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Experimental line broadening and line shift coefficients of the acetylene $\nu_1 + \nu_3$ band pressurized by hydrogen and deuterium and comparison with calculations

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ABSTRACT

Theoretical and experimental values have been determined for the pressure broadening of the $\nu_1 + \nu_3$ band of acetylene by hydrogen and deuterium at 195 K, and experimental values of the pressure shifts have been determined. Theoretical values have been calculated on the basis of a recent potential energy surface using the close coupling scheme. We discuss the detailed contribution of the various rotational angular momenta of the perturbing gas and the *ortho* and *para* contribution to the total pressure broadening cross-sections. We give routes to circumvent the computational cost of such calculations. Experimental values have been measured using a tunable diode laser spectrometer assuming a Voigt line shape. These pressure broadening parameters are compared with measurements performed recently at room temperature and with present measurements performed at 195 K in the $\nu_1 + \nu_3$ band of acetylene. A satisfactory agreement is obtained with the present results and available ones at 295 K.

1. Introduction

An overview of the general interest of the acetylene molecule and of the acetylene–hydrogen system has been recently presented [1]. Here, we will only remind the reader of the main interests in planetology and astrophysical sciences. Acetylene is produced photochemically in environments where methane is present: it is a minor constituent of several planetary atmospheres, including the Earth, the Jovian planets, and Saturn's moon Titan. One of the main objectives of the Cassini–Huygens mission is the study of the composition of Saturn's atmosphere. The Hydrogen Deuterium Absorption Cell (HDAC) is part of the UltraViolet Imaging Spectrograph (UVIS) experiment onboard the Cassini spacecraft, a remote sensing instrument for atomic D/H measurements on Saturn and Titan. The isotopic D/H ratio is still a puzzling question about the evolution of the universe. Since deuterium is a tracer of star and galaxy evolution, the recent discovery made by using NASA's Far Ultraviolet Spectroscopic Explorer (FUSE) could radically alter theories about how stars and galaxies form [2].

Accurate pressure broadening and shift coefficients are required for extracting the partial pressure of acetylene from atmospheric spectroscopic measurements, and increasingly high quality astronomical observations demand correspondingly high quality laboratory measurements. While the environment of these atmospheric observations is typically at low temperatures (100–200 K for the stratospheres of Jupiter and Saturn, for instance [3,4]), most laboratory measurements of pressure broadening and shifts are performed at room temperature. Relatively few measurements of the temperature dependence of pressure broadening of acetylene are available, and even fewer on the temperature dependence of pressure-induced shifts.

A previous paper [5] reported the pressure broadening and shifts of the acetylene $\nu_1 + \nu_3$ band by H_2, D_2, N_2, air, and the rare gases at 295 K. That paper concluded that the pressure broadening cross-sections of acetylene by D_2 are 10–20% larger than the cross-sections for acetylene pressure broadening by H_2 at room temperature, and it pointed out that more data would be required to determine the cause of this difference. Since that time, this study was extended down to 195 K for the rare gases [6], demonstrating that there is satisfactory agreement between experiment and close coupling calculations over a range of temperatures.

The theoretical studies of weakly bound acetylene–rare gas complexes have been reinvestigated during the last few years [7–9] and applications to the calculations of C_2H_2–rare gas pressure broadening were performed on the potential energy surfaces (PES) proposed. Pursuing these studies, one of the present authors was involved in the determination of the first full, four dimensional, ab initio PES

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for the C_2H_2–H_2 system [1]. On this new PES H_2-pressure broadening coefficients of isotropic Raman lines were calculated. Results were found to be encouraging when compared to measurements performed at 143 K.

This paper reports the collisional broadening and shifts for acetylene in baths of H_2 and D_2 at 195 K and compares the experimental pressure broadening (PB) coefficients at 195 and 295 K with quantum dynamical values. The theoretical motivation of the present work is fivefold: (i) continue to test this potential; (ii) show that the difference between collisional width of Raman isotropic lines and infrared lines is the same as when the perturber is an atom; (iii) try to understand the different behavior of H_2, D_2 collisional-induced width of acetylene lines; (iv) compare the *ortho* and *para* (H_2 or D_2) partial contributions to the linewidth; and (v) give routes to avoid time consuming calculations and provide benchmark calculations for more approximate methods. The experimental motivation is to provide additional data on the temperature dependence of the pressure broadening and shift coefficients, to determine whether the difference between the H_2 and D_2 cross-sections persists at low temperature, and to ascertain the origin of this difference.

The next section will be devoted to points (ii)–(v). In Section 3 the experimental set up will be briefly described and the associated results will be given. The comparison of our experimental results and other measurements [10–12] with our theoretical results are presented in Section 4. Concluding remarks and perspectives are summarized in Section 5.

2. Calculations of pressure broadening cross-sections

2.1. Theoretical framework

The collisional broadening cross-sections calculated within the impact approximation are derived [1,13–16] from binary diffusion *S*-matrix elements for two rigid linear rotors obtained from the MOLSCAT [17] quantum dynamical code. These matrix elements are computed with the close-coupling method, as described by the references in Green [15] and in Hutson and Green [17] .

The main difference in the way of performing such calculations for the present work as compared to the study of Raman isotropic *Q* lines [1] is that we have to include in the rotational basis both even and odd j_1 acetylene rotational quantum numbers because we are interested in *R* or *P* infrared lines.[1] This greatly increases the duration of a single MOLSCAT run (about eightfold for H_2 as the perturbing molecule).[2] Therefore, we do not present thermally averaged pressure broadening cross-sections but cross-sections obtained at the single relative kinetic energy, $\overline{E}_{\text{kin}} = \frac{4}{\pi} k_B T$, associated with the mean relative speed, $\bar{v} = \sqrt{\frac{8k_BT}{\pi\mu}}$, for a given temperature *T*; μ is the reduced mass of the colliding pair ($\mu = 1.871$ u for C_2H_2–H_2, $\mu = 3.488$ u for C_2H_2–D_2). As shown in reference [1], this approximation should be reasonable. Note also that the calculations with deuterium are more time consuming than with hydrogen because the rotational constant is roughly divided by two and the associated de Broglie wavelength is shorter ($\sim 1/\sqrt{2}$ for the same initial kinetic energy). However, thanks to the D_2 or H_2 *ortho*/*para* separation and the potential symmetry, calculations can be performed separately for these two species.

One can define a *para* and an *ortho* partial PB cross-section for D_2 as:

$$\sigma_{pD_2}(j_1;T) = \sum_{j_2\ \text{odd}} \rho_{j_2}(T)\sigma(j_1,j_2;\overline{E}_{\text{kin}}) \tag{1a}$$

$$\sigma_{oD_2}(j_1;T) = \sum_{j_2\ \text{even}} \rho_{j_2}(T)\sigma(j_1,j_2;\overline{E}_{\text{kin}}) \tag{1b}$$

and thus a total pressure broadening cross-section:

$$\sigma(j_1;T) = \frac{2}{3}\sigma_{oD_2}(j_1;T) + \frac{1}{3}\sigma_{pD_2}(j_1;T) \tag{2}$$

For H_2 a similar relation holds (see Eq. (5) of reference [1]):

$$\sigma(j_1;T) = \frac{1}{4}\sigma_{pH_2}(j_1;T) + \frac{3}{4}\sigma_{oH_2}(j_1;T) \tag{3}$$

In these equations j_1 stands for the initial rotational quantum number of the C_2H_2 optical transition and j_2 is the initial rotational quantum number for the collision partner; j_2 is even for *p*-H_2 and *o*-D_2, while j_2 is odd for *o*-H_2 and *p*-D_2. The complete close coupling expression of $\sigma(j_1,j_2;\overline{E}_{\text{kin}})$ is given in reference [15]. The ρ's are the H_2 or D_2 (unit) normalized populations. In each case the summation in (1) was limited to $j_2 \leqslant 5$, as this has been done in conjunction for the calculation of the partition functions allowing the determination of the populations. The cross-sections $\sigma(j_1,j_2 = 4 \text{ or } 5;\overline{E}_{\text{kin}})$ have been fixed to $\frac{1}{2}(\sigma(j_1,j_2 = 2;\overline{E}_{\text{kin}}) + \sigma(j_1,j_2 = 3;\overline{E}_{\text{kin}}))$ if the calculation of $\sigma(j_1,j_2 = 3;\overline{E}_{\text{kin}})$ is necessary (at room *T*) or to $\frac{1}{2}(\sigma(j_1,j_2 = 1;\overline{E}_{\text{kin}}) + \sigma(j_1,j_2 = 2;\overline{E}_{\text{kin}}))$ if the calculation of $\sigma(j_1,j_2 = 3;\overline{E}_{\text{kin}})$ is unnecessary; the latter half sum also provides in this case $\sigma(j_1,j_2 = 3;\overline{E}_{\text{kin}})$. The H_2 and D_2 populations and the discussions following this subsection justify these approximations.

2.2. Comparison between cross-sections of isotropic Raman Q lines and IR R lines

Fig. 1 shows calculated pressure broadening cross-sections $\sigma(j_1,j_2;\overline{E}_{\text{kin}})$ at various kinetic energies, associated with T = 143, 195 and 296 K, for the significantly populated rotational states of the H_2 molecule. We observe that the differences between the cross-sections for *Q* lines and *R* lines are large for low j_1 values (except for $j_1 = 0$ where reorientation is not possible) and negligible for higher j_1 values, and that these differences decrease as the energy increases (because the collisions are more inelastic). This is due to the fact that these cross-sections for Raman isotropic *Q* lines are solely provided by 2-states to 2-states ordinary inelastic cross-sections. These detailed contributions, shown in Fig. 1, explain the differences noticed in Figs. 5 and 6 of reference [1], where experimental collisional half widths at half maximum (HWHM) of IR lines are compared to calculated pressure broadening coefficients of isotropic Raman *Q* lines. These behaviors with j_1 and energy are well known when the perturber is an atom [18,19]. Fig. 2 gives another example of such differences when the colliding partner of the acetylene molecule is the deuterium molecule. Finally, note that for both perturbers the $\sigma(j_1,0,\overline{E}_{\text{kin}})$ cross-section is always the smallest and that the other ones are close together.

2.3. Comparison between ortho and para pressure broadening cross-sections

Figs. 3 and 4 reinforce the last comments. The difference observed between $j_2 = 0$ and other j_2 values has been explained in reference [1] for *Q* lines and is still apparent for IR lines. This is obvious because most of the broadening comes from inelastic collisions (see Figs. 1 and 2).

In Fig. 3 and 4 the *ortho* and *para* partial pressure broadening cross-sections are also represented (by "unphysical" lines for clarity instead by symbols) as well as the total cross-sections, as de-

[1] Throughout this paper we use lower case *j* to denote the angular momentum of the isolated molecules to avoid confusion with the total angular momentum *J* of the collision.

[2] For instance, at a kinetic energy of 261 cm^{-1} for the $j_2 = 3$ PB contribution to the *R*(4) line, the duration of a MOLSCAT run is about 3 weeks on an Intel Xeon dual core processor.