Journal of Quantitative Spectroscopy & Radiative Transfer 112 (2011) 1429–1437

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

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

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ARTICLE INFO

Article history:
Received 10 December 2010
Received in revised form
11 February 2011
Accepted 15 February 2011
Available online 19 February 2011

Keywords:
Collisional broadening
Linewidths
Acetylene
Hydrogen
Classical
Semiclassical and quantum methods

ABSTRACT

Quantum close coupling (CC) calculations of H_2-broadening coefficients of infrared and isotropic Raman lines of acetylene (C_2H_2) are performed for temperatures between 77 and 2000 K. They are used to test three more approximate methods, the quantum coupled states (CS) theory, the semiclassical Robert–Bonamy (RB) formalism and the full classical (FC) model of Gordon. In order to allow a clear and well founded comparison, all the dynamical calculations were performed employing the same *ab initio* potential energy surface free of any adjustable parameters. It is shown that below room temperature both the coupled states method and full classical method fail at reproducing the close coupling pressure broadening coefficients while above room temperature they are correct and predict comparable accurate values for temperatures greater than about 1000 K. The values provided by the RB method are clearly not satisfactory even at the highest temperature examined. However, the temperature dependence of the RB results follows the functional form used for interpolating and extrapolating CC, CS and FC pressure broadening coefficients.

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1. Introduction

Interactions of the acetylene (ethyne) with rare gases have been extensively investigated in recent years [1–3]. An *ab initio* potential energy surface (PES) and a semi-empirical one have also been proposed for the acetylene–dihydrogen system [4,5]. The interests of such systems have been thoroughly discussed and encompass, at least for the C_2H_2–H_2 system, a large variety of chemical-physics fields.

When compared with experimental data, calculations of pressure broadening (PB) coefficients of acetylene lines may allow to test [4,6–9] an existing PES or help in the determination of a semi-empirical PES [2,3,5]. Obviously, to do so, accurate computational methods are required. The most accurate quantum mechanical close coupling (CC) method has been mainly used in these studies. Moreover, when a robust PES is available, i.e. a PES which has been tested on various experimental data, it can be used to compare the methods employed to calculate PB coefficients. This is the main purpose of the present work.

Few studies [10–13] were performed with the objective of comparing, in the same paper, quantum mechanical,

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0022-4073/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jqsrt.2011.02.011

semiclassical (SC) or fully classical (FC) methods for the evaluation of PB coefficients starting with the same potential. For C_2H_2–He a comparative study [14,15] using the semiclassical method of Robert and Bonamy [16] (denoted as RB hereafter) with the full three-dimensional classical method of Gordon [17,18] (denoted also as C3D hereafter) has been performed. Using the same *ab initio* potential as Thibault who performed very accurate quantum dynamical calculations [8] for both infrared and isotropic Raman lines, the authors of Refs. [14,15] obtained only moderately good results with the C3D method and poor results with the RB method. For the C_2H_2–Ar system, quantum dynamical calculations performed on the same potential as in [19] were successfully compared with experimental PB coefficients for isotropic Raman lines [7] and for infrared lines [2] and provide benchmark calculations for other methods. In that case too [19] the C3D method does a much better job than the RB method. Moreover, it has been shown in that study [19] that the use of an isotropic potential to drive the collision, as this is the case in the RB framework, leads to serious problems. Very recently, Ivanov and Buzykin [20] published a comparative study of Ar and He broadening of acetylene lines by using C3D classical method and by three most general and less approximate than RB semiclassical methods (see references therein [20]). The main conclusion of their work is that using simplified trajectories (including "exact" isotropic ones) in conjunction with an accurate *ab initio* interaction PES does not give good pressure broadening coefficients.

It has been argued in Refs. [14,15,19] that close coupling (CC) or coupled states (CS) calculations [21] are too time consuming and that therefore alternative methods should be used. This is not completely true for such systems at low and room temperatures because the well of the respective PESs is not deep and because the reduced mass is not very large. Moreover, for the acetylene molecule one can benefit from the fact that the ortho- and para-species do not interconvert. These arguments of saving time were possibly urgent 30 or 20 years ago but not nowadays due to the improvements of the computational facilities (the increase of the speed and main memory of the machines, the use of clusters, parallelization of numerical codes, etc.). However, at elevated temperatures where high j (≥ 30) rotational levels of C_2H_2 are populated the CC method becomes anyway time consuming and alternative methods are undoubtedly necessary. Nonetheless, one of the aims of the present work is to find when semi- or full classical methods may become sufficiently accurate, specifically for the domains of rotational quantum number j and temperature.

In line with these previous studies, the present paper compares the results of the C3D, RB, CS and CC methods, using the same *ab initio* PES [4], for the case of the H_2 collision induced broadening of acetylene lines. The line broadening calculations are performed for infrared absorption lines and isotropic Raman Q branch for j quantum number between 0 and 30 and a number of temperatures from 77 K up to 2000 K.

The rest of this paper is composed as follows. The dynamical calculations are briefly described in Section 2. In Section 3 we compare thermally averaged pressure broadening coefficients with the coefficients obtained at the mean relative velocity associated with a given temperature. Section 4 contains the results of CC, CS, SC and FC calculations of hydrogen pressure-induced broadening coefficients of isotropic Raman lines between 77 and 2000 K. Additional comparisons for IR lines of acetylene in hydrogen bath are also reported. Discussions are proposed in Section 5. The final Section 6 resumes our conclusions and gives our perspectives.

2. Dynamical calculations

All the dynamical calculations were performed on the same *ab initio* PES of Ref. [4]. The interaction energy $V(R,\theta_A,\theta_B,\phi)$ depends on the intermolecular distance R defined as the distance between the center of mass of each molecule with the z-axis being along R and oriented from the acetylene molecule to the hydrogen molecule and on the Jacobi angular coordinates which describe the relative orientation of the two molecules. This potential is able to reproduce the H_2 broadening of isotropic Raman lines measured at 143 K [4], infrared lines broadened by H_2 and D_2 between 173 and 300 K [6], and also integral cross-sections [5]. It compares well with a semi-empirical PES derived from first chemical principles, fitted on integral cross-sections and adjusted on PB coefficients [5].

The *ab initio* potential has been developed over 23 bispherical harmonics between 2 and 20 Å by step of 0.05 (for technical details see Ref. [4] and references therein) in order to provide a fine grid of radial components $V_{L_AL_BL}(R)$ (see Eqs. (1) and (2) of [4]). For their implementation in the RB code a transformation has been performed to obtain the usual [16,22] radial functions used with this method (Eq. (33) of Ref. [16]):

$$u_{L_A,L_B,M}(R)=\sum_L \sqrt{2L+1}\begin{pmatrix} L_A & L_B & L \\ M & -M & 0 \end{pmatrix} V_{L_A,L_B,L}(R) \tag{1}$$

Therefore, our RB code is based on the numerical approach developed in [22]. The contribution of the first order (S_1) term of the perturbative S [16] scattering operator is omitted because our potential has no vibrational dependence (this will not affect the inter-comparison because all our calculations are performed within a rigid rotor approximation). In addition, we neglect the imaginary contribution of the second order (S_2) term [16]. Gamache and coworkers using their complex RB formalism [23] have shown [23,24] that this omission can lead to serious errors even for the linewidths. However, in our rigid rotor approximation this omission has no effect on Raman Q lines [16,22,23,24]. Moreover, since H_2 pressure induced shifts measured in the ν_5 band [25] and in the $\nu_1+\nu_3$ band [6,26] are very weak, it is also expected that this omission does not affect the calculation of IR linewidths.

Using this RB method, the calculations were performed at the single kinetic energies associated with the mean relative speed at a given temperature T. The traditional parabolic trajectories were used following the method described in the original RB article [16]. For IR lines calculations were performed at T=173, 195 and 295 K and for Q lines at T=143, 295, 450, 600, 800, 1000, 1500

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