

## COLLISIONAL EXCITATION OF NH<sub>3</sub> BY HE AND H<sub>2</sub> : TOWARDS A NEW INTERPRETATION OF THE INVERSION EFFECT

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**Abstract.** New calculations, including the ammonia inversion degree of freedom as an average on the potential energy surface, are reported as an attempt to overcome the longstanding gap between theoretical and experimental results about rotational excitation of NH<sub>3</sub> by He and H<sub>2</sub> collisions in interstellar medium conditions.

### 1 Introduction

From its first detection in the interstellar medium, in 1968, as the first polyatomic molecule, ammonia has been the object of many studies through both theoretical (e.g. Green 1980) and experimental (e.g. Oka 1973) means. In fact, its large abundance there (also in a rich variety of isotopical forms), its inversion-splitting occurrence in the range of 1 cm<sup>-1</sup> and its typical collision-dominated population of levels, have made it a very good probe of various temperatures and gas densities. Collisions with hydrogen molecules are of particular interest since H<sub>2</sub> is the most abundant colliding partner in the dense interstellar medium. However, for simplicity, most of the studies were carried on NH<sub>3</sub> interacting with atomic helium, because the excitation effect of this atom, in the temperature range of interest, was assumed very similar to the para-H<sub>2</sub> one (Paper I). Furthermore, the inversion motion of the ammonia in the collision was never taken explicitly in account, except in a study involving Argon as the colliding partner (Van der Sanden et al. 1992), where only small effects were observed. After more than 30 years however a persistent disagreement (both for He and H<sub>2</sub> collisions) between the theoretical works and some double resonance experiments (Paper II) is still object of debate while a full dimensional study has never been performed. This work is intended then to provide collisional data, for NH<sub>3</sub>-He, with a better approximation in the treatment of the inversion with respect to the previous ones, in order to underline its role in the description of the collisional event and to have a new comparison with the reported experimental data.

### 2 Method

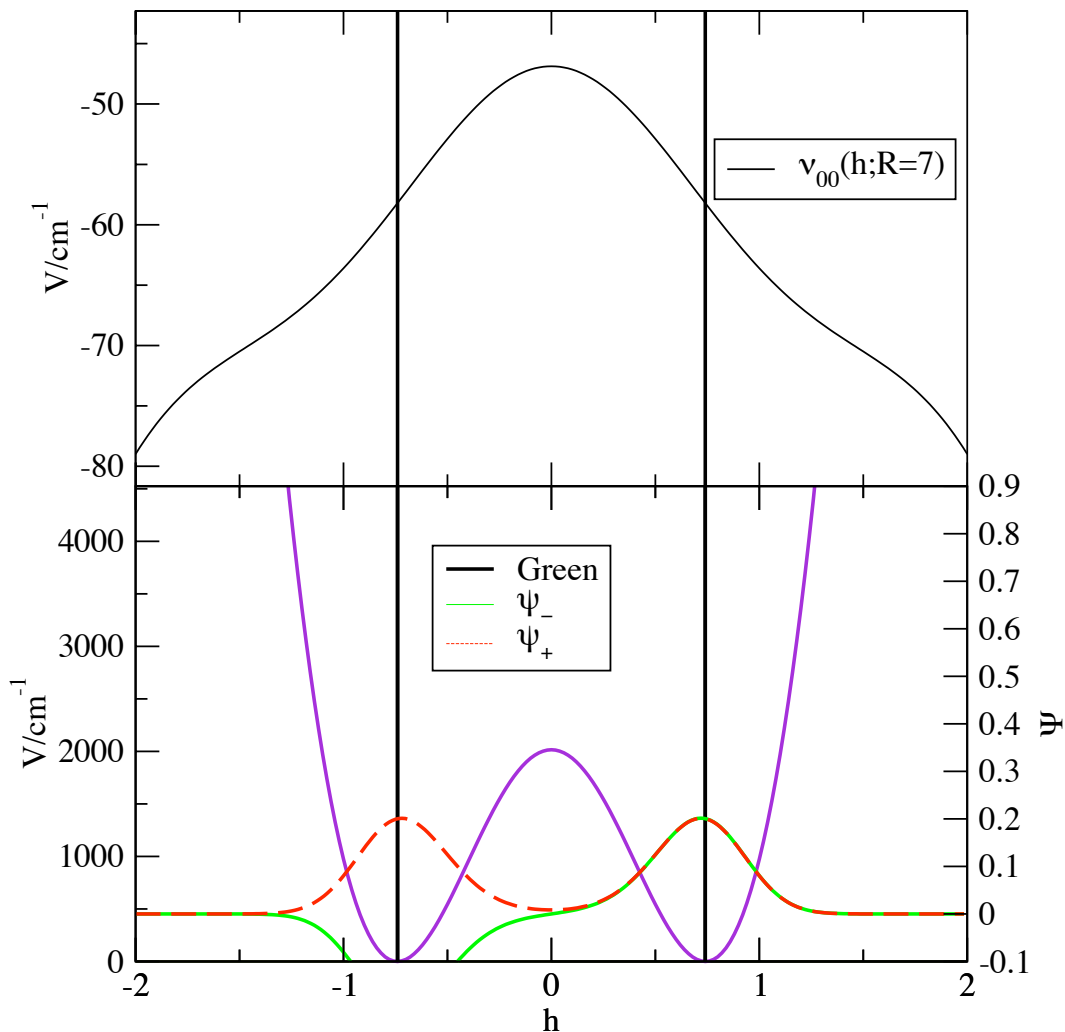
In the present work we take profit from a recent, accurate Potential Energy Surface (Hodges & Wheatley 2001) for the intermolecular interaction NH<sub>3</sub>-He, including the inversion motion in the collision by averaging the expansion coefficients of the potential on the first tunnelling doublet NH<sub>3</sub> wavefunctions, as described in Van der Sanden (1992):

$$V_{int}(R, \theta, \phi; h) = \sum_{l,m} \nu_{lm}(R; h) Y_{lm}(\theta, \phi) \quad (2.1)$$

$$\bar{\nu}_{lm}(R) = \begin{cases} \langle + | \nu_{lm}(R; h) | + \rangle; & l + m \text{ even} \\ \langle + | \nu_{lm}(R; h) | - \rangle; & l + m \text{ odd} \end{cases} \quad (2.2)$$

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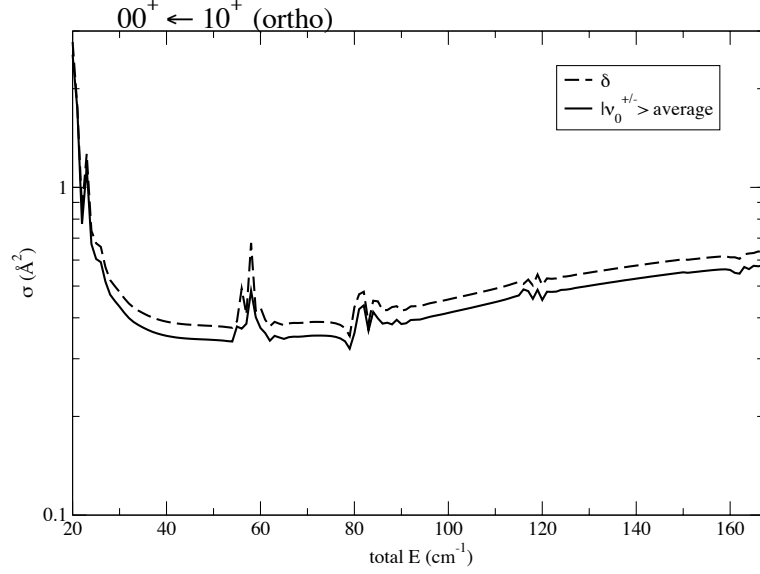


**Fig. 1.** Potential energy curve for ammonia inversion and relative wavefunctions used for the average of the intermolecular potential. The two vertical lines show the corresponding  $\delta$  function used in Paper I.

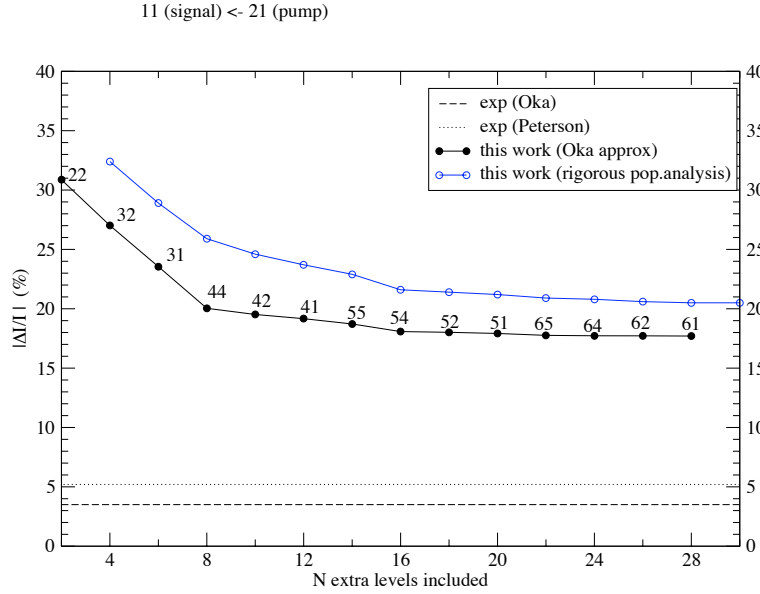
Then close coupling calculations (MOLSCAT code, Hutson & Green 1995) were performed, separately for ortho and para ammonia rotational levels, using the resulting PES and, for comparison, the original PES at the equilibrium value of it ( $\delta$  approximation, Green 1980)

### 3 Results

Results for the cross section (fig.2) compared with calculations at fixed  $\text{NH}_3$  geometries (as the ones performed in Paper I), as well for the collisional rates, show a slight correction that is not sufficient to reproduce the behaviour of the double resonance experiments (fig.3). In the figure we attempt to reproduce the experimental observables with the present rates, both by an approximated formula given by Oka (paper II), and with a more detailed derivation, considering the population analysis of all the rotational levels. The discrepancy seems to be related to different propensity rules in theory and experiments. In fact, a comparison of parity averaged cross sections (tab.1) give a very good agreement with corresponding state to state experimental values from crossed beam experiments (Schleipen et al 1991)



**Fig. 2.** Cross Section for a selected  $\text{NH}_3$  rotational transition, by He collision, with different approximations.



**Fig. 3.** Relative change in a doublet signal intensity for a pump probe experiment, and theoretical simulation of it with the present rates.

We can conclude that keeping into account the complete intermolecular Potential Energy Surface, dependent on the inversion coordinate  $h$ , by averaging it on the ammonia wavefunctions of the first vibrational doublet, provides a correction that it is not sufficient to involve a dramatic modification of the resulting cross sections and rates ( $< 10\%$ ), with respect to the previous "rigid" approximation (Machin & Roueff 2005). The unsolved discrepancy with some experimental works (Paper II), concerning especially a large difference in collisional propensity rules, points out the need of a full theoretical vibro-rotational treatment for this system as well as new experiments providing selected state-to-state rates.

**Table 1.** Parity averaged cross sections from ground para level( $11^-$ )

jk	Crossed Beams (Schleipen)	This work
21	2.67	2.70
22	1.56	1.77
31	1.24	1.19
32	1.17	1.02
41	0.50	0.17
42	0.69	0.29
44	1.46	1.74
54	0.61	0.36
55	0.33	0.28

## References

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