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A quantum study of argon induced line mixing in ammonia doublets

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Abstract. We present a theoretical study of pressure broadening and coupling coefficients for selected doublets of the ν_4 band of ammonia in argon bath. Generalized spectroscopic kinetic energy dependent cross sections are determined quantum mechanically making use of available $\text{NH}_3\text{-Ar}$ potential energy surfaces. Thermally averaged values at various temperatures are also provided. Results are in overall good agreement with data available in the literature. A further study focusses on the speed dependence of the corresponding line shape parameters. The pressure broadening coefficients are found to have a well marked speed dependence while the intradoublet coupling terms show a small speed dependence at room temperature.

1. Introduction

The perturbation of the spectra of ammonia in argon baths has led to numerous studies [1–11]. Most of these studies dealt with the pressure broadening and shift coefficients but some also addressed the line mixing effect. To our knowledge the speed dependence of the pressure broadening and shift has received little attention for this system [3, 6, 12] and the speed dependence of the line mixing completely disregarded. Recently, on the basis of the quadratic [13] or hypergeometric [14] models often used to model the speed dependence of the collisional broadening, Boulet et al. [11] have suggested that the speed dependence of intradoublet coupling coefficients could be observed in the ν_4 band of ammonia in argon. In order to check this proposition we have performed dynamical calculations on a potential energy surface (PES) [15].

2. Methodology

As it is well known [1], generalized spectroscopic cross sections are evaluated from S-matrix elements. In order to determine the scattering matrix, we employed the close coupling method (CC) or the coupled states approximation (CSA), together with the semi-empirical PES of Schmuttenmaer et al. [15]. This potential has been shown in previous works to be of good quality [16, 17] Additional calculations were performed with the most recent ab initio PES of Loreau et al. [17]. The results are very similar to the ones obtained with the semi-empirical PES, therefore only the results obtained with the later are presented here. Full dimensional $\text{NH}_3\text{-Ar}$ PES is not available. Therefore, we neglect the influence of the ammonia ν_4 vibration. We



thus use the pure rotational energy levels and their associated wavefunctions in the ground state. The doublet arising from the inversion motion of ammonia are modeled using the delta function model of Davis et al. [18]. These states are constructed according to symmetry considerations including the exchange of the hydrogen atoms [19]. Figure 1 shows the selection rules and position of the studied doublets.

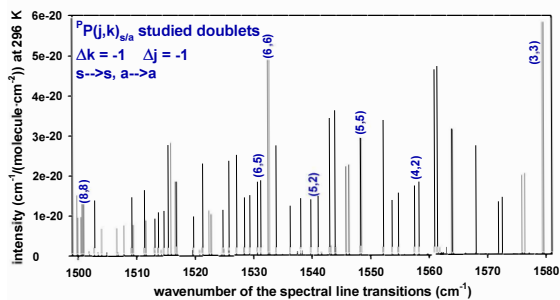


Figure 1. Spectral domain of the ν_4 band including the studied doublets (tick spectrum from HITRAN database [20]). j stands for the rotational quantum number and k is the absolute value of its projection on the C_3 axis.

3. Results and discussions

3.1. Pressure broadening

We first discuss the pressure broadening cross sections and illustrate the discussion with the $^P P(5,5)_s$ line which is a representative line. Figure 2 shows the kinetic energy dependent cross section for this line. The random phase approximation [21, 22] that reduces such a cross section to an average of the inelastic cross sections out of the levels involved in the optical transitions and neglects the contribution of the elastic collisions is very good. In addition we note that the intradoublet inelastic contribution does not amount to the full inelastic contribution and that its contribution decreases as the kinetic energy increases (as expected because more and more states are energetically accessible). The thermal average at 296 K leads for the $^P P(5,5)_{s/a}$ lines

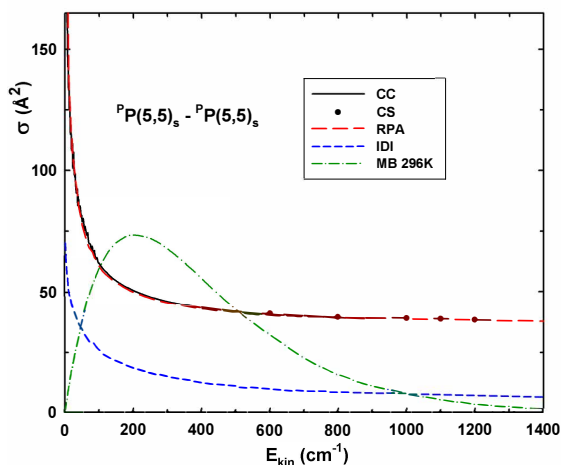


Figure 2. Cross sections for the $^P P(5,5)_s$ line as a function of the kinetic energy. Real part of the diagonal cross section is evaluated with the CC method (black solid line) and with the CSA (black solid disks). The total inelastic contribution (RPA) is presented in red dashed line and the contribution from the intradoublet inelastic (IDI) cross section in blue dashed line. The Maxwell-Boltzmann (MB) kinetic energy distributions at 296 K is displayed in green dash-dotted lines.

to a value of $46.23 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ which is about 5 to 10% smaller than the experimental values [4, 5]. Such a disagreement is also obtained for the other studied lines. We infer that the underestimation observed in the theoretical results is due to the neglect of the rovibrational dephasing.

The pressure broadening (or line coupling) coefficient is given by a Maxwell-Boltzmann average over the relative speed v_r of the product $v_r \sigma$. Figure 3 shows $v_r \sigma$ for the $^P P(5,5)_s$ line as the function of square root of E_{kin} , thus puts into focus the v_r dependence of this product. The

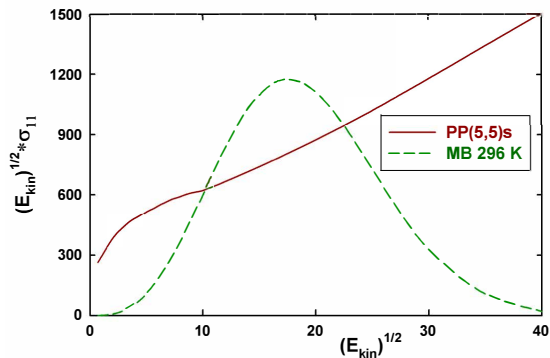


Figure 3. Relative speed dependence of the diagonal relaxation matrix element for the $^P P(5,5)_s$ line. The green dashed line represents the Maxwell-Boltzmann relative speed distribution at 296 K in arbitrary units.

observed dependence is not proportional to v_r^a , where the exponent a is a constant, therefore the hypergeometric function model [14] is not valid. However, at room T and thus considering the portion of the curve over the width of the Maxwell-Boltzmann distribution (see the green dashed curve), a nearly linear dependence is seen. The slope leads to the ammonia speed dependence of the pressure broadening coefficient and a "local" validity of the hypergeometric function in this domain as shown in figure 4. It is also shown in figure 4 that locally the alternative quadratic model [13, 20] works well too. Finally, we note that this speed dependence is important. Very similar results are obtained for the other studied lines.

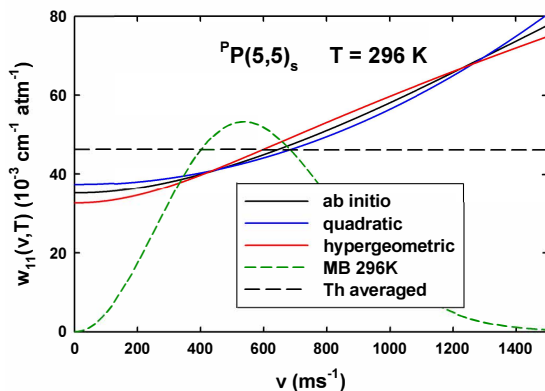


Figure 4. Speed dependence, at 296 K, of the pressure broadening coefficient of the $^P P(5,5)_s$: ab initio results (black line), quadratic model (blue line), hypergeometric model (red line). In addition, the theoretical thermally averaged value is represented by the black dashed line and the speed distribution by the green dashed line.

3.2. Line coupling

As stated in the introduction, there is also an interest in considering the coupling between lines. As is illustrated on figure 5 the intradoublet $^P P(5,5)_s - ^P P(5,5)_a$ cross section is bigger than the coupling of the $^P P(5,5)_s$ transition with other lines. Therefore, at low pressure (at least below 1 atm) to model the line shape it is sufficient to construct a 2×2 W-relaxation matrix, setting $W_{11} = W_{22}$ to the pressure broadening coefficients and $W_{12} = W_{21}$ to the intradoublet line mixing coefficients. Table 1 provides the off diagonal relaxation matrix elements at 296 K for the studied doublets. The comparison with available experimental values is good, in particular for the largest line coupling terms.

Figure 6 displays the relative speed dependence of the products $v_r \sigma_{12}$ for the studied doublets as a function of the root square of the kinetic energy. We see that such products rapidly increase and then vary smoothly. We remind the reader [14] that if they were constant then there would not be ammonia speed dependence. Thus we expect a small absolute speed dependence at room temperature. In fact, this is indeed what we obtain as shown by figure 7. Nevertheless, the speed

dependence of the intradoublet coupling coefficients should be visible at lower temperatures (below ~ 193 K).

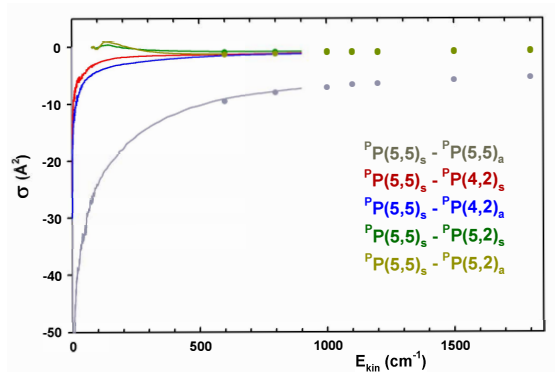


Figure 5. Real part of the coupling cross sections of the $^P P(5,5)_s$ with other studied lines as a function of the kinetic energy. Solid lines: CC values, solid disks: CSA values. Note the threshold, of about 78 cm^{-1} , for the upwards cross sections with the doublet $^P P(5,2)_{s,a}$.

Table 1. Calculated line coupling coefficients, in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ at 296 K, within the inversion doublets and experimental values [5]. $\Delta\sigma$ is the intradoublet line spacing in cm^{-1} .

Line	$\Delta\sigma$	Calc.	Exp.
$^P P(3,3)_{s/a}$	0.275	7.2	4.6
$^P P(4,2)_{s/a}$	0.769	2.6	
$^P P(5,2)_{s/a}$	1.244	1.8	
$^P P(5,5)_{s/a}$	0.245	14.0	14.9
$^P P(6,5)_{s/a}$	0.545	8.9	6.0
$^P P(6,6)_{s/a}$	0.233	17.4	18.0
$^P P(8,8)_{s/a}$	0.210	23.4	24.7

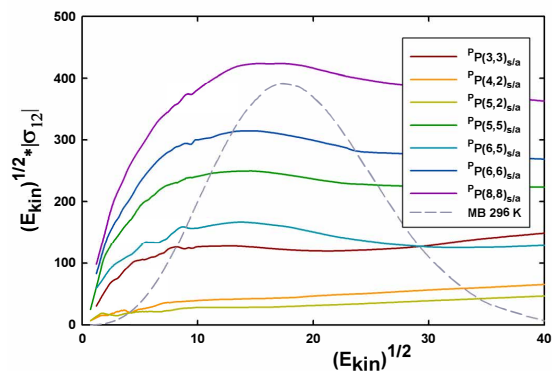


Figure 6. Relative speed dependence of off-diagonal relaxation matrix elements w_{12} for the studied doublets. The grey dashed line represents the Maxwell-Boltzmann relative speed distribution at 296 K in arbitrary units.

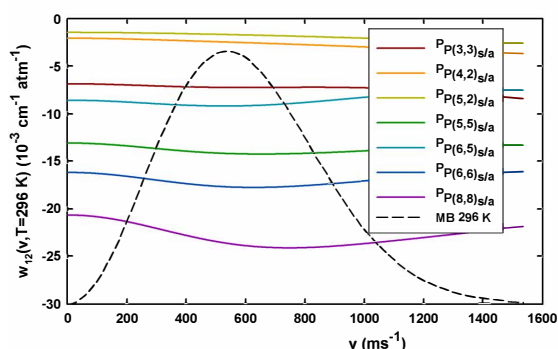


Figure 7. Speed dependence at 296 K of the intradoublets relaxation matrix studied. The Maxwell-Boltzmann ammonia speed distribution in arbitrary units is shifted to the lowest tick mark of the y-axis.

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