Ab initio line-shape parameters for speed-dependent hard-collision profiles: applications to rovibrational lines of H$_2$, D$_2$, HD in He or H$_2$

Franck Thibault$^1$ and Piotr Wcisło$^2$

$^1$Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France
$^2$Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

Franck.Thibault@univ-rennes1.fr

Abstract. We review our recent studies on the spectral line shapes of H$_2$, including its isotopologues, self-perturbed or perturbed by helium. Line shape parameters are derived following the generalized Hess method and making use of the close-coupling formalism.

1. Introduction

We review some recent works, we and others, have presented about molecular hydrogen and its isotopologues in helium or hydrogen baths. In particular we are interested in the effect of the collisions with the bath on the shapes of molecular transitions in H$_2$, D$_2$ and HD.

First, we show how line shape parameters may help in the validation of a potential energy surface (PES). We also discuss the influence of the PES on pressure broadening (PB) and pressure shifting (PS) cross sections. In a second step we remind the reader the general theoretical frame of our ab initio calculations: the generalized method (GHM) [1-3]. Within this framework, line shape parameters are deduced from quantum dynamical calculations and generalized spectroscopic collision integrals. We make the link between Hess’ profile [1] and the so-called Hartmann-Tran profile (HTP) which is recommended by the IUPAC [4] and adopted by the HITRAN database. These parameters may also be used in conjunction with the speed-dependent billiard-ball model of Ciurylo and collaborators [5]. Three recent applications making use of our generalized Hess parameters (GHPs) are reviewed.

It is well known that the Dicke narrowing of a spectral line is related to the frequency of the velocity changing (VC) collisions. This narrowing parameter is often deduced from the mass diffusion coefficient. We will discuss the differences that exist between this approximate value and the one deduced from the generalized Hess method (GHM) [2,3].

2. Interests of ab initio calculations

A line shape is a manifestation of the interaction of an optically active molecule with the surrounding perturbers constituting the bath. Hence to describe a line shape one needs a PES. Performing dynamical calculations on that PES provides line-shape parameters that can be compared to experimental values. Thus this is a test of the PES, but the results may depend on the theoretical method. Having accurate experimental line-shape parameters, coming from the literature for instance, one may compare different
theoretical calculations in order to compare these methods [6] which can be fully quantum dynamical, semi-classical or fully classical. The close-coupling formalism is essentially exact but its application is very time consuming as compared for instance with the coupled-states method or semi-classical methods. Thus such intercomparisons can be useful to see when a given formalism may be applied. This may depend on the studied system and for a given system on the temperature. In addition, theoretical calculations of the PB and PS coefficients may be used to help in the construction of semi-empirical surfaces [7]. However, depending on the rovibrational quantum numbers \( v, j \), and on the temperature, the PB and PS coefficients may be more or less sensitive to a given part of a PES or to the relative importance of the isotropic and anisotropic components.

Theoretical calculations can fill the gaps between different experimental sets of data or complete them. Databases need a large number of line shape-parameters useful to model spectra of planetary atmospheres at various temperatures and pressures. This is a role of ab initio calculations. Applications devoted to the HITRAN database are discussed here and further in section 4.3.

Finally, ab initio calculations can make the link between the narrowing parameter poorly deduced from a mass diffusion coefficient and the true one. This last point is postponed to section 4.4.

2.1 Test of \( \text{H}_2\text{-He PESs} \)

A couple of years ago we have tested four PESs in their capability to produce accurate observed linewidths and lineshifts [8]. Namely we have intercompared the Schaefer and Köhler (SK) [9], the modified Muchnik and Russek (mMR) [10,11], the Boothroyd et al. (BMP) [11] and the Bakr et al. (BSP) [12] PESs. The close coupling method was used to calculate PB and PS coefficients. The calculations of these coefficients for the isotropic Raman \( Q(1) \) line of the fundamental band of \( \text{D}_2 \) in helium readily lead us to reject the mMR and BMP PESs. The calculations of such parameters for the purely rotational Stokes \( S_0(1) \) line of \( \text{H}_2 \) in He neither help us to differentiate between the two last PESs tested. We have thus extended these calculations to the isotropic Raman \( Q(1) \) line of the 1-0 band of \( \text{H}_2 \) in He. Inspection of the PS coefficients, given in table 1, clearly shows that the BSP PES provides results in better agreement with the experimental values.

| Table 1. Calculated PS coefficients and experimental values (in \( 10^{-3} \text{ cm}^{-1} \text{ amagat}^{-1} \)) for the isotropic Raman \( Q(1) \) line of \( \text{H}_2 \) in He for selected temperatures. |
|---|---|---|---|
| \( T / K \) | SK | BSP | Exp.[13] |
| 296 | 11.66 | 10.33 | 9.66 |
| 795 | 22.88 | 20.77 | 18.59 |

In addition, the calculated half widths at half maximum (HWHM) obtained with the speed-dependent billiard-ball profile (SDBBP) of Ciurylo et al [5] also leads to the same conclusion, see table 2. Note that the calculated PB coefficients using the SK and BSP PESs are increased by the same amount when taking into account the inhomogeneous broadening essentially due to the speed dependence of the shift.

| Table 2. PB coefficients and HWHM (in \( 10^{-3} \text{ cm}^{-1} \text{ amagat}^{-1} \)) for the isotropic Raman \( Q(1) \) line of \( \text{H}_2 \) in He for selected temperatures. |
|---|---|---|---|
| \( T / K \) | PBC | HWHM |
| | SK | BSP | BSP\(^a\) | Exp.[13] |
| 296 | 1.39 | 1.14 | 1.81 | 1.76 |
| 795 | 4.50 | 3.98 | 5.00 | 5.26 |

\(^a\) Taking into account the inhomogeneous broadening.
The better agreement obtained with the BSP PES is certainly related with a better description of the H\textsubscript{2} intramolecular motion dependence of this PES.

2.2 Analysis of the different contributions coming from a PES to the PB and PS coefficients

In order to separate the isotropic component of a PES from its anisotropic ones and to perform dynamical calculations it is useful to expand a diatom-atom PES over Legendre polynomials:

\[ V(r_{\text{int}}, R, \theta) = \sum_{\lambda} V_{\lambda}(r_{\text{int}}, R) P_{\lambda}(\cos \theta), \]

where \( r_{\text{int}} \) describes the intramolecular motion, \( R \) is the distance between the center of masses and \( \theta \) is the angle formed by \( r_{\text{int}} \) and \( R \). For a homonuclear molecule like H\textsubscript{2} only even values of \( \lambda \) are involved.

In the coupled equations a number of radial coupling terms are thus involved:

\[ V_{\lambda, v, v', j}(R) = \int_0^\infty \chi_{v, j}(r_{\text{int}}) V(r_{\text{int}}, R) \chi_{v', j}(r_{\text{int}}) dr_{\text{int}}, \]

in which \( \chi_{v, j}(r_{\text{int}}) \) are rovibrational wavefunctions of the monomer. In practice, we are interested in an optical rovibrational line \( v_j \rightarrow v'_j \), thus \( v \) and \( v' \) stand both for \( v_i \) and/or \( v_f \). Therefore, we are interested in collisional coupling inside a given vibrational state, \( v_i \) or \( v_f \), or between \( v_i \) and \( v_f \). In fact, because vibrational relaxation (or excitation) is in general much smaller than rotational collisional transfers ([8] and references therein) non-diagonal in \( v \) radial coupling terms can be neglected. One may also disregard the centrifugal effects: in other words it is possible to replace in equation (2) \( \chi_{v, j}(r_{\text{int}}) \) by \( \chi_{v, 0}(r_{\text{int}}) \)? The answer is yes when one considers optical rovibrational transitions because this effect is masked by the vibrational dependence of the potential, but the answer is no when one considers purely rotational transitions (at least for hydrides) [8].

The anisotropic components of a PES are also responsible for inelastic collisions and it is well known that a PB cross section can be written as a sum of an inelastic contribution and a purely dephasing one due to elastic collisions:

\[ \text{Re} \left( \sigma^{(q)}(E_{\text{kin}}) \right) = \sigma_{\text{inelastic}} + \text{Re} \left( \sigma^{(q)}_{\text{dephasing}}(E_{\text{kin}}) \right), \]

where \( q \) stands for the order of the matter-radiation interaction and \( E_{\text{kin}} \) is the relative center of mass kinetic energy. Figure 1 provides such an example of these two contributions.

At low kinetic energy, where the rotational level \( j = 3 \) is not accessible, the total cross section is the purely dephasing one. In fact, this contribution comes essentially from a vibrational dephasing as seen from a calculation performed keeping only the isotropic component of the PES in \( v = 0 \) and in \( v = 1 \). This can also be shown by looking at the kinetic energy dependence of the PS cross sections (see Fig.11 of Ref. [8]).
2.3 Calculations to provide a large set of data

A priori, ab initio calculations can be performed for any kind of optical transition at any temperature. This is not possible for a given experiment. Indeed, experiments are generally performed at a given temperature or for a limited range of temperatures and for a given spectral region ranging from one line to a more or less wide spectral band. Thus theoretical calculations are complementary to experimental studies. Moreover, in a fitting or multispectrum analysis calculated line-shape parameters may be used as initial values in the process. However, to be able to provide line-shape parameters for a number of rovibrational transitions at any temperature one needs a robust PES. Again a good example is H₂ in He for which the quantum dynamical calculations are not too time consuming. For this system, we have improved and extended the BSP PES [12] in order to study overtones [14]. In the later reference the line-shape parameters for Q lines from \( v = 0 \) up to \( v = 5 \) and \( j = 0 \) up to \( j = 5 \) are provided. Recently, we have extended this study to O and S lines [15]. All these parameters will be adapted, along with their speed and temperature dependences, in the HITRAN database [16].

3. Theoretical frame

By approximating the collision operator by two relaxation frequencies, \( \tilde{\omega}_A \) and \( \tilde{\omega}_R \), a long time ago Hess [1] solved a semi-classical kinetic equation which takes into account the internal motion and the drift term due to the translational motion, treated classically, leading to the Dicke narrowing. The solution of this Boltzmann-like kinetic equations leads to Hess profile:

\[
I_{\text{Hess}}(\Delta \omega) = \frac{1}{\pi} \text{Re} \left( \int \frac{W(\tilde{\omega})d\tilde{\omega}}{\tilde{\omega}_C + \tilde{\omega}_A - i \left( \Delta \omega - \tilde{\omega}_C \right)} \right),
\]

where \( W(\tilde{\omega}) \) is the Maxwell-Boltzmann velocity distribution of the active molecule and \( \Delta \omega \equiv \omega - \omega_0 \), with \( \omega_0 \) being the angular frequency of the transition. The complex PB, PS coefficient is denoted \( \tilde{\omega}_A = \Gamma + i \Delta = n_b \tilde{\omega}_0^0(q) \). The (complex) frequency (in rad/s) of the velocity changing collisions is given by \( \tilde{\omega}_C = (\tilde{\omega}_R - \tilde{\omega}_A) \). The key quantity, \( \tilde{\omega}_R \), was given by the generalized Hess method (GHM) by Monchick and Hunter [3]. It takes into account the correlation between the translational and internal motions and is expressed in terms of two, mass weighted, collision integrals:

\[
\tilde{\omega}_R = n_b \frac{m_a}{m_a + m_b} \tilde{\omega}_0^0(q) + \frac{2}{3} n_b \frac{m_b}{m_a + m_b} \tilde{\omega}_1^0(q).
\]

These collision integrals read:

\[
\tilde{\omega}_L^{s,s'}(q) = \langle v_s ' \rangle \int dx x^{s-s'+2/2} e^{-x} \frac{1}{\sigma_f^* \left( E_{\text{kin}} = x k_B T \right)}
\]

and are obtained from the generalized spectroscopic cross sections \( \sigma_f^* \), the close coupling expressions of which are given in [2,3]. It should be noticed that for \( \lambda = 0 \), the expression of \( \sigma_f^* \) is completely identical with the “standard” close-coupling expression of the PB and PS cross sections derived from Fano’s relaxation operator. The cross section for \( \lambda = 1 \) has no classical equivalent. We will discuss below the difference between \( \tilde{\omega}_C \) and the (real) frequency of the VC collisions derived from a mass diffusion coefficient.

In the following we call \( \tilde{\omega}_A \) and \( \tilde{\omega}_C \) the generalized Hess parameters (GHPs). Note that these parameters contribute both to the broadening and the shifting of a line because they are complex valued (see equation (4)).
4. Applications
In the following subsections we present a few applications already performed or in course.

4.1 Accurate deuterium spectroscopy

The aim of that study was to provide both an experimental and theoretical line position of the S(2) quadrupole line of the 2-0 band of D₂ [17]. Experimental spectra of D₂ were recorded, at 294.9 K, with a frequency stabilized cavity ring-down spectrometer coupled with an optical frequency comb referenced to a primary time standard. Speed dependent PB and PS coefficients (and obviously the corresponding thermally averaged values) were calculated for the same temperature. Non Voigt effects were clearly seen on the recorded profiles at various pressures above about 247 Torr (see Fig.4 of reference 17). The SDBBP [5] leads to the best agreement with the experimental profiles, thus allowing an accurate determination of the transition energy of that line. The resulting value is in very good agreement with recent measurements performed in Grenoble [18] in the Doppler regime, as can be seen in Fig. 6 of Ref. [17]. These experimental values agree with the state of the art theoretical value, which takes into account QED and relativistic corrections, at the 3 sigma level (cf Table 3 of Ref. [17]). Comparison between theory and experiment at this level of accuracy allows a new physics beyond the standard model (such as long-range hadronic interaction or additional dimensions) to be searched [21]. Nevertheless, we will be able to improve our experimental analysis since a new ab initio PES will be soon available and instead of fitting the frequency of the VC collisions as this was done in conjunction with the SDBBP we will also provide the speed dependence of the real and imaginary parts of $\tilde{\omega}_{VC}$ (a new code has been written for diatomic – diatomic GHPs).

4.2 Pure rotational Stokes lines of D₂ in Helium

The present authors have contributed to an analysis of the very first rotational anisotropic Raman lines, S₀(j = 0-2), of D₂ in helium baths at 77, 195 and 300 K [19]. As for H₂ in He, the speed dependence of the collisional widths and shifts is very strong. Thus for instance, as can be seen in figure 2, if one models the S₀(0) line taking only into account this speed dependence using a weighted sum of Lorentzian a strong asymmetric line shape is obtained. Now considering in addition the effects of the VC collisions (figure 2) the profile is symmetrized. The final line shape is a Lorentzian with a HWHM close to $\gamma P = Re(\tilde{\omega}_{s})$ at high pressure. Thus if one adjusts such an experimental line we could conclude that there is no speed dependence neither nor Dicke effect! In conclusion ab initio calculations again help to understand the formation of a line shape. Furthermore, that study [19] allows an accurate determination of the line positions of these Stokes lines. The results are in good agreement with previous experimental results and theoretical calculations [20].

![Figure 2](attachment://Figure_2.png)

Figure 2. Simulations of the D₂ S₀(0) line at $T = 77$ K and $p = 1$ atm. The black solid line is the weighted sum of Lorentzians. The dashed blue line is the speed-dependent hard-collision profile. The red solid line (covered by the dashed blue line) is the simple Lorentz profile obtained with the thermally averaged values of the collisional shift and widths.
4.3 Generalized Hess Parameters for the HITRAN database

One of the main goals of (our) ab initio studies is to provide line-shape parameters for the HITRAN database. The later database had retained the Hartmann-Tran profile [4]. Disregarding the speed dependence the HTP can be written as:

\[
I_{HTP}(\Delta \omega) = \frac{1}{\pi} \text{Re} \left\{ \int \frac{W(\tilde{\nu})d\tilde{\nu}}{1 - (\nu_{VC} - \eta \tilde{\nu})} \frac{W(\nu_{VC} + (1 - \eta) \tilde{\nu} - i (\Delta \omega - \tilde{k} \cdot \tilde{v} \nu_{VC})}{W(\nu_{VC} + (1 - \eta) \tilde{\nu} - i (\Delta \omega - \tilde{k} \cdot \tilde{v} \nu_{VC})} \right\}.
\]

(7)

Comparing this profile with Hess’ profile, given by equation (4), our GHPs can be readily used in the HTP making the substitutions: \( \tilde{\nu} \rightarrow \tilde{\nu}_t \), \( \nu_{VC} \rightarrow \tilde{\nu}_{VC} \) and setting the empirical correlation parameter \( \eta \) to zero.

Since we are calculating kinetic energy dependent cross sections we are also able to provide the speed dependence of the GHPs. The method for calculating the speed dependence of the frequency of the VC collisions is presented in the supplementary material of [19] since it differs from the method used for the width and the shift.

In a near future, we will present an article devoted to the adaption in a suitable form for the full HTP parameters for O, Q and S lines of H\(_2\) in He for rovibrational transitions from \( \nu = 0 \) up to 9 and \( j = 0 \) to 5 [16].

4.4 Differences between \( \nu_{\text{diff}} \) and \( \tilde{\nu}_{VC} \)

As an initial value in a line fitting procedure with a hard or soft collision profile, the frequency of the velocity-changing collisions derived from a diffusional motion model, \( \nu_{\text{diff}} \), is often used. Either this frequency is fixed or it is adjusted. \( \nu_{\text{diff}} \) is inversely proportional to the mass diffusion coefficient \( D_{ab} \),

\[
\nu_{\text{diff}} = \frac{k_B T}{m_o D_{ab}}.
\]

The big difference between the later frequency and the real part of the GHP \( \tilde{\nu}_{VC} \) is that this last frequency describes the transport of the optical excitation. It can be shown, that only for structureless particles, thus driven by one and only one central potential, that the real part of the cross section \( \text{Re}(\sigma_{\text{diff}}^{\nu_{\text{diff}}}) \) reduces to a momentum-transfer cross sections (see also the discussions in the appendices A and B of [14]). A number of experimental articles have shown that the optical frequency of the VC collisions is different to \( \nu_{\text{diff}} \) and that it depends on the rovibrational transition. This dependence appears naturally in the GHM.

In references [14,19] we have compared \( \nu_{\text{diff}} \) and \( \text{Re}(\tilde{\nu}_{VC}) \) for H\(_2\) and D\(_2\) in He, respectively, and have shown that they are quite close because the H\(_2\)-He interaction is mostly isotropic and because at room \( T \) or lower the role of the inelastic collisions is small. Figure 3 shows the same comparison for HD in He. As compared to H\(_2\) or D\(_2\) in He, the differences between the classical values and the GHPs at different temperatures are larger. This is due to the fact that the interacting potentials are the same for the 3 considered cases but for HD in He due to the lack of symmetry odd \( \lambda \) values are also involved (see equation 1). Finally, we observe that the (quantum) frequency of the VC collisions is slightly different for the two lines considered.
Figure 3. Comparison of the frequency of the VC collisions obtained with the GHP $Re(\omega_{VC})$ with the diffusional frequency $\nu_{diff}$ at various temperatures. The GHM allows the distinction of these frequencies for the purely rotational $R(0)$ and $S_0(2)$ lines.

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