Rotational excitation of the interstellar NH$_2$ radical by H$_2$

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We present quantum close-coupling calculations for the rotational excitation of the interstellar amido radical NH$_2$ due to collisions with H$_2$ molecules. The calculations are based on a recent, high-accuracy full-dimensional NH$_2$ potential energy surface adapted for rigid-rotor scattering calculations. The collisional cross section calculations are performed for all transitions among the first 15 energy levels of both ortho- and para-NH$_2$ and for total energies up to 1500 cm$^{-1}$. Both para- and ortho-H$_2$ colliding partners are considered. The cross sections for collision with para- and ortho-H$_2$ are found to differ significantly, the magnitude of the ortho-H$_2$ ones being dominant. No strong propensity rules are observed but transitions with $\Delta k = 0$ are slightly favored. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4975324]

I. INTRODUCTION

Neutral nitrogen hydrides (NH, NH$_2$, and NH$_3$) are highly abundant species in a variety of astrophysical regions. Among them, the NH$_2$ radical, even if not generally the most abundant one, is of key importance for the chemistry of these media. It was detected for the first time in the interstellar medium (ISM) by van Dishoeck et al., who pointed out that this simple hydride is crucial for testing the production pathways in nitrogen-bearing molecules. Indeed, the NH$_2$ chemistry is directly related to that of the abundant and ubiquitous ammonia, NH$_3$. In addition, NH$_2$ exhibit spin symmetry states whose relative abundances are sensitive to the H$_2$ ortho-to-para ratio (OPR) in the gas phase. NH$_2$ observations may be able to put constraints on the H$_2$ OPR in dense gas.

The Infrared Space Observatory was later used to observe infrared absorption lines of NH$_2$ and, recently, the Herschel Space Observatory with the Heterodyne Instrument for the Far-Infrared (HIFI) allowed the observation of several low-lying rotational transitions of NH$_2$ at a very high spectroscopic resolution. These (absorption) lines were employed to derive NH$_2$:NH$_3$ abundance ratios of $\sim$2:1:1 in lukewarm diffuse clouds and $\sim$3:1:20 in the colder envelope of low-mass protostars. Emission lines were also detected more recently in denser and hot ISM regions. In addition, anomalous (non statistical) ortho-to-para ratios of NH$_2$ and NH$_3$ were derived in the diffuse gas. These ratios were successfully reproduced by gas-phase models including a rigorous nuclear-spin chemistry, suggesting that NH$_2$ just like NH$_3$, is mainly formed in the gas-phase via a series of successive hydrogen abstraction reactions NH$_2^+$ + H$_2$ ($n = 0$–3) followed by electronic dissociative recombination. A recent study has also emphasized the importance of the H-exchange reaction NH$_2$ + H in the ortho-para conversion of NH$_3$.

However, the analysis of the NH$_2$ rotational spectra, especially those in emission, was hampered by the lack of collisional rate coefficients. Without these data, only approximate estimates of the molecular column density are possible assuming local thermodynamic equilibrium (LTE), which is generally not a good approximation. Persson et al. estimated collisional rate coefficients assuming quenching rate coefficient of $5 \times 10^{11}$ cm$^3$ s$^{-1}$ and state-specific downward rates for radiatively allowed transitions that scale in proportion to radiative line strengths. Such estimates are very approximate and the accurate determination of the NH$_2$ abundance would greatly benefit from accurate collisional data. The main collider in the dense ISM is generally molecular hydrogen, H$_2$.

Scattering studies implying nonlinear polyatomic molecules and H$_2$ are still sparse. To date, calculations of rate coefficients for the collisional excitation by para- and ortho-H$_2$ (hereafter p-H$_2$ and o-H$_2$, respectively) have been performed only for the four interstellar molecules H$_2$CO, NH$_3$, CH$_3$OH, H$_2$O, and SO$_2$. To the best of our knowledge, there are no collisional data available for the NH$_2$–H$_2$ system. The only relevant study for astrophysics implying the NH$_2$ molecules is the measurement of integral cross sections for NH$_2$–He rotational transitions performed by Dagdagian. However, no rate coefficients were given in this work. NH$_2$–H collisions were also studied but the NH$_2$ molecule was in its first excited electronic state that is negligibly populated in atmospheric media.

NH$_2$ is an asymmetrical rotor with two forms caused by the different relative orientations of the hydrogen nuclear
spins. In collision with H₂, the two forms behave like two distinct species: ortho-NH₂ and para-NH₂ (hereafter denoted as o-NH₂ and p-NH₂, respectively). In addition, NH₂ has a complex rotational structure resulting from the open-shell character of the NH₂ ground electronic state \( ^2B_1 \). Hence, each rotational level is split by spin-rotation interaction in a fine structure of two sublevels identified by the total angular momentum \( j_z \) with \( j_z = N_z + S \) (where \( N_z \) is the rotational angular momentum and \( S \) is the electronic spin). Moreover, fine structure levels are further split into three components through hyperfine interactions, due to the coupling between the nitrogen nuclear spin and the total angular momentum \( j_z \). Finally, a second hyperfine structure resulting from the coupling between the nuclear spins of the hydrogen nuclei splits all o-NH₂ sublevels into three new sublevels.

The calculation of collisional cross sections taking into account this complex structure is an extremely challenging task. Calculations of collisional data for open-shell molecules in collision with H₂ have been achieved only recently,²⁰ for linear molecules and cannot be easily extended to a polyatomic top. This is why, in the present work, we neglect the fine and hyperfine structure of the NH₂ target and we provide data for transitions between rotational levels. Collisional data including these specific structures may be deduced from the present calculations using decoupling approximations.²¹,²²

In this paper, we used a new accurate full-dimensional NH₂ potential energy surface (PES)²³ to compute the cross sections for the collisional excitation of the first 15 rotational levels of both o- and p-NH₂ by H₂. The paper is organized as follows. The PES and the scattering calculations are presented in Section II. In Section III, we report state-to-state resolved cross sections for the rotational excitation of NH₂ by H₂. Concluding remarks are drawn in Section IV.

II. METHODS

A. Potential energy surface

The NH₂ radical is known to react with H₂ to form NH₃ through an exothermic pathway by a direct hydrogen abstraction mechanism. This reactive channel NH₂ + H₂ → NH₃ + H was found to have a barrier of 3340 cm⁻¹.²³ The reaction is thus quite slow with rate coefficients lower than \( 10^{-13} \) cm³ s⁻¹ for temperatures lower than 500 K.²³,²⁴ Under such circumstances, neglecting the reactive pathway in the treatment of the NH₂–H₂ collision should have only a small influence on the description of the inelastic processes,²⁵,²⁶ as long as low to moderate collision energies are considered. We also note that the hydrogen exchange process is also negligibly small under such conditions.

An accurate rigid-rotor five-dimensional PES was then constructed for the NH₂–H₂ system in its electronic and vibrational ground state, suitable for low-energy inelastic rotational calculations, from the recently computed nine-dimensional global PES of NH₂.²³ This PES was determined at the UCCSD(T)-F12a/aug-cc-pVTZ level of theory and the \( \textit{ab initio} \) points were fitted using the permutation-invariant polynomial neutral network (PIP-NN) method²⁷ with a root mean squared error (RMSE) of 27 cm⁻¹. The RMSE of 27 cm⁻¹ is for the full nine-dimensional PES (including the reactive path).

The fitting RMSE for the non-reactive NH₂–H₂ region relevant for this work is much smaller, of the order of few cm⁻¹.

In this work, the intermolecular potential is described as a function of five coordinates, namely, the intermolecular distance \( R \) from the NH₂ center of mass to the H₂ center of mass, and four relative angles \((\theta, \varphi)\) and \((\theta', \varphi')\) which describe, respectively, the collision direction and the H₂ orientation relative to the NH₂ body-fixed system. The body-fixed Jacobi coordinate system used in our calculations is presented in Fig. 1.

As the original routine from Li and Guo²⁵ employs internuclear coordinates, the following transformation was employed to determine the Cartesian positions of the two hydrogen atoms (\( H_2 \) with coordinates \((x_a, y_a, z_a) \) and \( H_b \) with coordinates \((x_b, y_b, z_b) \) of the H₂ molecule in the NH₂ body-fixed coordinate system:

\[
x_a = R \sin \theta \cos \varphi + r_{H_i} \sin \theta' \cos \varphi' \frac{m_{H_i}}{2m_{H_i}}, \quad (1)
\]

\[
y_a = R \sin \theta \sin \varphi + r_{H_i} \sin \theta' \sin \varphi' \frac{m_{H_i}}{2m_{H_i}}, \quad (2)
\]

\[
z_a = R \cos \theta + r_{H_i} \cos \theta' \frac{m_{H_i}}{2m_{H_i}}, \quad (3)
\]

\[
x_b = R \sin \theta \cos \varphi - r_{H_i} \sin \theta' \cos \varphi' \frac{m_{H_i}}{2m_{H_i}}, \quad (4)
\]

\[
y_b = R \sin \theta \sin \varphi - r_{H_i} \sin \theta' \sin \varphi' \frac{m_{H_i}}{2m_{H_i}}, \quad (5)
\]

\[
z_b = R \cos \theta - r_{H_i} \cos \theta' \frac{m_{H_i}}{2m_{H_i}}, \quad (6)
\]

where \( r_{H_i} \) is the bond length of H₂ fixed at its vibrationally averaged distance \( \langle r_{H_i} \rangle_0 = 1.149 \) a₀. The NH₂ molecule, which lies in the (xoz) plane (see Fig. 1), was also kept rigid with an averaged geometry taken from the experimental work of Davies et al.²⁸ \( \langle r_{NH} \rangle_0 = 1.936 \) a₀ and \( \langle HNH \rangle_0 = 103.33^\circ \). We note that employing state-averaged geometries is a reliable approximation for including zero-point vibrational effects within a rigid-rotor PES, as discussed in previous studies on H₂-O–H₂.²⁹,³⁰ In addition, it was shown recently for the CO–H₂ system that state-averaged geometries also give scattering results very close to full-dimensional calculations.³¹

![FIG. 1. Jacobi coordinate system of the NH₂–H₂ complex.](image-url)
Here, the lowest vibrational bending frequency of NH$_2$ is $\approx$1500 cm$^{-1}$. Hence, vibrational excitation is closed at the investigated energies and can be safely neglected in the scattering calculations.

The original fit of Li and Guo$^{23}$ was employed to generate interaction energies on a very dense grid of 81,000 geometries in $R$, $\theta$, $\varphi$, $\theta'$, and $\varphi'$. An asymptotic potential of 2062.47 cm$^{-1}$ (corresponding to the above monomer averaged geometries) was subtracted from these interaction energies. 27 values in $R$ were selected in the range [3.75–20.00]Å and this radial grid was combined with 3000 random angular geometries $\theta$, $\varphi$, $\theta'$, $\varphi'$. The PES $V(R, \theta, \varphi, \theta', \varphi')$ was expanded over all angular functions for all $R$-functions using the following expression:

$$V(R, \theta, \varphi, \theta', \varphi') = \sum_{p_1q_1p_2q_2} t_{p_1q_1p_2q_2}(R) P_{p_1q_1p_2}(\theta, \varphi, \theta', \varphi'), \quad (7)$$

where

$$t_{p_1q_1p_2q_2}(\theta, \varphi, \theta', \varphi') = (1 + \delta_{q_10})^{-1} \sum_{r_1 r_2 r} \left( \begin{array}{c} p_1 \\ r_1 \\ p_2 \\ r_2 \\ p \end{array} \right) \times Y_{p_1 q_1}(\theta, \varphi) Y_{p_2 q_2}(\theta', \varphi') \times \left[ \delta_{q_1 r_1} + (-1)^{p_1+q_1+p_2+q_2} \delta_{q_2 r_1} \right], \quad (8)$$

where $(3j)$ is a “3-j” symbol, $Y_{pq}$ is a spherical harmonic, $\delta_{q_1}$ is a Kronecker delta, equal to one if $i = j$ and to zero otherwise, and the sum is over $r_1$, $r_2$, $r$. The indices $p_1$, $p_2$, and $p$ refer to the tensor ranks of the angle dependence of the NH$_2$ orientation, the H$_2$ orientation, and the collision vector orientation, respectively. In Eq. (8), the index of the $C_{2v}$ symmetry of NH$_2$ requires that $q_1$ be even and the homonuclear symmetry of H$_2$ similarly constrains $p_2$ to be even. The expansion coefficients $v_{p_1q_1p_2q_2}(R)$ were obtained through a least-squares fit on the random grid of 3000 orientations at each intermolecular separation. We initially included all anisotropies up to $p_1 = 10$, $p_2 = 6$, and $p = 16$, resulting in 810 basis functions. We then selected only significant terms using a Monte Carlo error estimator (defined in the work of Rist and Faure$^{24}$), resulting in a final set of 146 expansion functions with anisotropies up to $p_1 = 10$, $p_2 = 6$, and $p = 13$. The RMSE was found to be lower than 1 cm$^{-1}$ for $R > 4.75$ Å. A cubic spline interpolation of the coefficients $v_{p_1q_1p_2q_2}(R)$ was finally performed over the whole $R$ range and it was smoothly connected using a switching function to standard extrapolations (exponential and power laws at the short- and long-range, respectively) in order to provide continuous radial expansion coefficients for the scattering calculations.

Two-dimensional plots of the NH$_2$–H$_2$ PES are presented in Figs. 3–5.

The global minimum of the 5D fitted PES is located at $\theta = \theta' = 0^\circ$ with a depth of $-213.00$ cm$^{-1}$ and at an intermolecular distance $R = 6.05$ Å. This minimum corresponds to the most stable configuration of the NH$_2$–H$_2$ complex so that H$_2$ is approaching the N atom of the NH$_2$ molecule along the $C_2$ axis.

In Fig. 3, we show a contour plot of the interaction energy for fixed $\theta' = \varphi = \varphi' = 0^\circ$. This plot shows the anisotropy of the interaction with respect to the NH$_2$ rotation.

![Contour plot of the 5D PES as function of $R, \theta$ for fixed $\theta' = \varphi = \varphi' = 0^\circ$. Energy is in cm$^{-1}$.](Image)

The shape of the two PESs is quite similar. Indeed, Valiron et al.$^{29}$ reported that the H$_2$O–H$_2$ global minimum is at the same configuration than that of NH$_2$–H$_2$, the well depth of H$_2$O–H$_2$ and NH$_2$–H$_2$ PESs being similar ($-235.14$ cm$^{-1}$ for the H$_2$O–H$_2$ complex vs. $-213$ cm$^{-1}$ for the NH$_2$–H$_2$ complex).

Furthermore, for both NH$_2$–H$_2$ and H$_2$O–H$_2$ PESs, a secondary minimum is found when H$_2$ is approaching along the direction of the NH (OH) bond with the H$_2$ molecule perpendicular to the NH$_2$ (H$_2$O plane). The H$_2$O–H$_2$ secondary minimum found at $\theta = 119^\circ$ and $\theta' = 90^\circ$ with a well depth equal to $-199.40$ cm$^{-1}$ is, however, deeper than that of NH$_2$–H$_2$ ($-122.29$ cm$^{-1}$) found at $\theta = 113^\circ$ and $\theta' = 90^\circ$.

![Sample of expansion coefficients ($v_{p_1q_1p_2q_2}$) of the NH$_2$–H$_2$ PES, as function of intermolecular distance $R$, for $p_1 = 0.1.2$ and $p_2 = 0.2$.](Image)
B. Scattering calculations

We used the fitted NH$_2$–H$_2$ PES to study the rotational excitation of NH$_2$ by H$_2$. We focus only on the collisional excitation of the rotational states of NH$_2$, since the computation of fine/hyperfine structure resolved cross sections is a true challenge. The rotational energy levels of NH$_2$ are labelled by three numbers: the angular momentum $N_1$ and the pseudo-quantum numbers $k_a$ and $k_c$ which correspond to the projection of $N_1$ along the axis of the least and greatest moments of inertia, respectively. The para states correspond to $k_a + k_c$ odd and the ortho states to $k_a + k_c$ even. Extension to the fine/hyperfine structure using approximate treatment will be considered in a future study.

The rotational levels of NH$_2$ were obtained using the rotational constants from Müller et al.$^{35}$ Figure 6 shows the rotational energy levels of both $\sigma$- and $\pi$-NH$_2$. For the H$_2$ molecule, the rotational states are denoted by $j_2$ throughout this paper. The para states of H$_2$ have even rotational states $j_2 = 0, 2, \ldots$ and the ortho states have odd rotational states, $j_2 = 1, 3, \ldots$.

As inelastic (nonreactive) collisions cannot interconvert the ortho- and para-forms, the calculations were done separately for the four spin combinations, namely, $\pi$-NH$_2$–$\pi$-H$_2$, $\pi$-NH$_2$–$\sigma$-H$_2$, $\sigma$-NH$_2$–$\pi$-H$_2$, and $\sigma$-NH$_2$–$\sigma$-H$_2$. NH$_2$ molecule is treated as a rigid rotor. We used the quantum close-coupling (CC) approach to obtain the inelastic cross sections as described in Phillips et al.$^{36}$ All scattering calculations have been performed with the version 14 of the MOLSCAT code.$^{37}$ The coupled equations were solved using the modified log-derivativeairy propagator of Alexander and Manolopoulos.$^{38}$ The reduced mass of the system is 1.790 367 amu.
Inelastic cross sections were obtained between levels with a rotational energy \( E_{\text{rot}} \leq 422 \text{ cm}^{-1} \), that is, up to \( N_{1_k,l_k} = 4_{40} \) for \( \alpha\text{-NH}_2 \) and \( N_{1_k,l_k} = 4_{44} \) for \( \rho\text{-NH}_2 \).

The collisions were studied for the total energy ranging from 32 to 1500 cm\(^{-1}\). The integration parameters were chosen to ensure convergence of the cross sections in this range. We carefully spanned the energy range to guarantee a good description of the resonances. For collision with \( \rho\text{-H}_2 \), the energy steps are 0.2 cm\(^{-1}\) below 100 cm\(^{-1}\), 0.5 cm\(^{-1}\) from 100 to 200 cm\(^{-1}\), 1.0 cm\(^{-1}\) from 200 to 500 cm\(^{-1}\), 2.0 cm\(^{-1}\) from 500 to 700 cm\(^{-1}\), 5.0 cm\(^{-1}\) from 700 to 1000 cm\(^{-1}\), and 20 cm\(^{-1}\) from 1000 to 1500 cm\(^{-1}\). For collision with \( \alpha\text{-H}_2 \), the energy steps are 0.2 cm\(^{-1}\) below 300 cm\(^{-1}\), 1.0 cm\(^{-1}\) from 300 to 500 cm\(^{-1}\), 2.0 cm\(^{-1}\) from 500 to 700 cm\(^{-1}\), 5.0 cm\(^{-1}\) from 700 to 1000 cm\(^{-1}\), and 20 cm\(^{-1}\) from 1000 to 1500 cm\(^{-1}\).

At each collision energy, the total angular momentum \( J_{\text{tot}} \) was set large enough to converge cross sections, the value of \( J_{\text{tot}} \) varies from 19 at low energies to 64 for energies larger than 1000 cm\(^{-1}\).

Since a given \( N_1 \) rotational number includes a large number of \( \text{NH}_2 \) sub-rotational energy, rotational levels with internal energies above \( E_{\text{max}} = 650 \text{ cm}^{-1} \) were eliminated for total energies \( E_{\text{rot}} \leq 200 \text{ cm}^{-1} \). This \( E_{\text{max}} \) parameter was progressively increased up to \( E_{\text{max}} = 2200 \text{ cm}^{-1} \) for \( E_{\text{rot}} = 1500 \text{ cm}^{-1} \). These large values of \( E_{\text{max}} \) are needed to converge cross sections. A similar effect was previously observed for methyl-formate (HCOOCH\(_3\)) colliding with helium\(^{39}\) and for formaldehyde (H\(_2\)CO) colliding with H\(_2\)\(^{40}\).

It was also crucial to optimize the rotational basis of \( \text{H}_2 \) in order to keep calculations feasible in terms of both central processing unit (CPU) time and memory. Tests of the \( \rho\text{-H}_2 \) and \( \alpha\text{-H}_2 \) basis were performed at different values of total energy. For collisions with \( \rho\text{-H}_2(j_2 = 0) \), the inclusion of the \( \text{H}_2(j_2 = 2) \) level was necessary to obtain cross sections converged to better than 5\%, even when these channels were energetically closed. For \( \alpha\text{-H}_2(j_2 = 1) \), it was found that inclusion of the \( \text{H}_2(j_2 = 3) \) level in the basis does not have a noticeable influence on the magnitude of the cross sections. Hence, for the determination of rotational excitation cross section of \( \text{NH}_2 \) in collision with \( \alpha\text{-H}_2 \), only the \( \text{H}_2(j_2 = 1) \) basis was retained.

### III. RESULTS

Figure 7 shows the collisional energy dependence of the de-excitation integral cross sections of \( \alpha\text{-} \) and \( \rho\text{-NH}_2 \) in collision with \( \alpha\text{-H}_2(j_2 = 1) \) and \( \rho\text{-H}_2(j_2 = 0) \). One can first observe resonances that appear for energies lower than 250 cm\(^{-1}\). These resonances in the de-excitation cross sections are related to the presence of the attractive potential well with a depth of \( \sim 213 \text{ cm}^{-1} \) that allows the \( \text{H}_2 \) molecule to be temporarily trapped and hence quasi-bound states to be formed before the complex dissociates. The cross sections for collisions with \( \rho\text{-H}_2(j_2 = 0) \) seem to display a richer resonance structure than the cross sections for collisions with \( \alpha\text{-H}_2(j_2 = 1) \) that appear to have a smoother energy dependence. Actually, there are many more, and hence overlapping, resonances for the cross sections for collisions with \( \rho\text{-H}_2(j_2 = 0) \) because of a larger number of (quasi-)bound states due to the contribution of an additional coupling term \( N_1 + j_2 = j_12 \) absent in collisions with \( \rho\text{-H}_2(j_2 = 0) \). Second, regarding the magnitude of the cross sections, we observe a global decrease of their intensity with increasing \( \Delta N_1 \). However it is interesting to note that for collisions with \( \rho\text{-H}_2(j_2 = 0) \), the magnitude of cross sections with \( \Delta N_1 = 2 \) can be larger than those with \( \Delta N_1 = 1 \), while the trend is a rather monotonous decrease for \( \alpha\text{-H}_2(j_2 = 1) \).

Also, when the collisional energy increases, the magnitude of the cross sections for \( \Delta N_1 = 1 \) and \( \Delta N_1 > 1 \) tends to be closer whether for collisions with \( \rho\text{-} \) or \( \alpha\text{-H}_2 \). This behavior is expected and observed for many systems like HNC–\( \text{H}_2\),\(^{41}\) HCl–\( \text{H}_2\),\(^{42}\) and O\(_2\)–\( \text{H}_2\).\(^{43}\)

**FIG. 7.** Rotational de-excitation cross sections of \( \rho\text{-} \) and \( \alpha\text{-NH}_2 \) by \( \rho\text{-} \) and \( \alpha\text{-H}_2 \). For collisions with both \( \rho\text{-} \) and \( \alpha\text{-H}_2,j_2 \) is unchanged.
that vanishes for collisions with quadrupole interaction that exists for collisions with coefficients with $p$ with $p$ with $p$ with $p$ only the terms with $j$ with $j$ with $j$ with $j$ sections with $p$-H$_2$(j$_2$ = 0) and the vertical axis presents the corresponding collisional cross sections with $o$-H$_2$(j$_2$ = 1). The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor 3.

In order to have an overview of the differences that exist between the excitation cross sections with $p$- and $o$-H$_2$ colliders, we show, in Fig. 8, a comparison between the two sets of cross sections for all the de-excitation transitions from all initial levels up to $N_{1k, k_a} = 4_{10}$ for $o$-NH$_2$ and up to $N_{1k, k_a} = 4_{11}$ for $p$-NH$_2$ at a fixed collision energy of 100 cm$^{-1}$. The horizontal axis presents the cross sections for collisions with $p$-H$_2$(j$_2$ = 0) whereas the vertical axis presents the cross sections for collisions with $o$-H$_2$(j$_2$ = 1).

Examination of the plots for collisions of $o$- and $p$-NH$_2$ with both $o$- and $p$-H$_2$ shows that the two sets of data agree generally within a factor of 3. The largest cross sections are those for collision with $o$-H$_2$, with only a few exceptions. This trend was already observed for several interstellar species like SiS,$^{64}$ HCl,$^{65}$ SO$_2$,$^{45}$ or H$_2$O.$^{46}$

This behavior can also be explained by looking at the radial coefficients $\psi_{pq|qp'}$ of the expansion Equation (7), as plotted in Fig. 2. The radial coefficients contributing to cross sections with $j_2 \rightarrow j_2'$ transitions are those with $p_2$ in the range $j_2 - j_2' < p_2 < j_2 + j_2'$. Then, for collisions with $p$-H$_2$(j$_2$ = 0) only the terms with $p_2 = 0$ contribute whereas for collisions with $o$-H$_2$(j$_2$ = 1) the $p_2 = 0$, 2 terms contribute. The radial coefficients with $p_2 = 2$ are not negligible compared to the one with $p_2 = 0$ explaining why the cross sections for collisions with $o$-H$_2$(j$_2$ = 1) are larger than the ones for collisions with $p$-H$_2$(j$_2$ = 0). The non-negligible contribution of the radial coefficients with $p_2 = 2$ can be explained notably by the dipole-quadrupole interaction that exists for collisions with $o$-H$_2$ and that vanishes for collisions with $p$-H$_2$.

Then, we were interested in the propensity rules in the NH$_2$–H$_2$ collisional system. Figures 9 and 10 show, at 3 different collisional energies (50, 500, and 1000 cm$^{-1}$), the rotational de-excitation cross sections from $p$-NH$_2$(N$_{1k, k_a} = 4_{23}$) and $o$-NH$_2$(N$_{1k, k_a} = 4_{13}$) for both $p$- and $o$-H$_2$ collisions.

![FIG. 8. Comparison between $p$- and $o$-H$_2$ de-excitation cross sections for $o$-NH$_2$ (upper panel) and $p$-NH$_2$ (lower panel) at a collision energy of 100 cm$^{-1}$. The horizontal axis represents the collisional cross sections with $p$-H$_2$(j$_2$ = 0) and the vertical axis represents the corresponding collisional cross sections with $o$-H$_2$(j$_2$ = 1). The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor 3.](image1)

![FIG. 9. Propensity rules for transitions out of the initial N$_{1k, k_a} = 4_{13}$ state of the $p$-NH$_2$ molecule in collision with $p$-H$_2$(j$_2$ = 0) (bottom panel) and $o$-H$_2$(j$_2$ = 1) (top panel), for kinetic energies = 50, 100, and 1000 cm$^{-1}$.](image2)

![FIG. 10. Propensity rules for transitions out of the initial N$_{1k, k_a} = 4_{13}$ state of the $o$-NH$_2$ molecule in collision with $p$-H$_2$(j$_2$ = 0) (bottom panel) and $o$-H$_2$(j$_2$ = 1) (top panel), for kinetic energies = 50, 100, and 1000 cm$^{-1}$.](image3)
TABLE I. Comparison of cross sections for transitions out of $\alpha$-NH$_2$(N$_{\ell\ell\ell}$ = 0$_{00}$) rotational level induced by collisions with $p$-H$_2$(j$_2$ = 0) and He.$^{18}$ $E_{\text{coll}}$ = 467 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Final level</th>
<th>$\alpha$-NH$_2$–p-H$_2$</th>
<th>$\alpha$-NH$_2$–He</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$_{11}$</td>
<td>(1)$^a$</td>
<td>(1)$^a$</td>
</tr>
<tr>
<td>2$_{02}$</td>
<td>(1)$^a$</td>
<td>(1)$^a$</td>
</tr>
<tr>
<td>2$_{12}$</td>
<td>0.01</td>
<td>$\leq 0.05 \pm 0.02$</td>
</tr>
<tr>
<td>3$_{33}$</td>
<td>0.37</td>
<td>0.07 $\pm 0.02$</td>
</tr>
<tr>
<td>4$_{04}$</td>
<td>0.23</td>
<td>0.06 $\pm 0.02$</td>
</tr>
</tbody>
</table>

$^a$Cross sections are separately normalized for each $\ell'_2$ = 0 and 1 manifold.

IV. CONCLUSION

We have presented in this paper a study of the interaction between NH$_2$ and hydrogen molecules. Cross sections for the rotational (de)excitation of $\alpha$- and $p$-NH$_2$ colliding with both $p$-H$_2$(j$_2$ = 0) and $\alpha$-H$_2$(j$_2$ = 1) have been computed. All transitions among both the 15 lowest levels of $\alpha$-NH$_2$ and $p$-NH$_2$ were considered.

The cross sections for collisions with para- and ortho-H$_2$ differ, the magnitude of the ortho-H$_2$ ones being dominant. Propensity rules are discussed and it is found that no rigorous selection rules are defined although transitions with $\Delta k_z = 0$ seem to be slightly favored.

The present results should therefore be adopted in any radiative transfer model of NH$_2$ in environments with $T \leq 150$ K. In particular, Persson et al.$^2$ used a non-LTE radiative transfer model using radiative coefficients estimated from an assumed quenching rate coefficient of $5 \times 10^{-11}$ cm$^3$ s$^{-1}$ and radiative selection rules, i.e., $\Delta N_l = 0, \pm 1; \Delta k_z = \pm 1, \pm 3$, etc.; $\Delta k_c = \pm 1, \pm 3$, etc. Our results indicate that inelastic cross sections corresponding to radiatively forbidden transitions (e.g., $\Delta k_z = 0$) can be as probable as (or even stronger than) those corresponding to radiatively allowed transitions. Hence, previously published NH$_2$ abundance should be revised accordingly, using our new data.

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