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Sándor Demes, François Lique, Jérôme Loreau, Alexandre Faure. Collision-induced excitation of ammonia in warm interstellar and circumstellar environments. *Monthly Notices of the Royal Astronomical Society*, 2023, 524 (2), pp.2368-2378. 10.1093/mnras/stad1970 . hal-04148649

**HAL Id: hal-04148649**

**<https://hal.science/hal-04148649>**

Submitted on 3 Jul 2023

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# Collision-induced excitation of ammonia in warm interstellar and circumstellar environments

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Accepted 30 June 2023, the published version available at <https://doi.org/10.1093/mnras/stad1970>

## ABSTRACT

Ammonia (NH<sub>3</sub>) is the first polyatomic molecule detected in the interstellar medium. Both its spectroscopic and collisional properties have been extensively studied earlier, and NH<sub>3</sub> was often used in laboratory astrophysics studies to compare high-level scattering calculations with state-of-the-art experiments. Nevertheless, some of its important collisional properties remain unresolved. In this paper we report state-to-state and thermally averaged collisional data for the rotational excitation of NH<sub>3</sub> by H<sub>2</sub> calculated with the close-coupling quantum theory. Both nuclear spin symmetries (*ortho/para*) of the colliders are studied. Similar research has been carried out previously, providing rate coefficients up to temperature of 200 K for rotational states with internal energy up to  $\sim 420$  cm<sup>-1</sup>. Here we have computed cross sections for collision energies up to 4700 cm<sup>-1</sup> and rate coefficients up to 500 K. Most of the rotation-inversion levels of ammonia have been considered below the first vibrational excitation threshold, leading to a total of 33 *ortho*- and 62 *para*-NH<sub>3</sub> states. We have compared our results with the most accurate data for He and H atoms available in the literature. The propensity rules have also been analysed in the case of high rotational levels of NH<sub>3</sub>. The rate coefficients obtained by averaging over the thermal H<sub>2</sub> relative populations exhibit significantly larger magnitudes than the state-to-state collisional data in the case of NH<sub>3</sub> transitions with large internal energy difference, when the rotational energy transfer between the colliders is strong.

**Key words:** molecular processes – molecular data – methods: laboratory: molecular – astrochemistry – ISM: molecules

## 1 INTRODUCTION

The first polyatomic molecule detected in the interstellar medium (ISM) was ammonia (NH<sub>3</sub>) (Cheung et al. 1968). Since the beginning of the era of radio astronomy, ammonia has gained great astronomical importance due to its specific and very favourable spectroscopic properties. Due to the features of its inversion-rotation transitions, which allow the detection of highly excited NH<sub>3</sub> lines, ammonia has been widely used to probe the physical conditions in a variety of interstellar environments (see the early review by Ho & Townes (1983) on the interstellar importance of ammonia). Consequently, NH<sub>3</sub> as well as its isotopologues are actively targeted in observational molecular astrophysics today, as indicated by numerous research papers in the past few years (Candelaria et al. 2023; De Simone et al. 2022; Bógnér et al. 2022; Galloway-Sprietsma et al. 2022; Feng et al. 2022; Zhou et al. 2020; Gao et al. 2019; Sipilä et al. 2019; Wong et al. 2018; Mills et al. 2018; Mills & Morris 2013). Some of these observations (see e.g. Candelaria et al. 2023; De Simone et al. 2022) report highly excited rotational lines of ammonia in warm interstellar environments. However, to adequately interpret such observations in interstellar clouds, accurate collisional data are required, as the population of rotational levels is dominantly determined by the competition between

radiative and collisional processes (Bouhafs et al. 2017). Rotationally inelastic collisions of NH<sub>3</sub> with the most abundant interstellar atoms and molecules (H<sub>2</sub>, H, He) are the most important processes from the point of view of astrophysical environments, including interstellar clouds, photodissociation regions (PDRs), pre-stellar cores as well as external galaxies. Even though a large number of sophisticated measurements have been carried out previously to study low-energy collisions of NH<sub>3</sub> with H<sub>2</sub> and other important colliders (see, for example, Daly & Oka 1970; Schleipen et al. 1993; Willey et al. 2002), the experiments usually do not provide direct state-to-state rate coefficients, which are the most important collisional quantities from an astrophysical point of view.

Up to this point, numerous theoretical investigations have been devoted to the study NH<sub>3</sub>-H<sub>2</sub> collisions, including the early study by Danby et al. (1988), which did not consider the rotational structure of hydrogen, assuming a collision with *p*-H<sub>2</sub> ( $j_{\text{H}_2} = 0$ ). The NH<sub>3</sub>-H<sub>2</sub> theoretical studies were later significantly improved by Maret et al. (2009) and then by Ma et al. (2015). It is also worth mentioning the accurate scattering calculations for deuterated isotopologues such as NHD<sub>2</sub>, NH<sub>2</sub>D, ND<sub>3</sub> performed by Daniel et al. (2014, 2016). Rotationally inelastic differential cross sections have also been measured and calculated for ND<sub>3</sub> in collision with H<sub>2</sub> (Tkáč et al. 2015) and D<sub>2</sub> (Gao et al. 2019) at some very limited collision energies. The satisfactory agreement between theory and experiment reported in

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these works could be referred to as a good probe of the accuracy of the methods commonly used in potential energy surface and scattering calculations. Although ammonia appears to be an extremely well studied system from this point of view, there are still several limitations on the existing collision data. The most complete set of data for  $\text{NH}_3\text{-H}_2$  collisions are provided by Bouhafs et al. (2017), where the authors studied all rotational transitions between levels with internal energies below  $417\text{ cm}^{-1}$  and provided rate coefficients up to kinetic temperature of 200 K.

Apart from collisions with  $\text{H}_2$ , a large number of experimental and theoretical studies have been devoted to the study of inelastic collisions of ammonia with other projectiles, dominantly by atomic species like H, He, Ar, Xe, Rb, *etc.* From an astrophysical point of view, the most important of these are the  $\text{NH}_3\text{-He}$  and  $\text{NH}_3\text{-H}$  collisions, the former being often used as a template for  $\text{H}_2$ . The  $\text{NH}_3\text{-He}$  collisions have been extensively studied since the first  $\text{NH}_3$  observations (see the measurement by Oka (1968) and the calculation by Green (1980)). For astrophysical applications, the most complete set of rate coefficients for collisions with helium is given by Machin & Roueff (2005), where the authors calculated accurate cross sections up to  $1500\text{ cm}^{-1}$  and rate coefficients up to 300 K. Later Yang & Stancil (2008) reproduced the rate coefficients of Machin & Roueff (2005), and significantly extended their range towards mK temperatures. While the authors of this work have also extended the collision energy range (from  $10^{-5}$  up to  $10^4\text{ cm}^{-1}$ ), unfortunately their work covers low-lying ammonia levels only (with internal energies below  $\sim 200\text{ cm}^{-1}$ ), which severely limits their astrophysical use.

It should be stressed again that without accurate and broadband collisional rate coefficients, the abundance of  $\text{NH}_3$  molecules in warm interstellar clouds could only be approximated, under the assumption of local thermodynamic equilibrium (LTE) conditions, which is usually not a good approximation in such media (Roueff & Lique 2013). Therefore, in the present work, we provide a complete set of collisional cross sections and thermal rate coefficients for the rotational excitation of  $\text{NH}_3$  by  $\text{H}_2$ , calculated on the basis of an accurate and well-tested 5-dimensional interaction potential (Maret et al. (2009)). The new collisional data have several crucial improvements over the results of Bouhafs et al. (2017): first, the present calculations include all rotational levels with internal energies up to  $\sim 800\text{ cm}^{-1}$ , and second, the rate coefficients are calculated up to higher temperatures (500 K). The paper is structured as follows: In Section 2 the details of the interaction potential (subsection 2.1) as well as the scattering calculations (subsection 2.2) are presented. The state-to-state collisional data are analysed and discussed in Section 3, with subsection 3.1 devoted to the cross sections, subsection 3.2 to the thermal rate coefficients, and subsection 3.3 to the collisional propensity rules. Our concluding remarks are given in Section 4.

## 2 METHODS

### 2.1 Potential energy surface

For the  $\text{NH}_3\text{-H}_2$  interaction potential, we have used the 5-dimensional potential proposed by Maret et al. (2009), in which all intramolecular coordinates are kept fixed (rigid rotor approximation). As it was discussed earlier by Maret et al. (2009) and later by Bouhafs et al. (2017), due to the good agreement between the theory based on this PES and the laboratory measurements, such an approximation is considered appropriate for collision energies below the first vibrational excitation threshold of ammonia ( $\nu_2 = 1$ ), *i.e.*  $E_c < 932.4\text{ cm}^{-1}$  (Rajamäki et al. 2003), provided that the collision

time-scales are faster than the inversion vibrational motion of ammonia. This allows one to compute reliable collisional rate coefficients at least up to 500 K kinetic temperatures.

Since the PES of Maret et al. (2009) has already been described in detail (see also Bouhafs et al. (2017)), we only briefly summarise its main points:

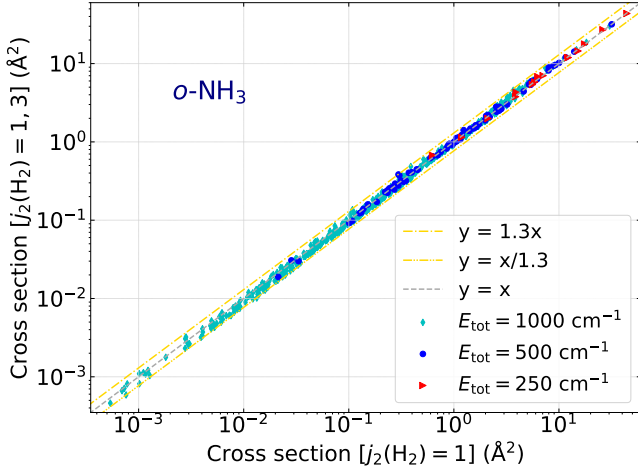
- For the geometries of the monomers, the ground-state averaged bond lengths  $r$  and bond angles  $\alpha$  were used ( $r_{\text{N-H}} = 1.9512 a_0$ ,  $\alpha_{\text{H-N-H}} = 107.38^\circ$  for  $\text{NH}_3$  and  $r_{\text{H-H}} = 1.4488 a_0$  for  $\text{H}_2$ ), as it was shown to be the most appropriate in the full-dimensional study of  $\text{H}_2\text{O-H}_2$  collision by Faure et al. (2005).
- The analytical PES was fitted on 29,000 *ab initio* CBS-extrapolated reference points with a 167-term angular expansion (with anisotropies up to  $l_1 = 10$  and  $l_2 = 4$ ) using a Monte Carlo error estimator (Rist & Faure 2012). The *ab initio* points were calculated using standard coupled-cluster theory with singles and doubles and perturbative corrections for triple excitations [CCSD(T)], with a simple complete basis set (CBS) extrapolation procedure.
- The accuracy of the final fit is  $< 1\text{ cm}^{-1}$  both in the long-range part and in the well region of the PES ( $R \gtrsim 5 a_0$ , where  $R$  is the intermolecular distance between the centres of mass of the colliders).
- The global minimum is about  $-267\text{ cm}^{-1}$  located at  $R = 6.1 a_0$ .

We have used the following units throughout this paper (unless otherwise noted): atomic units ( $a_0$ ) for distances ( $1 a_0 \approx 5.29177 \times 10^{-9}\text{ cm}$ ), wave numbers ( $\text{cm}^{-1}$ ) for energies ( $1\text{ cm}^{-1} \approx 1.4388\text{ K}$ ).

### 2.2 Scattering calculations

In this work, we have computed state-to-state rotational (de)excitation cross sections and thermal rate coefficients for the collision of *ortho(o)*- and *para(p)*- $\text{NH}_3$  with both *ortho*- and *para*- $\text{H}_2$ . Previously, similar calculations were performed by Bouhafs et al. (2017) for collision energies of  $0.1 - 1600\text{ cm}^{-1}$ , including rotational states with an internal energy up to  $417\text{ cm}^{-1}$ . Our current work is an extension of this latter with several substantial improvements. Most importantly, we have significantly increased the number of states, involving all rotation-inversion levels up to  $800\text{ cm}^{-1}$  (*i.e.* somewhat below the first vibrational excitation threshold of  $\text{NH}_3$  at  $\nu_2 \approx 932.4\text{ cm}^{-1}$ ), which can be treated effectively within the limits of the rigid-rotor approximation. Consequently, we have also greatly increased the collision energy range, allowing very accurate thermal rate coefficients to be derived up to 500 K, and with some limitations even up to 800 K. This is a significant improvement compared to the work of Bouhafs et al. (2017), where the largest kinetic temperature presented is 200 K.

The general methodology we used in the current work is very similar to that previously applied by Bouhafs et al. (2017). In order to avoid discrepancies between different theories, we did not use any approximate methods (*e.g.* coupled states), and we calculated the cross sections by the most accurate close-coupling (CC) quantum approach in the whole energy range, using the recent version 5 of the HIBRIDON scattering code (Alexander et al. 2023). In the case of collisions with *p*- $\text{H}_2$  projectiles, they were computed up to a total energy of  $4500\text{ cm}^{-1}$ , while for *o*- $\text{H}_2$  energies up to  $4700\text{ cm}^{-1}$  were considered. As described in detail by the authors of previous  $\text{NH}_3$  studies (Rist et al. 1993; Danby et al. 1988; Maret et al. 2009; Bouhafs et al. 2017), the rotation-inversion levels of a symmetric top molecule can be denoted by  $j_k^\epsilon$ , where  $j$  is the total angular momentum quantum number, and  $k$  is its projection on the  $C_3$  principal rotational axis, while  $\epsilon$  is the symmetry index (Rist et al. 1993). In order to be consistent with the spectroscopy literature, in the



**Figure 1.** Ratio of the state-to-state cross sections for the  $o\text{-NH}_3\text{-}o\text{-H}_2$  collision as computed with ( $j_2 = 1$ ) vs. ( $j_2 = 1, 3$ ) rotational basis sets. All possible de-excitation transitions are compared at 250, 500 and 1000  $\text{cm}^{-1}$  total energies ( $E_{\text{tot}}$ ).

present work we use in the following the  $j_k^\pm$  notation, involving the inversion symmetry (defined as  $+/- = -\epsilon(-1)^J$ ), contrary to Bouhafs et al. (2017) who used the  $\epsilon$  symmetry index. *Ortho*- $\text{NH}_3$  requires that  $k = 3n$  ( $n$  are integer numbers), while all other  $k$  quantum numbers refer to *p*- $\text{NH}_3$ , defining about twice as many rotational levels in favour of the latter below a certain internal energy limit. It is worth mentioning that the electric dipole transition rules prevent radiative transitions to occur between different  $k$ -ladders ( $\Delta j = 0$ ,  $\Delta k = 0$ ,  $\epsilon = \pm$ ), so the lowest inversion doublets in each  $k > 0$  ladder are metastable and can only be relaxed through collisions (Maret et al. 2009).

We have calculated the collisional data for transitions between all rotational states below  $\sim 800 \text{ cm}^{-1}$ , including levels up to  $10_0^-$  for *o*- $\text{NH}_3$  and  $9_5^-$  for *p*- $\text{NH}_3$ , thus all states with  $j \leq 8$  (and also some of those with  $j = 9$  and  $j = 10$ ) are studied. For a detailed list of the rotational levels considered in this work, see Tables A1-A2 in Appendix A. In the case of the  $\text{H}_2$  projectile, the 3 lowest rotational states are considered in the scattering calculations, including  $j_2 = 0, 2$  for *p*- $\text{H}_2$  and only  $j_2 = 1$  for *o*- $\text{H}_2$  ( $j_2$  refers to the rotational state of  $\text{H}_2$  throughout the paper). The collisional data calculated with a larger  $j_2 = 1, 3$  basis for *o*- $\text{H}_2$  show rather small differences as compared to the results obtained with a smaller  $j_2 = 1$  basis (see Fig. 1). The systematic comparison of all state-to-state cross sections at some particular energies (since large-scale scattering calculations with  $j_2 = 1, 3$  are unfeasible) shows that the larger *o*- $\text{H}_2$ -basis has no significant impact on the results, the average errors between the two datasets presented in Fig. 1 vary only between 3.7% (at 250  $\text{cm}^{-1}$ ) and 7.6% (at 1000  $\text{cm}^{-1}$ ). The contribution from a larger  $\text{H}_2$  rotational basis is usually  $< 10\%$ , and higher rotational terms ( $j_2 > 3$ ) would have even less remarkable effects on the collisional data. It is worth noting that due to the wide range of collision energies, we have computed many transitions with the  $j_2 = 2$  excited state of  $\text{H}_2$  as the collider, which has not been done in any of the previous works. Since all 4 nuclear spin combinations are treated separately (the selection rules prevent *ortho*-to-*para* transitions), the calculations involving the *p*- $\text{NH}_3$  species are computationally more expensive, which is also the case with *p*- $\text{H}_2$ , due to the larger rotational basis.

As is typical for full quantum CC calculations, both the rotational

basis ( $j_{\text{max}}$ ) and the maximum total angular momentum ( $J_{\text{tot}}$ ) values were constrained depending on the collision energy. Their particular values were determined from the results of systematic convergence test calculations, using the following thresholds: in the case of the rotational basis size, a maximum mean deviation criteria of 1% was set for total energies up to 2000  $\text{cm}^{-1}$ , which was then gradually increased up to 5% at the highest energies ( $> 4000 \text{ cm}^{-1}$ ), leading to  $j_{\text{max}}$  up to 17. The largest total angular momentum parameters were set by stricter convergence-threshold criteria: a maximum of 0.01% mean deviation was allowed up to 2000  $\text{cm}^{-1}$ , which was increased up to 0.1% at higher energies. We used the Airy propagator at long range radial distances and the log-derivative propagator in the short range. The best parameters for the propagator model (*i.e.* the initial and final distance of propagation and the switching point between the two propagators) were also chosen by convergence tests, so that the mean deviation in the cross sections never exceeds 0.01% due to these parameters. Finally, we also found an upper boundary for the significant rotational levels, which is about 1550  $\text{cm}^{-1}$ . Excluding all levels above this threshold does not change the cross sections by more than 0.01% on average, while such a limitation on the levels can save considerable computational time. Bouhafs et al. (2017) showed that the  $\text{NH}_3\text{-H}_2$  cross sections are characterised by strong and dense resonances caused by the potential well (*i.e.* at collision energies up to  $\sim 267 \text{ cm}^{-1}$ ). Consequently, a rather small energy step size should be used in the scattering calculations. We applied  $E_{\text{step}} = 1.0 \text{ cm}^{-1}$  up to 1200  $\text{cm}^{-1}$  total energy, which was then gradually increased until 100  $\text{cm}^{-1}$  at the highest energies.

The rate coefficients were calculated by integration over a Maxwell-Boltzmann distribution of relative velocities as follows:

$$k_{i \rightarrow f}(T) = \left( \frac{8}{\pi \mu k_B^3 T^3} \right)^{\frac{1}{2}} \int_0^\infty \sigma_{i \rightarrow f} E_c e^{-\frac{E_c}{k_B T}} dE_c. \quad (1)$$

Here  $E_c$  is the collision or kinetic energy,  $\sigma_{i \rightarrow f}$  is the cross section for a transition from a particular initial state ( $i$ ) to a given final state ( $f$ ),  $\mu$  is the reduced mass of the ‘projectile + target’ molecular system and  $k_B$  is the Boltzmann constant. It is necessary to mention that the computed cross sections would allow to obtain rate coefficients up to  $\sim 800 \text{ K}$ , however at such temperatures the rotational levels above the  $v_2 = 1$  vibrational threshold can be significantly populated (effectively up to about  $\sim 1500 \text{ cm}^{-1}$ ). These high-lying states are not straightforward to implement in our CC-formalism, first, due to the lack of vibrational dependence in the PES, and second, since the total number of levels would be extremely large, making the calculations not feasible (with our calculations we reached about 11,000 as a maximum number of coupled channels, which is pushing the currently accepted upper limit of the CC-formalism). Also, at these temperatures we should consider more  $\text{H}_2$ -levels ( $j_2 = 3 - 5$ ), since they can be also efficiently populated. We should keep in mind then that our collisional data would be not complete at 800 K due to the lack of significantly populated states, both in terms of  $\text{NH}_3$  and  $\text{H}_2$  levels, which may lead to unknown uncertainties in radiative transfer models. Our calculations show that the inclusion of higher levels does not change the collisional data below  $v_2 = 1$ , so we can confirm that the collisional data reported in this work, which include all ammonia levels below  $\sim 800 \text{ cm}^{-1}$ , are consistent and robust. The rotational levels of  $\text{H}_2$  ( $j_2 = 0 - 2$ ) considered in this work allowed one to compute accurate and consistent collisional data for all  $\text{NH}_3$ -transitions involving these states up to 500 K kinetic temperature. According to our rough estimations, a total of about 1.5 million

CPU-hours have been spent to perform the scattering calculations reported in this work.

In addition to the state-to-state collisional data we also report thermally averaged rate coefficients with respect to the  $\text{H}_2$  projectile in order to efficiently model excitation of ammonia in warm environments. For any transition of the target molecule the rate coefficients averaged over a thermal distribution of the  $\text{H}_2$  projectile can be obtained as follows:

$$\bar{k}_{j \rightarrow j'}(T) = \sum_{j_2} n_{j_2}(T) \sum_{j'_2} k_{j j_2 \rightarrow j' j'_2}(T), \quad (2)$$

where  $n_{j_2}(T)$  is the relative population of the projectile:

$$n_{j_2}(T) = \frac{(2j_2 + 1) \exp\left(-\frac{E_{j_2}}{k_B T}\right)}{\sum_{j'_2} (2j'_2 + 1) \exp\left(-\frac{E_{j'_2}}{k_B T}\right)}. \quad (3)$$

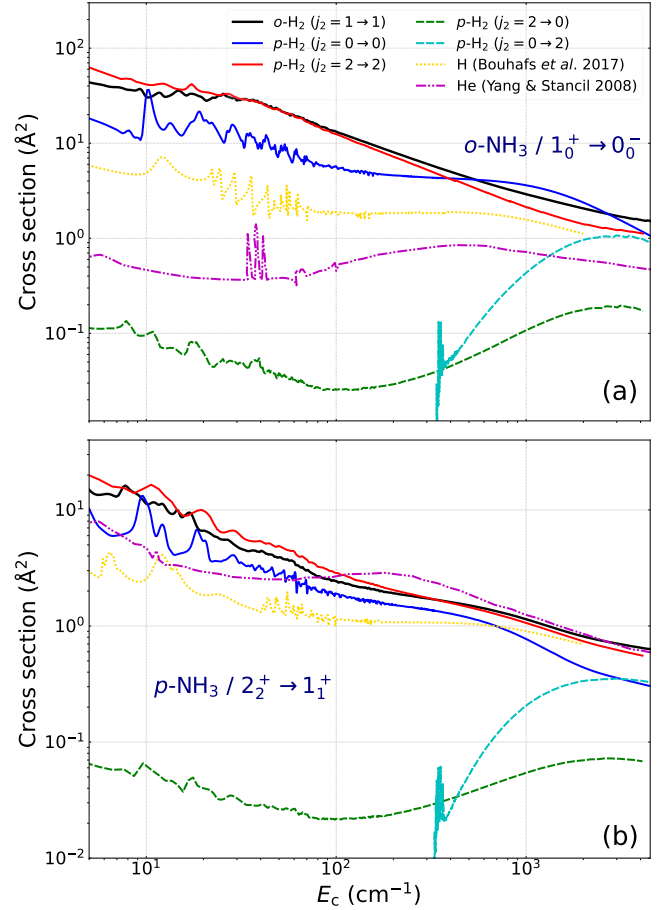
In Eq(s). 2-3  $j$  and  $j'$  denote the initial and final rotational levels of ammonia (defined by the  $j, k \in$  quantum numbers),  $j_2$  and  $j'_2$  refer to the initial and final rotational states of  $\text{H}_2$ , respectively, while  $E_{j_2}$  and  $E_{j'_2}$  are the corresponding internal energy of the projectile. The sum  $(2j_2 + 1)$  defines the degeneracy of the particular  $\text{H}_2$  levels for a particular nuclear symmetry. We computed thermalized rate coefficients for all  $\text{NH}_3$  transitions induced by  $p\text{-H}_2$  in  $j_2 = 0$  and  $j_2 = 2$ . Higher levels ( $j_2 > 2$ ) are not significantly populated at temperatures below 500 K. In the case of  $o\text{-H}_2$ , we cannot provide thermalized rate coefficients due to the lack of data with the  $j_2 = 3$  collider, but since the results obtained with  $o\text{-H}_2(j_2 = 1)$  are in a fairly good agreement with the thermally averaged  $p\text{-H}_2$  data, one can assume that thermalized rate coefficients are those with  $j_2 = 1$ . Somewhat larger deviations are found for a few transitions only, which are related to near-resonant effects. It is worth to mention that, since the rate coefficients are computed below 500 K only, near-resonance effects due to  $j_2 = 1 \leftrightarrow 3$  transitions (which involves an energy transfer of  $\sim 587 \text{ cm}^{-1}$ ) can be neglected.

### 3 RESULTS AND DISCUSSION

#### 3.1 Cross sections for rotational excitation

In Fig(s). 2-3 the variation of the state-to-state rotational de-excitation cross sections is presented for some selected transitions of  $\text{NH}_3$  as a function of the collision energy. Our current results for collisions with  $o\text{-H}_2(j_2 = 1)$  and  $p\text{-H}_2$  (both  $j_2 = 0$  and  $j_2 = 2$ ) are compared with the most accurate data for collisions with atomic hydrogen (Bouhafs et al. 2017) and helium (Yang & Stancil 2008). We do not aim to make a comparison with the most recent  $\text{NH}_3\text{-H}_2$  theoretical data from Ma et al. (2015); Bouhafs et al. (2017), since these authors used a very similar methodology and PES, so their results are in a perfect agreement with ours for the common transitions. Those transitions of  $\text{NH}_3$  are also presented in which  $p\text{-H}_2$  is changing its rotational state, (these are the so-called  $\text{H}_2$ -inelastic processes). We considered two of these, which are relevant at temperatures  $< 500 \text{ K}$ : the  $j_2 = 0 \rightarrow 2$  excitation and the  $j_2 = 2 \rightarrow 0$  de-excitation process. For sake of clarity, in the remainder of the text, we will indicate both the initial and final levels of  $\text{H}_2$  even for elastic transitions (e.g.  $j_2 = 0 \rightarrow 0$  for the collision with ground state  $p\text{-H}_2$ , etc).

Fig. 2.a shows the cross sections for the transition from the first excited state of  $o\text{-NH}_3$  ( $1_0^+$ ) to its ground state ( $0_0^+$ ). As can be seen, significant differences are found depending on the type of the projectile ( $o/p\text{-H}_2$ , H or He). For example, collisions with helium are characterised by much smaller cross sections compared to the data for



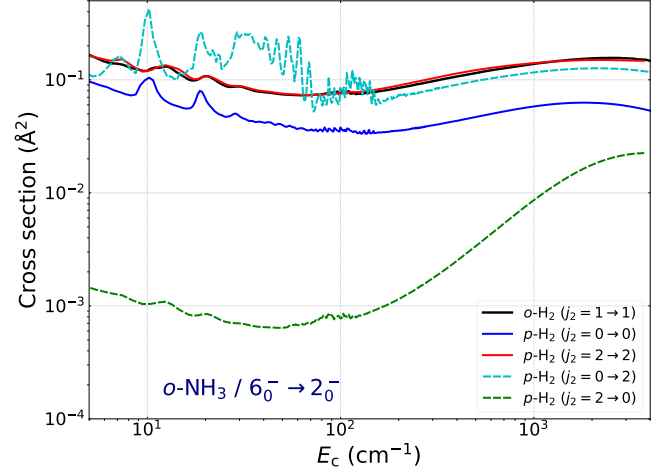
**Figure 2.** The variation of rotational de-excitation cross sections for the  $1_0^+ \rightarrow 0_0^-$  de-excitation transition of  $o\text{-NH}_3$  (panel a) and  $2_2^+ \rightarrow 1_1^+$  transition of  $p\text{-NH}_3$  (panel b). The collisions with  $o\text{-H}_2(j_2 = 1 \rightarrow 1)$  and  $p\text{-H}_2$  (all states involving  $j_2 = 0$  and  $j_2 = 2$ ) are compared with the corresponding results of Bouhafs et al. (2017) for collision with H and those of Yang & Stancil (2008) with He.

$\text{H}_2$  or even atomic H projectiles. With respect to  $\text{H}_2$ , the differences can be more than an order of magnitude, especially in the low-energy regime (below  $\sim 100 \text{ cm}^{-1}$ ). As the collision energy increases, the cross sections become somewhat closer to each other, but the differences are still very significant (at least a factor of 8 around  $\sim 500 \text{ cm}^{-1}$ ). As also observed previously for  $\text{H}_2\text{O}$  (Daniel et al. 2011) and  $\text{NH}_2\text{D}$  (Daniel et al. 2016), the cross sections for collisions with ground state  $o\text{-H}_2(j_2 = 1 \rightarrow 1)$  and with excited  $p\text{-H}_2(j_2 = 2 \rightarrow 2)$  are quite close in general, although at low collision energies  $j_2 = 2$  is somewhat larger, while the opposite is true at high energies. The differences increase slowly with increasing  $E_c$  and reach a maximum of about a factor of 1.5. However, the cross sections involving ground state  $p\text{-H}_2(j_2 = 0 \rightarrow 0)$  are significantly different: they are quasi-constant at  $E_c \sim 100 - 1000 \text{ cm}^{-1}$ , are usually much lower in magnitude than the other  $\text{H}_2$ -elastic data, and are characterized by a superimposed, dense resonant structure. A similar behaviour has been found by Lanza et al. (2014) when comparing the cross sections calculated for the HCl molecule in collision with ground-state  $o/p\text{-H}_2$  and excited  $p\text{-H}_2(j = 2)$  projectiles. These differences are related to the properties of the PES and its expansion coefficients. While the  $\text{NH}_3\text{-}p\text{-H}_2(j_2 = 0 \rightarrow 0)$  scattering matrices and cross sections depend only on the  $l_2 = 0$  terms of the interaction potential ( $l_2$  is the

tensor rank which defines the angular dependence on the  $\text{H}_2$  orientation, see Rist et al. (1993) for details), higher  $\text{H}_2$ -levels ( $j_2 > 0$ ) are also affected by the  $l_2 = 2$  ( $j_2 = 1$ ) and  $l_2 = 2, 4$  ( $j_2 = 2$ ) expansion terms (note that  $l_2$  must be even for homonuclear diatoms). In particular, the quadrupole behaviour of  $\text{H}_2$  (represented by the  $l_2 = 2$  term) plays an important role at long-range. Since the magnitude of the  $l_2 = 2$  terms is comparable to that of the  $l_2 = 0$  terms, larger cross sections are observed for the  $\text{NH}_3$ - $o$ - $\text{H}_2$  ( $j_2 = 1$ ) scattering process. However, the terms  $l_2 \geq 4$  are negligible compared to  $l_2 = 0, 2$ . It is worth noting that the  $o$ - $\text{H}_2$  and  $p$ - $\text{H}_2$  ( $j_2 = 2$ ) cross sections also involve multiple resonances, but they are very close together, leading to a strong overlapping and broadening, and thus these resonance peaks cannot be clearly identified. If we examine the  $1_0^+ \rightarrow 0_0^-$   $\text{NH}_3$  transition accompanied with the  $j_2 = 0 \rightarrow 2$   $\text{H}_2$ -inelastic process, we can clearly see the threshold above  $\sim 337 \text{ cm}^{-1}$  where this channel opens, and right above this a strong, dense resonance behaviour. The corresponding cross section then increases rapidly, approaching the magnitude of the  $\text{H}_2$ -elastic cross sections at higher collision energies. Due to this, such process can have a significant impact on the high-temperature thermalized rate coefficients. The transition accompanied with  $\text{H}_2$  de-excitation ( $j_2 = 2 \rightarrow 0$ ) is somewhat different. It does not have a threshold, but at low collision energies it is by about two orders of magnitude lower than all other processes. The cross section of this process does not vary strongly with the energy, however it exhibits a wide, shallow minimum centered around  $100 \text{ cm}^{-1}$ . The impact of this process on the rate coefficients is rather negligible even at higher kinetic temperatures.

In the case of the  $2_2^+ \rightarrow 1_1^+$  transition of  $p$ - $\text{NH}_3$  (Fig. 2.b), the overall trends are similar. A remarkable difference is that above  $\sim 100 \text{ cm}^{-1}$  collision energies, the cross sections for helium are slightly larger than all our  $\text{H}_2$  data. This can be related to a broad maximum in the He cross sections, which is associated to the formation of shape (orbiting) resonances due to the opening of some initially closed channels above the van der Waals region of the  $\text{NH}_3$ -He PES (see Yang & Stancil (2008) for details). The cross sections for collisions with atomic hydrogen are usually lower than all other data, except for collision energies  $\geq 800 \text{ cm}^{-1}$ , where they are comparable to or even exceed the  $p$ - $\text{H}_2$  ( $j_2 = 0 \rightarrow 0$ ) cross sections. It is also worth mentioning that these cross sections generally possess very similar resonance structure qualitatively as compared to the corresponding data with ground-state  $p$ - $\text{H}_2$  projectile. This is related to the similar characteristics and shape of their interaction potentials, considering only the  $l_2 = 0$  terms in the  $\text{NH}_3$ - $\text{H}_2$  PES.

Fig. 3 shows the cross sections for a near-resonant transition. In the case of a near-resonant transition the internal energy change within the target molecule is accompanied with a very close internal energy change within the projectile. Such effects were studied in detail earlier for collision of  $\text{HCl}$  with  $\text{H}_2$  by Lanza et al. (2014). The  $6_0^- \rightarrow 2_0^-$   $\text{NH}_3$  transition with an energy gap of  $\sim 356.5 \text{ cm}^{-1}$  is quasi-resonant with the  $j_2 = 0 \rightarrow 2$  transition in  $p$ - $\text{H}_2$  ( $\sim 356.3 \text{ cm}^{-1}$ ). The energy released by de-excitation of  $\text{NH}_3$  can be almost entirely transferred to  $\text{H}_2$ , which is efficiently excited from  $j_2 = 0$  to  $j_2 = 2$ . On the other hand, the  $\text{H}_2$  de-excitation ( $j_2 = 2 \rightarrow 0$  process) releases such a portion of energy, which can be captured by  $\text{NH}_3$ , initiating a very efficient excitation in it ( $2_0^- \rightarrow 6_0^-$ ). We can see in Fig. 3 a very pronounced near-resonant rotational energy transfer. The  $j_2 = 0 \rightarrow 2$  cross section is very large, comparable with the  $\text{H}_2$ -elastic cross sections for all collision energies. Below  $\sim 150 \text{ cm}^{-1}$ , when the rotational energy transfer is the most efficient, its magnitude exceeds that of all  $\text{H}_2$  state-conserving processes. In this energy interval it shows a very pronounced resonance structure. Due to near-resonant effects the corresponding  $\text{NH}_3$  de-excitation



**Figure 3.** The variation of the near-resonant  $6_0^- \rightarrow 2_0^-$  rotational transition of  $o$ - $\text{NH}_3$  in collision with  $p$ - $\text{H}_2$  (involving all state-changing and state-conserving processes with  $j_2 = 0, 2$ ) as well as with  $o$ - $\text{H}_2$  ( $j_2 = 1 \rightarrow 1$ ).

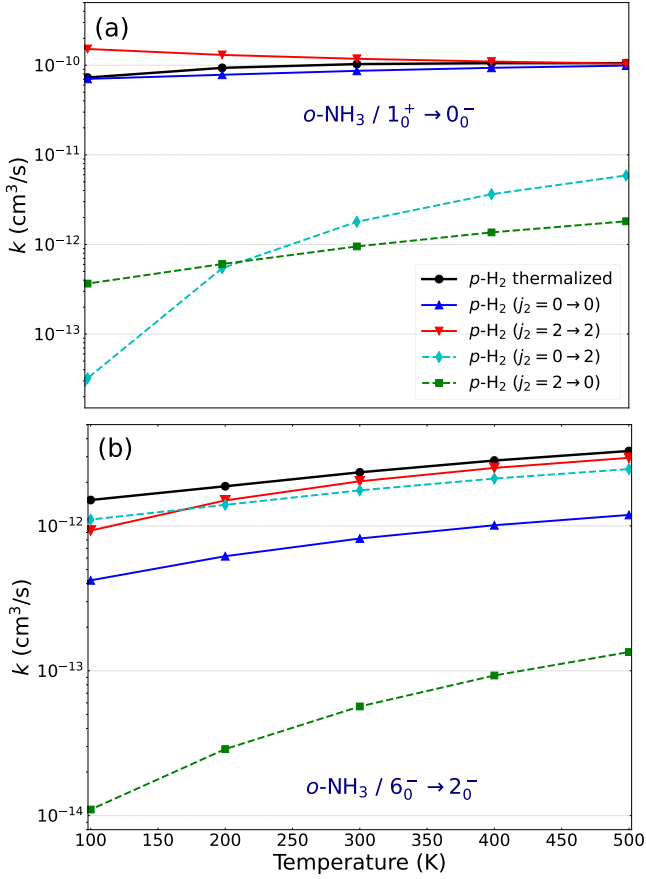
transition exhibit significantly larger thermalized rate coefficients as compared to any of the pure  $\text{H}_2$ -elastic processes.

Based on the comparative analysis of the cross sections one can draw a conclusion that generally they do not correlate well with respect to the type of collider. We found no clear scaling rules between the collisional data calculated with  $\text{H}_2$  ( $j_2 = 0, 1, 2$ ) and those with He or H. These dissimilarities and random trends between the cross sections are expected to be present in the rate coefficients as well. The only relatively good agreement (within a factor of  $\sim 1.5$ ) is observed between the  $o$ - $\text{H}_2$  ( $j_2 = 1$ ) and excited  $p$ - $\text{H}_2$  ( $j_2 = 2$ ) cross sections. As a consequence, neither He nor H atomic colliders, nor the structureless ground state  $p$ - $\text{H}_2$  can be used as a template for collisions with molecular hydrogen at temperatures where its excited states ( $j_2 \geq 1$ ) are effectively populated, *i.e.* at  $T_{\text{kin}} > 100 \text{ K}$ . This has also been reported previously by several authors, see for example the review by Roueff & Lique (2013). Also, the cross sections can be strongly affected by near-resonant rotational energy transfer in the case of transitions from higher initial levels of  $\text{NH}_3$ , which is necessary to take into account when computing the rate coefficients.

### 3.2 Rate coefficients

Once the state-to-state cross sections were calculated, the corresponding thermal rate coefficients  $k(T)$  were derived for all 4 nuclear spin combinations of the  $\text{NH}_3$ - $\text{H}_2$  collision. In the case of  $p$ - $\text{H}_2$  collider, in addition to the state-to-state collisional data, we also report the thermally averaged rate coefficients over the  $j_2 = 0, 2$  levels.

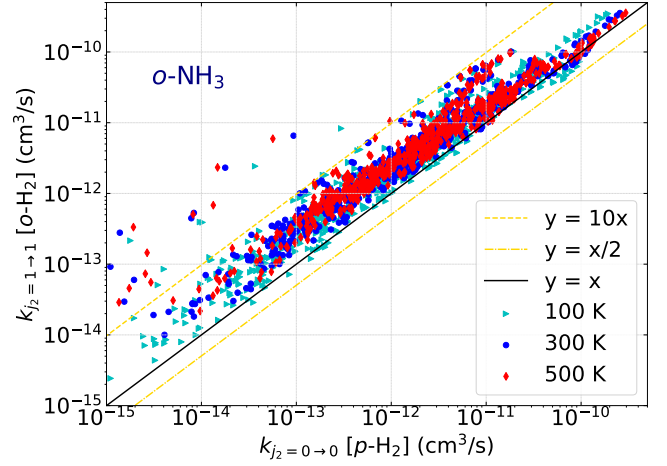
In Fig. 4 we examine the temperature dependence of the rate coefficients for a fundamental ( $1_0^+ \rightarrow 0_0^-$ ) and a near-resonant ( $6_0^- \rightarrow 2_0^-$ ) rotational transition of  $o$ - $\text{NH}_3$ . Since the  $j_2 = 1 \rightarrow 1$   $o$ - $\text{H}_2$  rate coefficients are very close to the  $j_2 = 2 \rightarrow 2$  excited  $p$ - $\text{H}_2$  data, we decided not to show them separately, but we also show the thermally averaged rate coefficients computed for  $p$ - $\text{H}_2$ . The general trends are similar to what was observed in the case of the cross sections. As one can see in Fig. 4.a, when the transition energy is low, the  $\text{H}_2$ -inelastic transitions are very weak and the thermalized rate coefficients are only governed by the  $\text{H}_2$ -elastic processes. Due to the variation of  $\text{H}_2$  population the thermal average is always found to be between the  $j_2 = 0 \rightarrow 0$  and  $j_2 = 2 \rightarrow 2$  data: at low temperatures closer



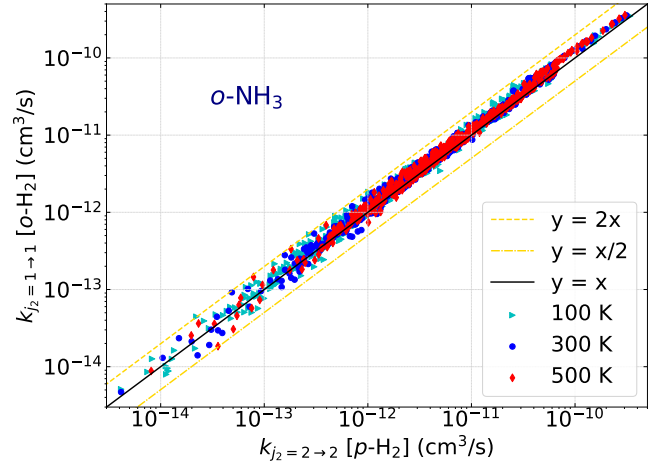
**Figure 4.** Thermal rate coefficients as a function of kinetic temperature for a fundamental low-energy ( $1_0^+ \rightarrow 0_0^-$ , panel a) and a near-resonant ( $6_0^- \rightarrow 2_0^-$ , panel b)  $o$ -NH<sub>3</sub> de-excitation transition calculated in collision with  $p$ -H<sub>2</sub> state-changing and state-conserving processes.

to the ground state, at 300 K along their average, while at 500 K close to the excited  $p$ -H<sub>2</sub> data. This trend is not valid however when the rotational energy transfer between the colliders is more efficient (the internal energy change  $\Delta E_{\text{int}}$  is large), especially in the case of near-resonant energy transfer. As one can see in Fig. 4.b, in the case of the  $6_0^- \rightarrow 2_0^-$  process with  $\Delta E_{\text{int}} \approx 356.5 \text{ cm}^{-1}$ , the  $j_2 = 0 \rightarrow 2$  H<sub>2</sub>-excitation process is very strong and significantly contributes to the thermal average. Due to this, the thermalized rate coefficients can be even higher than the  $j_2 = 2 \rightarrow 2$  (and thus  $j_2 = 1 \rightarrow 1$ ) H<sub>2</sub>-elastic data. Since the  $j_2 = 0 \rightarrow 2$  process is involved in the thermal average with a weight given by the relative population of its  $j_2 = 0$  state, this effect is more pronounced at 100 K. The  $j_2 = 2 \rightarrow 0$  H<sub>2</sub>-inelastic rate coefficients are very weak, as expected.

The relative ratios of the rate coefficients are also analysed to compare the magnitude and the variation of  $k(T)$  with respect to the state of the H<sub>2</sub>-projectile. Fig. 5 shows a comparison of the rate coefficients for all rotational transitions considered for  $o$ -NH<sub>3</sub> (with  $E_{\text{int}} \leq 800 \text{ cm}^{-1}$ ) in collision with  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) and ground state  $p$ -H<sub>2</sub> ( $j_2 = 0 \rightarrow 0$ ) at 100, 300 and 500 K kinetic temperatures. Fig. 6 compares the rate coefficients of  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) and excited  $p$ -H<sub>2</sub> ( $j_2 = 2 \rightarrow 2$ ) for the same transitions and temperatures, while Fig. 7 shows the ratio between state-to-state  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) and thermalized  $p$ -H<sub>2</sub> rate coefficients. As can be seen in Fig. 5, the correlation between the collisional data calculated for collisions with  $o$ -H<sub>2</sub> and ground state  $p$ -H<sub>2</sub> is generally modest, as expected from the



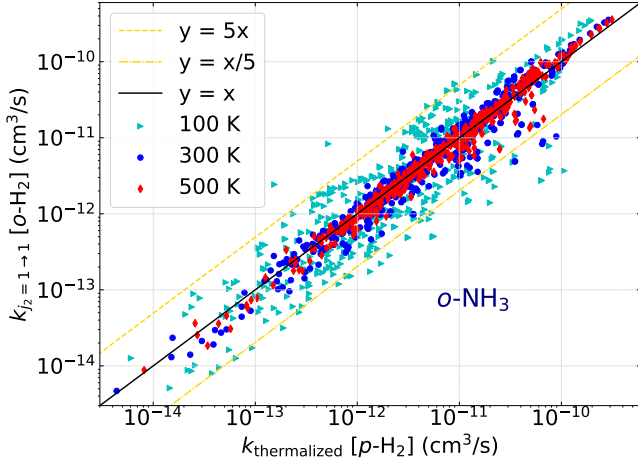
**Figure 5.** Ratio of the state-to-state rate coefficients for the collision of  $o$ -NH<sub>3</sub> with  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) vs.  $p$ -H<sub>2</sub> ( $j_2 = 0 \rightarrow 0$ ). All rotational de-excitation transitions are considered below  $\sim 800 \text{ cm}^{-1}$  internal energy at kinetic temperatures of 100, 300 and 500 K.



**Figure 6.** Same as Fig. 5 but the ratio is calculated from collisional data for  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) and  $p$ -H<sub>2</sub> ( $j_2 = 2 \rightarrow 2$ ) colliders.

behaviour of the corresponding cross sections. For the majority of the transitions we find that  $o$ -H<sub>2</sub> can de-excite ammonia more intensely, since the corresponding rate coefficients are significantly larger. Most commonly, we observe about 4-5 times larger  $k(T)$  values in favour of this projectile, but for some low-magnitude transitions the differences can be larger than one order of magnitude, and even reach two orders of magnitude. Also, these largest deviations do not depend on the temperature. There is some correlation between the two data sets for the largest rate coefficients, greater than  $\sim 10^{-10} \text{ cm}^3/\text{s}$ . In this range, the rate coefficients typically agree within 30 – 40%, and the larger deviations are observed at 100 K. Our analysis again confirms that ground-state H<sub>2</sub> ( $j_2 = 0$ ) cannot be used as a template for ‘normal’ H<sub>2</sub> in warm clouds, where its excited levels can be significantly populated.

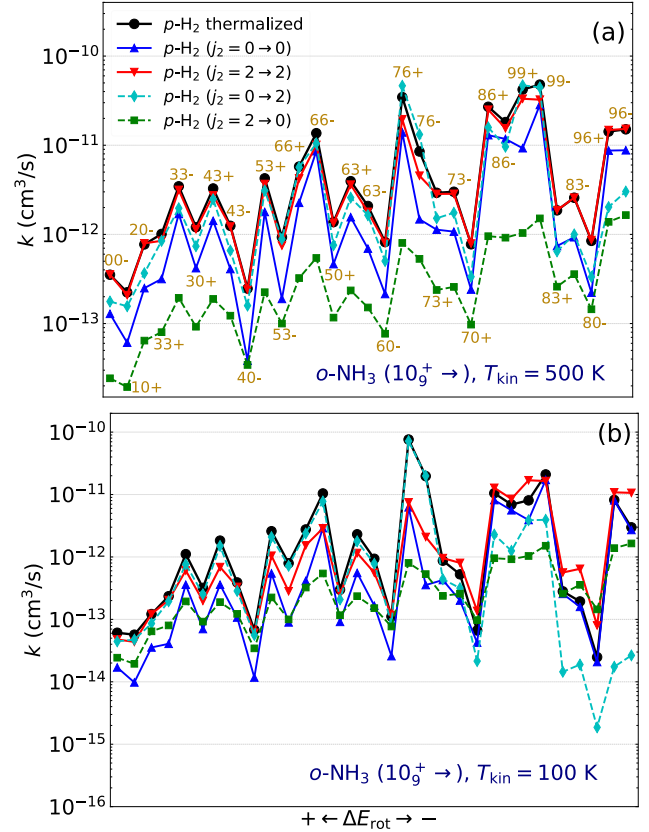
Fig. 6 reveals different rate coefficient relationships. In this plot the  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) data are compared with excited  $p$ -H<sub>2</sub> ( $j_2 = 2 \rightarrow 2$ ) and the correlation between them is much stronger: we observe differences up to a factor of 2 at most. The deviations are



**Figure 7.** Same as Fig. 5 but the ratio is calculated from collisional data for  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) and thermalized  $p$ -H<sub>2</sub> colliders.

larger for less dominant transitions (below  $\sim 10^{-12}$  cm<sup>3</sup>/s). For all other transitions, the two sets of  $k(T)$  are in a very good agreement, usually within 50%. We found the following mean relative errors (involving all transitions in the statistics): 20.8%, 17.0% and 15.9% at 100, 300 and 500 K, respectively. It is worth noting that partially these differences may arise from the fact that  $j_2 = 3$  was not included in the basis set for  $o$ -H<sub>2</sub> (the impact of adding  $j_2 = 3$  can lead to a factor of  $\sim 1.3$  differences, see Fig. 1). The same tendencies were observed with the  $p$ -NH<sub>3</sub> rate coefficients. In general, all the effective rate coefficients in NH<sub>3</sub>-H<sub>2</sub> collision with ( $j_2 \geq 1$ ) are quantitatively similar at higher temperatures, independently from the nuclear spin symmetry of H<sub>2</sub>, as was found also in the case of the NH<sub>2</sub>D-H<sub>2</sub> (Daniel et al. 2014) and H<sub>2</sub>O-H<sub>2</sub> (Daniel et al. 2011) collisions. Thus, in the absence of appropriate collisional data, H<sub>2</sub> in either  $j_2 = 1$  or  $j_2 = 2$  can be a reliable template for any excited states of  $o/p$ -H<sub>2</sub> ( $j_2 \geq 1$ ).

In order to examine the direct impact of thermal averaging over H<sub>2</sub>-population on the rate coefficient, we also analysed their relative ratio with respect to the state-to-state  $o$ -H<sub>2</sub> ( $j_2 = 1$ ) data in Fig. 7. As one can be seen in Fig. 7, we observe that at higher temperature (500 K) the thermalized rate coefficients correlate with the state-to-state  $o$ -H<sub>2</sub> data. This correlation is not as strong as in the case of the  $p$ -H<sub>2</sub> ( $j_2 = 2 \rightarrow 2$ ) data (see Fig. 6), but the general agreement at this temperature is usually within a factor of 2. While we found somewhat less coherence in this case, only some specific transitions possess larger ratios than a factor of 2 at 500 K, and these are exclusively the ones impacted by the near-resonance effects. The absolute mean deviation is  $\sim 15.4\%$ , which is very close to what was found in the case of the  $j_2 = 2 \rightarrow 2$  vs.  $j_2 = 1 \rightarrow 1$  processes ( $\sim 15.9\%$ ). On the other hand, when analysing the ratios at 100 K, we found unexpectedly large deviations, usually within a factor of 5, but for some near-resonant transitions they can be as large as an order of magnitude. If we examine the magnitude of the H<sub>2</sub>-inelastic transitions which contribute to the thermal average (see Eq. 2), we can easily find the origin of these effects: in the case of transitions accompanied with a significant rotational energy transfer, *i.e.* when the internal energy change is larger than the energy gap between the  $j_2 = 0$  and 2  $p$ -H<sub>2</sub> levels, the  $j_2 = 0 \rightarrow 2$  transition becomes very efficient, which significantly contributes to the thermalized rate coefficients at 100 K. Similar effects were reported also by Daniel et al. (2011). Since the considered NH<sub>3</sub> levels involve a large number of such transitions,



**Figure 8.** Propensity rules showing the variation of the rate coefficients for de-excitation transitions from the  $10_0^+$  state of  $o$ -NH<sub>3</sub> accompanied with different  $p$ -H<sub>2</sub>-elastic/inelastic and thermally averaged processes at higher (500 K, panel a) and lower (100 K, panel b) kinetic temperatures. The transition energy (rotational energy difference,  $\Delta E_{\text{rot}}$ ) is decreasing from left to right (see Appendix A for the full description of rotational levels and energies).

we observe a strong change in the distribution of the relative ratios shown in Fig. 7 w.r.t. Fig. 6, and the corresponding thermalized rate coefficients over the  $p$ -H<sub>2</sub> states are significantly larger than those of for  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ). Such effects are probably also present in the case of collisions with  $o$ -H<sub>2</sub>, but since the energy gap between the  $j_2 = 1, 3$  levels is much higher ( $\sim 587$  cm<sup>-1</sup>), the number of impacted transitions would be significantly less and are usually of low-magnitude (as expected from the energy-gap law). Thus, it is not advised to use thermalized  $p$ -H<sub>2</sub> rate coefficients to model the excitation due to  $o$ -H<sub>2</sub> at lower temperatures, but the differences between these collisional data is strongly decreasing at higher temperatures.

### 3.3 Propensity rules

In Fig(s). 8-9, the collisional propensity rules are analysed based on the state-to-state and thermalized rate coefficients. Fig. 8 presents  $k(T)$  for all possible de-excitation paths from the  $10_0^+$  level of  $o$ -NH<sub>3</sub> at kinetic temperatures of 500 K (a) and 100 K (b). Both the ( $j_2 = 0 \rightarrow 0, j_2 = 2 \rightarrow 2$ ) H<sub>2</sub>-elastic as well as the ( $j_2 = 0 \rightarrow 2, j_2 = 2 \rightarrow 0$ ) H<sub>2</sub>-inelastic processes are analysed along with the thermally averaged  $p$ -H<sub>2</sub> rate coefficients. In Fig. 9 the collisional propensities for transitions out of the  $9_7^-$  level of  $p$ -NH<sub>3</sub> are analysed, involving also de-excitation due to  $o$ -H<sub>2</sub> ( $j_2 = 1 \rightarrow 1$ ) collision.

As one can see, there is no clear evidence for general propensity trends with respect to the quantum numbers, but the same qualitative



behaviour is observed for all H<sub>2</sub>-processes. In Fig. 8.a, the transitions to states with  $k = 0$  are usually the smallest. Also, there is a preference for transitions towards  $j = k$  final states. Somewhat smaller differences are found for processes where only the inversion symmetry is changing (e.g.  $6_3^+$  and  $6_3^-$ ). We can observe some general propensity tendencies for the transitions analysed, which are very similar both at 100 and 500 K, but there are no clear scaling rules that generally apply to all transitions. For example, in the case of  $p$ -NH<sub>3</sub> we found that the  $9_7^+$  and  $8_7^+$  (i.e.  $\Delta k = 0$ ) final states are the most dominant in Fig 9, but there are some larger  $\Delta k$  transitions too with strong de-excitation rate coefficients, including the  $8_4^+$  or  $7_4^+$  channels. In general, the most favoured transitions are those when  $\Delta k = 0, 3$  or even  $\Delta k = 6$ , while all other transitions are hindered and significantly less efficient, especially in the case of large- $j$  jumps. This can be explained by the expansion terms of the PES. For example, in the case of H<sub>2</sub>( $j_2 = 0$ ) in the  $v_{lm}$  radial coefficients  $m$  has to be a multiple of 3 at arbitrary  $l$ . Transitions that change in the  $k$ -ladder are governed by terms with  $m = \Delta k$ , and these terms are smaller when  $m$  increases. This makes favourable those transitions, when  $\Delta k$  is a multiple of 3 (e.g.  $9_7^- \rightarrow 8_7^\pm, 8_4^\pm, 8_1^\pm$ ). For transitions when  $\Delta k$  is not a multiple of 3, higher order expansion terms are required, since these states are not directly coupled (Rist et al. 1993; Loreau & van der Avoird 2015). These effects are also similar to the dipole selection rules, which favour  $\Delta j = 0, 1$  and  $\Delta k = 0$  transitions. No clear propensities can be observed w.r.t. the symmetry index or inversion symmetry: transitions to a given  $j_k$  level with  $\pm$  are comparable and imply rather similar rate coefficients. However, it is worth mentioning that we found pronounced tendencies involving inversion symmetry change in the most efficient  $\Delta j = 1; \Delta k = 0$  transitions (e.g., see the  $10_9^+ \rightarrow 9_9^-$  and the  $9_7^- \rightarrow 8_7^+$  processes in Fig(s). 8-9). These can be also explained due to the expansion terms of the PES. The symmetry-changing transitions require that  $l + m$  to be odd, while the transitions that conserve inversion require terms with even  $l + m$  (Rist et al. 1993). These rules are more general for H<sub>2</sub>( $j_2 = 0$ ), since for H<sub>2</sub>( $j_2 \geq 1$ ) additional coupling terms are involved in the expansion scheme. We also found that, in general, the propensities are rather invariant to temperature. Stronger propensities are observed usually with respect to the projection quantum number  $k$  as opposed to the change in the main rotational quantum number  $j$ , so that the collision aims to conserve the projection of the NH<sub>3</sub> angular momentum on the C<sub>3</sub> molecular axis.

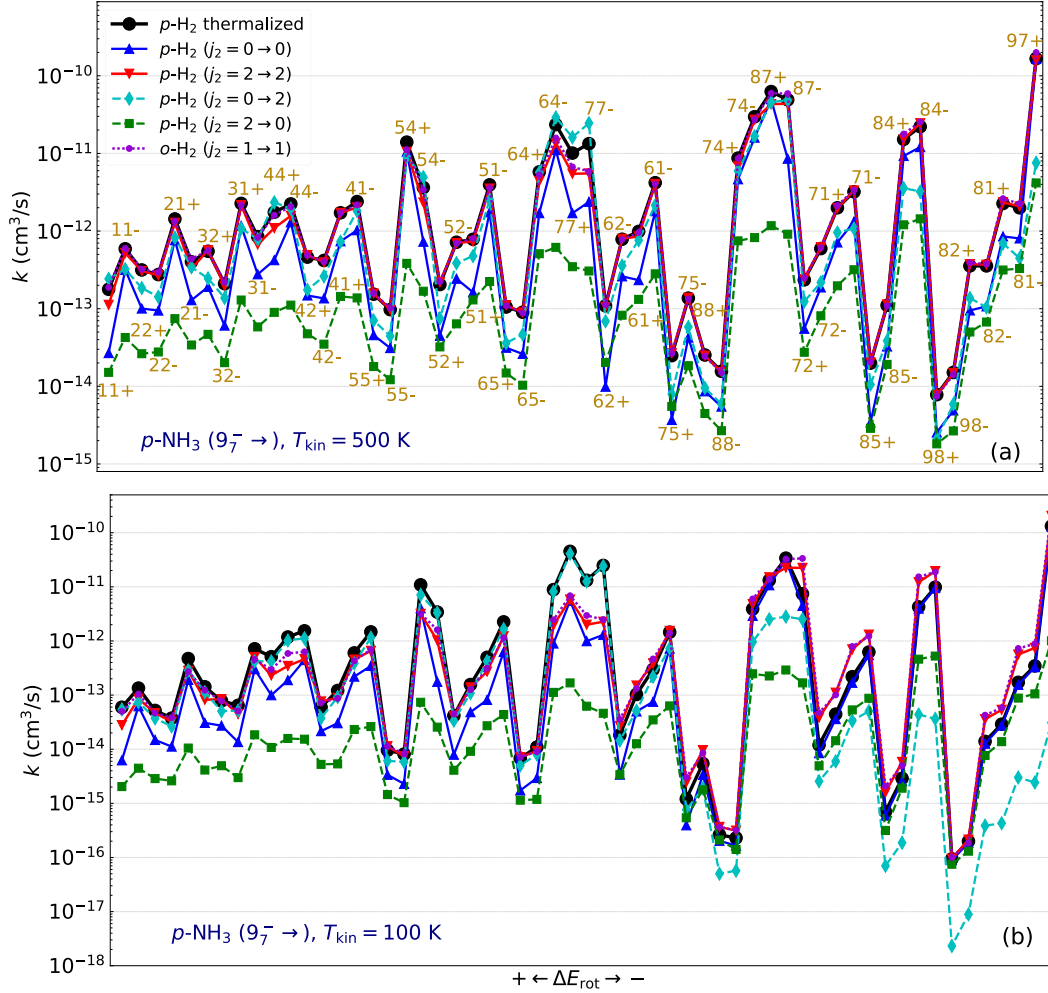
Both in the case of  $o$ -NH<sub>3</sub> (Fig. 8) and  $p$ -NH<sub>3</sub> (Fig. 9) de-excitation transitions only the H<sub>2</sub>-elastic processes are dominant when the rotational energy release ( $\Delta E_{\text{rot}}$ ) is low, and their statistical average dominates in the thermalized rate coefficients. With increasing  $\Delta E_{\text{rot}}$ , the  $j_2 = 0 \rightarrow 2$  H<sub>2</sub>-inelastic process becomes more significant due to the more efficient rotational energy transfer. We can clearly locate those transitions (with  $\Delta E_{\text{rot}} \approx 336 - 369 \text{ cm}^{-1}$ ), in which the near-resonant effects are the strongest. For these the thermalized rate coefficients can be about an order of magnitude larger than any of the pure H<sub>2</sub>-elastic data. At 100 K the dependence of the magnitude of H<sub>2</sub>-inelastic transitions on  $\Delta E_{\text{rot}}$  is more pronounced: when the energy release is small, the  $j_2 = 0 \rightarrow 2$  process is very weak, and the thermalized rate coefficients are almost entirely determined by the  $j_2 = 0 \rightarrow 0$  rate coefficients. At higher  $\Delta E_{\text{rot}}$  however, the  $j_2 = 0 \rightarrow 2$  channel is significantly stronger, and its contribution becomes dominant in the thermally averaged collisional data.

## 4 CONCLUSIONS

In this paper we have presented rotational (de)excitation cross sections and rate coefficients for the collision of ammonia (NH<sub>3</sub>) with molecular hydrogen (H<sub>2</sub>). Both the *ortho/para* nuclear spin configurations were considered in the case of the colliding partners, so that all 4 possible nuclear symmetry combinations of the NH<sub>3</sub>-H<sub>2</sub> complex are studied. In the case of *para*-H<sub>2</sub>, the thermally averaged rate coefficients were also computed based on the temperature-dependent relative population of  $j_2 = 0$  and  $j_2 = 2$  hydrogen levels.

The cross sections possess pronounced resonance properties, typically up to collision energies of  $250 - 300 \text{ cm}^{-1}$ , which correlate with the well depth of the interaction potential. The resonance behaviour is less pronounced in the case of collisions with excited H<sub>2</sub>( $j_2 > 0$ ) due to the strong overlap between the dense peaks. At higher collision energies the cross sections show the usual, monotonic decreasing behaviour. We found very significant differences (typically within a factor of 2 - 5) between the collisional data calculated with *ortho*-H<sub>2</sub>( $j_2 = 1$ ) and ground state *para*-H<sub>2</sub>( $j_2 = 0$ ) colliders, in favour of the former. However, there is a good overall agreement between the state-to-state cross sections and rate coefficients obtained for H<sub>2</sub>-elastic collisions with *ortho*-H<sub>2</sub>( $j_2 = 1$ ) and excited *para*-H<sub>2</sub>( $j_2 = 2$ ), which are related to the  $l_2$  expansion terms of the PES. We have presented a comparison at the level of cross sections with the most accurate data for collisions of NH<sub>3</sub> with helium (Yang & Stancil 2008) and hydrogen atoms (Bouhafs et al. 2017). We found large relative differences (typically 1-2 orders of magnitude) with respect to our H<sub>2</sub> collisional data, but we did not observe any systematic scaling rules between the different projectiles. The mutual analysis of thermally averaged and state-to-state rate coefficients has also showed that the impact due to the  $j_2 = 0 \rightarrow 2$  excitation of *para*-H<sub>2</sub> can be very significant. The thermalized rate coefficients thus can have a much larger magnitude compared to the respective state-to-state data, especially when a near-resonance occurs between *para*-H<sub>2</sub> and NH<sub>3</sub> transitions. We can draw a conclusion that neither He and H, nor the simple ground state  $p$ -H<sub>2</sub>( $j_2 = 0$ ) can be used as a template for appropriate modelling of collisions with molecular hydrogen at high temperatures ( $\gtrsim 100 \text{ K}$ ). Clearly, projectile- and state-specific, accurate collisional data are needed to interpret the ammonia observations in warm interstellar environments, considering at least the three lowest rotational levels of H<sub>2</sub>( $j_2 = 0, 1, 2$ ).

When analysing the collisional propensity rules, we did not find any universal tendencies for the favourable de-excitation routes that can be validated for arbitrary rotational states. Nevertheless, one can observe some general trends, which are generally related to the connections between the quantum numbers of the initial and final rotational states. These usually correspond to the well-known dipole selection rules. For example, some propensities are found for a well-defined combination of  $j$  and  $k$  rotational quantum numbers, which clearly depend on the parameters of the initial state. Among them, the  $\Delta j = 0, \pm 1$  transitions are the most favourable, but only when  $\Delta k = 0$ . For transitions involving different  $k$ -ladders, we found that  $\Delta k = -3$  or  $-6$  are very efficient de-excitation routes too, but positive jumps in the  $k$ -ladder are not favourable (obviously, the opposite rule holds for the reverse excitation transitions). In general, we observed about an order of magnitude lower rate coefficients towards final states obeying  $|\Delta k| = 1, 2$  with respect to the initial state. Consequently, the collisional propensity rules are more stringent and more pronounced in relation to the projection quantum number  $k$  than in the case of the main rotational quantum number  $j$ . Our new set of state-to-state and thermalized rate coefficients should help to accurately model



**Figure 9.** Same as Fig. 8 but for de-excitation transitions from the  $9_7^-$  initial state of  $p$ -NH<sub>3</sub> at  $T_{\text{kin}} = 500$  K (panel a) and  $T_{\text{kin}} = 100$  K (panel b).

non-LTE rotational spectra of NH<sub>3</sub> (within  $v_2 = 0$ ) up to about 500 K, *i.e.* covering warm interstellar and circumstellar environments.

[leidenuniv.nl/~moldata/](https://leidenuniv.nl/~moldata/) and BASECOL <https://basecol.vamdc.eu/> data bases.

## ACKNOWLEDGEMENTS

We acknowledge financial support from the European Research Council (Consolidator Grant COLLEXISM, Grant Agreement No. 811363) and the Programme National “Physique et Chimie du Milieu Interstellaire” (PCMI) of CNRS/INSU with INC/INP cofunded by CEA and CNES. We wish to acknowledge the support from the CEA/GENCI for awarding us access to the TGCC/IRENE super-computer within the A0110413001 project. F.L. acknowledges the Institut Universitaire de France.

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material at MNRAS online. The collisional data presented in this article will be made publicly available also through the EMAA <https://emma.osug.fr/> (doi:10.17178/EMAA), LAMDA <https://home.strw.leidenuniv.nl/~moldata/> and BASECOL <https://basecol.vamdc.eu/> data bases.

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## APPENDIX A: ROTATIONAL LEVELS OF AMMONIA FOR WHICH COLLISIONAL DATA ARE CALCULATED IN THIS WORK

The complete set of the rotational levels considered in this work for both *ortho/para*-NH<sub>3</sub> target species are given in Tables A1-A2, respectively. It is worth to emphasise that for the definition of the NH<sub>3</sub> levels, the notation with the inversion symmetry +/- is used rather than the  $\epsilon$  symmetry index.

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**Table A1.** The full list of rotational energy levels for *ortho*- $\text{NH}_3$  considered in the present study. The corresponding energies are taken from JPL data base (Pickett et al. (2010), Species Tag: 17002, version 5, compiled by S. Yu, 1 Sep. 2010). The rotational energies computed by the HIBRIDON code, which were used in the scattering calculations, are in a good overall agreement with these data with a mean deviation of  $\sim 1\%$ .

<i>ortho</i> - $\text{NH}_3$ rotational levels					
state label	internal energy [cm <sup>-1</sup> ]	rotational state $J_k^\pm$	state label	internal energy [cm <sup>-1</sup> ]	rotational state $J_k^\pm$
(1)	0.000000	0 <sub>0</sub> <sup>-</sup>	(18)	421.664932	7 <sub>6</sub> <sup>+</sup>
(2)	19.096483	1 <sub>1</sub> <sup>+</sup>	(19)	422.429625	7 <sub>6</sub> <sup>-</sup>
(3)	59.619617	2 <sub>0</sub> <sup>-</sup>	(20)	520.828585	7 <sub>3</sub> <sup>+</sup>
(4)	85.068186	3 <sub>3</sub> <sup>+</sup>	(21)	521.429579	7 <sub>3</sub> <sup>-</sup>
(5)	85.864408	3 <sub>3</sub> <sup>-</sup>	(22)	553.599742	7 <sub>0</sub> <sup>+</sup>
(6)	118.444459	3 <sub>0</sub> <sup>+</sup>	(23)	579.986473	8 <sub>6</sub> <sup>+</sup>
(7)	164.537707	4 <sub>3</sub> <sup>+</sup>	(24)	580.677592	8 <sub>6</sub> <sup>-</sup>
(8)	165.294507	4 <sub>3</sub> <sup>-</sup>	(25)	591.793694	9 <sub>9</sub> <sup>+</sup>
(9)	198.500538	4 <sub>0</sub> <sup>-</sup>	(26)	592.710260	9 <sub>9</sub> <sup>-</sup>
(10)	263.723260	5 <sub>3</sub> <sup>+</sup>	(27)	678.494549	8 <sub>3</sub> <sup>+</sup>
(11)	264.433261	5 <sub>3</sub> <sup>-</sup>	(28)	679.043432	8 <sub>3</sub> <sup>-</sup>
(12)	282.781115	6 <sub>6</sub> <sup>+</sup>	(29)	711.559858	8 <sub>0</sub> <sup>-</sup>
(13)	283.616894	6 <sub>6</sub> <sup>-</sup>	(30)	757.592095	9 <sub>6</sub> <sup>+</sup>
(14)	296.848422	5 <sub>0</sub> <sup>+</sup>	(31)	758.209168	9 <sub>6</sub> <sup>-</sup>
(15)	382.525089	6 <sub>3</sub> <sup>+</sup>	(32)	789.887816	10 <sub>9</sub> <sup>+</sup>
(16)	383.184131	6 <sub>3</sub> <sup>-</sup>	(33)	790.695217	10 <sub>9</sub> <sup>-</sup>
(17)	416.094413	6 <sub>0</sub> <sup>-</sup>			

**Table A2.** The same as Table A1, but for *para*- $\text{NH}_3$  rotational levels considered in the present study.

<i>para</i> - $\text{NH}_3$ rotational levels								
state label	internal energy [cm <sup>-1</sup> ]	rotational state $J_k^\pm$	state label	internal energy [cm <sup>-1</sup> ]	rotational state $J_k^\pm$	state label	internal energy [cm <sup>-1</sup> ]	rotational state $J_k^\pm$
(1)	15.379581	1 <sub>1</sub> <sup>+</sup>	(22)	282.823311	5 <sub>2</sub> <sup>-</sup>	(43)	539.051568	7 <sub>2</sub> <sup>+</sup>
(2)	16.169945	1 <sub>1</sub> <sup>-</sup>	(23)	293.174912	5 <sub>1</sub> <sup>+</sup>	(44)	539.628351	7 <sub>2</sub> <sup>-</sup>
(3)	44.002570	2 <sub>2</sub> <sup>+</sup>	(24)	293.836648	5 <sub>1</sub> <sup>-</sup>	(45)	549.965265	7 <sub>1</sub> <sup>+</sup>
(4)	44.793872	2 <sub>2</sub> <sup>-</sup>	(25)	323.575629	6 <sub>5</sub> <sup>+</sup>	(46)	550.527020	7 <sub>1</sub> <sup>-</sup>
(5)	55.145322	2 <sub>1</sub> <sup>+</sup>	(26)	324.333901	6 <sub>5</sub> <sup>-</sup>	(47)	620.272295	8 <sub>5</sub> <sup>+</sup>
(6)	55.915816	2 <sub>1</sub> <sup>-</sup>	(27)	356.790867	6 <sub>4</sub> <sup>+</sup>	(48)	620.899680	8 <sub>5</sub> <sup>-</sup>
(7)	103.628679	3 <sub>2</sub> <sup>+</sup>	(28)	357.491173	6 <sub>4</sub> <sup>-</sup>	(49)	653.077294	8 <sub>4</sub> <sup>+</sup>
(8)	104.390346	3 <sub>2</sub> <sup>-</sup>	(29)	373.455885	7 <sub>7</sub> <sup>+</sup>	(50)	653.656966	8 <sub>4</sub> <sup>-</sup>
(9)	114.743221	3 <sub>1</sub> <sup>+</sup>	(30)	374.313652	7 <sub>7</sub> <sup>-</sup>	(51)	654.853426	9 <sub>8</sub> <sup>+</sup>
(10)	115.484885	3 <sub>1</sub> <sup>-</sup>	(31)	400.854489	6 <sub>2</sub> <sup>+</sup>	(52)	655.642555	9 <sub>8</sub> <sup>-</sup>
(11)	138.564636	4 <sub>4</sub> <sup>+</sup>	(32)	401.484415	6 <sub>2</sub> <sup>-</sup>	(53)	696.601988	8 <sub>2</sub> <sup>+</sup>
(12)	139.369840	4 <sub>4</sub> <sup>-</sup>	(33)	411.830973	6 <sub>1</sub> <sup>+</sup>	(54)	697.123674	8 <sub>2</sub> <sup>-</sup>
(13)	183.035703	4 <sub>2</sub> <sup>+</sup>	(34)	412.444450	6 <sub>1</sub> <sup>-</sup>	(55)	707.445146	8 <sub>1</sub> <sup>+</sup>
(14)	183.759649	4 <sub>2</sub> <sup>-</sup>	(35)	462.219782	7 <sub>5</sub> <sup>+</sup>	(56)	707.953272	8 <sub>1</sub> <sup>-</sup>
(15)	194.112947	4 <sub>1</sub> <sup>+</sup>	(36)	462.913756	7 <sub>5</sub> <sup>-</sup>	(57)	710.063268	9 <sub>7</sub> <sup>+</sup>
(16)	194.817912	4 <sub>1</sub> <sup>-</sup>	(37)	476.471115	8 <sub>8</sub> <sup>+</sup>	(58)	710.754928	9 <sub>7</sub> <sup>-</sup>
(17)	204.475777	5 <sub>5</sub> <sup>+</sup>	(38)	477.355693	8 <sub>8</sub> <sup>-</sup>	(59)	719.386458	10 <sub>10</sub> <sup>+</sup>
(18)	205.294109	5 <sub>5</sub> <sup>-</sup>	(39)	495.241772	7 <sub>4</sub> <sup>+</sup>	(60)	720.340610	10 <sub>10</sub> <sup>-</sup>
(19)	237.859254	5 <sub>4</sub> <sup>+</sup>	(40)	495.882832	7 <sub>4</sub> <sup>-</sup>	(61)	797.581238	9 <sub>5</sub> <sup>+</sup>
(20)	238.614878	5 <sub>4</sub> <sup>-</sup>	(41)	532.100983	8 <sub>7</sub> <sup>+</sup>	(62)	798.141563	9 <sub>5</sub> <sup>-</sup>
(21)	282.143792	5 <sub>2</sub> <sup>+</sup>	(42)	532.875927	8 <sub>7</sub> <sup>-</sup>			