecule does not participate in transitions.

Therefore, the correct expression for $\langle \hat{S} \rangle$ should be

$$\langle \hat{S} \rangle = \sum_2 \left\{ \sum_{2'} \langle \langle j2'i2' | S | j2i2 \rangle \rangle \right\} \langle \langle 22 |, \quad (7)$$

where $\langle \langle 22 |$ stand for axes in the Liouville space and $\sum_{2'} \langle \langle j2'i2' | S | j2i2 \rangle \rangle$ are the corresponding coordinates, not that given in the right-hand side of Eq. (6). The latter is nothing but one of this vector's coordinates along a specified axis labeled by 2 and 2'. As a result, after applying the cumulant expansion and deriving a similar expression for $\exp\{-iS_1 - S_2\}$, these S_1 and S_2 are Hilbert operators, not numbers given by their corresponding matrix elements. It is well known that for an operator A , $\langle \alpha | \exp\{A\} | \beta \rangle \neq \exp\{\langle \alpha | A | \beta \rangle\}$ including $\alpha = \beta$ unless A is a diagonal with respect to α and β . Therefore, this derivation is not correct because it is implicitly based on a similar replacement of $\langle \alpha | \exp\{A\} | \beta \rangle$ by $\exp\{\langle \alpha | A | \beta \rangle\}$. Again, another subtlety led to an error in the derivation. At this stage, we would like to note that although this alternative derivation contains an error, it is helpful for exhibiting more clearly what kind of extra unnecessary approximations are embedded in the current RB formalism.

In summary, we have shown that there are subtle errors in the attempts to derive the RB formulas, and we can conclude that expressions for the half-widths and shifts using the RB formulation are not “exact”; that is, they contain some other tacit approximations. However, by making a series expansion, it is easy to show that the current RB formulas match $\langle m(0) \rangle_{\text{bath}}$ given by the Anderson-Tsao-Curnutte [17,18] theory up to the second order of the perturbation expansion of \hat{S} ,

$$\begin{aligned} \langle m(0) \rangle_{\text{bath}} = & \frac{1}{2\pi} \left\langle \left\{ -\hbar^{-1} \int_{-\infty}^{+\infty} dt \sum_{2,2'} \langle \langle j2'i2' | \hat{V}(t) | j2i2 \rangle \rangle \rho_b + i\hbar^{-2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^t dt' \right. \right. \\ & \left. \left. \times \sum_{2,2'} \langle \langle j2'i2' | \hat{V}(t) \hat{V}(t') | j2i2 \rangle \rangle \rho_b + \dots \right\} \right\rangle_{v,b}, \quad (8) \end{aligned}$$

where the average over the internal degrees of the bath molecule is explicitly given and the average over the translation motion is indicated by $\langle \dots \rangle_{v,b}$. This implies these formulas should work well for cases where the interaction potentials are weak. For other cases, the calculated values become less reliable due to the extra approximations involved. These extra approximations introduced could interweave with those caused by the currently adopted level of approximation (e.g., isolated lines, trajectories determined by the isotropic potential, simple anisotropic models, etc.) in the RB expressions. In light of the discussion above, one may ask why no one has found the problem for so many years? First, as shown above, the errors are very subtle. Second, the RB formulas are still valid as good approximations, especially for weak interactions. As a result, these formulas have been successfully used for many molecular pairs and the results obtained were in fair agreement with experimental data. It is this success that led researchers to accept the correctness of the RB formulas and to search in other directions in order to make further improvements.

2. Modification of the RB formalism

We now present a correct way for applying the cumulant expansions within the RB formalism. Instead of choices used previously, one can choose an average of \hat{S} over the internal degrees of the bath molecule as the average used in the cumulant expansion,

$$\langle \hat{S} \rangle = Tr_{\text{internal}} \left\{ I_b \hat{S} \rho_b \right\} = \sum_{2,2'} \langle \langle j2'i2' | \hat{S} | j2i2 \rangle \rangle \rho_b(2), \quad (9)$$

where we have inserted I_b , a unit vector in the line space of the bath molecule, to emphasize that the trace is carried out for the Liouville operator \hat{S} . It is worth mentioning here that the average of the Liouville operator \hat{S} over the bath molecular internal degrees is carried out by summations not only over 2, but also over 2'. Except for the weighting factor ρ_b in the summation over 2, averages over 2 and 2' are treated on an equal footing. This differs from an average of a Hilbert operator in which the summation is weighted by ρ_b over 2

alone. It is easy to show that the normalization condition $\langle 1 \rangle = 1$ is satisfied. In addition, contrary to the previous case, after making the average the remaining $\langle \hat{S} \rangle$ is no longer an operator acting on the states of the bath molecule. Although it is still an operator in the line space of the absorber, according to our assumption it is diagonal. As a result, one is able to apply the cumulant expansion and derive an “exact” expression for $\langle \hat{S} \rangle$

$$\langle \hat{S} \rangle = e^{-i(S_1)_{j_2} - (S_2)_{j_2}}, \quad (10)$$

where the simple notation $\langle A \rangle_{j_2}$ is defined as a weighted average of A over the angular momentum quantum number j_2 of the bath molecule

$$\langle A \rangle_{j_2} = \sum_{j_2} (2j_2 + 1) e^{-E(j_2)/kT} A(j_2) / Q_b \quad (11)$$

and S_1 and S_2 to be averaged over j_2 are exactly the same as those appearing in the RB formulas. Except for this modification, the RB formalism, including the classical treatment of the translation motion that is carried out by averaging over the velocity v and the impact parameter b indicated by $\langle \dots \rangle_{v,b}$ later, remains unaffected. As a result, the only difference in the expressions for $\langle m(0) \rangle_{\text{bath}}$ is to replace $\langle \{ \exp(-iS_1 - S_2) \}_{j_2} \rangle_{v,b}$ by $\langle \{ \exp(-i(S_1)_{j_2} - (S_2)_{j_2}) \} \rangle_{v,b}$. Then, one can easily write down new formulas for the half-widths and shifts directly from those provided by Robert et al. For the half-widths, the RB formula [8] and the new one are given by

$$\gamma_{\text{RB}} = \frac{n_b}{2\pi c} \int_0^{+\infty} v f(v) dv \int_0^{+\infty} 2\pi b db \langle 1 - \cos(S_1 + \text{Im}(S_2)) e^{-\text{Re}(S_2)} \rangle_{j_2} \quad (12)$$

and

$$\gamma_{\text{new}} = \frac{n_b}{2\pi c} \int_0^{+\infty} v f(v) dv \int_0^{+\infty} 2\pi b db \left[1 - \cos(\langle S_1 \rangle_{j_2} + \text{Im}(\langle S_2 \rangle_{j_2})) e^{-\text{Re}(\langle S_2 \rangle_{j_2})} \right], \quad (13)$$

respectively, where $f(v)$ is the Maxwell–Boltzmann distribution function. Meanwhile, for the shifts, the RB formula [8] and the new one are given by

$$\delta_{\text{RB}} = \frac{n_b}{2\pi c} \int_0^{+\infty} v f(v) dv \int_0^{+\infty} 2\pi b db \langle \sin(S_1 + \text{Im}(S_2)) e^{-\text{Re}(S_2)} \rangle_{j_2} \quad (14)$$

and

$$\delta_{\text{new}} = \frac{n_b}{2\pi c} \int_0^{+\infty} v f(v) dv \int_0^{+\infty} 2\pi b db \sin(\langle S_1 \rangle_{j_2} + \text{Im}(\langle S_2 \rangle_{j_2})) e^{-\text{Re}(\langle S_2 \rangle_{j_2})}. \quad (15)$$

In contrast with the RB formulas Eqs. (12) and (14) where the summation over j_2 is outside of the cumulant expansion and the other summation over j'_2 is inside, in the new Eqs. (13) and (15), both the summations over j_2 and j'_2 are inside and are treated on an equal footing. The new treatment is consistent with how one should treat the average of a Liouville operator over the internal degrees of the bath molecule mentioned above, and thus this treatment is more physically realistic. Finally, we would like to emphasize that these different orders of averaging over bath degrees of freedom are not arbitrary. It is the subtle error in applying the cumulant expansion in the RB formalism and the proper way to do this in the present study that leads to the differences.

3. Numerical comparisons

We have done numerical calculations to compare the differences between the two formulations for several molecular pairs of interest. Our purpose is to show effects resulting from the derivation error in the RB formalism. For illustration purposes, we use a simple anisotropic potential model that consists of the dipole–dipole, dipole–quadrupole, quadrupole–dipole, and quadrupole–quadrupole interactions. With respect to the isotropic potential, we use a Lennard–Jones model with vibrational dependence described by the two parameters a_{01} and y [19]. The translation motion is assumed to follow a parabolic trajectory [1]. As shown in Figs. 1 and 2, for the half-widths and shifts, respectively, for the fundamental band of HF perturbed by N_2 , the

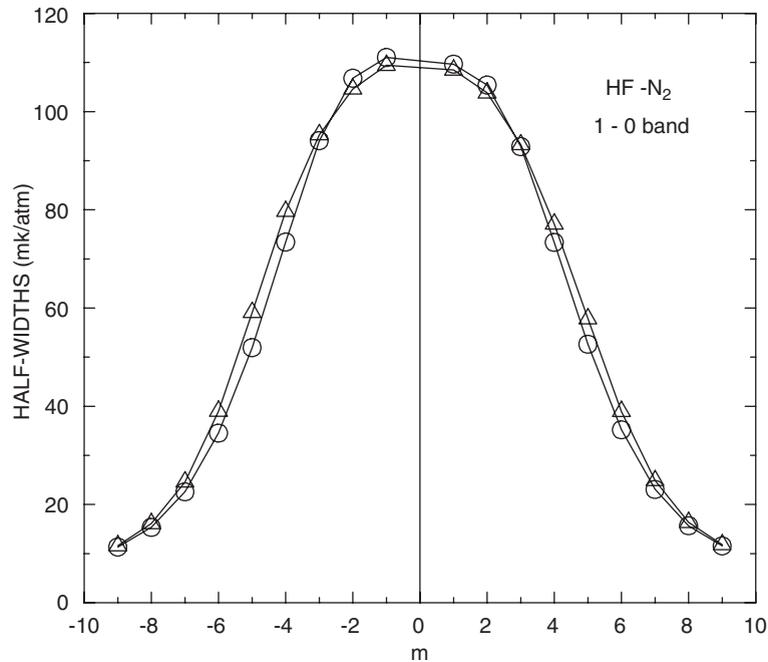


Fig. 1. Calculated half-widths of the 1–0 band of HF broadened by N_2 at 296 K. Values derived from the RB and the new formulas are denoted by \circ and Δ , respectively. Experimental values at 295 K by Pine and Looney [20] are presented by +.

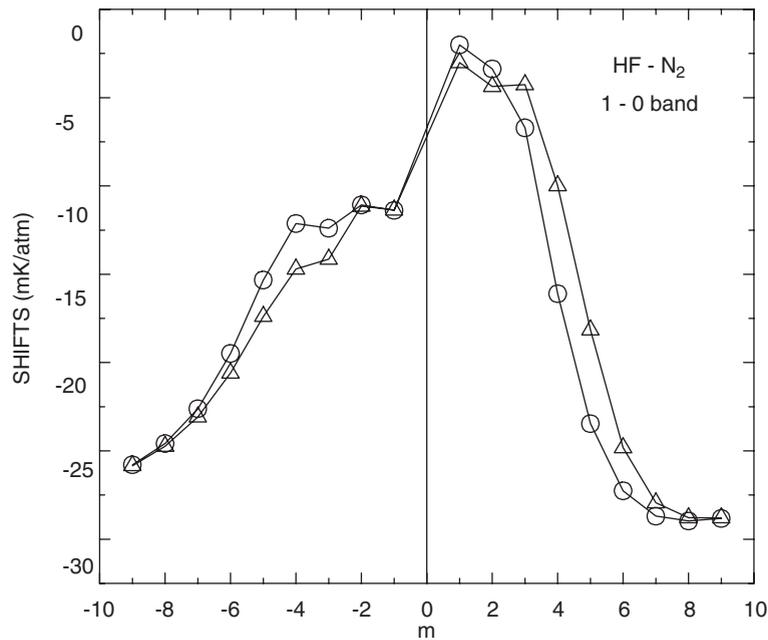


Fig. 2. Calculated shifts of the 1–0 band of HF broadened by N_2 at 296 K. Values derived from the RB and the new formulas are denoted by \circ and Δ , respectively. Experimental values at 295 K by Pine and Looney [20] are presented by +.

values obtained from these two formulas differ slightly; the shifts differ more than the widths. For comparison, we also show the experimental values [20]. This behavior is expected because the dipole moment of N_2 is zero and the interaction between HF and N_2 is relatively weak.

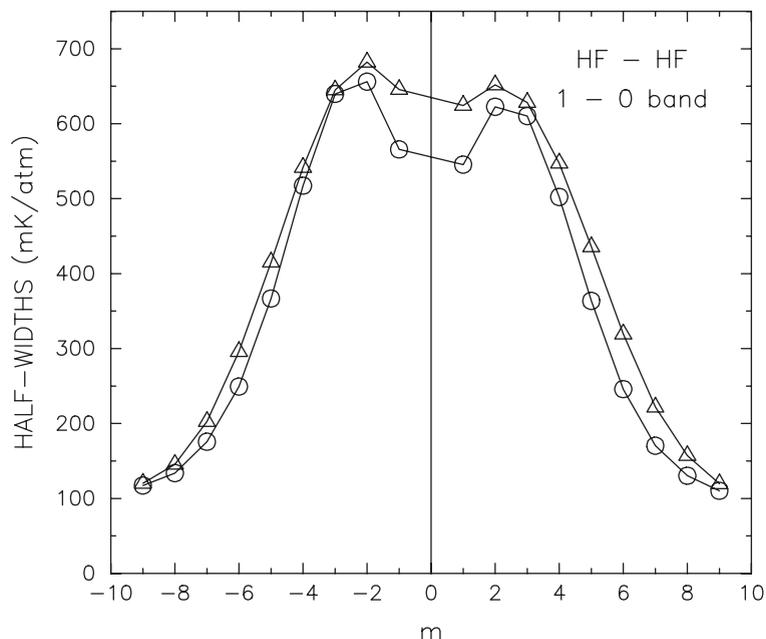


Fig. 3. The same as Fig. 1 except for HF broadened by HF. Experimental values at 295 K by Pine and Fried [21] are presented by +.

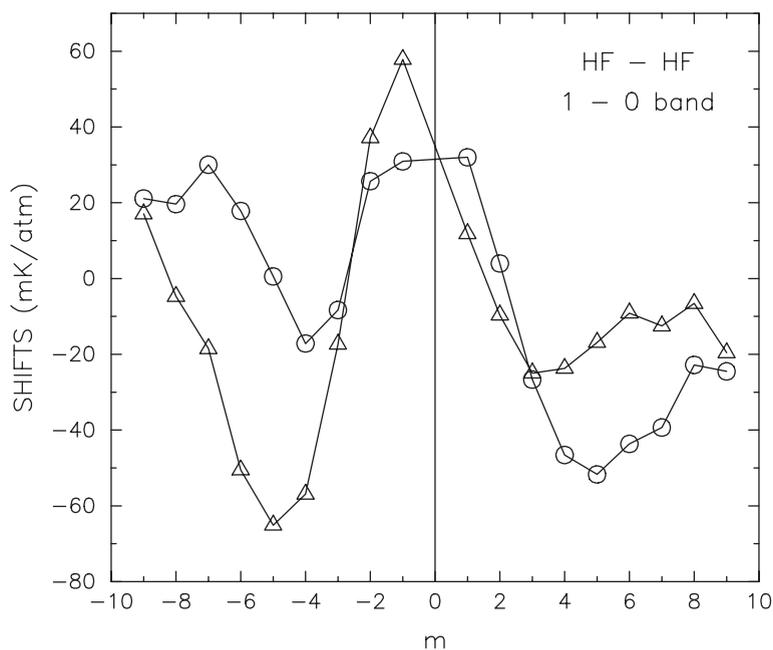


Fig. 4. The same as Fig. 2 except for HF broadened by HF. Experimental values at 295 K by Pine and Fried [21] are presented by +.

We next consider a pair of HF–HF molecules whose interaction is very much stronger than that for HF–N₂. We see from Fig. 3 that, in general, values of the half-width obtained from the new expression (Eq. (13)) are larger than those found from Eq. (12). On the other hand, one can see from Fig. 4 that in comparison with the shifts based on the RB theory, the new calculated values change dramatically. The experimental data [21] are shown for comparison. Additional comparisons for the magnitudes of the differences in widths and shifts

between the RB formalism and the modified RB formalism for a number of vibrational bands of H₂O, O₃ and CH₄, are given in Antony et al. [22].

In summary, we have shown that there is an error in the RB formalism that occurred when these authors applied the cumulant expansion in their derivation. As a result, the current RB formulas implicitly contain other approximations, which could affect the theoretical predictions based on approximations adopted intentionally. We have shown how to fix this problem within the RB framework, and provided expressions for the calculation of half-width and shift without introducing any extra approximations. Numerical tests show that the invalid assumption nature of the current RB formulas could distort the theoretical predictions significantly, especially for cases where interactions between the absorber and bath molecules are strong. This implies that results obtained through improvements of the RB formalism made by many researchers could also be affected. In order to make further refinements of the theory, one has to use comparisons between the undistorted predictions and experimental measurements as a guide.

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