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An experimental and theoretical study of nitrogen-broadened acetylene lines

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ABSTRACT

We present experimental nitrogen-broadening coefficients derived from Voigt profiles of isotropic Raman Q-lines measured in the ν_2 band of acetylene (C_2H_2) at 150 K and 298 K, and compare them to theoretical values obtained through calculations that were carried out specifically for this work. Namely, full classical calculations based on Gordon's approach, two kinds of semi-classical calculations based on Robert–Bonamy method as well as full quantum dynamical calculations were performed. All the computations employed exactly the same *ab initio* potential energy surface for the C_2H_2–N_2 system which is, to our knowledge, the most realistic, accurate and up-to-date one. The resulting calculated collisional half-widths are in good agreement with the experimental ones only for the full classical and quantum dynamical methods. In addition, we have performed similar calculations for IR absorption lines and compared the results to bibliographic values. Results obtained with the full classical method are again in good agreement with the available room temperature experimental data. The quantum dynamical close-coupling calculations are too time consuming to provide a complete set of values and therefore have been performed only for the R(0) line of C_2H_2. The broadening coefficient obtained for this line at 173 K and 297 K also compares quite well with the available experimental data. The traditional Robert–Bonamy semi-classical formalism, however, strongly overestimates the values of half-width for both Q- and R-lines. The refined semi-classical Robert–Bonamy method, first proposed for the calculations of pressure broadening coefficients of isotropic Raman lines, is also used for IR lines. By using this improved model that takes into account effects from line coupling, the calculated semi-classical widths are significantly reduced and closer to the measured ones.

1. Introduction

Many experimental infrared studies have been devoted to the nitrogen broadening of acetylene lines of various fundamentals or combination bands [1–9]. Table 1 of the recent studies of Predoi-Cross and collaborators [8,9] gives an exhaustive summary. In the present work, we complete

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Table 1
Pressure broadening coefficients for the R(0) line at room temperature (297 ± 2 K), 173 K and 100 K (as a reference for future use, for instance, for Titan's atmosphere).

	Room *T*	173 K	100 K
Calculated	120.45 (a) 119.75 (b) 121.05 (c) 121.30 (d)	175.75 (a) 177.95 (b) 176.30 (c) 177.95 (d)	259.05 (a) 264.85 (b) 258.50 (c) 264.85 (d)
Experimental	116.60 (e) 119.95 (f) 116.15 (g) 110.00 (h)	161.10 (i) 168.00 (j)	

(a) CC ThAv, (b) CC MThV, (c) CC/CS ThAv, (d) CC/CS MThV, (e) ν_5 band [1] 297 K, (f) $\nu_1+\nu_3$ band [5] 295 K, (g) $\nu_1+\nu_5$ band 297 K [2], (h) $\nu_1+\nu_3$ band [8], (i) $\nu_4+\nu_5$ band [6] 173.2 K, (j) ν_5 band 173.4 K [3].

these studies by performing the very first broadening measurement of isotropic Raman Q-branch lines in the ν_2 band at 150 K and 298 K. The motivation of this and similar works are well known, with the data obtained being of interest to (and finding application in) fields as diverse as the study of planetary atmospheres –including the Earth – combustion processes or pollution control.

Due to the interest of the C_2H_2–N_2 system many theoretical calculations of the nitrogen broadening of acetylene lines have also been performed [1,3,4,8–11]. However, these calculations were almost all conducted with the semi-classical method of Robert and Bonamy [12] using semi-empirical potentials. For instance, in Ref. [8] various isotropic parts of this system were tested in order to get a good agreement with the experimental data. A few calculations were also performed on the basis of the energy corrected sudden approximation, for which no potential energy surface was used and for which the nitrogen molecule was reduced to a pseudo-atom [13,14]. The very first realistic dynamical calculations performed on an *ab initio* potential energy surface (PES) [15] were done in Ref. [9] using the full classical method of Gordon [16,17]. In the present study, starting with the same PES [15], we are extending this effort. We intercompare the full classical method (FC) with semi-classical (SC) methods [12,18–20], quantum dynamical calculations, available experimental results for infrared lines and our results for isotropic Raman lines. In addition, this study completes a series of papers [21–23] devoted to a comparison of the full classical, the close-coupling (CC) and the Robert–Bonamy (RB) methods. In that series it has been shown that the traditional RB formalism is unable to provide accurate pressure broadening coefficients without adjusting some intermolecular parameters. More recently, Ma et al. [20] have shown that by considering effects from the line coupling in the standard [12] RB method, one is able to obtain a much better agreement with experimental values at least for self-perturbed nitrogen isotropic Raman lines. The latter study has been completed by a comparison of the full relaxation matrix as obtained with this refined method with quantum dynamical calculations [24,25]. Meanwhile, this refined version of semi-classical RB model has been adapted to the case of IR lines [26].

The aim of such comparative studies, including full classical ones, is to find well founded alternative methods to the quantum dynamical calculations, in particular to the CC method, which still remain very time consuming even for simple systems like N_2–N_2 or C_2H_2–N_2.

In the following sections we briefly recall a few points about the methods used. Then the experimental set up and reduction of data are given. The results of our calculations are compared with our experimental Raman data and, finally, with bibliographic infrared data.

2. Theoretical methods

Binary collisions and the impact approximation for lines without line mixing [27] are the shared features of the methods summarized below. We disregard any translational effects (velocity or speed dependence) on the lineshape. Since the PES [15] is only four dimensional in the Jacobi coordinates, our calculations are performed within the rigid rotor approximation. We are therefore unable to provide any lineshift coefficients as well as to discuss any vibrational dependence of the collisional linewidths. The latter seems to be quite insensitive to the different kinds of transitions involving different vibrational modes [7] but the situation is not so clear regarding, for instance, Fig. 6 of [6], Fig. 13 of [7], Fig. 5 of [8] and Fig.4 of [9]. However, such experimental differences may arise because of the different lineshape models used. Regardless, our aim is not to provide accurate pressure broadening coefficients but to compare the methods we have used starting with the same PES.

2.1. Potential energy surface used

The calculations have been performed on the four-dimensional *ab initio* PES of Thibault et al. [15]. This PES has been expanded over bispherical harmonics (see Refs. therein [23]):

$$V(R,\theta_1,\theta_2,\Phi)=\sum_{L_1,L_2,L}V_{L_1L_2L}(R)\times A_{L_1L_2L}(\theta_1,\theta_2,\Phi) \qquad (1)$$

where (θ_1, θ_2, Φ) are the three angular Jacobi coordinates which describe the relative orientation of the two monomers. R is the distance between the two monomer centers of mass and defines the intermolecular z axis, $\theta_{\{1,2\}}$ defines the bending angle of the monomer axis relative to the intermolecular axis (the indices “1” and “2” refer to the acetylene and nitrogen molecules respectively) and Φ is the rotational angle around the collisional z axis oriented from “1” to “2”. The values L_1, L_2 and L are even because the colliding pair is formed of centrosymmetric molecules and $|L_1-L_2|\le L\le|L_1+L_2|$. In Eq. (1) 85 terms have been used, up to $(L_1,L_2,L)=(8,8,16)$. The angular functions $A_{L_1L_2L}(\theta_1,\theta_2,\Phi)$ are defined in the case of two linear molecules by a normalized product of spherical harmonics for monomers 1 and 2 as

$$A_{L_1L_2L}(\theta_1,\theta_2,\Phi) = \left(\frac{2L+1}{4\pi}\right)^{1/2}\sum_m \langle L_1mL_2-m|L0\rangle Y_{L_1}^{m}(\theta_1,0)Y_{L_2}^{-m}(\theta_2,\Phi) \qquad (2)$$

where $Y_{L_1}^{m}$ and $Y_{L_2}^{-m}$ are the ordinary spherical harmonics, $\langle ....|..\rangle$ is a Clebsch–Gordan coefficient, and $|m|\le \min(L_1,L_2)$.