Collisonal excitation of singly deuterated ammonia NH$_2$D by H$_2$.

F. Daniel$^1$*, A. Faure$^1$, L. Wiesenfeld$^1$, E. Roueff$^2$, D.C. Lis$^{3,4}$, P. Hily–Blant$^1$*

$^1$IPAG, Observatoire de Grenoble, Université Joseph Fourier, CNRS UMR5571, B.P. 53, 38041 Grenoble Cedex 09, France
$^2$LERMA and UMR 8112, Observatoire de Paris, Place J. Janssen, 92190 Meudon, France
$^3$Sorbonne Universités, Université Pierre et Marie Curie, Paris 6, CNRS, Observatoire de Paris, UMR 8112, LERMA, Paris, France
$^4$California Institute of Technology, Cahill Center for Astronomy and Astrophysics 301-17, Pasadena, CA 91125, USA

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ABSTRACT

The availability of collisional rate coefficients with H$_2$ 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$_2$D / para–H$_2$(Jr = 0, 2) collisional system, for energy levels up to Jr = 7 (E$_a$=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 Jr = 4$_2$ (E$_a$=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 Jr = 4$_2$, while we estimate an accuracy of 30% for higher levels.

Key words: molecular data – molecular processes – scattering

1 INTRODUCTION

Singly deuterated ammonia, NH$_2$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$_2$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. 2004; Saito et al. 2006; 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 deuteron fractionation was derived to be several 10$^{-2}$. 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$_2$D has been detected at much higher frequencies thanks to Herschel. In Orion KL [Neill et al. 2013], several excited levels of NH$_2$D up to Jr,Kr = 7$_3$ (E$_a$=600 K) 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$_2$) = 10$^7$ -10$^9$ cm$^{-3}$.

In order to interpret the NH$_2$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$_2$H that the rate coefficients with He and H$_2$ can differ by factors 3–30, depending on the transition [Machin & Roueff 2007; Wiesenfeld et al. 2011]. Thus, a dedicated calculation for NH$_2$D with H$_2$ 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$_2$D / He rate coefficients is insufficient to accurately model the observations, at least under cold dark clouds conditions.

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

* E-mail: fabien.daniel@obs.ujf-grenoble.fr

$^1$ NH$_2$D is an asymmetric top whose rotational energy structure can be described with the $J$, $K_a$, $K_c$ quantum numbers. Alternatively, one may use the pseudo quantum number $\tau = K_a - K_c$. In what follows, we mainly use the $J_a$ notation to describe the rotational energy levels but can alternatively make use of the $K_a, K_c$ 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$_2$D-H$_2$ potential energy surface (PES) was derived from the NH$_2$H$_2$ PES computed by [Maret et al. (2009)], but in the principal inertia axes of NH$_2$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$_2$D. In the original NH$_2$H$_2$ PES, the ammonia and hydrogen molecules were both assumed to be rigid, which is justified at temperatures lower than $\sim$1000 K. The NH$_3$ and H$_2$ geometries were taken at their ground-state average values, as recommended by [Faure et al. (2005)] in the case of the H$_2$O-H$_2$ system. The rigid-rotor NH$_2$H$_2$ 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$_2$D was assumed to be identical to that of NH$_3$, i.e. the effect of deuteration substitution on the ammonia geometry was neglected. This assumption was previously adopted for the similar ND$_2$H-H$_2$ system by [Wiesenfeld et al. (2011)]. We note that internal geometry effects are indeed expected to be only moderate ($\leq$ 30%) at the temperatures investigated here, as shown by [Scribano et al. (2010)] for the D$_2$O-H$_2$ system. The main impact of the isotopic substitution on the NH$_2$H$_2$ PES is therefore the rotation of the principal inertia axes.

We have thus expressed the NH$_2$H$_2$ PES of [Maret et al. (2009)] in the principal inertia axes of NH$_2$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$_2$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$_2$D center of mass in the NH$_2$H$_2$ reference frame were found to be $X_{C(M)}=0.101312$ Bohr and $Y_{C(M)}=-0.032810$ Bohr, where $X_{C(M)}$ and $Y_{C(M)}$ were calculated for the ground-state average geometry of NH$_2$H$_2$ used by [Maret et al. (2009)]. The NH$_2$D-H$_2$ 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$_2$D and $l_2=4$ for H$_2$, resulting in a total of 210 angular basis functions. The root mean square residual was found to be lower than 1 cm$^{-1}$ for intermonomer separations $R$ larger than 5 Bohr, with a corresponding mean error on the expansion coefficients smaller than 1 cm$^{-1}$.

3 COLLISIONAL DYNAMICS

In order to describe the NH$_2$D energy structure, we adopted the same approach than [Machin & Roueff (2006)], i.e. we assumed that NH$_2$D is a rigid rotor and we neglected the inversion motion corresponding to the tunneling of the nitrogen atom through the H$_2$D plane. The spectroscopic constants, adapted from the CDMS 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$_2$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$0.4 cm$^{-1}$ 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$_2$D. Finally, we also considered H$_2$D as a rigid rotor and adopted a rotational constant of 59.2817 cm$^{-1}$ (Huber & Herzberg 1979). The reduced mass of the collisional system is $\mu = 1.81299890$ amu.

In order to solve the collisional dynamics, we used the MOLSCAT code. Since NH$_2$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$_2$D energy levels up to $J_{\text{f}} = 7_{\text{f}}$ 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 $E_{\text{t}} \sim 3000$ cm$^{-1}$. We thus performed a few calculations at some specific values of the total energy for which we determined the number of NH$_2$D rotational energy levels, as well as the integration step required to insure a convergence better than 1% below 530 cm$^{-1}$ 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 $J_z = 2$ level of para–H$_2$ 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 $J_z = 0$ or $J_z = 0.2$ basis can differ by up to a factor 7. An example of the influence of the $J_z = 2$ energy level of H$_2$ on the cross sections is given in Fig. 2. This figure will be further discussed below.

At low total energy (i.e. $E_{\text{t}} < 110$ cm$^{-1}$), we performed dynam-

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<td>20</td>
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<tr>
<td>1355 – 2800</td>
<td>50</td>
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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 100–110 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 energy levels, since our calculations show that typically, the cross sections have resonances for kinetic energies up to $\sim 150$ cm$^{-1}$ above the threshold of the transition. Thus, because the NH$_2$D energy levels are close in energy, and because we are interested in the levels up to $J_\tau$, we reduced the step between consecutive energies, and because we are interested in the levels up to $J_\tau$, we reduced the step between consecutive energies, or $J_2$ threshold of the transition. Thus, because the NH$_2$D 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 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 I. 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 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 Å$^2$ have ratios equal to zero. The transitions which are predicted to be null with the CS formalism correspond to $J_\tau = 0$, where $\tau$ ranges from $\tau = -J + 1$ to $\tau = J - 1$ in a step of 2. The transitions concerned correspond to H$_2$ transitions with $J_2 = 0 \rightarrow 0$. In Fig. 2, we report the de-excitation transitions connected to the $|0\rangle$ 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 in this example, the total energy is 110 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 Å$^2$, the CS method is accurate within a factor $\sim 1.2$ for most transitions. On the other hand, reducing the basis of the 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 cm$^{-1}$, since the reduced amount of computational time (typically reduced by a factor 10–20) enables to adopt a fine energy grid.

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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 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 transition by a dotted vertical line.

Figure 4. Cross sections for the transitions connected to the fundamental energy level and for levels up to $J_{\tau} = 4_4$. 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.
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\(^{-1}\), 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 those predicted to be null with the CC formalism. To do so, we extrapolate the behaviour observed for the rates with levels such that \(J < 4\) and derive the following expression:

\[
R(J_i \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left( \frac{1}{1.35} \right)^{J_i - 1} \times \left( \frac{1}{2.5} \right)^{i - 1} \tag{1}
\]

with \(\tau_i = -J + 1 + 2(i - 1)\) ; \(i \in [1; n]\) and 
\[
E = \left( \frac{2J + 1}{2} \right)
\]

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 other sources of error. A second limitation comes from the fact that the PES was calculated for the equilibrium geometry of the \(\text{NH}_3\) molecule. The PES was corrected for the displacement of the center of mass between \(\text{NH}_3\) and \(\text{NH}_2\)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 \(\text{NH}_2\)D, rather than taking the \(\text{NH}_3\) internal geometry,
can lead to noticeable effects. Such a modification was tested for D₂O by Scribano et al. (2010), where rate coefficients for this isotopologue were calculated using the H₂O internal geometry. Differences of the order of 30% were found and we might expect differences of the same order for NH₂D. Finally, a third source of error relates to the scaling of the CS cross sections (noted $R^*(i \rightarrow j)$). The minimum and maximum values of the ratios $R^*(i \rightarrow j)/R^*(i \rightarrow j)$ 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 $J_r = 3$. In the lower panel of this figure, we report the same quantities, but for levels up to $J_r = 4_2$ 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 $3_{1}$-1 transitions, 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 $\sim 2$ but most of the transitions (93% of the 253 transitions considered) 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 $R^*(i \rightarrow j)/R^*(i \rightarrow j)$, we can expect that the transitions that involve an energy level above $J_r = 4_2$ will have a typical accuracy of 30%, since these transitions

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that with temperature increasing from 10K to 300K. However, as can be seen with an average ratio slightly increasing from 2 to 2.4 with temperature, we expect a larger fraction of the H$_2$ excitation. The previous discussion dealt with rate coefficients for the levels up to $J_e = 3$. 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 $J_e = 4$ 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 $J_e = 4$. For higher energy levels, the accuracy should be of the order of 30%. This holds true for all transitions except for the transitions $J_e \to 0$ 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 $J > 4$, 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$_3$ 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$_2$ 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. $T \ll 50K$). However, at higher gas temperatures, we expect a larger fraction of the H$_2$ molecules in excited states ($J_2 > 0$). As discussed in Sec. 3, the cross sections with $J_2 = 2 \to 2$ are of larger magnitude than the cross sections associated with the $J_2 = 0 \to 0$ transitions. This is shown in Fig. 7( where we represent the ratio of the rate coefficients with $J_2 = 2 \to 2$ to that with $J_2 = 0 \to 0$, for temperatures of 10 and 300K. On average, the rate coefficients with $J_2 = 2 \to 2$ 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 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$_2$ 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$_2$ rather than para–H$_2$ and in such a case, it should be necessary to calculate the corresponding rate coefficients. However, in the case of the H$_2$O / H$_2$ collisional system it was found that the effective rate coefficients for $J_e = 2$ and $J_2 = 1$ agree within $\sim 30\%$ (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$_2$ symmetry. As a consequence, in astrophysical applications, the thermalized rate coefficients with ortho–H$_2$ or para–H$_2$ lead to similar line intensities at high temperatures (Daniel et al. 2012). To conclude, this means that in principle, the rate coefficients with $J_2 = 2 \to 2$ can serve as a template to emulate the rate coefficients of ortho–H$_2$ ($J_e = 1 \to 1$). We checked this assumption by performing a few calculations with...
orth–H$_2$ as a collisional partner. In Fig. 5 we compare the cross sections of the $2_2 \rightarrow 1_4$ 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 $\sigma_j(2 \rightarrow 2)/\sigma_j(1 \rightarrow 1)$ is $\mu \sim 1$, with a standard deviation $\sigma$ that vary with energy in the range $\sigma = 0.15 - 0.30$. For each energy, ~70% of the transitions vary by less than $1 \sigma$ around $\mu$ and ~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–H$_2$ rate coefficients.

5 DISCUSSION

Prior to this work, the only available rate coefficients for NH$_2$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 H$_2$. However, for many molecules, large differences exist and the rates do not scale accordingly to the factor ~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 ND$_2$H. Indeed, for this particular isotopologue, the He and H$_2$ rate coefficients were found to vary by factors in the range 3–30 [Machin & Roueff 2007, Wiesenfeld et al. 2011]. In Fig. 5 we give the ratios of the current NH$_2$D / H$_2$ rate coefficients with the rates calculated with He [Machin & Roueff 2006], as a function of the magnitude of the H$_2$ rate coefficients and for temperatures of $T = 10K$ and $T = 100K$. The comparison concerns the transitions that involve levels up to $J_r = 2_{12}$ (the highest level considered in Machin & Roueff 2006). From this figure, it appears that the H$_2$ and He rate coefficients show large variations, as expected from the previous studies of ND$_2$H. At $T = 10K$, 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 $T = 100K$, 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 coefficients 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 ND$_2$H / 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 H$_2$. As discussed in Sec. 3 considering a $J_2 = 0$ basis for H$_2$ can induce variations as large as a factor ~7 and the magnitude of the effects are presumably similar for ND$_2$H. We thus performed a few additional calculations for the ND$_2$H / H$_2$ system. These calculations are similar to the ones presented in Wiesenfeld et al. (2011) except for the H$_2$ basis which is now set to $J_2 = 0, 2$. In Fig. 5 we compare the cross sections of NH$_2$D and ND$_2$H for the six de–excitation transitions possible when considering the levels up to $J_r = 1_1$. 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 cm$^{-1}$, differences of a factor ~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 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 CD$_2$H / H$_2$ rate coefficients, it should be more accurate to take the CH$_2$D / H$_2$ rate coefficients than the CD$_2$H / He one.

**Figure 8.** Comparison between the current NH$_2$D / H$_2$ rate coefficients with the rates calculated with He as a collisional partner (Machin & Roueff 2004).

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

We reported the calculation of collisional rate coefficients for the NH$_2$D / H$_2$ system for NH$_2$D rotational energy levels up to $J_r = 7$; ($E \sim 735$K) and for temperatures in the range $T = 5–300$K. 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$_3$ / H$_2$ potential energy surface presented in Maret et al. (2009). The dynamical calculations were performed at the close-coupling level at low total energy ($E < 110$ cm$^{-1}$) and with the coupled–states formalism at higher energies. For the levels up to $J_r = 4$ 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 $J_r \rightarrow 0_r$ transitions with $J_r$ varying from $-J_r+1$ to $J_r-1$ 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 $J > 4$, 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$_3$.

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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 cm$^{-1} < E < 250$ 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:

\[ f(E) = \sum_{i=1,3} a_i E_i^{-2} \]  \[(A1)\]

\[ g(E) = \sum_{i=1,3} a_i E_i^{-2} + a_4 E^{-0.1} \]  \[(A2)\]

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$_{2,3}$–1$_{1,1}$, 3$_{2,1}$–1$_{1,1}$ or 3$_{0,2}$–2$_{0,0}$ 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...
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 $3000 \text{ cm}^{-1}$, we extrapolate the ratios at energies higher than $250 \text{ cm}^{-1}$. To do so, we proceed as follows. We first fit a linear function using the ratios obtained with this function is lower by at least a factor 3 by comparison to the $\chi^2$ obtained with the function $f(E)$.

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extrapolate the behaviour observed for the rates with levels such
that \( J < 4 \). In Fig. B2 we show the various rate coefficients cal-
culated for the levels up to \( J = 3 \). 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. More-
over, 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 transi-
tions from \( J = 2 \) and \( J = 3 \), are approximated in this way by using
the analytical expressions:

\[
R(2_1 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left( \frac{1}{1.3} \right) \tag{B1}
\]

\[
R(2_2 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left( \frac{1}{1.3} \right)^2 \times \frac{1}{2.45} \tag{B2}
\]

\[
R(3_2 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left( \frac{1}{1.4} \right)^2 \times \frac{1}{3} \tag{B3}
\]

\[
R(3_1 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left( \frac{1}{1.4} \right)^2 \times \frac{1}{3} \times \frac{1}{2.4} \tag{B4}
\]

\[
R(3_0 \rightarrow 0_0) = R(1_0 \rightarrow 0_0) \times \left( \frac{1}{1.4} \right)^2 \times \frac{1}{3} \times \frac{1}{2.4} \tag{B5}
\]

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 re-
sulting expression corresponds to Eq. (1) of Sections 4.

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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).