

# Collisional excitation of singly deuterated ammonia NH<sub>2</sub>D by H<sub>2</sub>

F. Daniel<sup>1</sup>\*, A. Faure<sup>1</sup>, L. Wiesenfeld<sup>1</sup>, E. Roueff<sup>2</sup>, D.C. Lis<sup>3,4</sup>, P. Hily-Blant<sup>1</sup> \*

<sup>1</sup> IPAG, Observatoire de Grenoble, Université Joseph Fourier, CNRS UMR5571, B.P. 53, 38041 Grenoble Cedex 09, France

<sup>2</sup> LERMA and UMR 8112, Observatoire de Paris, Place J. Janssen, 92190 Meudon, France

<sup>3</sup> Sorbonne Universités, Université Pierre et Marie Curie, Paris 6, CNRS, Observatoire de Paris, UMR 8112, LERMA, Paris, France

<sup>4</sup> California Institute of Technology, Cahill Center for Astronomy and Astrophysics 301-17, Pasadena, CA 91125, USA

Accepted XXX. Received XXX; in original form XXX

## ABSTRACT

The availability of collisional rate coefficients with H<sub>2</sub> is a pre-requisite for interpretation of observations of molecules whose energy levels are populated under non local thermodynamical equilibrium conditions. In the current study, we present collisional rate coefficients for the NH<sub>2</sub>D / para-H<sub>2</sub>(J<sub>2</sub> = 0, 2) collisional system, for energy levels up to J<sub>τ</sub> = 7<sub>7</sub> (E<sub>u</sub>~735 K) and for gas temperatures in the range T = 5 – 300K. The cross sections are obtained using the essentially exact close-coupling (CC) formalism at low energy and at the highest energies, we used the coupled-states (CS) approximation. For the energy levels up to J<sub>τ</sub> = 4<sub>2</sub> (E<sub>u</sub>~215 K), the cross sections obtained through the CS formalism are scaled according to a few CC reference points. These reference points are subsequently used to estimate the accuracy of the rate coefficients for higher levels, which is mainly limited by the use of the CS formalism. Considering the current potential energy surface, the rate coefficients are thus expected to be accurate to within 5% for the levels below J<sub>τ</sub> = 4<sub>2</sub>, while we estimate an accuracy of 30% for higher levels.

**Key words:** molecular data – molecular processes – scattering

## 1 INTRODUCTION

Singly deuterated ammonia, NH<sub>2</sub>D, was first tentatively detected toward the Kleinmann-Low nebula in Orion (Rodriguez Kuiper et al. 1978) and toward Sgr B2 (Turner et al. 1978). However, due to the molecular richness of these objects, a blending with transitions from other molecular species could not be discarded at that time. The first unambiguous detection of NH<sub>2</sub>D was subsequently performed by Olberg et al. (1985) in the cold environment of L183, S140 and DR21(OH) at 85 GHz and 110 GHz, thanks to the high spectral resolution of the observations which enabled to resolve the hyperfine structure of the lines. Since then, its centimeter and millimeter rotational transitions have been used as tracers of the physical conditions and chemistry of the molecular gas over a wide range of conditions, ranging from cold prestellar cores (e.g. Tiné et al. 2000; Saito et al. 2000; Shah & Wootten 2001; Hatchell 2003; Roueff et al. 2005; Busquet et al. 2010) to warm star-forming regions (e.g. Walmsley et al. 1987; Pillai et al. 2007). In cold environments, the deuterium fractionation was derived to be several 10<sup>-2</sup>. Such high fractionation ratios are within the values predicted by gas phase models at low temperatures (Roueff et al. 2005). In warm environments such as Orion KL, the fractionation ratio was derived to be 0.003 by Walmsley et al. (1987) and interpreted as a possible signature of mantle evaporation. More recently, NH<sub>2</sub>D has been detected at much higher

frequencies thanks to Herschel. In Orion KL (Neill et al. 2013), several excited levels of NH<sub>2</sub>D up to J<sub>K<sub>a</sub>,K<sub>c</sub></sub> = 7<sub>5,3</sub> (E<sub>u</sub> ~ 600 K)<sup>1</sup> were detected and the fractionation ratio was derived to be 0.0068. The temperature and density associated to the emitting regions were estimated to T ~ 100–300K and n(H<sub>2</sub>) ~ 10<sup>7</sup> -10<sup>8</sup> cm<sup>-3</sup>.

In order to interpret the NH<sub>2</sub>D observations, a key ingredient of the modelling are the collisional rate coefficients. Before the current calculations, the only available rate coefficients considered He as a collisional partner (Machin & Roueff 2006). However, it was shown in the case of ND<sub>2</sub>H that the rate coefficients with He and H<sub>2</sub> can differ by factors 3–30, depending on the transition (Machin & Roueff 2007; Wiesenfeld et al. 2011). Thus, a dedicated calculation for NH<sub>2</sub>D with H<sub>2</sub> is required in order to interpret the observations of this molecule. Indeed, as discussed by Daniel et al. (2013), a simple scaling of the NH<sub>2</sub>D / He rate coefficients is insufficient to accurately model the observations, at least under cold dark clouds conditions.

The paper is organized as follow. The potential energy surface is described in Section 2 and the collisional dynamics based on

<sup>1</sup> NH<sub>2</sub>D is an asymmetric top whose rotational energy structure can be described with the J, K<sub>a</sub>, K<sub>c</sub> quantum numbers. Alternatively, one may use the pseudo quantum number τ = K<sub>a</sub> − K<sub>c</sub>. In what follows, we mainly use the J<sub>τ</sub> notation to describe the rotational energy levels but can alternatively make use of the J<sub>K<sub>a</sub>,K<sub>c</sub></sub> notation, which is usually employed in astrophysical studies.

this surface in Section 3. We then describe the rate coefficients in Section 4 with some emphasis placed on their expected accuracy. In Section 5, we discuss the current results with respect to other related collisional systems and finally, we present conclusions in Section 6.

## 2 POTENTIAL ENERGY SURFACE (PES)

The rigid-rotor NH<sub>2</sub>D-H<sub>2</sub> potential energy surface (PES) was derived from the NH<sub>3</sub>-H<sub>2</sub> PES computed by Maret et al. (2009), but in the principal inertia axes of NH<sub>2</sub>D. The scattering equations to be solved (see below) are indeed written for a PES described in the frame of the target molecule, here NH<sub>2</sub>D. In the original NH<sub>3</sub>-H<sub>2</sub> PES, the ammonia and hydrogen molecules were both assumed to be rigid, which is justified at temperatures lower than  $\sim 1000$  K. The NH<sub>3</sub> and H<sub>2</sub> geometries were taken at their ground-state average values, as recommended by Faure et al. (2005) in the case of the H<sub>2</sub>O-H<sub>2</sub> system. The rigid-rotor NH<sub>3</sub>-H<sub>2</sub> PES was computed at the coupled-cluster CCSD(T) level with a basis set extrapolation procedure, as described in Maret et al. (2009) where full details can be found. In the present work, the geometry of NH<sub>2</sub>D was assumed to be identical to that of NH<sub>3</sub>, i.e. the effect of deuterium substitution on the ammonia geometry was neglected. This assumption was previously adopted for the similar ND<sub>2</sub>H-H<sub>2</sub> system by Wiesenfeld et al. (2011). We note that internal geometry effects are indeed expected to be only moderate ( $\lesssim 30\%$ ) at the temperatures investigated here, as shown by Scribano et al. (2010) for the D<sub>2</sub>O-H<sub>2</sub> system. The main impact of the isotopic substitution on the NH<sub>3</sub>-H<sub>2</sub> PES is therefore the rotation of the principal inertia axes.

We have thus expressed the NH<sub>3</sub>-H<sub>2</sub> PES of Maret et al. (2009) in the principal inertia axes of NH<sub>2</sub>D. The transformation can be found in Wiesenfeld et al. (2011) (Eqs. 2-3) where the  $\gamma$  angle is equal to -8.57 degrees for NH<sub>2</sub>D, as determined experimentally by (Cohen & Pickett 1982). The shift of the center of mass was also taken into account: the coordinates of the NH<sub>2</sub>D center of mass in the NH<sub>3</sub>-H<sub>2</sub> reference frame were found to be  $X_{CM}=0.101312$  Bohr and  $Y_{CM}=-0.032810$  Bohr, where  $X_{CM}$  and  $Y_{CM}$  were calculated for the ground-state average geometry of NH<sub>3</sub> used by Maret et al. (2009). The NH<sub>2</sub>D-H<sub>2</sub> PES was generated on a grid of 87 000 points consisting of 3000 random angular configurations combined with 29 intermolecular distances in the range 3-15 Bohr. This PES was finally expanded in products of spherical harmonics and rotation matrices, as in Wiesenfeld et al. (2011) (see their Eq. 4), using a linear least-squares fit procedure. We selected iteratively all statistical significant terms using the procedure of Rist & Faure (2011) applied at all intermolecular distances. The final expansion included anisotropies up to  $l_1=10$  for NH<sub>2</sub>D and  $l_2=4$  for H<sub>2</sub>, resulting in a total of 210 angular basis functions. The root mean square residual was found to be lower than 1 cm<sup>-1</sup> for intermonomer separations  $R$  larger than 5 Bohr, with a corresponding mean error on the expansion coefficients smaller than 1 cm<sup>-1</sup>.

## 3 COLLISIONAL DYNAMICS

In order to describe the NH<sub>2</sub>D energy structure, we adopted the same approach than Machin & Roueff (2006), i.e. we assumed that NH<sub>2</sub>D is a rigid rotor and we neglected the inversion motion corresponding to the tunneling of the nitrogen atom through the H<sub>2</sub>D plane. The spectroscopic constants, adapted from the CDMS

**Table 1.** Step between the consecutive total energies used to characterize the cross sections.

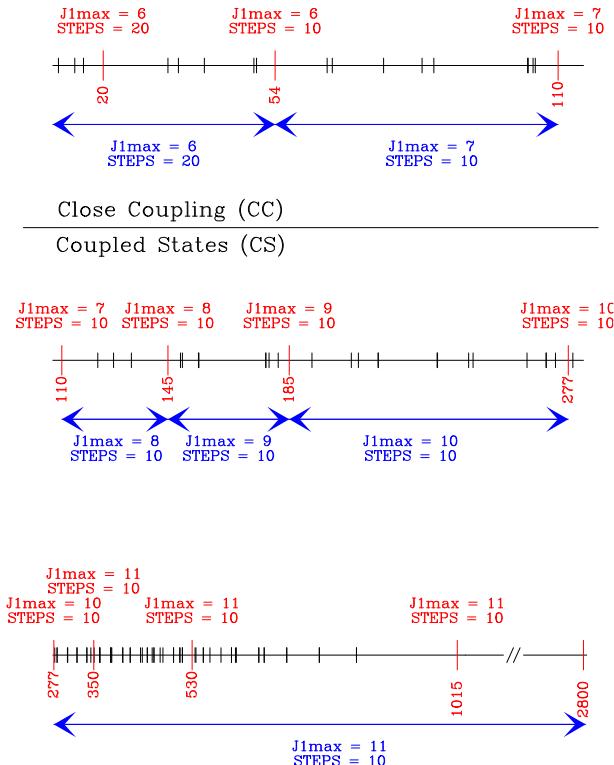
Energy range (cm <sup>-1</sup> )	step in energy (cm <sup>-1</sup> )
< 110	0.1
110 – 277	0.2
277 – 630	0.5
630 – 690	2
690 – 755	4
755 – 1355	20
1355 – 2800	50

catalogue (Müller et al. 2001) and from Coudert et al. (1986), are given in Table 2 of Machin & Roueff (2006). As outlined in Machin & Roueff (2006), neglecting the inversion motion leads to neglecting the difference between the ortho and para states of NH<sub>2</sub>D, which are thus treated as degenerate. Indeed, by considering the inversion motion, every rotational state would be split in two states which are either symmetric or anti-symmetric under exchange of the protons. By combining the symmetry of each state with the symmetry of the nuclear wave functions, each state will either correspond to an ortho or para state to ensure that the overall wavefunction is anti-symmetric under the exchange operation. Since the collisional transitions are only possible within a given symmetry, the treatment of the collisional dynamics would be essentially similar for each species, except for the slight differences of energy between the ortho and para states, which is of the order of  $\sim 0.4$  cm<sup>-1</sup> independently of the rotational state (Coudert & Roueff 2006). Hence, by neglecting the inversion motion, we obtain a set of rate coefficients which applies to both the ortho and para symmetries of NH<sub>2</sub>D. Finally, we also considered H<sub>2</sub> as a rigid rotor and adopted a rotational constant of 59.2817 cm<sup>-1</sup> (Huber & Herzberg 1979). The reduced mass of the collisional system is  $\mu = 1.812998990$  amu.

In order to solve the collisional dynamics, we used the MOLSCAT code<sup>2</sup>. Since NH<sub>2</sub>D is observed in warm media and since the transitions detected include levels up to  $J = 7$ , our goal was set accordingly. We performed the calculations in order to provide rate coefficients for the NH<sub>2</sub>D energy levels up to  $J_\tau = 7$  and for the temperature range  $T = 5 – 300$ K. A first step consisted of adjusting the convergence of the dynamical calculations for these levels and for total energies up to  $E_t \sim 3000$  cm<sup>-1</sup>. We thus performed a few calculations at some specific values of the total energy for which we determined the number of NH<sub>2</sub>D rotational energy levels, as well as the integration step required to insure a convergence better than 1% below 530 cm<sup>-1</sup> and better than 5% above this threshold. These test calculations are summarized in Fig. 1 and the parameters used for each energy range are also indicated. We found that including the  $J_2 = 2$  level of para-H<sub>2</sub> in the dynamical calculations had a large impact on the resulting cross sections. Indeed, at some specific energies, we found that the cross sections obtained with the  $J_2 = 0$  or  $J_2 = 0, 2$  basis can differ by up to a factor 7. An example of the influence of the  $J_2 = 2$  energy level of H<sub>2</sub> on the cross sections is given in Fig. 2. This figure will be further discussed below.

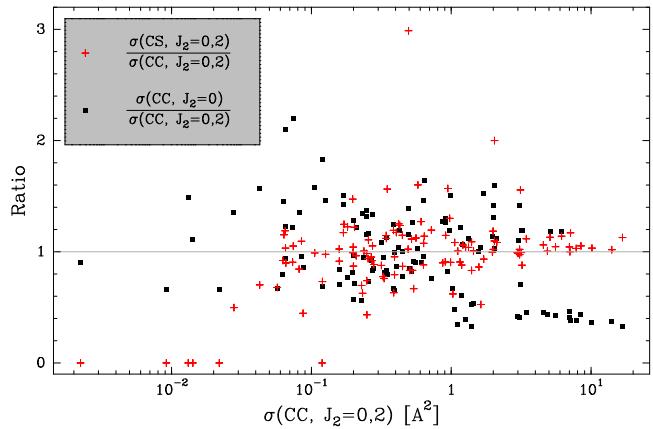
At low total energy (i.e.  $E_t < 110$  cm<sup>-1</sup>), we performed dynam-

<sup>2</sup> J. M. Hutson and S. Green, MOLSCAT computer code, version 14 (1994), distributed by Collaborative Computational Project No. 6 of the Engineering and Physical Sciences Research Council (UK).



**Figure 1.** Parameters that describe the convergence of the dynamical calculations performed with MOLSCAT. J1max stands for the maximum quantum number of  $\text{NH}_2\text{D}$  and STEPS is inversely proportional to the integration steps of the propagator. In red, we indicate the total energies at which we checked for the convergence of these two parameters. In blue, we indicate the values used for each energy range. Additionally, we also reported the energy levels of  $\text{NH}_2\text{D}$  which appear as vertical lines.

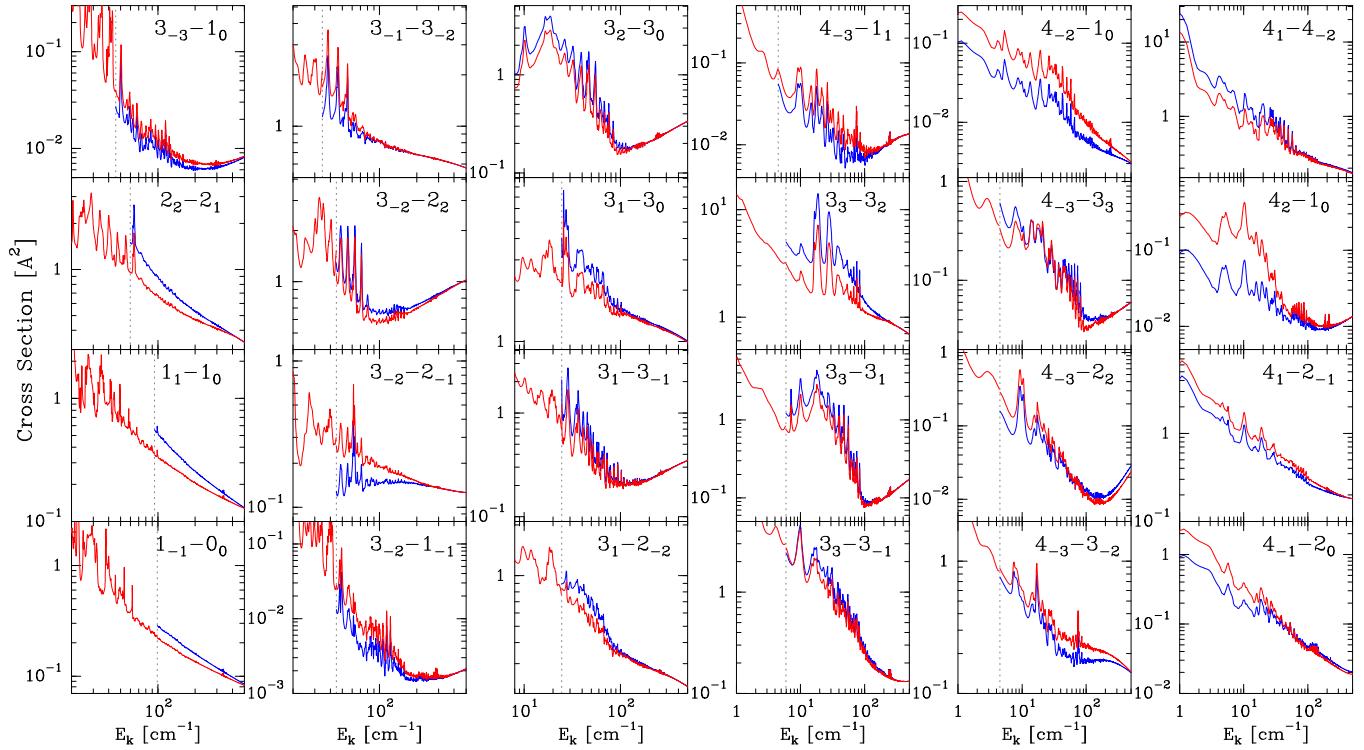
ical calculations with the accurate close-coupling (CC) formalism. However, because of the increase of the computational time with the number of channels, the cost in term of CPU time became prohibitive at high energy. As an example, in the range  $100\text{--}110\text{ cm}^{-1}$ , the CPU time typically ranged from 40 to 90 hours per energy, the amount of time being dependent on how far the energy is from the last opened energy level. In order to keep the CPU time spent within a reasonable amount of time, we had two options. We could either increase the step between two consecutive energy grid points, or switch to an approximate method in order to solve the collisional dynamics. While the first option could be a good choice for the low lying energy levels, it would turn to be a bad choice for the highest ones, since our calculations show that typically, the cross sections have resonances for kinetic energies up to  $\sim 150\text{ cm}^{-1}$  above the threshold of the transition. Thus, because the  $\text{NH}_2\text{D}$  energy levels are close in energy, and because we are interested in the levels up to  $J_\tau = 7$  ( $E \sim 512\text{ cm}^{-1}$ ), an accurate description of the resonances for all the transitions require the step between consecutive energies to be low (i.e. typically of  $0.2\text{ cm}^{-1}$ ) up to a total energy of  $\sim 660\text{ cm}^{-1}$ . Therefore, we made the choice to use an approximate method to solve the dynamics. We considered two options: reducing the basis of  $\text{H}_2$  still using the CC formalism or using the coupled-states (CS) formalism (McGuire & Kouri 1974) with the  $J_2 = 0, 2$  basis for  $\text{H}_2$ . In Fig. 2, we show the ratio of the cross-sections obtained with those two treatments with respect to the cross sections obtained with the CC formalism and with the  $J_2 = 0, 2$  basis for  $\text{H}_2$ .



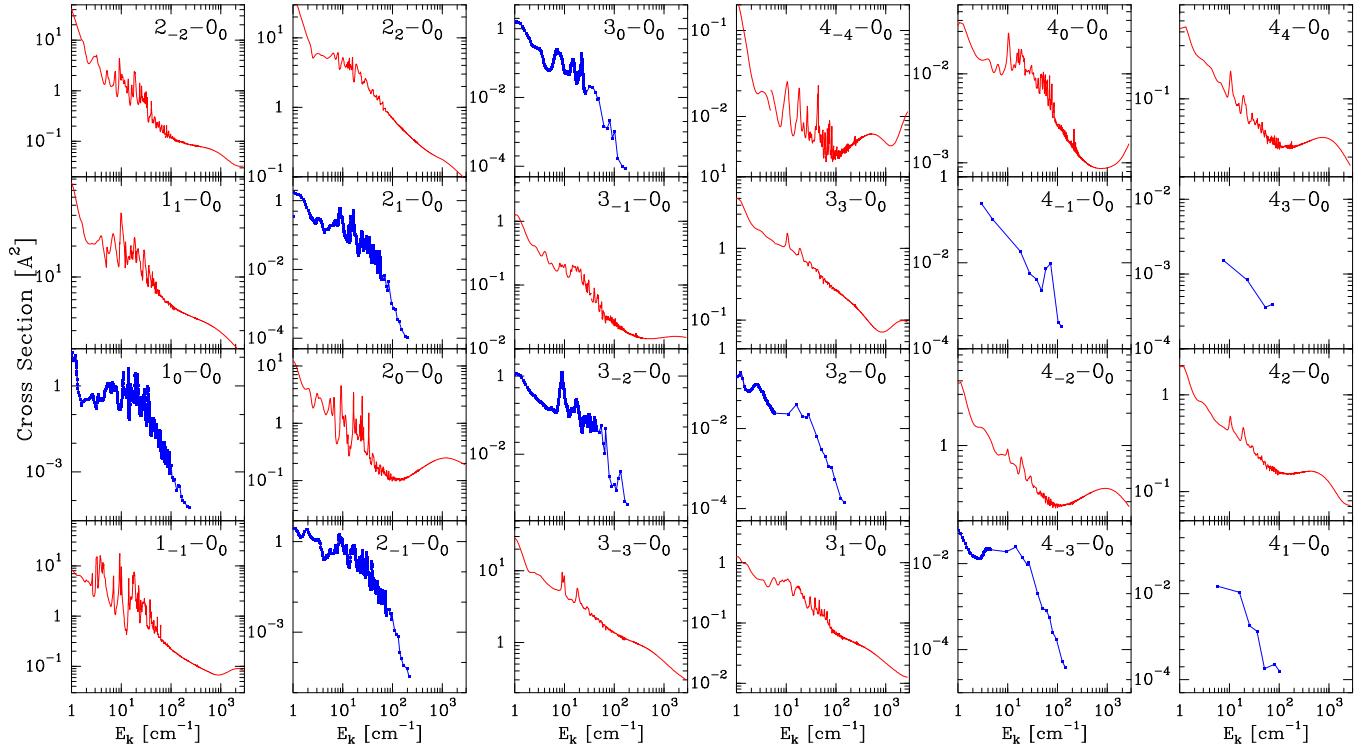
**Figure 2.** Ratio at  $110\text{ cm}^{-1}$  between two approximate sets of cross sections with respect to CC cross sections obtained with a  $J_2 = 0, 2$  basis of  $\text{H}_2$ . The first approximate set (red crosses) corresponds to cross sections obtained with the CS formalism and with a  $J_2 = 0, 2$  basis of  $\text{H}_2$ . The second set (black points) is obtained with the CC formalism but the basis of  $\text{H}_2$  is reduced to  $J_2 = 0$ .

In this example, the total energy is  $110\text{ cm}^{-1}$  but we checked that the conclusions are similar at other values. Considering this figure, it appears that the CS method gives a fairly accurate description of the dynamics, especially for the transitions with the highest cross sections. Indeed, it can be seen that for the transitions with cross sections higher than  $2\text{ \AA}^2$ , the CS method is accurate within a factor  $\sim 1.2$  for most transitions. On the other hand, reducing the basis of the  $\text{H}_2$  molecule with the CC formalism introduces larger errors, up to a factor  $\sim 3$  in this case. We thus made the choice to use the CS approximation to perform the dynamical calculations above  $110\text{ cm}^{-1}$ , since the reduced amount of computational time (typically reduced by a factor 10–20) enables to adopt a fine energy grid. The step between consecutive energies is given in table 1. In order to emphasize on the necessity to resort to an approximate method to perform the dynamical calculations, we note that the total CPU time spent to obtain the rate coefficients was  $\sim 170\,000$  hours ( $\sim 19$  years), a time however substantially reduced by the availability of a cluster of cores (336 cores of 2.26 GHz). Finally, in order to obtain a set of rate coefficients as accurate as possible, we scaled the CS cross sections by performing a few calculations with the CC formalism, up to total energies of  $250\text{ cm}^{-1}$ . These calculations enable to scale the transitions that involve the levels up to  $J_\tau = 4$  and the procedure used to perform the scaling is described in the appendix. The scaled and original CS cross sections are reported in Fig. 3 for a few transitions. Note that as expected from formal criteria (see Heil et al. 1978, and references therein), we observe that the accuracy of the CS formalism increases with the kinetic energy.

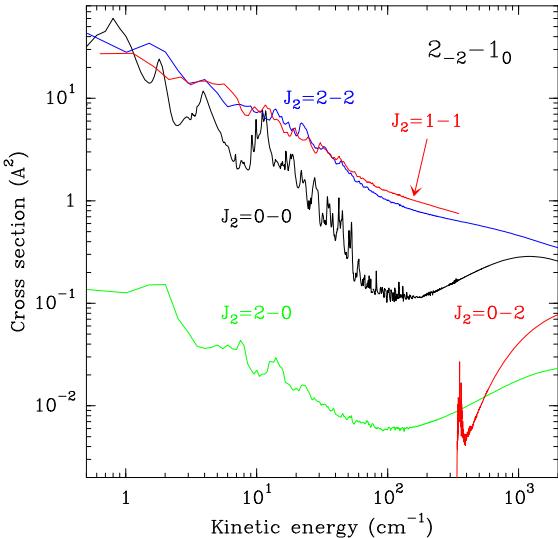
Apart from its accuracy, the CS formalism has the additional drawback that some transitions are predicted to be null while they should not be, which is a consequence of the neglect of small coupling terms. This can be seen in Fig. 2 where a few transitions below  $0.2\text{ \AA}^2$  have ratios equal to zero. The transitions which are predicted to be null with the CS formalism correspond to  $J_\tau \rightarrow 0$  where  $\tau$  ranges from  $-\tau + 1$  to  $\tau - 1$  in a step of 2. The transitions concerned correspond to  $\text{H}_2$  transitions with  $J_2 = 0 \rightarrow 0$ . In Fig. 4, we report the de-excitation transitions connected to the  $0_0$  level for the levels up to  $J_\tau = 4$ . For the transitions with non-null CS cross sections (indicated in red in Fig. 2), the values reported



**Figure 3.** Cross sections as a function of the kinetic energy  $E_k$ . The blue curve corresponds to the CS calculations. The red curve corresponds to the CC calculations, below a total energy of  $110 \text{ cm}^{-1}$  and to the scaled CS calculations above this threshold. The correspondence between this particular value of the total energy and the kinetic energy is indicated for each transitions by a dotted vertical line.



**Figure 4.** Cross sections for the transitions connected to the fundamental energy level and for levels up to  $J_r = 4_4$ . The red curves correspond to CC plus scaled CS cross sections. The blue curves correspond to CC calculations and are truncated in energy since the CS formalism predict null cross sections.



**Figure 5.** Cross sections associated to the  $2_{-2} \rightarrow 1_0$  NH<sub>2</sub>D transition and corresponding to the various  $J_2 \rightarrow J'_2$  H<sub>2</sub> transitions with para-H<sub>2</sub> either in its fundamental state ( $J_2 = 0$ ) or first excited state ( $J_2 = 2$ ). The cross section with ortho-H<sub>2</sub> ( $J_2 = 1 - 1$ ) is also indicated, for a reduced range of kinetic energies.

correspond to the CC and scaled-CS cross sections. For the other transitions (indicated in blue), we report the CC points we calculated. For the latter, we included the reference CC points used to scale the CS cross sections, i.e. for total energies between 110 and 250 cm<sup>-1</sup>, which explains why the step in energy is large for the highest kinetic energies. First, when considering this figure, it is important to notice that the cross sections predicted to be null with the CS formalism are indeed of lower magnitude by comparison with other transitions. Additionally, from the few transitions available, it appears that these cross sections decrease quickly with increasing kinetic energy. As an example, the  $1_0 \rightarrow 0_0$  transition decreases by 4 orders of magnitude between 1 cm<sup>-1</sup> and 110 cm<sup>-1</sup>. Finally, all these transitions seem to share a similar shape. These peculiarities of the null CS cross sections makes it possible to calculate the rate coefficients for the levels up to  $J_\tau = 3_2$ , with a reasonable accuracy up to 300 K, despite the truncation in energy of the grid. This point will be further discussed in the next Section where we also derive analytical formulae which are used to estimate the null  $J_\tau \rightarrow 0_0$  rate coefficients for the levels above  $J_\tau = 3_2$ .

Finally, since we performed calculations with a  $J_2 = 0, 2$  basis for H<sub>2</sub> and since the energy grid was well sampled, the cross sections that involve the excited  $J_2 = 2$  state of H<sub>2</sub> can be used to derive the corresponding rate coefficients. Indeed, the convergence criteria previously discussed also apply to the transitions  $J_2 \rightarrow J'_2$  with either  $J_2$  or  $J'_2$  equal to 2. In Fig. 5, we give a characteristic example of such transitions and show the transitions related to the  $2_{-2} \rightarrow 1_0$  state-to-state transition of NH<sub>2</sub>D and that involve the various possible rotational states of H<sub>2</sub>. From this figure, it appears that the transitions which are inelastic for H<sub>2</sub> are of lower magnitude than the elastic transition, by typically one or two orders of magnitude. Moreover, we find that the  $J_2 = 2 \rightarrow 2$  transitions are larger than the transitions  $J_2 = 0 \rightarrow 0$ . These conclusions apply to the whole set of transitions and were already reached for other molecular systems (see e.g. Dubernet et al. 2009; Daniel et al. 2010, 2011; Wiesenfeld & Faure 2013).

#### 4 RATE COEFFICIENTS

The collisional de-excitation rate coefficients are calculated by averaging the cross sections with a Maxwell–Boltzmann distribution that describes the distribution of velocity of the molecules in the gas (see e.g. eq. (5) in Wiesenfeld et al. 2011). In Table 2, we give the de-excitation rate coefficients for levels up to  $J_\tau = 2_2$ , with  $J_2 = 0 \rightarrow 0$ , and for temperatures in the range T = 5–100K. The way these rates are obtained is further discussed below. This table is directly comparable to Table 7 of Machin & Roueff (2006) where the same quantities are given for the NH<sub>2</sub>D / He system. The whole set of rate coefficients, with higher temperatures and with a more extended set of molecular levels will be made available through the LAMDA (Schöier et al. 2005) and BASECOL (Dubernet et al. 2013) databases.

##### 4.1 Null CS cross sections

As outlined in Section 3, the transitions  $J_\tau \rightarrow 0_0$  where  $\tau$  ranges from  $\tau = -J + 1$  to  $\tau = J - 1$  with a step of 2 are predicted to be equal to zero with the CS formalism. Using the available CC calculations, we are however able to calculate these rate coefficients for the transitions with  $J \leq 3$  and up to 300 K with a reasonable accuracy (see Appendix B). Since the current set of rate coefficients considers levels up to  $J_\tau = 7_7$ , it is necessary to estimate the rate coefficients for the transitions that connect the fundamental energy level to the levels with  $J \geq 4$  which are predicted to be null with the CS formalism. To do so, we extrapolate the behaviour observed for the rates with levels such that  $J < 4$  and derive the following expression :

$$R(J_{\tau_i} \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left(\frac{1}{1.35}\right)^{J-1} \times \left(\frac{1}{2.6}\right)^{i-1} \quad (1)$$

with  $\tau_i = -J + 1 + 2 \times (i - 1)$  ;  $i \in \llbracket 1; n \rrbracket$

and  $n = E\left(\frac{2J+1}{2}\right)$

We can expect large errors of the corresponding rate coefficients, typically of a factor 10 or higher, since this expression is established on the basis of a poor statistics. However, since the corresponding rate coefficients should play only a minor role in the pumping scheme, these uncertainties should not have noticeable consequences on the predicted line intensities. In any astrophysical application, this assumption should however be checked. For example, as was done in Daniel et al. (2013), the sensitivity of the line intensities to the corresponding rate coefficients can be assessed by considering randomly scaled values for these rates around their nominal value.

##### 4.2 Rate coefficients accuracy

The accuracy of the current rate coefficients is limited by the following assumptions. A first source of error comes from the neglect of the inversion motion. However, we expect that this hypothesis should only have marginal effects on the rate coefficients, at least in comparison to the other sources of error. A second limitation comes from the fact that the PES was calculated for the equilibrium geometry of the NH<sub>3</sub> molecule. The PES was corrected for the displacement of the center of mass between NH<sub>3</sub> and NH<sub>2</sub>D, but the variation of the bond length from NH to ND was neglected. The effect introduced by taking into account the vibrationally averaged geometry of NH<sub>2</sub>D, rather than taking the NH<sub>3</sub> internal geometry,

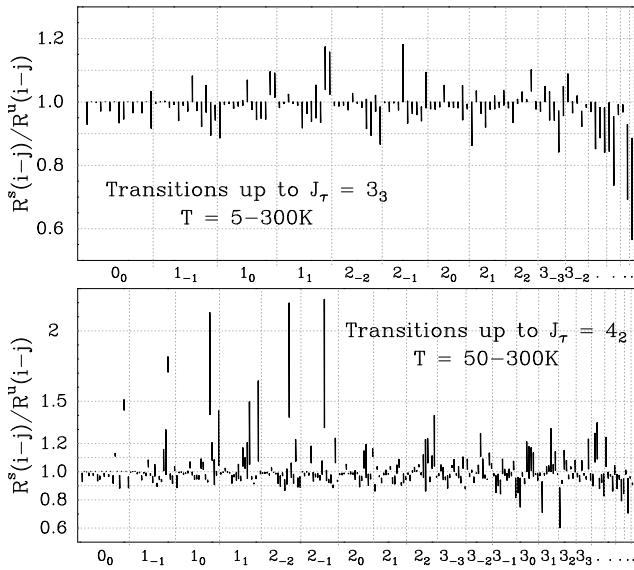
**Table 2.** De-excitation rate coefficients for NH<sub>2</sub>D / H<sub>2</sub> (J<sub>2</sub> = 0-0) as a function of temperature and for NH<sub>2</sub>D levels up to J<sub>T</sub> = 2<sub>2</sub>.

Transition	Rate coefficients (cm <sup>3</sup> s <sup>-1</sup> )					
	5K	10K	25K	50K	75K	100K
1 <sub>0,1</sub> → 0 <sub>0,0</sub>	1.24(-11)	1.17(-11)	9.58(-12)	6.86(-12)	5.41(-12)	4.58(-12)
1 <sub>1,1</sub> → 0 <sub>0,0</sub>	2.00(-12)	2.06(-12)	1.62(-12)	9.69(-13)	6.45(-13)	4.66(-13)
1 <sub>1,1</sub> → 1 <sub>0,1</sub>	1.17(-10)	1.20(-10)	1.16(-10)	1.06(-10)	1.02(-10)	1.01(-10)
1 <sub>1,0</sub> → 0 <sub>0,0</sub>	5.56(-11)	6.65(-11)	7.22(-11)	6.93(-11)	6.79(-11)	6.80(-11)
1 <sub>1,0</sub> → 1 <sub>0,1</sub>	1.46(-11)	1.38(-11)	9.61(-12)	6.05(-12)	4.56(-12)	3.89(-12)
1 <sub>1,0</sub> → 1 <sub>1,1</sub>	1.55(-11)	1.52(-11)	1.16(-11)	8.35(-12)	6.79(-12)	5.90(-12)
2 <sub>0,2</sub> → 0 <sub>0,0</sub>	9.34(-12)	6.89(-12)	4.68(-12)	3.24(-12)	2.62(-12)	2.29(-12)
2 <sub>0,2</sub> → 1 <sub>0,1</sub>	2.76(-11)	2.73(-11)	2.70(-11)	2.61(-11)	2.58(-11)	2.60(-11)
2 <sub>0,2</sub> → 1 <sub>1,1</sub>	1.79(-11)	1.42(-11)	9.32(-12)	5.85(-12)	4.39(-12)	3.70(-12)
2 <sub>0,2</sub> → 1 <sub>1,0</sub>	2.28(-11)	2.17(-11)	1.84(-11)	1.47(-11)	1.30(-11)	1.22(-11)
2 <sub>1,2</sub> → 0 <sub>0,0</sub>	2.00(-12)	1.89(-12)	1.29(-12)	7.45(-13)	4.94(-13)	3.58(-13)
2 <sub>1,2</sub> → 1 <sub>0,1</sub>	7.80(-12)	7.14(-12)	5.16(-12)	3.42(-12)	2.58(-12)	2.14(-12)
2 <sub>1,2</sub> → 1 <sub>1,1</sub>	2.69(-11)	2.71(-11)	2.60(-11)	2.48(-11)	2.46(-11)	2.47(-11)
2 <sub>1,2</sub> → 1 <sub>1,0</sub>	1.25(-11)	1.05(-11)	6.61(-12)	3.85(-12)	2.76(-12)	2.27(-12)
2 <sub>1,2</sub> → 2 <sub>0,2</sub>	9.57(-11)	9.58(-11)	1.05(-10)	1.09(-10)	1.11(-10)	1.13(-10)
2 <sub>1,1</sub> → 0 <sub>0,0</sub>	5.35(-12)	4.60(-12)	3.43(-12)	2.50(-12)	2.14(-12)	2.04(-12)
2 <sub>1,1</sub> → 1 <sub>0,1</sub>	5.38(-11)	5.58(-11)	6.03(-11)	6.10(-11)	6.13(-11)	6.20(-11)
2 <sub>1,1</sub> → 1 <sub>1,1</sub>	2.90(-11)	3.06(-11)	2.92(-11)	2.44(-11)	2.10(-11)	1.88(-11)
2 <sub>1,1</sub> → 1 <sub>1,0</sub>	8.99(-12)	7.69(-12)	5.67(-12)	4.23(-12)	3.57(-12)	3.22(-12)
2 <sub>1,1</sub> → 2 <sub>0,2</sub>	1.48(-11)	1.47(-11)	1.16(-11)	8.26(-12)	6.95(-12)	6.54(-12)
2 <sub>1,1</sub> → 2 <sub>1,2</sub>	2.35(-11)	2.37(-11)	2.33(-11)	2.26(-11)	2.25(-11)	2.28(-11)
2 <sub>2,1</sub> → 0 <sub>0,0</sub>	8.19(-13)	6.91(-13)	4.63(-13)	2.76(-13)	1.87(-13)	1.37(-13)
2 <sub>2,1</sub> → 1 <sub>0,1</sub>	2.36(-11)	2.51(-11)	2.60(-11)	2.27(-11)	1.99(-11)	1.81(-11)
2 <sub>2,1</sub> → 1 <sub>1,1</sub>	5.44(-11)	5.61(-11)	6.01(-11)	6.14(-11)	6.23(-11)	6.35(-11)
2 <sub>2,1</sub> → 1 <sub>1,0</sub>	3.14(-12)	2.78(-12)	2.10(-12)	1.48(-12)	1.21(-12)	1.10(-12)
2 <sub>2,1</sub> → 2 <sub>0,2</sub>	3.05(-11)	2.54(-11)	1.97(-11)	1.66(-11)	1.55(-11)	1.50(-11)
2 <sub>2,1</sub> → 2 <sub>1,2</sub>	2.33(-11)	1.91(-11)	1.31(-11)	9.46(-12)	8.31(-12)	8.10(-12)
2 <sub>2,1</sub> → 2 <sub>1,1</sub>	3.16(-11)	3.87(-11)	4.37(-11)	4.23(-11)	4.12(-11)	4.09(-11)
2 <sub>2,0</sub> → 0 <sub>0,0</sub>	1.63(-11)	1.58(-11)	1.43(-11)	1.21(-11)	1.06(-11)	9.73(-12)
2 <sub>2,0</sub> → 1 <sub>0,1</sub>	6.02(-12)	5.20(-12)	4.03(-12)	3.11(-12)	2.68(-12)	2.46(-12)
2 <sub>2,0</sub> → 1 <sub>1,1</sub>	3.85(-12)	3.24(-12)	2.46(-12)	1.87(-12)	1.63(-12)	1.57(-12)
2 <sub>2,0</sub> → 1 <sub>1,0</sub>	7.38(-11)	7.42(-11)	7.48(-11)	7.43(-11)	7.48(-11)	7.60(-11)
2 <sub>2,0</sub> → 2 <sub>0,2</sub>	2.24(-11)	1.98(-11)	1.57(-11)	1.20(-11)	1.00(-11)	8.82(-12)
2 <sub>2,0</sub> → 2 <sub>1,2</sub>	1.57(-11)	1.72(-11)	1.88(-11)	1.85(-11)	1.82(-11)	1.82(-11)
2 <sub>2,0</sub> → 2 <sub>1,1</sub>	1.33(-11)	1.25(-11)	8.88(-12)	5.83(-12)	4.48(-12)	3.84(-12)
2 <sub>2,0</sub> → 2 <sub>2,1</sub>	9.50(-12)	8.68(-12)	9.44(-12)	9.41(-12)	9.05(-12)	8.78(-12)

can lead to noticeable effects. Such a modification was tested for D<sub>2</sub>O by Scribano et al. (2010), where rate coefficients for this isotope were calculated using the H<sub>2</sub>O internal geometry. Differences of the order of 30% were found and we might expect differences of the same order for NH<sub>2</sub>D. Finally, a third source of error resides in the use of the CS formalism at high temperatures. As described in Sec. 3 and in Appendix A, the CS calculations were scaled according to some reference calculations performed with the CC formalism. However, an inherent limitation of this procedure comes from the uncertainty introduced by the scattering of the ratios which are due to the resonances. Moreover, the ratios were extrapolated at the highest energies. Finally, for the transitions that involve energy levels higher than the 4<sub>2</sub> level, we directly computed the rate coefficients using the original CS cross sections.

In order to have an estimate of the error introduced in the rate coefficients due to the use of the CS formalism, we compared the rate coefficients calculated with the scaled CS cross sections (noted  $R^s(i \rightarrow j)$ ) to the rates calculated with the unscaled cross

sections (noted  $R^u(i \rightarrow j)$ ). The minimum and maximum values of the ratios  $R^s(i \rightarrow j)/R^u(i \rightarrow j)$  found in the range  $T = 5 - 300$  K are reported in the upper panel of Fig. 6 for all the de-excitation transitions up to  $J_T = 3_3$ . In the lower panel of this figure, we report the same quantities, but for levels up to  $J_T = 4_2$  and for the temperature range  $T = 50 - 300$  K. From this figure, it can be seen that for the transitions that involve levels up to the 3<sub>-1</sub> (E~75 cm<sup>-1</sup>), the scaled and unscaled rate coefficients differ by less than 20% (upper panel). On the other hand, for higher energy levels, the differences can be as high as a factor ~2 but most of the transitions (93% of the 253 transitions considered here) show differences below a factor 1.3. We note that the reason why the lowest energy levels are less affected by the scaling of the cross sections comes from the fact that a larger part of the grid correspond to CC calculations for these levels. Finally, given the variations observed for the  $R^s(i \rightarrow j)/R^u(i \rightarrow j)$  ratios, we can expect that the transitions that involve an energy level above  $J_T = 4_2$  will have a typical accuracy of 30%, since these transitions



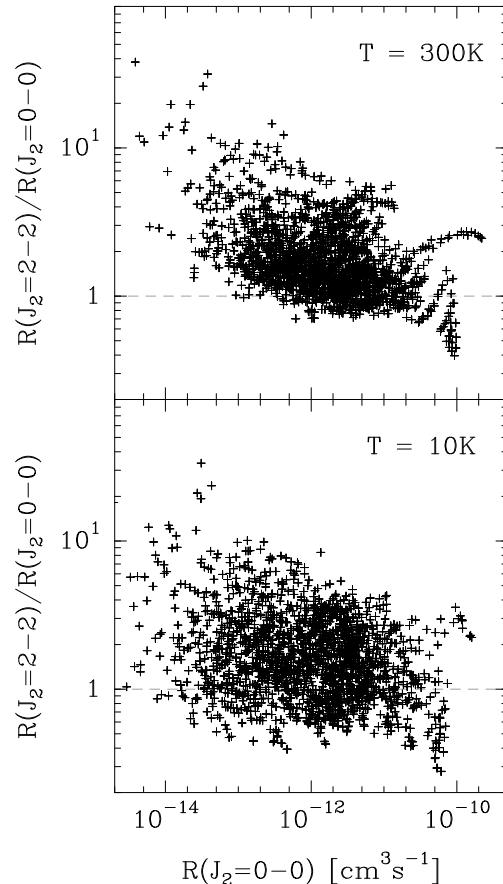
**Figure 6.** **Upper panel:** range of the variations found in the temperature range  $T = 5 - 300$  K, between the scaled and unscaled collisional rate coefficients for the levels up to  $J_\tau = 3_3$ . The x-axis gives the final level of the de-excitation collisional rate coefficient. For each final level, the variations are given for all the de-excitation rates, ordered by increasing value of the upper energy level state. **Lower panel:** same as the upper panel but for the transitions which consider levels up to  $J_\tau = 4_2$  and for the temperature range  $T = 50 - 300$  K.

are directly calculated from the CS cross sections.

To summarize the previous considerations, considering the current PES, we expect that the current rate coefficients will be accurate within 5% for the transitions up to  $J_\tau = 4_2$ . For higher energy levels, the accuracy should be of the order of 30%. This holds true for all transitions except for the transitions  $J_\tau \rightarrow 0_0$  where  $\tau$  ranges from  $\tau = -J + 1$  to  $\tau = J - 1$  with a step of 2. For these transitions and for the levels such that  $J < 4$ , the rates should be accurate to within 30%. For higher levels, i.e. with  $J \geq 4$ , we can expect an error up to a factor 10 in the rate coefficients. Most importantly, a dominant source of error resides in the fact that the PES was calculated for a molecular geometry which corresponds to the NH<sub>3</sub> internal geometry. Thus, we might expect an additional 30% uncertainty on the rate coefficients (Scribano et al. 2010).

#### 4.3 Thermalized rate coefficients

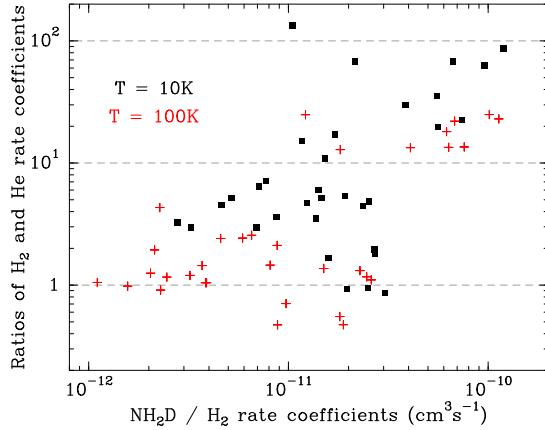
The previous discussion dealt with rate coefficients where para-H<sub>2</sub> was restricted to its fundamental state  $J_2 = 0$ . Such rate coefficients are enough to tackle astrophysical applications that deal with cold media (i.e.  $T < 50$ K). However, at higher gas temperatures, we expect a larger fraction of the H<sub>2</sub> molecules in excited states ( $J_2 > 0$ ). As discussed in Sec. 3, the cross sections with  $J_2 = 2 \rightarrow 2$  are of larger magnitude than the cross sections associated with the  $J_2 = 0 \rightarrow 0$  transitions. This is shown in Fig. 7 where we represent the ratio of the rate coefficients with  $J_2 = 2 \rightarrow 2$  to that with  $J_2 = 0 \rightarrow 0$ , for temperatures of 10 and 300K. On average, the rate coefficients with  $J_2 = 2 \rightarrow 2$  are of larger magnitude, with an average ratio slightly increasing from 2 to 2.4 with temperature increasing from 10K to 300K. However, as can be seen



**Figure 7.** Ratio of the rate coefficients associated to the  $J_2 = 2 \rightarrow 2$  over the rate with  $J_2 = 0 \rightarrow 0$ , as a function of the magnitude of the rate coefficients associated to the para-H<sub>2</sub> fundamental state. The ratios are given at T= 10 K (lower panel) and T = 300K (upper panel).

from Fig. 7, the variation in magnitude of the rate coefficient depends on the absolute magnitude of the rate, the variation being larger for the rates of lower magnitude. Moreover, as seen in Fig. 7, there is a large scatter of the ratios. Thus, by varying the relative populations of the fundamental and first H<sub>2</sub> excited states, the number of collisionally induced events will be modified accordingly, i.e. the number of events becomes larger with increasing the fractional abundance of the first excited state. To take this effect into account, we define thermalized rate coefficients, following the definition given in Dubernet et al. (2009) (i.e. Eq. (4) in this reference).

Finally, we stress that in hot media, the relevant collisional partner will be ortho-H<sub>2</sub> rather than para-H<sub>2</sub> and in such a case, it should be necessary to calculate the corresponding rate coefficients. However, in the case of the H<sub>2</sub>O / H<sub>2</sub> collisional system it was found that the effective rate coefficients for  $J_2 = 2$  and  $J_2 = 1$  agree within ~30% (Dubernet et al. 2009; Daniel et al. 2010, 2011). More generally, these studies showed that apart from the rate coefficients in  $J_2 = 0$ , all the effective rate coefficients with  $J_2 > 0$  are qualitatively similar, independently of the H<sub>2</sub> symmetry. As a consequence, in astrophysical applications, the thermalized rate coefficients with ortho-H<sub>2</sub> or para-H<sub>2</sub> lead to similar line intensities at high temperatures (Daniel et al. 2012). To conclude, this means that in principle, the rate coefficients with  $J_2 = 2 \rightarrow 2$  can serve as a template to emulate the rate coefficients of ortho-H<sub>2</sub> ( $J_2 = 1 \rightarrow 1$ ). We checked this assumption by performing a few calculations with



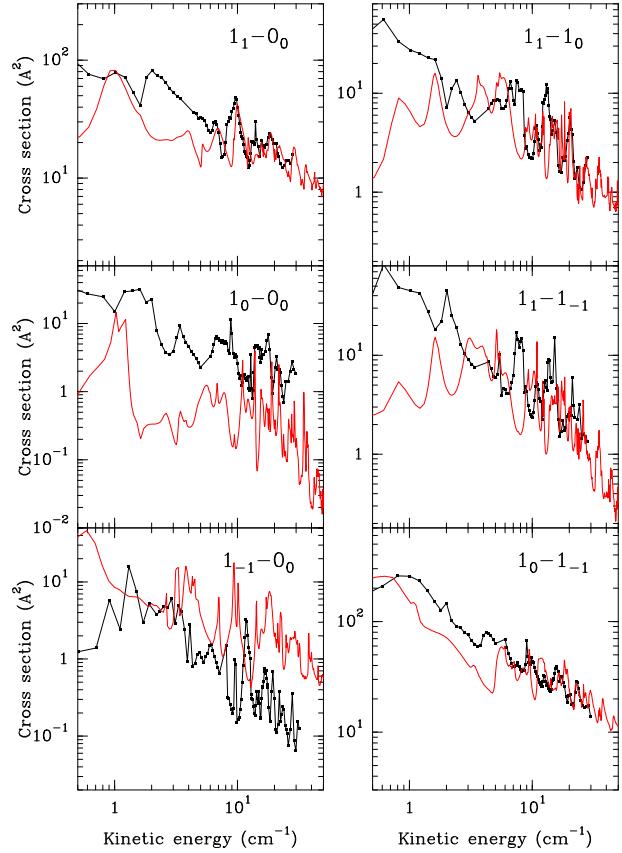
**Figure 8.** Comparison between the current  $\text{NH}_2\text{D} / \text{H}_2$  rate coefficients with the rates calculated with He as a collisional partner (Machin & Roueff 2006).

ortho– $\text{H}_2$  as a collisional partner. In Fig. 5, we compare the cross sections of the  $2_{-2} - 1_0$  transition associated with either  $J_2 = 2 \rightarrow 2$  or  $J_2 = 1 \rightarrow 1$ . It can be seen that these two cross sections are qualitatively similar for the energy range considered here. Such an agreement is also found on a more general basis. Considering a statistics over the  $i \rightarrow j$  transitions, we obtained that, whatever the energy, the mean value  $\mu$  of the ratios  $\sigma_{ij}(2 \rightarrow 2)/\sigma_{ij}(1 \rightarrow 1)$  is  $\mu \sim 1$ , with a standard deviation  $\sigma$  that vary with energy in the range  $\sigma = 0.15 - 0.30$ . For each energy,  $\sim 70\%$  of the transitions vary by less than  $1\sigma$  around  $\mu$  and  $\sim 95\%$  of the transitions are within  $2\sigma$ . Thus, this confirms that the rate coefficients in  $J_2 = 2 \rightarrow 2$  are a good approximation for the ortho– $\text{H}_2$  rate coefficients.

## 5 DISCUSSION

Prior to this work, the only available rate coefficients for  $\text{NH}_2\text{D}$  were calculated with He as a collisional partner. Rate coefficients with He are often used as a template to estimate the rate coefficients with  $\text{H}_2$ . However, for many molecules, large differences exist and the rates do not scale accordingly to the factor  $\sim 1.4$  deduced from the difference in the reduced masses of the two colliding systems. Concerning the deuterated isotopologues of ammonia, such a conclusion was already reached for  $\text{ND}_2\text{H}$ . Indeed, for this particular isotopologue, the He and  $\text{H}_2$  rate coefficients were found to vary by factors in the range 3–30 (Machin & Roueff 2007; Wiesenfeld et al. 2011). In Fig. 8, we give the ratios of the current  $\text{NH}_2\text{D} / \text{H}_2$  rate coefficients with the rates calculated with He (Machin & Roueff 2006), as a function of the magnitude of the  $\text{H}_2$  rate coefficients and for temperatures of  $T = 10\text{K}$  and  $T = 100\text{K}$ . The comparison concerns the transitions that involve levels up to  $J_\tau = 2_2$  (the highest level considered in Machin & Roueff 2006). From this figure, it appears that the  $\text{H}_2$  and He rate coefficients show large variations, as expected from the previous studies of  $\text{ND}_2\text{H}$ . At  $T = 10\text{K}$ , the ratios are in the range 1–100. Moreover, it appears that the largest differences are also found for the largest rate coefficients. At higher temperatures, we obtain the same trend except that the range of variations is reduced. For example, at  $T = 100\text{K}$ , the ratios for the lowest rate coefficients are around 1 while they are around 20 for the highest rates.

Finally, one may wonder if it is possible to infer the rate co-



**Figure 9.** Comparison between the  $\text{NH}_2\text{D}$  (red) and  $\text{ND}_2\text{H}$  (black) cross sections calculated with  $\text{H}_2$  ( $J_2 = 0, 2$ ).

efficients of singly deuterated ammonia from the rates of doubly deuterated ammonia, or vice-versa. A direct comparison of the current rates with the values reported by Wiesenfeld et al. (2011) for  $\text{ND}_2\text{H} / \text{H}_2$  would not be totally meaningful, at least quantitatively, since in the latter study, the dynamical calculations were performed with a  $J_2 = 0$  basis for  $\text{H}_2$ . As discussed in Sec. 3, considering a  $J_2 = 0, 2$  basis for  $\text{H}_2$  can induce variations as large as a factor  $\sim 7$  and the magnitude of the effects are presumably similar for  $\text{ND}_2\text{H}$ . We thus performed a few additional calculations for the  $\text{ND}_2\text{H} / \text{H}_2$  system. These calculations are similar to the ones presented in Wiesenfeld et al. (2011) except for the  $\text{H}_2$  basis which is now set to  $J_2 = 0, 2$ . In Fig. 9, we compare the cross sections of  $\text{NH}_2\text{D}$  and  $\text{ND}_2\text{H}$  for the six de-excitation transitions possible when considering the levels up to  $J_\tau = 1_1$ . From this figure, it appears that on the average, the cross sections are of the same order of magnitude for the two colliding systems. The differences are definitely lower than those found with He as a collisional partner. However, above  $5 \text{ cm}^{-1}$ , differences of a factor  $\sim 3$  or higher may occur when considering individual transitions. This implies that a dedicated calculation is necessary to infer accurate rate coefficients for a particular isotopologue. Furthermore, given the differences obtained between the rate coefficients calculated with  $\text{H}_2$  or He, the current comparison shows that in the absence of a dedicated calculation, the rate coefficients of a deuterated isotopologue should be preferentially taken from another isotopologue with the same symmetry rather than scaled from the He rates. As an example, to emulate the  $\text{CD}_2\text{H} / \text{H}_2$  rate coefficients, it should be more accurate to take the  $\text{CH}_2\text{D} / \text{H}_2$  rate coefficients than the  $\text{CD}_2\text{H} / \text{He}$  one.

## 6 CONCLUSIONS

We reported the calculation of collisional rate coefficients for the NH<sub>2</sub>D / H<sub>2</sub> system for NH<sub>2</sub>D rotational energy levels up to  $J_\tau = 7_7$  ( $E \sim 735\text{K}$ ) and for temperatures in the range T = 5–300K. These rate coefficients will be made available through the BASECOL (Dubernet et al. 2013) and LAMDA (Schöier et al. 2005) databases. The current rate coefficients were calculated by adapting the NH<sub>3</sub> / H<sub>2</sub> potential energy surface presented in Maret et al. (2009). The dynamical calculations were performed at the close-coupling level at low total energy ( $E < 110\text{ cm}^{-1}$ ) and with the coupled-states formalism at higher energies. For the levels up to  $J_\tau = 4_2$  the CS cross sections were scaled according to some reference points performed with the accurate CC formalism. For these transitions and for the current PES, the accuracy of the rate coefficients is expected to be of the order of 5%. For higher energy levels, the accuracy is limited by the use of the CS formalism, and the corresponding rate coefficients are expected to be accurate within 30%. These uncertainties concern all the transitions except the  $J_\tau \rightarrow 0_0$  transitions with  $J_\tau$  varying from  $-J+1$  to  $J-1$  in a step of two. For these latter transitions, we expect the rate coefficients to be accurate within 30% for the levels with  $J \leq 3$  while for the levels such that  $J \geq 4$ , the rate coefficients have uncertainties of the order of a factor 10. We note that these errors only consider the accuracy of the dynamical calculations and do not take into account other sources of uncertainty like the accuracy of the PES or the neglecting of the inversion motion. For what concerns the PES, we might expect an additional 30% uncertainty on the rate coefficients, which is to be added in quadrature to the previously mentioned uncertainties, since the current PES was calculated for an internal geometry suitable to NH<sub>3</sub>.

## ACKNOWLEDGMENTS

All (or most of) the computations presented in this paper were performed using the CIMENT infrastructure (<https://ciment.ujf-grenoble.fr>), which is supported by the Rhône-Alpes region (GRANT CPER07\_13 CIRA: <http://www.ci-ra.org>). D.L. support for this work was provided by NASA (*Herschel* OT funding) through an award issued by JPL/Caltech. This work has been supported by the Agence Nationale de la Recherche (ANR-HYDRIDES), contract ANR-12-BS05-0011-01 and by the CNRS national program “Physico-Chimie du Milieu Interstellaire”.

## REFERENCES

- Busquet, G., Palau, A., Estalella, R., et al. 2010, A&A, 517, L6  
 Cohen, E. A., & Pickett, H. M. 1982, Journal of Molecular Spectroscopy, 93, 83  
 Coudert, L., Valentin, A., & Henry, L. 1986, Journal of Molecular Spectroscopy, 120, 185  
 Coudert, L. H., & Roueff, E. 2006, A&A, 449, 855  
 Daniel, F., Dubernet, M.-L., Pacaud, F., & Grosjean, A. 2010, A&A, 517, A13  
 Daniel, F., Dubernet, M.-L., & Grosjean, A. 2011, A&A, 536, A76  
 Daniel, F., Goicoechea, J. R., Cernicharo, J., Dubernet, M.-L., & Faure, A. 2012, A&A, 547, A81  
 Daniel, F., Gérin, M., Roueff, E., et al. 2013, A&A, 560, A3  
 Dubernet, M.-L., Daniel, F., Grosjean, A., & Lin, C. Y. 2009, A&A, 497, 911  
 Dubernet, M.-L., Alexander, M. H., Ba, Y. A., et al. 2013, A&A, 553, A50  
 Faure, A., Valiron, P., Wernli, M., et al. 2005, JCP, 122, 221102  
 Hatchell, J. 2003, A&A, 403, L25  
 Heil, T. G., Kouri, D. J., & Green, S. 1978, JCP, 68, 2562  
 Huber, K. P., Herzberg, G., Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules, van Nostrand, New York, 1979  
 Machin, L., & Roueff, E. 2006, A&A, 460, 953  
 Machin, L., & Roueff, E. 2007, A&A, 465, 647  
 Maret, S., Faure, A., Scifoni, E., & Wiesenfeld, L. 2009, MNRAS, 399, 425  
 McGuire, P., & Kouri, D. J. 1974, JCP, 60, 2488  
 Müller, H. S. P., Thorwirth, S., Roth, D. A., & Winnewisser, G. 2001, A&A, 370, L49  
 Neill, J. L., Crockett, N. R., Bergin, E. A., Pearson, J. C., & Xu, L.-H. 2013, ApJ, 777, 85  
 Olberg, M., Bester, M., Rau, G., et al. 1985, A&A, 142, L1  
 Pillai, T., Wyrowski, F., Hatchell, J., Gibb, A. G., & Thompson, M. A. 2007, A&A, 467, 207  
 Rist, C. & Faure, A., 2011, J. Math. Chem., 50, 588  
 Rodriguez Kuiper, E. N., Kuiper, T. B. H., & Zuckerman, B. 1978, ApJL, 219, L49  
 Roueff, E., Lis, D. C., van der Tak, F. F. S., Gerin, M., & Goldsmith, P. F. 2005, A&A, 438, 585  
 Saito, S., Ozeki, H., Ohishi, M., & Yamamoto, S. 2000, ApJ, 535, 227  
 Schöier, F. L., van der Tak, F. F. S., van Dishoeck, E. F., & Black, J. H. 2005, A&A, 432, 369  
 Scribano, Y., Faure, A., & Wiesenfeld, L. 2010, JCP, 133, 231105  
 Shah, R. Y., & Wootten, A. 2001, ApJ, 554, 933  
 Tiné, S., Roueff, E., Falgarone, E., Gerin, M., & Pineau des Forêts, G. 2000, A&A, 356, 1039  
 Turner, B. E., Zuckerman, B., Morris, M., & Palmer, P. 1978, ApJL, 219, L43  
 Walmsley, C. M., Hermsen, W., Henkel, C., Mauersberger, R., & Wilson, T. L. 1987, A&A, 172, 311  
 Wiesenfeld, L., Scifoni, E., Faure, A., & Roueff, E. 2011, MNRAS, 413, 509  
 Wiesenfeld, L., & Faure, A. 2013, MNRAS, 432, 2573

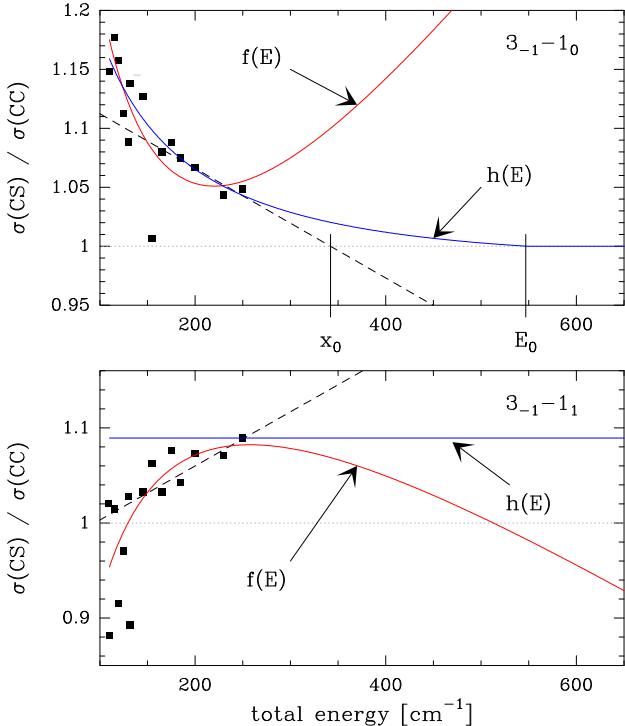
## APPENDIX A: SCALING OF THE CS CROSS-SECTIONS

In order to obtain accurate cross sections, we scaled the CS cross sections according to a few calculations performed with the CC formalism. These CC calculations were performed for total energies in the range  $110\text{ cm}^{-1} < E < 250\text{ cm}^{-1}$ . The ratio of the CC and CS cross sections is reported in Fig. A2 for a few transitions. In order to correct the CS cross sections, we performed an analytical fit of the ratio and to that purpose, we used two fitting functions :

$$f(E) = \sum_{i \in \{1,3\}} a_i E^{i-2} \quad (\text{A1})$$

$$g(E) = \sum_{i \in \{1,3\}} a_i E^{i-2} + a_4 e^{-0.1 E} \quad (\text{A2})$$

where  $E$  corresponds to the total energy. The latter functional form was used to reproduce the oscillating behaviour seen in some transitions (like e.g. the transitions  $2_{-1}-1_{-1}$ ,  $3_0-1_{-1}$  or  $3_0-2_0$  shown in Fig. A2). The choice of the functional form is made automatically, and for a given transition the function  $g(E)$  is selected as soon as



**Figure A1.** Extrapolation of the CS / CC ratios (see text for details).

the  $\chi^2$  obtained with this function is lower by at least a factor 3 by comparison to the  $\chi^2$  obtained with the function  $f(E)$ .

Considering the behaviour of the ratios reported in Fig. A2, it appears that the ratios depend on the total energy and, in most cases, tend to get close to 1 at the highest energies. Since we are interested in scaling the cross sections up to  $\sim 3000 \text{ cm}^{-1}$ , we extrapolate the ratios at energies higher than  $250 \text{ cm}^{-1}$ . To do so, we proceed as follow. We first fit a linear function using the ratios obtained at the highest energies. This leads to two possible behaviours depending on the energy where the resulting line crosses the  $y = 1$  axis (denoted  $x_0$  in what follows). In the first case,  $x_0 > 250 \text{ cm}^{-1}$ , and we then use the  $f(E)$  functional form to extrapolate the ratios at high energy. In the fitting procedure, we put as an additional constraint that the ratio is 1 at  $E_0 = 1.5 x_0$ . Above  $E_0$ , the ratio is set to one. In the second case,  $x_0 < 250 \text{ cm}^{-1}$ . In this case, we fix the ratio above  $250 \text{ cm}^{-1}$  and keep the value obtained at this latest energy. This extrapolation procedure thus gives the function  $h(E)$ . These two cases are illustrated in Fig. A1 where we show the result of the fitting procedure for the  $3_1 - 1_0$  transition (case 1) and  $3_1 - 1_1$  transition (case 2).

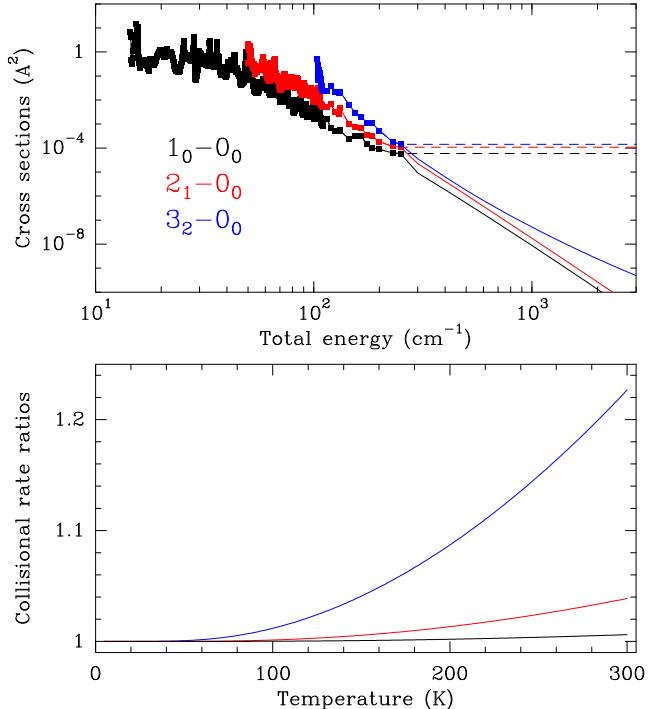
Finally, to insure the continuity between the two fitting functions, we define the function  $\phi(E)$ , which gives the correction of the CS cross sections in the range  $110 < E < 3000 \text{ cm}^{-1}$ :

$$\phi(E) = f(E) \text{ or } g(E) \quad \text{if } E < 170 \text{ cm}^{-1} \quad (\text{A3})$$

$$\phi(E) = (1-w)f(E) + w h(E) \quad \text{if } 170 < E < 250 \text{ cm}^{-1} \quad (\text{A4})$$

$$\phi(E) = h(E) \quad \text{if } E > 250 \text{ cm}^{-1} \quad (\text{A5})$$

where  $w$  is a weighting function that vary linearly between 0 and 1 in the range  $170 < E < 250 \text{ cm}^{-1}$ . The resulting fit is shown in Fig. A2 for a few transitions which are characteristic of the behaviour observed on the whole sample of transitions.

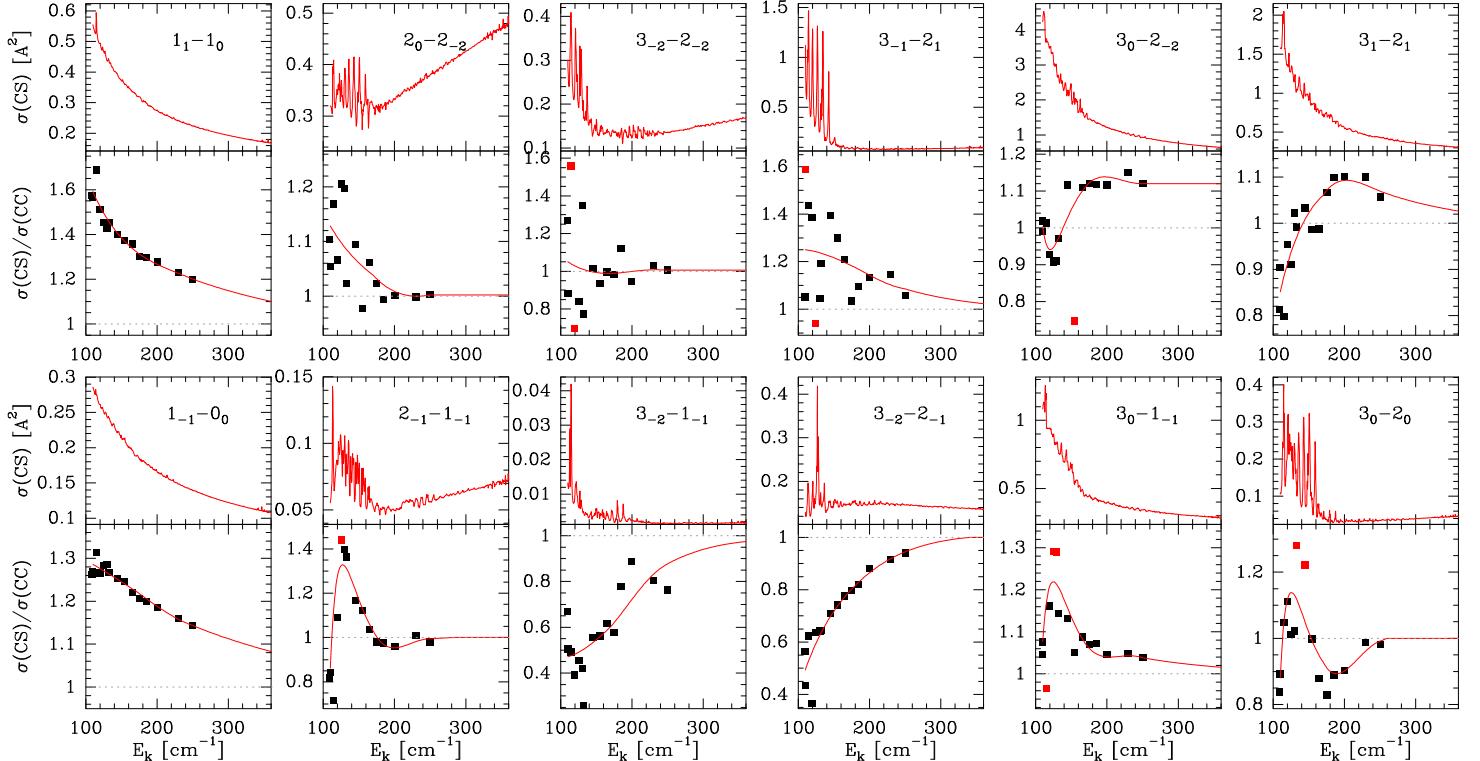


**Figure B1.** The upper panel gives the CC cross sections of the  $1_0 \rightarrow 0_0$ ,  $2_1 \rightarrow 0_0$  and  $3_2 \rightarrow 0_0$  transitions as a function of the total energy. The plain curves correspond to an extrapolation of these cross section based on a polynomial fit. The dashed curves, which assume constant values above  $250 \text{ cm}^{-1}$ , would correspond to an upper limit of the cross sections at high energies. The lower panel give the ratios of the rate coefficients obtained with the two extrapolations considered in the upper panel (same color code).

## APPENDIX B: NULL CS CROSS SECTIONS

As outlined in Section 3 and 4, the transitions  $J_\tau \rightarrow 0_0$  where  $\tau$  ranges from  $\tau = -J+1$  to  $\tau = J-1$  in a step of 2 are predicted to be equal to zero with the CS formalism. Since we performed CC calculations below  $110 \text{ cm}^{-1}$  with some additional points between  $110$  and  $250 \text{ cm}^{-1}$ , we are however able to calculate the rate coefficients for a few of these transitions and up to  $300 \text{ K}$ , despite the lack of calculated points above  $250 \text{ cm}^{-1}$ . This is due to the fact that the corresponding cross sections decrease sharply with the kinetic energy. This is illustrated in Fig. B1 for the  $1_0 \rightarrow 0_0$ ,  $2_1 \rightarrow 0_0$  and  $3_2 \rightarrow 0_0$  transitions. The upper panel in this figure shows the available CC points as well as two possible extrapolations of the cross sections above  $250 \text{ cm}^{-1}$ . The first extrapolation is obtained using a polynomial fit of the CC cross sections (plain curves) while the second way of extrapolating takes a constant value for the cross sections above a total energy of  $250 \text{ cm}^{-1}$  (dashed curves). These two limiting cases seem reasonable in view of the overall behaviour of the cross sections shown in Fig. 4. Using these two extrapolations, we then calculated the corresponding rate coefficients for  $T = 5 - 300 \text{ K}$  and their ratios are indicated in the bottom panel of Fig. B1. It can be seen that for these transitions, the rate coefficients are identical, within 2%, below  $T = 100 \text{ K}$ . For larger temperatures, we obtain larger differences, the discrepancies being the highest at  $300 \text{ K}$ . However, the variations are always below 25% and this conclusion holds true for the 7 transitions that consider the levels below the  $J_\tau = 3_2$  level.

Since the current set of rate coefficients considers levels up to  $J = 7$ , it is necessary to complete the current set. To do so, we



**Figure A2.** In each panel, the upper plot shows the unscaled CS cross sections in  $\text{\AA}^2$ . In the lower plot, the black dots correspond to the ratios of the CC and CS cross sections and the red curves show a fit of these ratios.

extrapolate the behaviour observed for the rates with levels such that  $J < 4$ . In Fig. B2, we show the various rate coefficients calculated for the levels up to  $J_\tau = 3_3$ . First, as can be seen in Fig. 4, the rate coefficients associated with the transitions predicted to be null with the CS formalism are systematically of lower magnitude than the rates of the other transitions. Thus, they should presumably play a minor role in the radiative transfer calculations. Moreover, all these transitions show a similar trend with temperature and are roughly proportional. As a consequence, it is possible to mimic the rate of a given transition using the rate coefficient, for example, of the  $1_0 \rightarrow 0_0$  transition. The dotted curves in Fig. B2, for the transitions from  $J = 2$  and  $J = 3$ , are approximated in this way by using the analytical expressions:

$$R(2_{-1} \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left(\frac{1}{1.3}\right) \quad (\text{B1})$$

$$R(2_1 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left(\frac{1}{1.3}\right) \times \frac{1}{2.45} \quad (\text{B2})$$

$$R(3_{-2} \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left(\frac{1}{1.4}\right)^2 \quad (\text{B3})$$

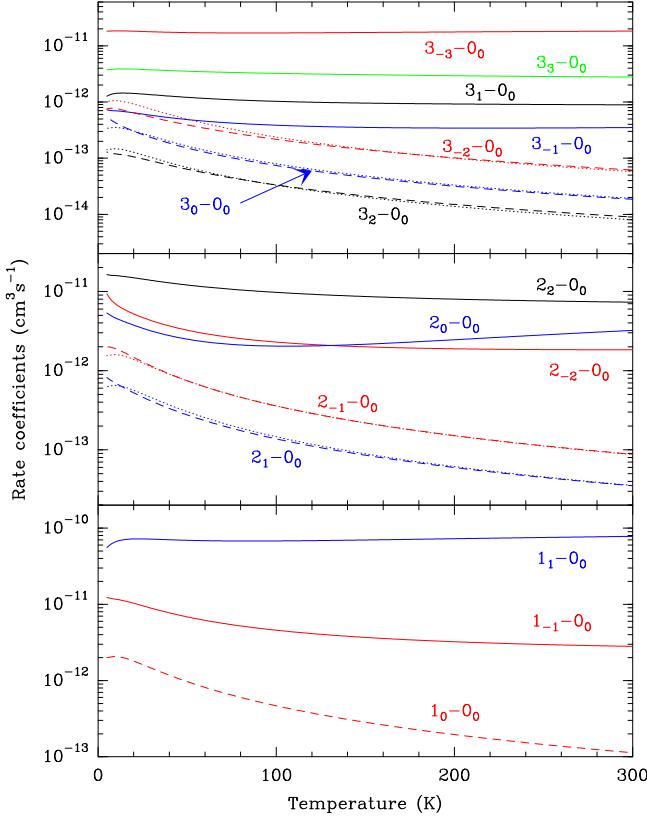
$$R(3_0 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left(\frac{1}{1.4}\right)^2 \times \frac{1}{3} \quad (\text{B4})$$

$$R(3_2 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left(\frac{1}{1.4}\right)^2 \times \frac{1}{3} \times \frac{1}{2.4} \quad (\text{B5})$$

It can be seen in Fig. B2 that this simple scaling of the  $1_0 \rightarrow 0_0$  rate coefficient can reproduce qualitatively the rate coefficients directly obtained from the integration of the cross sections (dashed curves).

From this trend, we can generalize the above equations and the resulting expression corresponds to Eq. (1) of Sections 4.

This paper has been typeset from a  $\text{\TeX}$  /  $\text{\LaTeX}$  file prepared by the author.



**Figure B2.** Rate coefficients for the transitions connecting the levels from  $J = 1$  (lower panel),  $J = 2$  (middle panel) and  $J = 3$  (upper panel) to the fundamental energy level. The transitions for which the CS formalism predict non null rate coefficients are indicated in plain curves. For the other transition for which the CS formalism predict null cross sections, the dashed curves correspond to the rate coefficients calculated from the available CC points. In the latter case, for the transitions from  $J = 2$  and  $J = 3$ , we also show rate coefficients which are scaled from the  $1_0 \rightarrow 0_0$  transition (dotted curves).