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Vibration-dependent trajectories and their effects on vibrational dephasing

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Abstract

We show that the expression for S_1 (i.e., the first term in the expansion of the S matrix) that is essential in calculating vibration-rotation pressure-broadened shifts is not properly given in the usual Robert–Bonamy (RB) formalism. The problem resulted when they considered effects of the vibrational dephasing on S_1; they tacitly made an assumption that the trajectories of interest are vibrationally independent. As a result, the current RB expression is an approximate one. Based on a vibration-dependent trajectory model, which is physically sound, we derive the correct expression for S_1. We present numerical calculations of the broadening and shifting cross sections and of the line shape parameters for the H_2–He pair and find for this molecular system, new results differ significantly from those calculated using the existing formalism. In addition, by comparing with those derived from close coupling calculations, we find that the new results are better than the old ones. Finally, we discuss how important effects from this modification could be for other molecular systems. We conclude that for certain molecular systems where the short-range collisions are the dominant source responsible for the line widths and shifts, and in addition, the isotropic potential has small depth, the present modification is a worthwhile step to be taken in order to refine the current RB formalism. Meanwhile, for other systems it may not be necessary.
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1. The Born–Oppenheimer approximation and vibration-dependent trajectories

It is well known that in many molecular collision theories, the Born-Oppenheimer approximation is introduced to simplify calculations. With this approximation, the total wavefunction is written as a product of two components associated with the translational and internal motions, respectively, and the original Schrödinger equation becomes two separated ones governed by two Hamiltonians. In addition, the Hamiltonian determining the translational motion consists of a kinetic operator K and a potential operator V_α. The latter can be expressed as [1]

$$V_\alpha = <\alpha|V|\alpha> + \sum_{\alpha'\neq\alpha} \frac{<\alpha|V|\alpha'><\alpha'|V|\alpha>}{E_\alpha - E_{\alpha'}} + \cdots, \qquad (1)$$

where V is the total potential between two molecules, α is a simple notation used to denote all internal quantum numbers, and E_α corresponds to its eigenvalues. It is worth mentioning that no matter if the translational motion is treated quantum mechanically or classically, V_α depends on the internal degrees of freedom.

In semi-classical theories [2–4], the translational motion is treated classically. In addition, if one assumes V_α is not sensitive to the rotational quantum numbers, one can

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conclude that the trajectories are vibrationally dependent, but rotationally independent. Finally, we note that at present, in most theoretical half-width and shift calculations, the trajectory is assumed to be governed by its isotropic potential only. In other words, one assumes that the anisotropic interaction does not play any role in determining the trajectories. With this restriction, only the isotropic part of V_α is of interest. For simplicity, we will not introduce a new notation and in the following, V_α should be understood as the isotropic part defined by Eq. (1). In addition, one must distinguish V_α and $V_{\rm iso}(R(t),\xi)$ which is introduced later. The former is given by Eq. (1) and does not operate on the internal states $|\alpha>$, although it does depend parametrically on them [1]. Meanwhile, the latter is an operator. At the lowest order adopted in the present study, $V_\alpha = <\alpha\,|V_{\rm iso}(R(t),\xi)\,|\alpha>$.

In the following, we provide details to show how to derive formulas for vibrational dephasing based on vibration-dependent trajectories.

2. General expressions for vibrational dephasing from S_1(b)

In calculating molecular line half-widths and shifts, the vibrational dephasing makes contributions to S_1, the first-order term in the expansion of the S matrix, defined by the following equation [4]

$$S_1(b) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t < f|V_{\rm iso}(R(t),\xi)|f> - \frac{1}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t < i|V_{\rm iso}(R(t),\xi)|i>, \tag{2}$$

where b is the impact parameter, i and f denote the initial and final internal states. For later convenience, the normalized vibrational coordinate ξ defined by $\xi \equiv (r - r_{\rm e})/r_{\rm e}$, where r is the vibrational displacement and $r_{\rm e}$ the equilibrium displacement, has been explicitly included as an argument in $V_{\rm iso}$ in Eq. (2). It is known for years [1,5], with semi-classical line shape theories, a part of the interaction, which does not operate on the internal degrees, is excluded in evaluating the S matrix. As a result, the usual separation of the interaction into its isotropic and anisotropic parts adopted in the RB formalism is not a proper practice and it may lead to confusion [5]. The rigorous distinction is to separate the interaction into two categories such that one operates on the internal degrees while the second does not [1,5]. Accordingly, one has to introduce a comprehensive expression for $V_{\rm iso}(R(t),\xi)$ to make an explicit separation between its vibration-independent and vibration-dependent parts, $V_0(R(t))$ and $\Delta V_{\rm iso}(R(t),\xi)$, as

$$\begin{aligned} V_{\rm iso}(R(t),\xi) &= V_{\rm iso}(R(t),\xi=0) + \Delta V_{\rm iso}(R(t),\xi) \\ &\equiv V_0(R(t)) + \Delta V_{\rm iso}(R(t),\xi). \end{aligned} \tag{3}$$

To make such a distinction for the isotropic potential $V_{\rm iso}(R(t),\xi)$ as shown above is the first step to remedy the problem. The next step is to ignore the component $V_0(R(t))$ in the expression for S_1 because it does not operate on the internal degrees [1]. As a result, a rigorously correct expression for S_1 should be written as

$$S_1(b) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t < f|\Delta V_{\rm iso}(R(t),\xi)|f> - \frac{1}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t < i|\Delta V_{\rm iso}(R(t),\xi)|i>. \tag{4}$$

One may ask why no one has challenged the previous expression for years? The answer is it happens that when one assumes further, with or without clearly making a statement, that the trajectories are assumed to be vibration-independent, the contributions to the first and second terms of Eq. (2) from $V_0(R(t))$ are exactly canceled out. This is just the case of the current RB formalism because these authors have tacitly made such an assumption there. Thus, within this limitation, Eq. (2) does not cause problems. Beyond this, to use Eq. (2) could cause errors. Therefore, one should use Eq. (4) as the expression for S_1. In the following, one has to keep in mind that it is $<\alpha|\Delta V_{\rm iso}(R(t),\xi)\ |\alpha>$ that appears in the integrand of Eq. (4) and V_α $(=<\alpha|V_{\rm iso}(R(t),\xi)|\alpha>)$ that determines trajectories.

3. Vibrational dephasing with straight line trajectories

In early line shape theories such as the Anderson-Tsao-Curnutte (ATC) formalism [2,3], the translational motion was simply assumed to be a movement with constant speed v along a straight line. In other words, the trajectories are only characterized by the impact parameter b and do not depend on V_α at all. Based on this trajectory model, if one chooses $t = 0$ when the two colliding molecules reach their distance of closest approach (equal to b), the translational motion R(t) is given by

$$R(t) = \sqrt{b^2 + (vt)^2}. \tag{5}$$

Usually one assumes $V_{\rm iso}(R(t),\xi)$ can be represented by a Lennard–Jones model which is expressed as an expansion in ξ by

$$V_{\rm iso}(R(t),\xi) = \frac{C_{12}}{R(t)^{12}}(1 + s_1\xi + t_1\xi^2) - \frac{C_6}{R(t)^6}(1 + s_2\xi + t_2\xi^2). \tag{6}$$

Then, its vibration-independent and vibration-dependent parts $V_0(R(t))$ and $\Delta V_{\rm iso}(R(t),\xi)$ can be easily identified as

$$\begin{aligned} V_0(R(t)) &= \frac{C_{12}}{R(t)^{12}} - \frac{C_6}{R(t)^6}, \\ \Delta V_{\rm iso}(R(t),\xi) &= \frac{C_{12}}{R(t)^{12}}(s_1\xi + t_1\xi^2) - \frac{C_6}{R(t)^6}(s_2\xi + t_2\xi^2). \end{aligned} \tag{7}$$

By introducing a dimensionless parameter $z = vt/b$ one is able to evaluate the expression for S_1 analytically [6]

$$S_1(b) = \frac{2C_{12}}{\hbar v b^{11}} \int_0^{+\infty} \mathrm{d}z \frac{1}{(1+z^2)^6} \times [< f|s_1\xi + t_1\xi^2|f > - < i|s_1\xi + t_1\xi^2|i >] - \frac{2C_6}{\hbar v b^5} \int_0^{+\infty} \mathrm{d}z \frac{1}{(1+z^2)^3} \times [< f|s_2\xi + t_2\xi^2|f > - < i|s_2\xi + t_2\xi^2|i >] = \frac{3\pi\varepsilon\sigma}{2\hbar v} \left\{ \frac{21}{32} \cdot \left(\frac{\sigma}{b}\right)^{11} [s_1(\xi_{(f)} - \xi_{(i)}) + t_1(\xi^2_{(f)} - \xi^2_{(i)})] - \left(\frac{\sigma}{b}\right)^5 [s_2(\xi_{(f)} - \xi_{(i)}) + t_2(\xi^2_{(f)} - \xi^2_{(i)})] \right\}, \tag{8}$$

where simple notations $\xi_{(f)} = <f|\xi|f>$, $\xi^2_{(f)} = < f|\xi^2|f >$, $\xi_{(i)} = <i|\xi|i>$, and $\xi^2_{(i)} = <i|\xi^2|i>$ are used. In deriving Eq. (8), we have replaced C_{12} and C_6 by the LJ parameters ε and σ according to the following relations $C_{12} = 4\varepsilon\sigma^{12}$ and $C_6 = 4\varepsilon\sigma^6$. It is worth mentioning that the derivation of Eq. (8) is based on the straight-line trajectory model. Therefore, this expression for S_1 is applicable within the ATC formalism.

4. Vibrational dephasing with "parabolic" trajectories

In the RB formalism [4], the straight-line trajectory model has been refined by a "parabolic" trajectory model in which effects from $V_0(R(t))$ have been taken into account. The translational motion is described by movements with an "apparent" speed v'_c along rectilinear paths or curves such that R(t) is given by

$$R(t) = r_c\sqrt{1+z^2}, \tag{9}$$

where z is a dimensionless parameter defined by $z = v'_c t/r_c$. In the above expression, r_c is the distance of closest approach defined in terms of the impact parameter b by

$$b^2 = r_c^2\left\{1 - \frac{8\varepsilon}{mv^2}\left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^6\right]\right\}, \text{or} \quad b^2 = r_c^2\left\{1 - \frac{2}{mv^2}V_0(r_c)\right\}. \tag{10}$$

In Eq. (10), two equations are given. The first is a special one applicable for the LJ potential model and the second is a general one presented here for later convenience. Meanwhile, v'_c is defined by

$$v_c^{2\prime} = v^2\left\{1 + \frac{8\varepsilon}{mv^2}\left[5\left(\frac{\sigma}{r_c}\right)^{12} - 2\left(\frac{\sigma}{r_c}\right)^6\right]\right\}, \text{or} \quad v_c^{2\prime} = v^2\left\{1 - \frac{2}{mv^2}V_0(r_c) - \frac{r_c}{mv^2}\cdot\frac{\mathrm{d}V_0(r_c)}{\mathrm{d}r_c}\right\}. \tag{11}$$

Similarly, there are two expressions given for v'_c in Eq. (11). By following the same derivation as for Eq. (8) without modification, it appears that one can easily obtain an expression for S_1 applicable for the "parabolic" trajectory model

$$S_1(r_c) = \frac{3\pi\varepsilon\sigma}{2\hbar v'_c}\left\{\frac{21}{32}\cdot\left(\frac{\sigma}{r_c}\right)^{11}[s_1(\xi_{(f)} - \xi_{(i)}) + t_1(\xi^2_{(f)} - \xi^2_{(i)})] - \left(\frac{\sigma}{r_c}\right)^5[s_2(\xi_{(f)} - \xi_{(i)}) + t_2(\xi^2_{(f)} - \xi^2_{(i)})]\right\}, \tag{12}$$

where S_1 has been expressed as a function of r_c. By comparing the above expression with Eq. (8), it is obvious that Eq. (12) is almost the same as the previous case except for replacing v by v'_c and b by r_c. An alternative expression commonly appearing in the literature [7] is given by

$$S_1(r_c) = \frac{3\pi\varepsilon\sigma}{2\hbar v'_c}a_{01}\left[\frac{21}{32}y\left(\frac{\sigma}{r_c}\right)^{11} - \left(\frac{\sigma}{r_c}\right)^5\right], \tag{13}$$

where $a_{01} = s_2(\xi_{(f)} - \xi_{(i)}) + t_2(\xi^2_{(f)} - \xi^2_{(i)})$ and $y = [s_1(\xi_{(f)} - \xi_{(i)}) + t_1(\xi^2_{(f)} - \xi^2_{(i)})]/a_{01}$.

5. Vibrational dephasing with "exact" trajectories

Recently, there have been attempts by Buldyreva et al. [8,9] to consider what they call the "exact" trajectory model. Their work is based on Bykov's method presented more than a decade ago [10], but no computation of line shapes was performed at that time. With this model, the trajectories result from solutions of the classical dynamic equations governed by the isotropic interaction V_α between two molecules which is represented again by $V_0(R(t))$. For this trajectory model, Buldyreva et al. [8,9] derive a formula within the RB formalism given by

$$S_1(r_c) = \frac{1}{\hbar}\int_{-\infty}^{+\infty}\mathrm{d}t < f|\Delta V_{\mathrm{iso}}(R(t),\xi)|f > - \frac{1}{\hbar}\int_{-\infty}^{+\infty}\mathrm{d}t < i|\Delta V_{\mathrm{iso}}(R(t),\xi)|i > = \frac{1}{\hbar}\int_{-\infty}^{+\infty}\mathrm{d}t[\Delta V_{\mathrm{iso}}(R(t))]_{fi} = \frac{2r_c}{\hbar v}\int_1^{+\infty} x\mathrm{d}x \frac{[\Delta V_{\mathrm{iso}}(xr_c)]_{fi}}{\{x^2 - 1 + 2V_0(r_c)/mv^2 - 2x^2V_0(xr_c)/mv^2\}^{1/2}}, \tag{14}$$

where $[\Delta V_{\mathrm{iso}}(R(t))]_{\mathrm{fi}} \equiv <f|\Delta V_{\mathrm{iso}}(R(t),\xi)|f> - <i|\Delta V_{\mathrm{iso}}(R(t),\xi)|i>$. Then, with Eq. (14) one can perform numerical calculations to find values of $S_1(r_c)$ for all trajectories of interest.

At this stage, there is nothing new. The above expressions for $S_1(r_c)$, especially the one given by Eq. (13), have been used by many researchers for many years. However, by carefully considering the derivation processes for $S_1(r_c)$ based on these trajectory models, we have found differences. First of all, the derivation for S_1 based on the straight line model is absolutely correct. On the other hand, we have found there are subtle problems involved in deriving the expressions based on both the "parabolic" and the "exact" trajectory models. For these two cases, in contrast with the fact that the trajectories are determined by $<\alpha|V_{\mathrm{iso}}(R(t),\xi)|\alpha>$ and the latter is vibrationally dependent, it has always been tacitly assumed that the translational motion is vibrationally independent. In the first case, only $V_0(R(t))$ (i.e., $<\alpha|V_{\mathrm{iso}}(R(t),\xi = 0)|\alpha>$) appears in Eqs. (9)–(11) which are used to describe the translational motion. This implies that during the collision process, no matter which vibrational states the absorber molecule occupies, the trajectories themselves and how fast the translation motion moves are the same.

Meanwhile, for the "exact' trajectory case, the problem is hidden more deeply. In deriving the second line of Eq. (14), the algebraic manipulation seems straightforward and the result looks faultless. However, by adding two integrands together and combining two integrations over t into one, one has tacitly assumed that the two arguments

R(t) in these two integrands move along the same trajectories with the same speed. This is just the same assumption made in the previous case. In summary, the current BR formalism, especially the expression for S_1, is based on an approximation such that the trajectories are vibration-independent. Fortunately, without this approximation it is easy to derive new correct expressions for S_1 for both the vibration-dependent "parabolic" and the vibration-dependent "exact" trajectory models.

6. A refinement of vibrational dephasing with "parabolic" trajectories

Rigorously speaking, the current expression for $S_1(r_c)$ in the RB formalism is applicable in calculating line half-widths and shifts not involving vibrational transitions. Although it is $V_0(R(t))$, not the more rigorous $<\alpha|V_{iso}(R,\xi)\ |\alpha>$ that appears in Eqs. (9)–(11), in practice this difference is trivial and can be considered simply as a notation change. However, for lines of interest where vibrational transitions take place, one has to take the vibrational dependence of the translational motion into account. As a result, the two integrations in the expression for S_1 should be treated separately

$$\begin{aligned} S_1(b) &= \frac{1}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t < f|\Delta V_{iso}(R(t),\xi)|f> - \frac{1}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t < i|\Delta V_{iso}(R(t),\xi)|i> \\ &= \frac{2r_{c,(f)}}{\hbar v'_{c,(f)}}\int_0^{+\infty} \mathrm{d}z < f|\Delta V_{iso}(R(z),\xi)|f> \\ &\quad - \frac{2r_{c,(i)}}{\hbar v'_{c,(i)}}\int_0^{+\infty} \mathrm{d}z < i|\Delta V_{iso}(R(z),\xi)|i> . \end{aligned} \tag{15}$$

In the above expression, $r_{c,(f)}$ and $r_{c,(i)}$ differ from each other and they also differ from r_c defined by Eq. (10) because these closest distances $r_{c,(f)}$ and $r_{c,(i)}$ are vibration-dependent. Similarly, one has to introduce two $v'_{c,(f)}$ and $v'_{c,(i)}$ to replace v'_c defined by Eq. (11) because these two are also vibration-dependent. In fact, one can find $r_{c,(f)}$ and $r_{c,(i)}$ from Eq. (10) by making a replacement of $V_0(r_c)$ by $V_\alpha(r_{c,(\alpha)})$. Similarly, one can get $v'_{c,(f)}$ and $v'_{c,(i)}$ from Eq. (11) with a similar replacement.

In the case where $V_{iso}(R,\ \xi)$ is given in terms of a LJ model as shown by Eq. (6), we can write $<f|V_{iso}(r_{c,(f)},\ \xi)\ |f>$ used to determine $r_{c,(f)}$ and $v'_{c,(f)}$ explicitly as

$$\begin{aligned} < f|V_{iso}(r_{c,(f)},\xi)|f > &= \frac{C_{12}}{r_{c,(f)}^{12}}(1+s_1\xi_{(f)}+t_1\xi_{(f)}^2) \\ &\quad - \frac{C_6}{r_{c,(f)}^{6}}(1+s_2\xi_{(f)}+t_2\xi_{(f)}^2). \end{aligned} \tag{16}$$

Meanwhile, $<f|\Delta V_{iso}(R(t),\xi)\ |f>$ appearing in Eq. (15) as an integrand of the first integration is given

$$\begin{aligned} < f|\Delta V_{iso}(R(z),\xi)|f > &= \frac{C_{12}(s_1\xi_{(f)}+t_1\xi_{(f)}^2)}{r_{c,(f)}^{12}(1+z^2)^6} \\ &\quad - \frac{C_6(s_2\xi_{(f)}+t_2\xi_{(f)}^2)}{r_{c,(f)}^{6}(1+z^2)^3}. \end{aligned} \tag{17}$$

Similarly, one can find $<i|V_{iso}(r_{c,(f)},\ \xi)\ |i>$ and $<i|\Delta V_{iso}(R(t),\ \xi)\ |i>$. Then, by performing the integrations analytically in Eq. (15), we find

$$\begin{aligned} S_1(b) &= \frac{3\pi\varepsilon\sigma}{2\hbar v'_{c,(f)}}\left[\frac{21}{32}\cdot\left(\frac{\sigma}{r_{c,(f)}}\right)^{11}(s_1\xi_{(f)}+t_1\xi_{(f)}^2) - \left(\frac{\sigma}{r_{c,(f)}}\right)^{5}\left(s_2\xi_{(f)}+t_2\xi_{(f)}^2\right)\right] \\ &\quad - \frac{3\pi\varepsilon\sigma}{2\hbar v'_{c,(i)}}\left[\frac{21}{32}\cdot\left(\frac{\sigma}{r_{c,(i)}}\right)^{11}(s_1\xi_{(i)}+t_1\xi_{(i)}^2) - \left(\frac{\sigma}{r_{c,(i)}}\right)^{5}\left(s_2\xi_{(i)}+t_2\xi_{(i)}^2\right)\right]. \end{aligned} \tag{18}$$

If potential parameters $s_1\xi_{(f)}+t_1\xi_{(f)}^2$, $s_2\xi_{(f)}+t_2\xi_{(f)}^2$, $s_1\xi_{(i)}+t_1\xi_{(i)}^2$, and $s_2\xi_{(i)}+t_2\xi_{(i)}^2$ are available, one can easily obtain the vibrational dephasing contributions to S_1(b) from Eq. (18) [11].

At this stage, we would like to discuss a problem associated with the argument of S_1. As shown by Eq. (18), the argument of S_1 is the impact parameter b, the same as that originally used in the ATC formalism, but not the closest approach r_c selected in the RB formalism. The key point here is between b and r_c, which one is a proper choice. In the ATC formalism, there is only one choice because $r_c = b$. Meanwhile, in the RB formalism, there are two choices, but to select r_c is better. However, after the vibration-dependent trajectory models are introduced, a new problem arises. Corresponding to a specified b value, there are two different trajectories. For the vibration-dependent "parabolic" trajectory model, the latter are described by $r_{c,(f)}$ and $v_{c,(f)}'$ and by $r_{c,(i)}$ and $v_{c,(i)}'$, respectively. Although it is still possible to describe all these $r_{c,(f)}$, $v_{c,(f)}'$, $r_{c,(i)}$, and $v_{c,(i)}'$ in terms of r_c, it requires extra work. As a result, to select r_c as the argument of S_1 becomes disadvantageous and to select b is a natural choice. It is worth mentioning that to choose b as the argument for S_1 will not cause any new challenge as one enters in the last stage of width and shift calculations by performing integrations over b. Of course, one has to make mathematical adjustments, such as to remove a Jacobian factor $\mathrm{d}b/\mathrm{d}r_c$ from the previous integrand and to change the integration limits accordingly.

7. A refinement of vibrational dephasing with "exact" trajectories

A general expression for S_1(b) is given by Eq. (4) from which numerical calculations can be carried out. One can follow Buldyreva's method [8,9] and express S_1 as

$$\begin{aligned} S_1(b) &= \frac{2r_{c,(f)}}{\hbar v}\int_1^{+\infty} x\mathrm{d}x\frac{\Delta V_{iso,(f)}(xr_{c,(f)})}{\{x^2-1+2V_{iso,(f)}(r_{c,(f)})/mv^2-2x^2V_{iso,(f)}(xr_{c,(f)})/mv^2\}^{1/2}} \\ &\quad - \frac{2r_{c,(i)}}{\hbar v}\int_1^{+\infty} x\mathrm{d}x\frac{\Delta V_{iso,(i)}(xr_{c,(i)})}{\{x^2-1+2V_{iso,(i)}(r_{c,(i)})/mv^2-2x^2V_{iso,(i)}(xr_{c,(i)})/mv^2\}^{1/2}}, \end{aligned} \tag{19}$$

where $\Delta V_{iso,(f)}(r) = <f|\Delta V_{iso}(r,\xi)|f>$, $\Delta V_{iso,(i)}(r) = <i|\Delta V_{iso}(r,\xi)|i>$, $V_{iso,(f)}(r) = <f|V_{iso}(r,\xi)|f>$, and $V_{iso,(i)}(r) = <i|V_{iso}(r,\xi)|i>$. In comparison with a case without considering vibration-dependent trajectories, there are no extra difficulties in evaluating the two integrations in the right side of Eq. (19). We note that the argument of

S_1 is the impact parameter b again. In this case, b is the only choice because it is impossible to describe the two trajectories calculated numerically in terms of r_c.

We would like to point out here that this refinement of the translation motion can also be extend into calculating the S_2 term because S_2 also depends on how the translational motion varies. In addition, one has to use b as the argument of S_2. Because the development is straightforward and S_2 is not the main subject in the present study, we will not discuss the extension here.

8. Numerical results

As an example, we present numerical calculations of the line broadening and line shifting for the isotropic Raman Q(1) line of $v = 1 \leftarrow v = 0$ band of H_2 broadened by He. For this pair, an accurate *ab initio* vibration-dependent potential surface is available [12] and has been used in previous calculations of line parameters for the same line [13–15]. As claimed by Joubert et al., this system is pertinent to specifically study the influence of the trajectory modification within the RB formalism [15], and it is a good candidate to test the new modification introduced here. We follow their arguments that for this system the vibrational dependence of the isotropic potential is the dominant source for the width and the shift of the Q(1) line, and contributions from the anisotropic potential can be neglected. As a result, the simplified expressions for the width and shift are given by

$$\begin{aligned}\gamma_{fi} &= \frac{n_b}{2\pi c}\sqrt{\frac{8kT}{\pi m}} \\ &\quad\times \int_0^\infty x\mathrm{e}^{-x}\mathrm{d}x \int_0^\infty 2\pi b[1-\mathrm{e}^{-\mathrm{Re}S_2(b,kTx)}\cos\eta_{fi}(b,kTx)]\mathrm{d}b \\ &\approx \frac{n_b}{2\pi c}\sqrt{\frac{8kT}{\pi m}}\int_0^\infty x\mathrm{e}^{-x}\mathrm{d}x\int_0^\infty 2\pi b[1-\cos\eta_{fi}(b,kTx)]\mathrm{d}b\end{aligned} \tag{20}$$

$$\begin{aligned}\delta_{fi} &= \frac{n_b}{2\pi c}\sqrt{\frac{8kT}{\pi m}} \\ &\quad\times \int_0^\infty x\mathrm{e}^{-x}\mathrm{d}x \int_0^\infty 2\pi b\mathrm{e}^{-\mathrm{Re}S_2(b,kTx)}\sin\eta_{fi}(b,kTx)\mathrm{d}b \\ &\approx \frac{n_b}{2\pi c}\sqrt{\frac{8kT}{\pi m}}\int_0^\infty x\mathrm{e}^{-x}\mathrm{d}x\int_0^\infty 2\pi b\sin\eta_{fi}(b,kTx)\mathrm{d}b,\end{aligned}$$

where n_b is the number density of the bath molecule, m is the reduced mass of the colliding pair, $x(= E/kT)$ is a dimensionless variable, and E is the initial translational kinetic energy. In the above expressions, $\eta_{fi}(b,E)$ is defined by

$$\eta_{fi}(b,E) = S_1(b,E) + ImS_2(b,E) \tag{21}$$

and is approximately represented by $S_1(b,E)$ here.

The original potential surface from Schaefer and Köhler [12] is given by tabulated values at dozens of R values and at five vibrational displacement r of H_2 (i.e., $r = 0.900$, 1.280, 1.449, 1.618, and 2.000 a.u.). In order to perform numerical calculations, we need to know $V_{iso}(R(t),\xi = 0)$ and $<\alpha|V_{iso}(R(t),\xi)\ |\alpha>$. The former is taken directly from the original values at $r_e = 1.449$ a.u. and the latter is calculated from the following formula

$$<\alpha|V_{iso}(R(t),\xi)|\alpha> = \int_0^{+\infty}\psi^2_{v_\alpha j=0}(r)V_{iso}(R(t),r)\mathrm{d}r, \tag{22}$$

where $\psi_{v_\alpha j}(r)$ is the ro-vibrational wave function of H_2. In practice, we do not carry out the integration of Eq. (22) directly, rather we calculate values of $<\alpha|V_{iso}(R(t),\ \xi)\ |\alpha>$ from polynomial expansions of $V_{iso}(R(t),\xi)$ derived from the least squares polynomial fitting over r and values of $<v = 0,\ j = 0\ \ |\xi^k|v = 0,\ j = 0>$ and $<v = 1,\ j = 0\ |\xi^k|\ v = 1,\ j = 0>$ with $k = 0,\ldots,5$ provided by Schwartz and Le Roy for matrix elements of H_2 [16]. After $<\alpha|V_{iso}(R(t),\xi)\ |\alpha>$ and $V_{iso}(R(t),\xi = 0)$ are available, values of $<\alpha|\Delta V_{iso}(R(t),\xi)\ |\alpha>$ are simply their differences.

As shown by Eq. (20), the width and shift are given by two-dimensional integrations over x and b. We do not present the definitions of the broadening and shifting cross sections here, rather we note that they are nothing but that represented by the integrations over b on the right-hand sides of Eq. (20). The calculated results are given in Figs. 1 and 2. From these two figures, we can draw several conclusions.

It is well known that values obtained from the close coupling calculation are the most accurate ones and they can serve as a bench mark to judge accuracies achieved by other methods. One of original purposes of the paper by Joubert et al. [15] was to study the effects from adopting a better trajectory model in calculations. Because advantages of the "exact" trajectory model over the "parabolic" one is obvious, one expects to find an improvement of agreement with the MOLSCAT [17] values for results obtained from this better model in the RB formalism. By comparing two dot-dashed lines representing these two different trajectory models, one can see that effects are significant because there are big gaps between these two lines. However, in comparisons with the dashed line denoting the MOLSCAT values, the expected improvement does not happen at all because the dashed line lies just at the middle between the two dot-dashed ones. One can also find the same features by checking Fig. 1(a) and (b) of the paper by Joubert et al. [15] On the other hand, if one compares the two solid lines derived from the new formula with the MOLSCAT values, the expected improvement is clearly demonstrated because values from the "exact" trajectory model are much closer to the latter than those from the "parabolic" model. This implies that the previous two results both from the RB formalism have been distorted and the source of the distortion is nothing but the vibration- independent trajectory assumption. The above comparisons can serve as an argument to justify the new modification suggested in the present study.

Secondly, by comparing the bold solid and the bold dot-dashed lines, the former is closer to the MOLSCAT values than the latter. The comparisons become more favorable

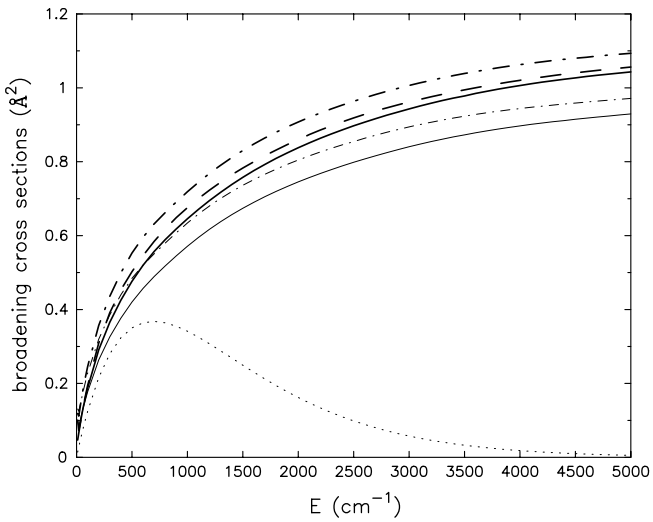

Fig. 1. Calculated broadening cross sections for the Q(1) line of $v = 1 \leftarrow v = 0$ band of H_2 broadened by He as function of the initial kinetic energy E. Values derived from the RB formalism are plotted by two dot-dashed lines: the bold one comes from the "exact" trajectory model and the thin one from the "parabolic" trajectory model. Similarly, results derived from the new formula with these two trajectory models are represented by two solid curves. In addition, values calculated from the MOLSCAT code are given by a bold dashed line. In order to be consistent, there is only the isotropic part of the potential surface used in the MOLSCAT calculations. For a reference, one (i.e., $T = 1000$ K) of the weighting functions introduced later in calculating the line parameters is plotted by a thin dotted line with arbitrary units.

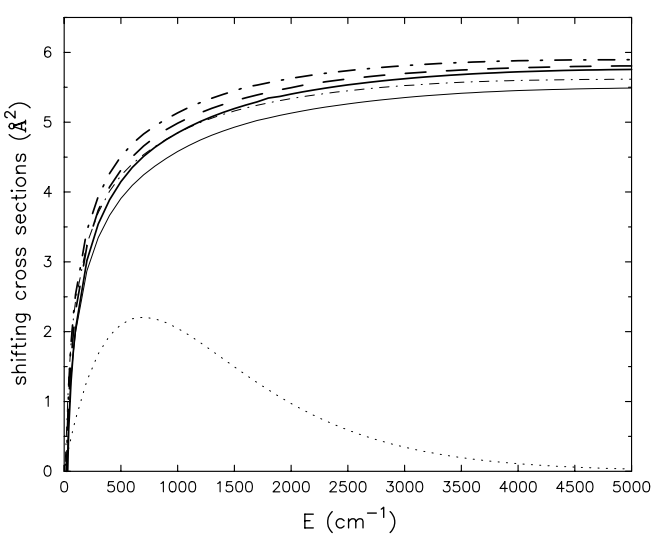

Fig. 2. The same as Fig. 1 except for the shifting cross sections.

for the new results as the energy increases. This is consistent with the fact that as the kinetic energy (or temperature) increases, the gap between classical theory and quantum theory becomes smaller. Finally, by comparing gaps between a bold and a thin line with the same format with gaps between a bold (or thin) dot-dashed and a bold (or thin) solid line, one can conclude that the effect from the modification of the trajectory model (i.e., from the "parabolic" to the "exact" trajectories) and the effect from the new modification suggested here (i.e., from the vibration-independent to the vibration-dependent trajectories) are comparable. In summary, one can conclude that at least for the H_2–He pair, when one makes refinements of the RB formalism by improving the trajectory modeling, it is worthwhile also to consider effects from the vibration-dependent trajectories. Of course, one cannot simply extend the above conclusion drawn from H_2–He to other systems without analyzing differences between their potential features.

After the broadening and shifting cross sections as functions of E are available, one can easily derive the line broadening and line shifting by performing the remaining integrations of the corresponding cross sections over x in Eq. (20). The calculated results are plotted in Figs. 3 and 4. We note that most of conclusions drawn from Figs. 1 and 2 are applicable for the Figs. 3 and 4 so we will not repeat them again. The only thing we would like to comment on here is that as shown by Fig. 4, it appears in comparison with the new shifting cross sections derived from the "exact" trajectory model, the new line shifting values become less favorable compared to the MOLSCAT values. The reason is that as shown by Fig. 2, the weighting function at $T = 1000$ K has its maximum value at $E = 695$ cm^{-1}. Maximum values of other weighting functions at lower temperatures become even smaller. Within this low-energy region, the shifting cross sections derived from MOLSCAT are in between those obtained from the RB formalism and the new formula with the "exact' trajectory model.

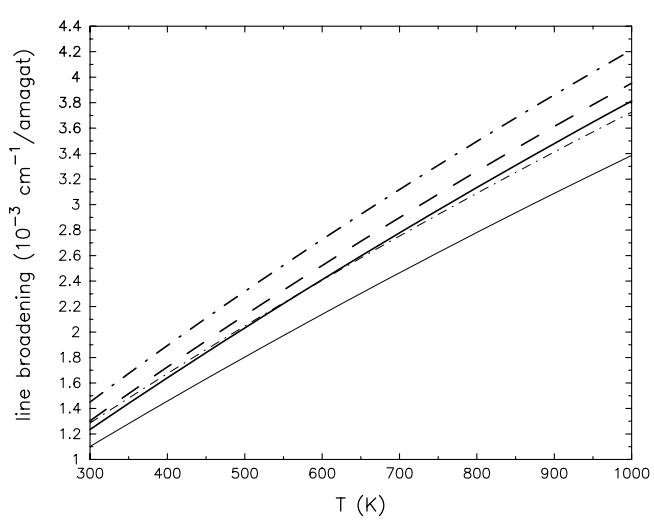

Fig. 3. Calculated line broadening for the Q(1) line of $v = 1 \leftarrow v = 0$ band of H_2 broadened by He as function of the temperature T. Values derived from the RB formalism are plotted by two dot-dashed lines: the bold one comes from the "exact" trajectory model and the thin one from the "parabolic" trajectory model. Similarly, results derived from the new formula with these two trajectory models are represented by two solid curves. In addition, values calculated from the MOLSCAT code are given by a bold dashed line.

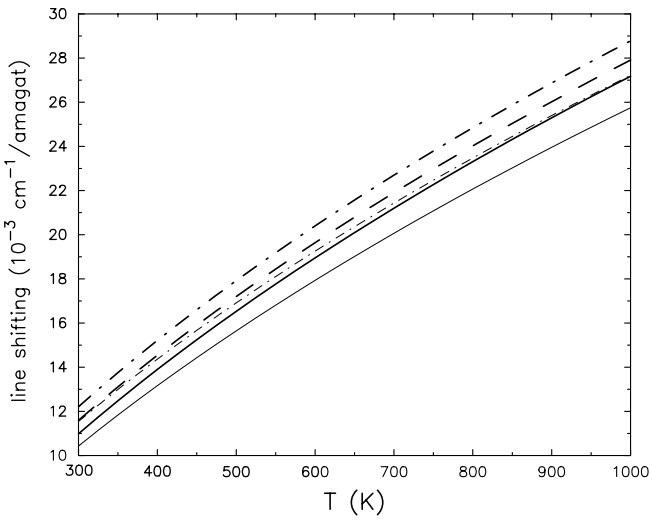

Fig. 4. The same as Fig. 3 except for the line shifting.

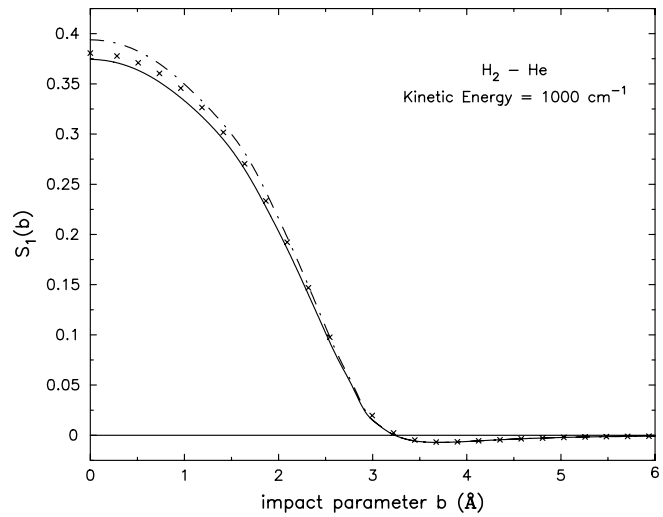

Fig. 5. Calculated S_1 as a function of b from the old and new formulas at the initial kinetic energy $E = 1000\ \mathrm{cm}^{-1}$ are plotted by a dot-dashed and solid lines. Values of the phase shifts derived from MOLSCAT for dozens of L values are also presented by crosses.

9. Conclusions

Because the new modification is built on sound physical considerations, it appears that a challenge may not come from the theoretical point of view, but from the practical point of view. In other words, whether to adopt it or not depends on how important the effects on the calculated widths and shifts from this modification are. In cases where the effects are negligible, the modification is not necessary. Otherwise, one should adopt it.

Based on the present study for the H_2–He system, we would like to make a few comments about this problem. In order to do this, we analyze profiles of $S_1(b)$ at a typical kinetic energy $E = 1000\ \mathrm{cm}^{-1}$ and present the calculated S_1 as a function of b from three different methods in Fig. 5. There values of S_1 derived from the previous and the new formulas with the "exact' trajectory model are plotted by dot-dashed and solid lines, respectively. Also, we have calculated the phase shifting from MOLSCAT for dozens of L values. According to the correspondence principle between the classical expression for the angular momentum mbv where v is the initial speed and its quantum analog $\hbar(L + 1/2)$, for a specified L we can find its corresponding b value. For $L = 0$, we assume that it corresponds to $b = 0$. Because the phase shifting represents the S_1 term, the MOLSCAT results can be plotted in the same figure and they are represented by x'es in Fig. 5. By comparing results derived from these three methods, it is obvious that as long as b is beyond 3.0 Å, they are the same. Meanwhile, for b less than 3.0 Å, there are significant differences, but the new values are closer to the MOLSCAT results.

One can infer additional information from this plot. In order to do this, we focus our attention on the two curves derived from the semi-classical method. We have already mentioned above that these two curves differ from each other significantly for $b < 3.0$ Å and become the same for $b > 3.0$ Å. It is worth mentioning that around the intramolecular separation $R = 3.0$ Å, the isotropic interaction of H_2–He changes signs from the positive repulsive to the negative repulsive part of the potential energy surface [12]. This means that σ, one of the effective LJ parameters for V_{iso}, is around 3.0 Å. Therefore, one can conclude that the new modification mainly affects short-range collisions with $b < \sigma$ and it does not significantly affect other collisions. This conclusion is not surprising. Meanwhile, in the range $b > \sigma$ where these two curves are identical, their values become negative and their magnitudes become very small as shown by a shallow dip of their profiles in the figure. It is worth mentioning that the shallowness of the depth results from the smallness of ε, another effective LJ parameter of V_{iso}, whose value is only about 13.6 K [12]. Based on these detailed analyses, we find that for the H_2–He system there is only one region (i.e., $b < \sigma$) in which $S_1(b)$ has larger magnitudes and this region is overlapped with the same region in which the modification of the vibration-dependent trajectories has the largest influence on $S_1(b)$. As a result, net effects on the cross sections and line shape parameters from the modification are fully exhibited. In order to understand the role played by the effective LJ parameter ε more clearly, let's assume that ε is several times larger than 13.6 K. In this case, the depth of S_1 would be several times larger than that shown in Fig. 5. As a result, there would be two regions in which $S_1(b)$ has large magnitudes. Among them, one (i.e., $b > \sigma$) is just a region which is not affected by the modification. Because a net effect results from an average process involving $S_1(b)$ over b with $2\pi b$ as the weighting function, this effect would be reduced significantly or even dramatically. In summary, with respect to the question about how important the modification could be, our answer is it depends on a system of interest. For systems similar to H_2–He with small ε values, the effect is important. For

other system with large ε values, the effect is not significant or even negligible.

The above comments result from analyzing the $S_1(b)$ term only because we have assumed that contributions from the $S_2(b)$ term for H_2–He are negligible. In general, this is not always true and the $S_2(b)$ term must be taken into account. It is well known that usually the S_2 term, especially its real part $\mathrm{Re}S_2(b)$, plays a crucial role in determining the pressure broadening and shifting. As shown by the first lines of expressions for γ and δ in Eq. (20), there is a factor $\exp(-\mathrm{Re}S_2(b,E))$ present. Usually, within the region for $b < \sigma$, values of $\mathrm{Re}S_2(b,E)$ are positive. As a result, this factor reduces contributions from $\cos\eta_{\mathrm{fi}}(b,E)$ and $\sin\eta_{\mathrm{fi}}(b,E)$ in these expressions. Of course, it reduces effects from changes of $\eta_{\mathrm{fi}}(b,E)$ caused by the modification introduced here as well. For systems which have strong anisotropic interactions, we expect that this effect could be significant or decisive. As a result, the effects from the new modification could be washed out, partially or completely. Of course, by applying the new modification to derivations of the $S_2(b)$ term itself, values of $S_2(b)$ at the region $b < \sigma$ could vary. But, we do not expect there would be big differences. Therefore, we expect that the above comments remain true when both S_1 and S_2 are derived from the vibration-dependent trajectory models. In summary, based on the considerations given above, we expect that for systems where the short-range collisions are the dominant source responsible for the line widths and shifts, and in addition, the isotropic interaction has small well depth, the vibration-dependent trajectory modification effects on the calculated line shape parameters could be significant. This means that people should consider this modification if they want to refine their calculated results. In other cases, however, the effects are not important or even negligible.

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