Comparison of quantum, semiclassical and classical methods in hydrogen broadening of nitrogen lines

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ABSTRACT

We use an accurate N_2–H_2 *ab initio* potential energy surface (PES) in order to inter-compare various methods commonly employed to calculate pressure broadening coefficients. Close-coupling (CC) calculations of the collisional linewidths of the isotropic Raman lines of N_2 perturbed by H_2 are performed for temperatures between 77 and 2000 K. The CC results compare well with available experimental values. Three less exact methods of calculation are also used: the full classical (FC) model of Gordon, the semiclassical (SC) formalism of Robert and Bonamy and the quantum dynamical coupled states (CS) method. The CS method provides good agreement with CC calculations for all studied temperatures, FC calculations can be considered as accurate above room temperature while the SC method gives overestimated values by about 20–30% in all cases. The temperature dependences of pressure broadening coefficients provided by each method are very similar at elevated (above room) temperatures.

1. Introduction

Molecular nitrogen (N_2) is one of the major components of atmospheric and combustion media. Several studies concerning collisional processes where N_2 is the active molecule have been carried out for both kinds of media [1–5]. For the atmospheric applications, the interest is mainly focused at low temperatures, contrarily to the high temperatures considered in the thermometry studies of combustion media, where N_2 is taken as a probe molecule for the determination of local temperature or concentration [6,7].

Experimental measurements of collisional broadening of the Raman Q-branch of the fundamental band of N_2 perturbed by H_2 were compared with semiclassical calculations in Ref. [4] and with quantum dynamical calculations in Ref. [5]. The analytical interaction potential used in the semiclassical ones corresponds to the addition of an electrostatic term and an atom–atom Lennard–Jones potential that takes into account the interaction at close intermolecular distances. In Ref. [4] the experimental measurements were obtained at 77 and 298 K. For room temperature a good agreement was found between experiments and calculations using a fitted value for the kinetic diameter of an atom–atom potential. Nevertheless, a discrepancy attributed to orbiting collisions, which are not taken into account in the semiclassical model of Robert and Bonamy (RB) [8], was observed at 77 K. On the other hand, close-coupling (CC) and couples states (CS) quantum dynamical calculations were performed on an *ab initio* potential energy surface (PES) [5,9,10]. The resulting pressure broadening coefficients compared well with measured values between 77 and 580 K.

It has been argued that the CC and CS methods are too much time consuming and therefore alternative methods

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should be used [11–13]. As discussed in Ref. [14], for simple molecular systems this could be true 20 years ago, but not in the present days, when the computational facilities have improved considerably since then. Also, for diatom–diatom collisions with ortho- and para-species, as it is the case for the N_2–H_2 system, ortho–para separation allows to speed up the calculations [14–17]. Moreover, when the temperature is larger than about one or two times the maximum well depth of the PES the construction of a grid of pressure broadening cross-sections at various kinetic energies is not useful and the approximation which consists in performing the calculation at the single kinetic energy associated with the mean thermal relative speed is justified, allowing an important economy of CPU time. We will discuss these aspects in Section 2. However, at high temperatures a great number of rotational levels are populated ($j \geq 30$) and so the CC and CS methods require large computation times and the use of alternative methods is appropriate. Therefore this study is also of some interest for thermometry applications based on nitrogen CARS spectra [6,7].

In this work, we present a comparison between full classical (FC), semiclassical (SC)[1] and quantum dynamical (CC and CS) calculations of the collisional broadening of N_2 perturbed by H_2, but now, the same *ab initio* PES is used in all the cases in order to properly compare the different methods of calculation. We have considered the Raman Q-branch lines of N_2 in N_2–H_2 mixtures for a large range of temperatures (77–2000 K) and N_2 rotational quantum numbers ($j=0$–30). This way, we can also determine the appropriate use of each method for each range of temperature. This work is therefore a continuation of our recent study [14] where we have dealt with the C_2H_2–H_2 system and where we concluded that: (1) the quantum CS approximation and the full classical method of Gordon [18,19] implemented by Ivanov [11–13,20,21] lead to similar results above room T; (2) the semiclassical method of Robert and Bonamy [8] is unable to provide accurate results using an *ab initio* PES for this system; (3) the temperature dependence of the PB coefficients is very similar for all methods considered, justifying the use of the RB method with effective potentials. And finally, because the PES of the present N_2–H_2 system is much less anisotropic (at least at short range) than that of C_2H_2–H_2 system, we should obtain a better agreement using the RB method.

In Section 2, very few dynamical details about the used PES are presented. We also discuss the ortho- and para-H_2 contributions to the total PB cross-sections and the utility of the thermal average operation. In Section 3, we compare calculated and experimental values of the collisional broadening coefficients and their temperature dependence as well as the results of the different theoretical methods between them. Section 4 resumes the conclusions of this work.

2. Dynamical calculations

The dynamical calculations were performed on the *ab initio* N_2–H_2 PES which is thoroughly discussed in Refs. [5,9,10]. Since one aim of the present work is to compare the methods of PB coefficient calculations, the four methods used here employed the same development over bispherical harmonics (the multipolar expansion) of the potential (see Eq. (8) of Ref. [5]). Therefore, there is no *ad hoc* expression nor n–m Lennard–Jones fitted form of any component of the PES as this is usually the case with the RB formalism. Since the PES is only four dimensional our calculations are performed within the rigid rotor approximation.

Quantum dynamical calculations were done with the MOLSCAT code [22]. Since very similar calculations were recently reported [5,14–17] we only provide very few details. Due to the fact that what we are primarily calculating are two states-to-two states cross-sections $\sigma(j_A j_B \rightarrow j'_A j'_B)$, where j_A and j_B are the pre-collisional rotational quantum numbers of N_2 (A) and H_2 (B), we have performed two kinds of MOLSCAT runs. One kind for ortho-nitrogen interacting with para-H_2 (pH_2) molecules and one kind for oN_2 interacting with ortho-H_2 (oH_2) molecules. This is due to the fact that the interactions are unable to convert an oH_2 molecule to a pH_2 molecule and conversely. Note that we have only performed such calculations for even nitrogen rotational j quantum numbers (oN_2). With the close-coupling method we have calculated such cross-sections for oN_2–pH_2 over a grid of 127 total energies between 15 and 1600 cm^{-1} and for oN_2–oH_2 over a grid of 115 total energies between 136 and 1500 cm^{-1}. With the coupled-states method, we build a grid of 86 energies between 13 and 3400 cm^{-1} for oN_2–pH_2 collisions and a grid of 82 energies between 133 and 4000 cm^{-1}.

At a detailed level, one can define a kinetic energy dependent partial PB cross-section as

$$\sigma(j_A, j_B; E_{kin}) = \sum_{j'_A \neq j_A, j'_B} \sigma(j_A j_B \rightarrow j'_A j'_B; E_{kin}) \qquad (1)$$

from which a thermally averaged PB cross-sections $\sigma(j_A j_B; T)$ can be obtained assuming a Maxwell–Boltzmann distribution, at a given temperature T, of the kinetic energies E_{kin}. For even rotational perturber states this allows to define a para-(partial) PB cross-section

$$\sigma_{pH_2}(j_A; T) = \sum_{j_B \; even} \rho_{j_B}(T) \sigma(j_A, j_B; T), \qquad (2)$$

and for odd rotational perturber states an ortho- (partial) PB cross-section

$$\sigma_{oH_2}(j_A; T) = \sum_{j_B \; odd} \rho_{j_B}(T) \sigma(j_A j_B; T) \qquad (3)$$

where

$$\sigma(j_A j_B; T) = \frac{1}{(k_B T)^2} \int \sigma(j_A j_B; E_{kin}) E_{kin} \exp(-E_{kin}/k_B T) dE_{kin}. \qquad (4)$$

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[1] Unless otherwise stated SC is equivalent to RB, the Robert–Bonamy semiclassical method; FC is the full classical method of Gordon [18,19] regenerated by Ivanov et al. (so called C3D method of Refs. [11–13,20,21]).