

Supplementary Material for :
Simulation of argon induced coupling coefficients of
NH₃ doublets and their speed dependence


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Abstract

In this Supplementary Material we provide additional informations for the
above entitled article.

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1. Table T1

Table 1: Characteristics of the studied lines of the ν_4 band of ammonia. j stand for the rotational quantum number and k for the absolute value of its projection (K) on the molecular axis. ϵ is the symmetry index. s/a specify the inversion motion symmetry. Prime (double prime) denote the final (initial) level quantum numbers. Line positions are from HITRAN2016 [1].

Line	j''	k''	ϵ''	j'	k'	ϵ'	position (cm ⁻¹)
$^P P(8,8)_s$	8	8	-1	7	7	1	1500.7334
$^P P(8,8)_a$	8	8	1	7	7	-1	1500.9439
$^P P(6,5)_s$	6	5	-1	5	4	1	1530.6141
$^P P(6,5)_a$	6	5	1	5	4	-1	1531.1591
$^P P(6,6)_s$	6	6	-1	5	5	1	1532.4503
$^P P(6,6)_a$	6	6	1	5	5	-1	1532.6830
$^P P(5,2)_s$	5	2	1	4	1	-1	1539.7596
$^P P(5,2)_a$	5	2	-1	4	1	1	1541.0041
$^P P(5,5)_s$	5	5	1	4	4	-1	1548.1839
$^P P(5,5)_a$	5	5	-1	4	4	1	1548.4290
$^P P(4,2)_s$	4	2	-1	3	1	1	1557.4800
$^P P(4,2)_a$	4	2	1	3	1	-1	1558.2494
$^P P(3,3)_s$	3	3	1	2	2	-1	1579.3616
$^P P(3,3)_a$	3	3	-1	2	2	1	1579.6363

2. Figure F1

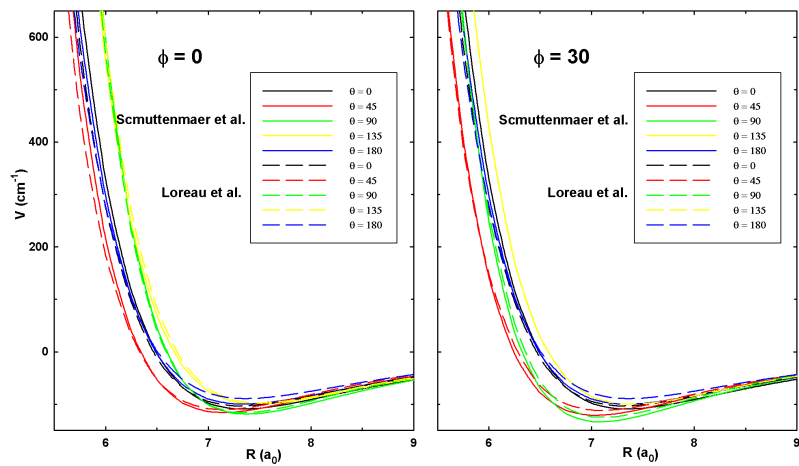


Figure 1: Comparison of the PESs of Schmittenmaer et al. [2] and Loreau et al. [3] along radial cuts for selected angular (θ) orientations. The left panel presents $\phi = 0^\circ$ and the right panel $\phi = 30^\circ$. For the Loreau et al. potential, the umbrella coordinate is fixed to its averaged value in the vibrational ground state.

3. Figure F2

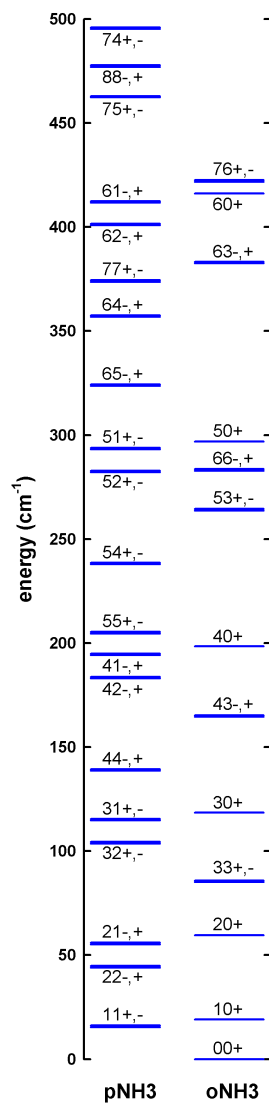


Figure 2: Diagram of ammonia rotational energy levels between 0 and 500 cm⁻¹ labeled as $jk\epsilon$ (+/- stand for $\epsilon=+1,-1$); for a doublet (thick line) the first sign is associated with the lowest state.

4. Figure F3

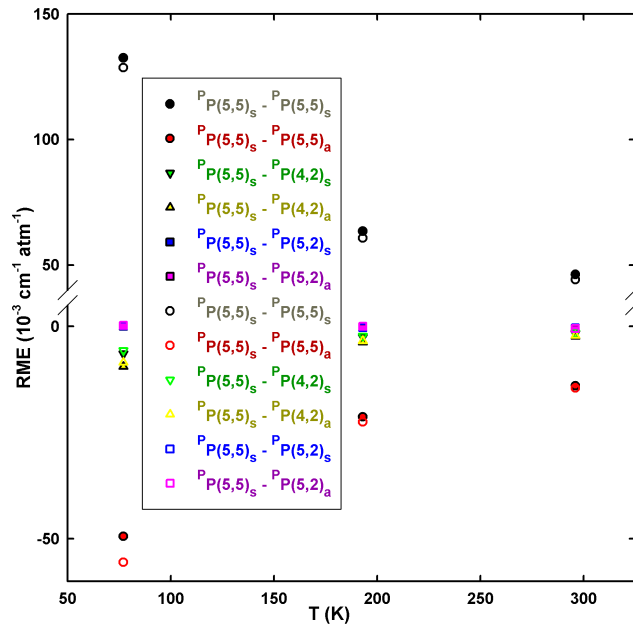


Figure 3: Relaxation matrix elements (RME) at 3 selected temperatures (77, 193 and 296 K) for the initial $^P P(5, 5)_s$ line coupled to other lines. Results obtained with Schmuttermaer *et al.* PES [2] (filled symbols) and Loreau *et al.* PES [3] (empty symbols).

5. Figure F4

We expand the various contributions leading to the total inelastic contribution to the pressure broadening cross sections (Eqs. 6 and 14 of the main article):

$$\begin{aligned}
 \sigma_{11}(v_r) &= \frac{1}{2} \{ \sigma_{out\ i}(v_r) + \sigma_{out\ f}(v_r) \} \\
 &= \frac{1}{2} \{ \sigma'_{out\ i}(v_r) + \sigma'_{out\ f}(v_r) \} + \sigma_{12}^{IDI}(v_r) \\
 &= \frac{1}{2} \{ \sigma'_{down\ i}(v_r) + \sigma'_{upw\ i}(v_r) + \sigma'_{down\ f}(v_r) + \sigma'_{upw\ f}(v_r) \} + \sigma_{12}^{IDI}(v_r) \\
 &= \frac{1}{2} \{ \sigma'_{down}(v_r) + \sigma'_{upw}(v_r) \} + \sigma_{12}^{IDI}(v_r).
 \end{aligned} \tag{1}$$

The indices i and f are the initial and final states of the line $|1\rangle$. The indices 'out i ' ('out f ') designates the sum of the inelastic cross sections out of the state i (f). They can be splitted into 2 parts: downwards and upwards ones. Primes exclude the inelastic cross sections to the line $|2\rangle$ with initial and final states i' and f' (the companion line constituting the doublet). The intradoublet inelastic (IDI) cross section (Eq. 8 of the main article) is recalled here:

$$\sigma^{IDI}(2; 1; E_{kin}) = \frac{1}{2} (\sigma(i' \leftarrow i; E_{kin}) + \sigma(f' \leftarrow f; E_{kin})). \tag{2}$$

In the main article (Fig. 7) we have summed the upwards and downwards contributions separately and drawn the full IDI contribution too. Figure 4 shows the various contributions for the ${}^P P(5, 5)_s$ line.

We remark that the change of variation with the kinetic energy of the intradoublet cross section occurs in the region where the upwards contributions start to contribute significantly (in the present case between 45 and 100 cm^{-1}).

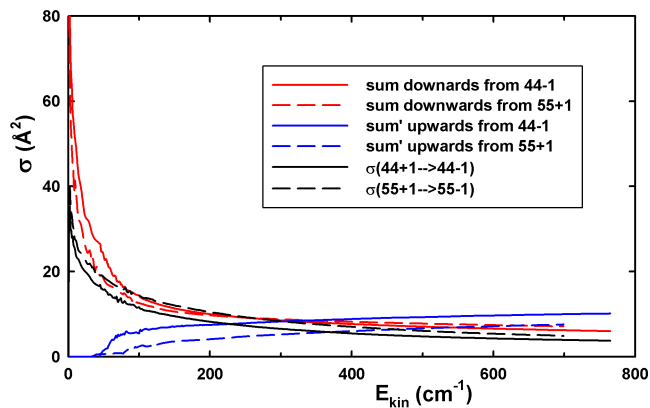


Figure 4: Illustration of Eq. (1) in the case of the $^P P(5, 5)_s$ line.

References

- [1] I. Gordon, L. Rothman, C. Hill, R. Kochanov, Y. Tan, P. Bernath, et al., The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf* 203 (2017) 3–69.
- [2] C. A. Schmuttenmaer, R. C. Cohen, R. J. Saykally, Spectroscopic determination of the intermolecular potential energy surface for Ar–NH₃, *The Journal of Chemical Physics* 101 (1994) 146–173.
- [3] J. Loreau, J. Liévin, Y. Scribano, A. van der Avoird, Potential energy surface and bound states of the NH₃–Ar and ND₃–Ar complexes, *The Journal of Chemical Physics* 141 (2014) 224303.