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Boulet

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Comparison of quantum, semiclassical and classical methods in the calculation of nitrogen self-broadened linewidths

FRANCK THIBAUT<sup>(1,\*)</sup>, LAURA GOMEZ<sup>(2)</sup>, SERGEY V. IVANOV<sup>(3)</sup>, OLEG G. BUZYKIN<sup>(4)</sup>, CHRISTIAN BOULET<sup>(5)</sup>

<sup>1</sup>Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes I, F-35042 Rennes, France

<sup>2</sup>Atmospheric Research and Instrumentation Branch. Instituto Nacional de Técnica Aeroespacial (INTA), 28850 Torrejón de Ardoz, Madrid, Spain

<sup>3</sup>Institute on Laser and Information Technologies, Russian Academy of Sciences, 2 Pionerskaya Str., 142190 Troitsk, Moscow Region, Russia

<sup>4</sup>Central Aerohydrodynamic Institute (TsAGI), Zhukovski, Moscow Region 140160, Russia

<sup>5</sup>Institut des Sciences Moléculaires d'Orsay, UMR CNRS 8214, Université Paris-Sud 11, F-91405 Orsay, France

Mail:

Franck THIBAUT

Université de Rennes I, Campus de Beaulieu

Institut de Physique de Rennes, UMR CNRS 6251, Bât. 11B

F-35042 Rennes, France

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\* Corresponding author. Tel. 33223236182 ; fax 33223235662  
E-mail address : Franck.Thibault@univ-rennes1.fr

## ABSTRACT

We perform dynamical calculations on two robust N<sub>2</sub>-N<sub>2</sub> potential energy surfaces in order to intercompare pressure broadening coefficients derived from close coupling and coupled states quantum dynamical methods, the semi-classical model of Robert and Bonamy and a full classical method. The coupled states and full classical results compare well with experimental results or with close coupling values when available. This study confirms that the classical method is a good alternative at room and high temperatures to quantum dynamical methods. The results obtained using the semi-classical method however deviate from the other sets of data at all temperatures considered here (77-2400K).

Keywords : Collisional broadening, linewidths, Raman spectroscopy, pressure broadening, nitrogen, classical, semiclassical and quantum methods

## 1. Introduction

Nitrogen is the most abundant molecule in our atmosphere and in that of Titan, and is also a major component in different combustion media. Therefore any physical, chemical or thermodynamical quantity, process or phenomenon involving this molecule in these environments is of great importance. Many diagnostics of temperature and pressure are based on spectroscopy of nitrogen through coherent Raman techniques. In this context, a number of lineshape studies, both experimental and theoretical, have been performed. Ref. [1] provides an exhaustive review of works performed on this subject before the 90's. The more recent Refs. [2-4] update this review.

In order to carefully interpret the results of Raman spectra it is necessary to have a good potential energy surface (PES) on which the calculations of lineshape parameters can be performed. Such calculations can provide pressure broadening coefficients which is what we propose to do here for self-broadening of nitrogen. Moreover, it is necessary to have reliable models in order to predict temperature dependence of broadening since the conditions of the probed  $N_2$  molecules may be very different in the upper atmosphere and in a flame. However, the main goal of the present work is not to provide, again [3-6], theoretical self-broadening coefficients for nitrogen but rather to compare a few dynamical methods available for calculating these coefficients.

Recently, some of us have intercompared the full classical method of Gordon [7,8], revived by Ivanov and coworkers [5,9,10], the semi-classical model of Robert and Bonamy [11] (referred to as RB hereafter) based on the well-known Anderson-Tsao-Curnutte method [12,13], and quantum dynamical calculations for the  $C_2H_2-H_2$  [14] and  $N_2-H_2$  [15] systems. In the present work, as in the latter references, the same development of the PESs is used with no adjusted expression of the isotropic part as is often done with semi-classical calculations and which was recently criticized by Ma and coworkers [6,16]. The main conclusions of these comparisons [14,15] were the following: 1) the close coupling (CC hereafter) method [17] provides accurate pressure broadening coefficients; 2) the less accurate coupled states (CS hereafter) method [18] is quite good above room temperature for  $C_2H_2-H_2$  and works well in the temperature range 77-580 K investigated for the  $N_2-H_2$  system; moreover this approximation should be better at higher temperatures; the full classical (FC hereafter) method is on the whole accurate above the room temperature; 3) the RB semi-classical formalism overestimates pressure broadening (PB) coefficients by at least 20% at all temperatures (up to 2000 K); 4) all considered methods predict a similar temperature dependence of the PB coefficients. However, we should acknowledge (as we mentioned in [15]) that these systems were not the most appropriate to test the RB model.

Indeed, the RB formalism assumes that the relative translational motion is independent of the rotational motion since the trajectory is driven by an effective central potential. This approximation will fail when non-resonant inelastic collisions play a significant role, since an important change in the kinetic energy of the colliding pairs will lead to difficulties in describing the trajectory at low kinetic energy [19,20]. This may be the case when the two colliding molecules have very different rotational constants. In contrast, in the case of self-broadening, one may reasonably hope that the interaction between translational and rotational motion does not change the translation enough, during resonant or quasi-resonant collisions, to produce any detectable effect. The present comparison therefore does not suffer the critique addressed against our preceding intercomparisons. Moreover, for this system a number of measured isotropic Raman collisional linewidths are available over a wide range of temperatures, from 77 K up to a few thousands kelvins. These will allow us to test thoroughly our methods from low to high temperatures.

In contrast to the  $C_2H_2-H_2$  or  $N_2-H_2$  systems for which quantum dynamical calculations are easily feasible up to about 1000 K in conjunction with the CC method and up to about 2000 K with the CS approximation [14,15,21], for the  $N_2-N_2$  system quantum calculations are feasible only up to about 400 K and 1000 K respectively with the CC and CS methods [22-24] (note that these limits depend in fact on the highest  $j$  values investigated). Therefore, for the  $N_2-N_2$  system and undoubtedly for heavier or more complex molecular systems, one has to resort to alternative methods, which motivates our continued comparison of the most rigorous quantum dynamical methods with the RB method and the full classical method. Finally, it should be remarked that such useful comparisons are so far very scarce (see the few references in [14]).

Section 2 describes the dynamical calculations. The various theoretical results are compared amongst themselves as well as with available experimental data in Sec. 3. The discussion constitutes the Section 4. Concluding remarks are given in Section 5.

## **2. Dynamical calculations**

The binary collisions and the impact approximations [2] are the common features of the methods summarized below. Since the PESs used are only four dimensional, our calculations are performed within the rigid rotor approximation. In view of the triple bond of the nitrogen molecule this should be very reasonable [25-27].

### *2.1 Potential energy surfaces used*

Dynamical calculations were performed on the ab initio PES [28,29] determined by the symmetry adapted perturbation theory (denoted hereafter as the SAPT PES) and on the scaled PES [30] (known as the PES8) derived from the PES of van der Avoird et al [31]. The PES8 has been recently used [24] for the determination of two-body rotational state-to-state rates which are closely related to the parameters that interest us in the present study. Both PESs were already used in the CC and CS calculations of pressure broadening coefficients in [4]. These PESs have been recently compared to other PESs [32]. The latter study states that the SAPT potential is the most accurate to date, even if its isotropic well depth seems to be slightly overestimated.

The PESs have been expanded<sup>†</sup> over bispherical harmonics [17,31]:

$$V(R, \theta_1, \theta_2, \Phi) = \sum_{L_1, L_2, L} V_{L_1 L_2 L}(R) \times A_{L_1 L_2 L}(\theta_1, \theta_2, \Phi) \quad (1)$$

where  $(\theta_1, \theta_2, \Phi)$  are the three angular Jacobi coordinates which describe the relative orientation of the two monomers.  $R$  is the distance between the two monomer centres of mass and defines the intermolecular axis,  $\theta_{\{1,2\}}$  defines the bending angle of the monomer axis relative to the intermolecular axis (the index “1” and “2” refers to one of the  $N_2$  molecules) and  $\Phi$  is the rotational angle around  $R$  of one monomer relative to the other (Fig. 1 of Ref. [33] provides a pictorial representation). The values  $L_1, L_2$  and  $L$  are even because the colliding pair is formed of homonuclear molecules and  $|L_1 - L_2| \leq L \leq |L_1 + L_2|$ . The angular functions  $A_{L_1 L_2 L}(\theta_1, \theta_2, \Phi)$  are defined in the case of two linear molecules by a normalized product of spherical harmonics for monomers 1 and 2 as:

$$A_{L_1 L_2 L}(\theta_1, \theta_2, \Phi) = \left( \frac{2L+1}{4\pi} \right)^{1/2} \sum_m \langle L_1 m L_2 - m | L 0 \rangle Y_{L_1}^m(\theta_1, 0) Y_{L_2}^{-m}(\theta_2, \Phi) \quad (2)$$

where  $Y_{L_1}^m$  and  $Y_{L_2}^{-m}$  are ordinary spherical harmonics,  $\langle \dots | \dots \rangle$  is a Clebsch-Gordan coefficient, and  $|m| \leq \min(L_1, L_2)$ . The expansion retained 30 angular functions and is identical to the one used by A. van der Avoird et al [31]. The radial coefficients  $V_{L_1 L_2 L}(R)$  were obtained through Gauss-Legendre quadratures over  $\theta_1$  and  $\theta_2$ , and by a Chebyshev quadrature over  $\Phi$  [21].

This expansion allows to economize CPU time and is well suited for use in the calculations of the PB cross sections with the MOLSCAT code [34]. For the dynamical treatment the radial coefficients  $V_{L_1 L_2 L}(R)$  for intermolecular distances not tabulated are obtained through standard interpolation methods [21]. Since the aim of the present work is to compare the

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<sup>†</sup>Note that in fact we are following the “normalization” of Ref. [17] which is closely related to the one of Ref. [31].

methods of PB coefficient calculations, these radial coefficients are the starting material for all the four methods used.

## 2.2 Quantum dynamical methods

For a review of the close coupling and coupled states approximation methods see Refs. [17] and [18] respectively. Briefly, the CS method is derived from the usual CC equations by approximating the collisional angular momentum operator, the Coriolis coupling term, to decouple partial waves. The resulting equations are identical in form to the CC equations except that now the equations are decoupled in the orbital momentum  $l$  and  $m_{12}$ , where  $m_{12}$  is the projection of  $\vec{j}_{12} = \vec{j}_1 + \vec{j}_2$  ( $\vec{j}_i$  being the internal angular momentum of molecule  $i$ ) on a collision fixed axis system. The CS approximation is expected to provide [22,23] quite good results at high kinetic energy without the high computational cost of a CC calculation. In [4] we have shown (see its Fig. 3) that the CS approximation should provide quite good results above room temperature.

For the present study, with the aim of testing various methods, we have performed a number of CS calculations for ortho-N<sub>2</sub> (oN<sub>2</sub>) perturbed by ortho- and para- N<sub>2</sub> (pN<sub>2</sub> states are associated with odd  $j$  values and have a statistical weight of 1/3). For oN<sub>2</sub>-oN<sub>2</sub> we have performed 63 (and 66 for oN<sub>2</sub>-pN<sub>2</sub>) Molscat runs for total energies between 0 and 1500 cm<sup>-1</sup>. Technical details are very similar to those given in [4]. We remind the reader that since we are dealing with isotropic Raman Q lines (with no vibrational dependence), what we are actually calculating are state-to-state cross-sections  $\sigma(j_1 j_2 \rightarrow j_1' j_2'; E_{kinetic})$ . These cross-sections, once thermally averaged over a Maxwell-Boltzmann distribution in kinetic energies, provide rotational relaxation or excitation rates. The pressure broadening coefficients are then obtained through weighted sums of these rates [4,23,35].

Close coupling calculations were performed in [4] up to total energies of 400 cm<sup>-1</sup>. Additional calculations are performed here in the range 300 - 500 cm<sup>-1</sup> in order to increase the accuracy of our CC/CS values [4] below room temperature. They were completed by our coupled states calculations at higher energies (up to 1500 cm<sup>-1</sup>, see above) in order to perform the thermal average up to room temperature. We emphasize that we have an independent set of thermally averaged coupled states pressure broadening coefficients and a mixed CC/CS set. Nonetheless, the CC/CS thermally averaged values are nearly unaffected by the CS calculations below room temperature for  $j$  values lower than 10. Therefore in the rest of this paper we will denote by CC our CC/CS values.

### 2.3 Semi-classical Robert-Bonamy method

There is a hierarchy of classical path methods. They all treat the relative translational motion classically but handle the internal ones quantum mechanically. Some determine the trajectories from the isotropic part  $V_0(R)$  ( $V_{000}(R)$  in our diatom – diatom case) of the full potential, but some others introduced an improved effective potential (in the sense that this effective central potential leads to better agreement with experimental values) or even make this effective potential depend on the rotational states, thus requiring a separate trajectory calculation for each initial state [19,20]. The popular RB approach [11] has its roots in the ATC theory [12,13]. It improves the latter by the non-perturbative treatment of the S scattering operator through the use of the linked cluster theorem, the introduction of short range anisotropic forces, and a more realistic description of the trajectory, driven by  $V_0(R)$ . A detailed discussion of this method is given by Ma and coworkers [6,16].

Our RB codes were developed following the numerical approach of Refs. [3,36]<sup>‡</sup>. Since all the necessary formulae are given in these references, they will not be replicated here. The potential used do not include vibrational dependence, and so, the contribution of the first order term of the perturbative expansion of the scattering operator S, known as  $S_1$  [11], has not been taken into account. Since all our calculations have been performed in the rigid rotor approximation, this will not affect the comparison. Moreover, due to the fact that  $N_2$  pressure induced lineshifts in the fundamental band are very weak [25-27], no effect on the linewidths calculations is expected. Similarly in the rigid rotor limit, the imaginary part of the second order term disappears since one has  $\text{Im}S_{2,\text{outer},i} = -\text{Im}S_{2,\text{outer},f}$  for Q lines. This relation, exact for Q lines (in the rigid rotor limit), can lead to erroneous linewidths calculations [37,38]<sup>§</sup> for other types of lines (O, P, R and S). Finally, since for isotropic Raman Q-branch lines the diagonal part of the so-called  $S_{2,\text{outer}}$  term is cancelled by the  $S_{2,\text{middle}}$  term (notation as in the ATC theory) associated with elastic contributions, we are left with the non-diagonal real part of  $S_2$  which comprises the contribution of the inelastic collisions only.

It has been shown in Ref. [4] that the time consuming operation consisting of performing the thermal average may be skipped even at  $T=77$  K without too much loss of accuracy (note that in CC or in CS this does not prevent the construction of a grid of total energies because the total energy is conserved). Ivanov and Buzykin [5], using the classical method found no significant

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<sup>‡</sup> it should be noticed that in Eq. (6) of Ref. [3] the Wigner 3j coefficients should be replaced by Clebsch-Gordan coefficients. Nonetheless, the code developed by Afzelius et al was correct.

<sup>§</sup>As pointed out by the referee there is a misunderstanding in Refs. [3,14] and some others: Gamache and coworkers [37,38] have shown that it is the omission of  $S_1 + \text{Im}S_2$  that can lead to serious errors and not the omission of  $\text{Im}S_2$  solely.

differences between thermally averaged PB cross-sections and the ones obtained at the mean thermal speed for temperatures greater than about 300 K. Full classical calculations performed here (Sec. 2.4) confirm the validity of this approximation, even at lower temperatures. The RB calculations performed here make use of this approximation.

We made use of two kinds of trajectories: the standard parabolic trajectory method as introduced by Robert and Bonamy [11] (denoted RB-PT) and an “exact” trajectory model [39-41] which is conceptually more justified. Both models assume that the trajectory is driven by the isotropic part of the potential. When an impact parameter  $b$  and a relative collisional speed are fixed, one obtains a trajectory specified by  $R(t)$ , the intermolecular distance, and an angle (the deflection angle for instance) as a function of time  $t$ . Having  $R(t)$  or  $t(R)$ , the rest of the theory is strictly identical (integrating over impact parameters in our approach). The “exact” trajectory model that we have followed is the one first implemented for calculations of N<sub>2</sub>-N<sub>2</sub> Raman linewidths by Afzelius et al [36] and derived through the resolution of the equation of motion (denoted RB-EM hereafter). In principle this method is equivalent to the standard RB-ET (exact trajectory) method [39-41], see [36].

Our expansions of the PESs have to be transformed in order to be used (Eq. (33) of [11]) in conjunction with the RB method, leading to:

$$U_{L_1, L_2, M}(R) = \frac{1}{(4\pi)^{3/2}} \sum_L (2L+1) \begin{pmatrix} L_1 & L_2 & L \\ M & -M & 0 \end{pmatrix} V_{L_1, L_2, L}(R). \quad (3)$$

It should be noticed that each pair  $(L_1, L_2)$  contributes additionally to the second order S<sub>2,outer</sub> term and comprises various contributions from the PES, for instance the radial terms  $U_{2,2,M}(R)$  comprise the long range quadrupole – quadrupole interaction, a dispersion contribution and a short range interaction contribution (see tables I and II of [31]). Later, we will briefly discuss the effect on the linewidths of the number of radial terms retained (sec. 3.2).

Finally, Ma et al [42] have shown that the manipulation of the cumulant expansion by Robert and Bonamy [11] was not correct due to the non-diagonality of the resolvent operator with respect to the perturber states in the Hilbert spaces. However using their new formulation they did not obtain a better agreement with experimental values (this, by no way signifies that they are wrong, this may reveal other drawbacks in the RB formalism). Buldyreva and coworkers [43] find no differences for linewidths of CH<sub>3</sub>Cl in O<sub>2</sub> using the two forms of the interruption function. It was therefore of interest to check this alternative form of the interruption function for N<sub>2</sub>-N<sub>2</sub>.

## 2.4 Full classical method

Exact classical equations of motion for the collision of two rigid linear molecules were applied to the calculations of collisional linewidths for N<sub>2</sub>-N<sub>2</sub> in [5] following the full classical impact treatment of Gordon [7,8]. This method was recently successfully applied to H<sub>2</sub>-broadening of acetylene [14] and nitrogen [15] lines above room temperature.

In this work, a temperature range between 77 and 2400 K was studied. Seventeen first-order Hamilton equations were used to describe the molecular collisions in an exact and classical way [5]. These equations were referred to a three-dimensional body-fixed coordinates framework. The starting intermolecular distance was chosen large enough (15 Å) to avoid any initial interaction between two N<sub>2</sub> molecules. The spin statistical weights of the perturbing molecules are considered in the usual way, while other collision parameters were set using a Monte-Carlo method. Rotation directions and the initial spatial orientation of the molecules are uniformly sampled, while the relative velocities are sampled according to the Maxwell distribution. In the present N<sub>2</sub>-N<sub>2</sub> study we first applied in our Monte-Carlo calculations the very effective algorithm of impact parameter  $b$  sampling [44] which gives a speed-up of approximately two.

The impact parameter was varied between 0 and 12 Å while the relative velocity was varied between 0.01 and 3 times the most probable relative speed ( $v_p$ ). In most of the cases, the statistical error of the calculated linewidths, associated with RMS error of the Monte-Carlo averaging, was kept lower than 1% (this took 30000-45000 trajectories per each  $j$  and  $T$ ). For a more detailed description of the method, see Refs. [5,45].

In previous studies on many other molecular systems we have checked that it is sufficient to set for the initial intermolecular distance the value  $R_{max} = 15$  Å. However, to remove any possible uncertainty in the present case, we have performed a series of special calculations to verify this point. We have compared linewidths for  $R_{max} = 15$  Å and for  $R_{max} = 20$  Å at 298 K and observed that the results are the same within RMS error. We have also tested different cut-offs  $b_{max}$  for the impact parameter, namely, for 10 Å, 12 Å and 14 Å. No systematic differences were observed between these calculations, and the value of difference was generally less than 3%.

The results presented in the next section were obtained at the mean thermal relative velocity (MTHV)  $\bar{v} = \sqrt{\frac{8k_B T}{\pi\mu}}$  associated with given temperature ( $\mu = 14$  u being the reduced mass of N<sub>2</sub>-N<sub>2</sub> pair and  $k_B$  being the Boltzmann constant), which allows to greatly reduce CPU time. The thermal average was only performed at the lowest temperature investigated (77 K). At this temperature, for both PESs, the values obtained at the mean thermal velocity are very close to those obtained while performing the thermal average. The relative differences increase with  $j$

and reach a maximum value of -8% for  $j=18$ . It was already noticed in [5] that “the error introduced by the MTHV model is only noticeable at low temperatures and high  $j$  values and rapidly fades when the temperature increases”. Therefore at higher  $T$ 's we make use of this approximation.

### 3. Intercomparisons

#### 3.1 Comparison amongst the different theories

First let us confirm [4,32] the good quality of the SAPT PES [28,29]. Close coupling calculations performed for temperatures below room temperature (Fig. 1-2) are in very good agreement with available experimental values [4,46-48]. The fact that these results are in better agreement with the experimental values than the CC/CS values of [4] (Fig. 6 of this Ref.) has been explained in Sect. 2.2. Having checked the quality of the PES used and the accuracy of our benchmark CC calculations we can pursue the comparisons.

With the SAPT PES, the results discussed in this section are obtained using the RB-EM model with 17 radial terms\*\*  $U_{L_1, L_2, M}(R)$  of the potential, i.e. up to  $L_1=L_2=L_{1,2\max} = 4$  (see Eq. (3)), and the correct expression of the interruption function [42]. Results presented with the quantum and full classical methods are obtained with the full expansion (Eq. (1)) of the SAPT PES.

At 77 K and 113 K (Fig. 1) the RB calculations largely overestimate the other sets of values by at least 50%. This is not surprising because the RB semi-classical method is known to be a poor approximation when the temperature (more precisely the mean relative kinetic energy  $4k_B T/\pi$ ) is lower than or comparable to the depth ( $\sim 83 \text{ cm}^{-1}$  or 120 K) of the isotropic part of the potential. More surprising are the quite good results given by both the FC and CS methods as compared with experimental values [4,46] and above all with the CC values. The fact that the CS values are lower than those of the CC calculation was predicted in [4] (Fig. 3 of this Ref.).

At higher temperatures, 194 and 298 K (Fig. 2) around  $j=8$  the RB semi-classical values still overestimate by about 50% while other values are in between  $\pm 10\%$ . Because of the differences at room temperature between the different set of experimental values [4,47,48] (see discussion in [4]) it is difficult to claim that the CS method is better than the FC method or vice-versa and this is of little interest here. We can simply remark that the CS values are in closer agreement with the CC results and that the FC values are systematically somewhat larger.

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\*\* Some are non-independent because  $U_{L_1, L_2, M}(R) = U_{L_2, L_1, M}(R)$ .

At 500 and 730 K (Fig. 3) the reported CS values are in good agreement with the experimental data of Rahn and Palmer [49]. The full classical values are still too large for the lowest  $j$  values but agreement with experiment improves as  $j$  increases. The overall agreement is again better as the temperature increases, a fact expected for a classical approximation (Fig. 4). At 1000 K CS linewidths for the lowest  $j$  values which are accurately calculated are in very good agreement with the experimental HWHM. The fact that the CS predictions are even better as the temperature increases is expected on the basis of this method which is a kind of sudden approximation, whose validity is better for close collisions. At higher temperatures we were not able to calculate the linewidths quantum dynamically even within the CS approximation because we were limited not by CPU time but mostly by size restrictions which will probably not pose a problem in a few years. Fortunately, the full classical method appears to be a good alternative here. Figure 5, compares experimental values [50] with classical values and semi-classical ones at  $T = 2080$  and  $2400$  K. Again the former are in very good agreement with the experimental values. Finally, we observe that the semi-classical RB results are really disappointing at all temperatures, with only slightly improved agreement as the temperature increases.

Before going further we should mention that very similar behavior and/or differences were obtained using the FC and RB methods in conjunction with the PES8. CC/CS calculations were performed on this surface in [4] up to room temperature. As with the SAPT PES, the classical results are close to the CC/CS values while the semi-classical ones are too large by at least 30%.

### 3.2. Some more details

As promised in sect. 2.3 we now compare various approximations within the RB semi-classical approach. Figure 6 displays the values obtained at room temperature using the PES8 [30]. The present calculated values obtained with the parabolic trajectory and potential terms up to  $L_1 = L_2 = L_{1,2\max} = 2$  (including 5  $U_{L_1, L_2, M}(R)$  curves) can be compared with those obtained by Afzelius et al [3] with the same conditions (see Fig. 3 of Ref. [3]). Such calculations were also repeated at higher  $T$ 's to check the excellent agreement with the values obtained by these authors [3]. Since the code we are using here is totally independent of the one used in [3,14,15,36], this validates our new RB code.

We have also calculated pressure broadening coefficients at room temperature (Fig. 6) using the PES8 and the RB -PT and -EM methods, including potential terms up to  $L_{1,2\max}=4$  (17 curves in total). We ascertained that, for both methods, including terms up to  $L_{1,2\max}=2$  or 4 leads to different results, and that including more terms leads to larger PB coefficients. Note that,

using 5 or 17 radial terms, we observe a similar behavior of the HWHM comparing the RB-EM values with the RB-PT values as the one observed in Fig. 1 for N<sub>2</sub>-N<sub>2</sub> and Fig. 2 for CO-CO in [36]. In particular, the calculated values with the exact trajectory are slightly larger for small  $j$  and smaller for high  $j$ 's than the ones computed with the parabolic trajectory. Slight differences due to the use of a different kind of trajectory have also been reported for the N<sub>2</sub>-N<sub>2</sub> system [6,41]. Moreover, similar differences [15] were also obtained while working the C<sub>2</sub>H<sub>2</sub>-H<sub>2</sub> and N<sub>2</sub>-H<sub>2</sub> linewidths. However, such (slight) differences tend to decrease as the temperature increases since the parabolic trajectory is a short time approximation of the exact trajectory (not shown but observed at higher  $T$ s). Nonetheless, using an exact trajectory scheme but with  $L_{1,2\max}=4$  leads to larger differences with the RB-EM method with  $L_{1,2\max}=2$  than between the RB-EM and RB-PT methods used in conjunction with  $L_{1,2\max}=4$ . For the present system, Ma et al [6] studied the convergence of the N<sub>2</sub>-N<sub>2</sub> HWHM with the expansion of the potential (see Fig. 11 of [6]). Therefore we follow the warnings/recommendations formulated by Ma et al [6,16] or Gamache et al [51] while truncating the expansion of potential. It should be noticed that the use of higher potential contributions significantly improves the full potential at short range and thus should primarily improve the calculations of HWHM of high  $j$  values (and at high energies).

Among the various assumptions made in developing the RB formalism, the application of the linked cluster theorem has been recently criticized by Ma et al. [42] who have proposed a new formulation of the cumulant exponentiation. The calculation denoted MTB (Ma-Tipping-Boulet) in Fig. 6 obtained with the correct formulation of the linked cluster theorem, the numerical solution of the equation of motion and 17 radial potential terms is our best calculation using the PES8. As expected from the work of Ma et al [42], for the current weakly interacting N<sub>2</sub>-N<sub>2</sub> system this correction is not large. Finally, on the whole, the various RB schemes used here (Fig. 6) lead to relative differences smaller than about 5% except for the highest  $j$  values.

#### 4. Discussion

Our discussion will focus on the failing of the RB semi-classical method, when starting from a given realistic potential. Remind that, in most applications of the RB formalism where the calculated values did not match the experimental data well, the strategy commonly used for improving the agreement was to tune some parameters rather than to criticize the formalism itself. This failing was already brought to the fore for the C<sub>2</sub>H<sub>2</sub>-H<sub>2</sub> [14] and N<sub>2</sub>-H<sub>2</sub> [15] systems. However, because of the large differences of the rotational constant of these interacting pairs it is difficult to conclude on the inability of the RB method starting with a true potential for these systems. This inability has also been seen for linear molecule - atom systems, even when using

an ab initio PES [9,10,45,52,53]. Possible solutions to this failing may be related to some major assumptions made in developing the formalism, such as (i) to assume the trajectories are only determined by the isotropic part of the potential; (ii) to consider contributions up to only the second order expansion of the linked cluster theorem.

Of course, the assumption that the trajectory is driven only by the isotropic part is not true. The “independence” of the classical path from the rotational motion is a high energy approximation because it assumes that the available kinetic energy is large compared with the gap between successive rotational levels. However, as the temperature (or the kinetic energy) increases, the interactions at shorter distances are more and more involved, and then one can expect that the anisotropic interactions affect more significantly the trajectories. Moreover, at high energies the collisions are more sudden and therefore orientational effects are more important than that at low translational energies where the molecule has more time to rotate during the collision and thus averaging the interactions. In other words there are serious questions about the reliability of semi-classical methods using a single trajectory for a system in which the rotational inelasticity is significant, when compared with thermal energies. From that point of view,  $N_2-N_2$  may appear, a priori, as a favorable case for semi-classical methods. We are not able to directly and quantitatively estimate the effect of ignoring the coupling between translation and rotation in the trajectory description within the RB formalism, but we can roughly estimate its importance in the full classical approach: as in [5] for the  $N_2-N_2$  system and as in [14,15], for  $C_2H_2-H_2$  and  $N_2-H_2$ , we at first consider the effect of performing full classical calculations using trajectories driven solely by the isotropic part of the potential instead than using true trajectories driven by the entire PES.

Figure 7 draws the FC pressure broadening coefficients calculated with trajectories driven by the complete PES and by the isotropic potential only and their ratios at various temperatures. In contrast to the Refs. [14,15] where the calculated values using “isotropic trajectories” were systematically larger than the true ones (as it is the case for the RB values), we have no clear indication in the present situation. It should be noted that the differences were larger for the  $H_2$ -broadening of acetylenes lines than for  $H_2$ -broadening of nitrogen lines simply because the  $C_2H_2-H_2$  potential is more anisotropic than the  $N_2-H_2$  potential. The present  $N_2-N_2$  potential is less anisotropic than the  $N_2-H_2$  one (see Fig. 1 of [28]) because of the symmetry of the colliding partners and this may explain why we observe smaller differences between the two kinds of calculations. Nevertheless, one may object that for  $N_2-N_2$  Ivanov and Buzykin [5] observed large differences between exact and isotropic classical calculations. This “contradiction” is explained very simply: the calculations of the trajectories in [5] were performed using a too approximate fit

of the true isotropic potential by a LJ expression. Such an approximation was deservedly criticized in [6,16]. In summary, classical calculations have confirmed that interaction between translational and rotational motions does not change the translation enough to produce a detectable change in the rotation. This result is a reasonable clue to the weak influence of the isotropic potential approximation for the trajectories, even if we cannot claim that it is a definitive proof since it has been obtained within the framework of the full classical model.

At this stage, it seems likely that the difficulties encountered with the RB formalism may be the use of the linked cluster theorem [54] to express the interruption function  $S(b)$  while limiting the evaluation of the linked clusters to *second order*. The validity of this approximation will be difficult to assess but it is quite clear that the next step towards a full understanding of the mechanism should be to look at the influence of third order terms  $S_3$  (and even of  $S_4$ ) in the expansion of the S matrix. This was also one of the conclusions of Ma et al [16].

As outlined before, in order to obtain “good” pressure broadening coefficients, a common strategy of the RB method standard users is to find an effective isotropic potential or to tune some parameters of the anisotropic part of the potential, like the dipole or quadrupole moments or the polarizabilities of molecules or the parameters of the atom-atom potential [2,5,14,15]. However, the changes of the isotropic part of the potential or of its anisotropic part are, in fact, correlated. Indeed, modifying the isotropic component of the potential changes the trajectories, the anisotropic component  $V_{\text{aniso}}(t)$  via  $t(R)$  is then evaluated along the trajectories and the Fourier components of  $V_{\text{aniso}}(t)$  are felt differently during the collision. This affects the rotational inelasticities.

Afzelius et al [3] in their  $\text{N}_2\text{-N}_2$  pressure broadening study chosen to modify the short range part of the PES to obtain a good agreement with experimental values. More precisely, they have modified the short range anisotropic overlap components [31] of the PES8 [30]. Figure 8 depicts this change on the main anisotropic components of the PES. This unphysical modification appears to be totally unjustified comparing this rescaled PES8 [3] with the original PES8 or the SAPT PES. The short range (anisotropic) forces were roughly divided by 2 as pressure broadening of non-polar molecules is sensitive to such forces. Table 1 shows how this modification changes the partial pressure broadening cross-sections (see Eq. (1) of Ref. [15]), namely, a summation of inelastic rotational state-to-state rotational cross-sections. Comparisons at a more detailed level show that the lowering of the partial pressure broadening cross-sections obtained with the rescaled PES8 arises from the rotational state-to-state cross-sections  $\sigma(j_1 j_2 \rightarrow j'_1 j'_2)$  involving large  $\Delta j_1$  or  $\Delta j_2$  collision-induced transitions. It is just the short range anisotropic part of the potential that mostly induces such transitions. For completeness we have

also repeated the calculations of Afzelius et al at 298 K (see Fig. 4 of [3]) using the rescaled PES8 and the RB method in conjunction with the parabolic trajectory and the interactions up to  $L_{\max}=4$ , i.e.  $L_{1,2\max}=2$  (Eq. (3)). Note that the RB-PT and RB-EM models were compared with the adjusted form of the PES8 in [36] with no significant differences. The PB coefficients obtained (Fig. 6) from the true PES8 [30] are reduced by more than 20% around  $j = 10$  using the rescaled PES8 [3]. Even if the effect of such a modification of a PES is well known and well understood, Figures 6 and 8 and Table 1 show how Afzelius et al [3,36] obtained a reasonable agreement with experimental data. To be fair, these authors themselves cast some doubts on their results. Indeed, they gave [3] “a word of caution”: “Although the RB theory can give excellent agreement with experimental data it is an approximate solution to the semiclassical collision problem, which in itself is not exact. Thus, it is not possible to distinguish if the results are biased by the RB calculation or by the PES employed” and concluded (still paraphrasing [3]) “the CC/CS results of Green and Huo [23] indicate that it is indeed the RB calculation that biased our calculations, hence further accurate CC–CS calculations would be highly valuable in order to test the underlying approximations”. This is what we did in [4] using the scaled (and not the rescaled) PES8 which leads to quite accurate PB coefficients from 77 to 298 K. Finally, it should be noted that our quantum calculations using the rescaled PES8 [3] confirms the conclusions of Ivanov and Buzykin [5] who have already compared pressure broadening coefficients calculated by means of the classical method with the original scaled PES8 [30] and the rescaled one [3] in atom-atom + quadrupole-quadrupole form.

## 5. Conclusion

In this work, we have calculated quantum dynamical, semi-classical and classical self-broadening coefficients of isotropic Raman lines over an extensive range of temperatures (77-2400K) using two accurate N<sub>2</sub>-N<sub>2</sub> PESs. The quantum close coupling method is the most rigorous and accurate and leads to a good agreement with available experimental data below room temperature. This quantum method provides benchmarks for the other methods. However, going to higher temperatures is too time consuming even for the simple N<sub>2</sub>-N<sub>2</sub> system. Therefore, we switched to the coupled states approximation which is known to be generally accurate at high temperature. With this approximate quantum method we even find a quite good agreement at the lowest temperature investigated. Unfortunately, we were only able to conduct such calculations up to 1000 K and for  $j$  values up to 14. The classical method of Gordon [7,8] revived by Ivanov and coworkers seems to be a good alternative to quantum CC/CS schemes at least at high temperatures, considering the results obtained here and in our preceding works

[14,15]. In the present study this robust method appears to be also good below the room temperature. In contrast, the results obtained within the semi-classical framework of Robert – Bonamy [11] are really disappointing. The RB results are much too large even for the highest temperatures, for which this method is expected to be more accurate on the basis of a classical translational motion. Unfortunately, it is exactly the high temperature domain which requires alternatives to quantum methods. This study confirms that any line broadening calculation performed on an accurate potential is not able to provide accurate values using the RB method in its present form. To obtain good agreement with experimental values a “good” potential has to be modified in part or by tuning a few parameters. This may allow experimental values to be completed by interpolating or extrapolating over  $j$  values. In addition, because the temperature dependence of the pressure broadening coefficients provided by the RB method is good (as a number of studies prove and which was checked in our recent studies [14,15] as well as for the  $N_2$ - $N_2$  system [3,36,46,48]) this approach may be pragmatically justified and explains why this computationally cheap method is so popular.

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## Figure captions

Fig. 1: Comparison of CC, CS, RB and FC pressure broadening coefficients, obtained with the SAPT PES, with experimental values at 77 K (a) and 113 K (b).

Fig. 2: Same as Fig. 1 but for 194 K (a) and 298 K (b).

Fig. 3: Comparison of CS, RB and FC pressure broadening coefficients, obtained with the SAPT PES, with experimental values at 500 K (a) and 730 K (b).

Fig. 4: Comparison of calculated pressure broadening coefficients ((a): CS, RB and FC; (b) RB and FC), obtained with the SAPT PES, with experimental values at 1000 K and 1700 K.

Fig. 5: Comparison of RB and FC pressure broadening coefficients, obtained with the SAPT PES, with experimental values at 2080 K (a) and 2400 K (b). Errors bars are three times the standard deviation [50].

Fig. 6: Semi-classical PB coefficients at 298 K obtained with the PES8 and using the standard RB model with parabolic (PT: lines) or exact (EM: triangles) trajectories, or the correct expression of PB coefficients as given by Ma et al [42] (denoted MTB: squares). The maximum  $L_{1,2}$  value entering in the development of the PES is also indicated. For future use in Section 4 another calculation (red diamonds) is also plotted.  $j$  stands for  $j_1$ .

Fig. 7: Classical PB coefficients at various  $T$ s calculated with the true trajectories guided by the full SAPT PES (symbols) or with trajectories simply driven by its isotropic part (dashed lines). Bottom: relative differences in percent.

Fig. 8: Comparison of the 4 main anisotropic radial terms (Eq. (3)) of the SAPT PES [28], scaled PES8 [28] and rescaled PES8 [3] (labeled PES8r). The isotropic components are not shown because they are identical for the scaled PES8 and rescaled PES8 and close to the SAPT isotropic part, see Fig. 2 of [4].)















