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Inelastic rate coefficients for collisions of N_2H^+ with H_2

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ABSTRACT

N_2H^+ is one of the first molecular ions observed in the interstellar medium and it is of particular interest to probe the physical conditions of cold molecular clouds. Accurate modelling of the observed lines requires the knowledge of collisional excitation rate coefficients. Thus, we have calculated rate coefficients for the excitation of N_2H^+ by H_2 , the most abundant collisional partner. The calculations are based on a new potential energy surface obtained from highly correlated ab initio calculations. This 4D-interaction surface exhibits a very deep well of $\approx 2530 \text{ cm}^{-1}$ making full converged scattering calculations very difficult to carry out, when one takes into account the rotational structure of H_2 . To overcome this difficulty, two approximate approaches, the Adiabatic Hindered Rotor approach (AHR) and the Statistical Adiabatic Channel Model (SACM), were tested by comparing the results with those obtained from full 4D Close-Coupling (CC) calculations. The AHR treatment, which reduces the scattering calculations to a 2D problem was found to give the best results at all temperatures and even for transitions involving high N_2H^+ rotational levels. State-to-state rate coefficients between the 26 first N_2H^+ rotational levels were calculated for temperatures ranging from 5 K up to 500 K. Using a recoupling technique, rate coefficients are obtained among hyperfine transitions.

Key words: Molecular data, Molecular processes, scattering, Interstellar: abundances.

1 INTRODUCTION

The study of physical and chemical conditions of interstellar clouds requires to model the emission of various neutral or ionic species. In particular, such studies allow the determination of the molecular abundances which put constraints on the interstellar chemistry. Several molecules can be used to probe various physical conditions of the clouds and thus to give information on the dynamical evolution of the cores and their capability to form stars. However, dense cores and especially prestellar cores suffer from strong depletion of the usual tracers (CO, CS, SO, (e.g. Pagani et al. 2005)) and it was found that only few species survive in the gas phase. Among them, nitrogen bearing molecules are the best known (NH_3 , N_2H^+ and possibly CN (Lee et al. 2001; Tafalla et al. 2002; Pagani et al. 2007; Hily-Blant et al. 2008)). Indeed, N_2H^+ was one of the first molecular ions detected in the

interstellar medium (Keto & Caselli 1975) and it is a particularly interesting tool to investigate cold cores (Pagani et al. 2007) as it is less depleted on the dust grain surfaces than most of the molecules. In addition, the hyperfine structure of N_2H^+ helps to discriminate between opacity and collisional excitation effects which puts constraints in the determination of the physical conditions.

Moreover, early stages of low-mass star formation are supposed to be submitted to intense ionization by energetic particles, the surrounding warm gas being enriched in molecular ions. The determination of $\text{HCO}^+/\text{N}_2\text{H}^+$ abundance ratio, measured from high energy lines, is considered as a possible way to investigate this process (Favre et al. 2017). Observations of transitions involving high rotational levels of HCO^+ and N_2H^+ towards a sample of protostars were performed with the Heterodyne Instrument for the Far-Infrared (HIFI) spectrometer on board of Herschel Space Observatory (Favre et al. 2017). The $j_1 = 6 - 5$ and $j_1 = 8 - 7$ lines of N_2H^+ were detected towards 6 protostars and the $j_1 = 11 - 10$ line was tentatively detected towards one source

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only. Modelling of these observations should require accurate collisional rate coefficients for high lying transitions with upper energy ≥ 100 K and for relatively high temperatures. In such conditions, rate coefficients for collisions with both para- and ortho- H_2 are required.

Collisional rate coefficients for N_2H^+ with para- H_2 ($j_2 = 0$) have been published by [Lique et al. \(2015\)](#), hyperfine-structure-resolved excitation rate coefficients were given for transitions between N_2H^+ j_1 rotational levels up to $j_1 = 7$ and temperatures ranging from 5 K to 70 K. These rate coefficients are based on the 4D potential energy surface (PES) ([Spielfiedel et al. 2015](#)) obtained from highly correlated ab initio calculations. The resulting rate coefficients differ significantly from the N_2H^+ -He values published by [Daniel et al. \(2005\)](#), with differences which cannot be reproduced by a simple scaling relationship. Recently, specific collisional rate coefficients for the $\text{N}^{15}\text{N}-\text{H}^+-\text{H}_2$ collisional system were computed in order to understand the enrichment process of molecules in ^{15}N atoms ([Daniel et al. 2016](#)). The differences between N^{15}NH^+ and N_2H^+ collisional data are minor so that the rate coefficients for the dominant isotopologue can be used safely for the minor ones.

While [Lique et al. \(2015\)](#) presented calculations for rotational levels $j_1 \leq 7$, we focus here on the computation of the collisional rate coefficients for the first 26 rotational levels and temperatures up to 500 K. Accurate data can be obtained at the full quantum time-independent Close-Coupling (CC) level of theory. However, due to the large well depth of the interaction surface ([Spielfiedel et al. 2015](#)) and the small rotational constant of N_2H^+ (1.55397 cm^{-1} ([Sastry et al. 1981](#))), the numerical solution of the coupled equations becomes impracticable due to memory and CPU requirements. So we have implemented a realistic although accurate approximate method to circumvent this problem. The Adiabatic Hindered Rotor approach (AHR) ([Zeng et al. 2011](#)) which reduces the 4D PES to a 2D PES was used for this purpose. The paper is organised as follows: Section 2 summarizes the ab initio calculations of the PES and provides a description of the scattering calculations. The validity of the reduced dimensional approach AHR is discussed. In Section 3, we present the resulting rate coefficients between rotational levels of N_2H^+ and in Section 4 the corresponding hyperfine resolved rate coefficients with conclusion set out in Section 5.

2 COMPUTATIONAL METHODOLOGY

2.1 Potential energy surface

All calculations presented here are based on the ab initio PES calculated by [Spielfiedel et al. \(2015\)](#). This PES is briefly described below and we refer the reader to [Spielfiedel et al. \(2015\)](#) for more details. Both molecules were treated as linear rigid rotors. The interaction potential was expressed in Jacobi coordinates $V(R, \theta_1, \theta_2, \varphi)$ (see Fig. 1 for the definition of the coordinates). The 4D $\text{N}_2\text{H}^+-\text{H}_2$ PES was computed at the coupled cluster with single, double and perturbative triple excitation [CCSD(T)] ([Hampel et al. 1992](#); [Watts et al. 1993](#)) level of theory with augmented correlation consistent triple zeta basis sets of [Woon & Dunning \(1994\)](#) for all atoms.

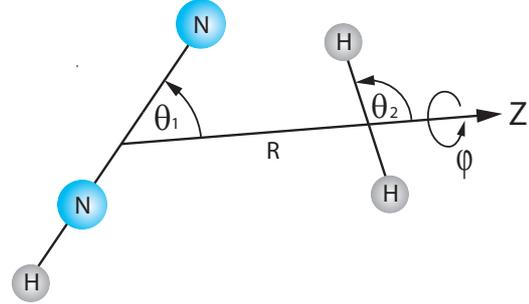


Figure 1. Jacobi coordinate system for the $\text{N}_2\text{H}^+-\text{H}_2$ complex.

Table 1. N_2H^+ rotational energy levels calculated from constants of [Sastry et al. \(1981\)](#)

j_1	$\epsilon_{j_1} \text{ (cm}^{-1}\text{)}$	j_1	$\epsilon_{j_1} \text{ (cm}^{-1}\text{)}$
0	0.000	13	281.550
1	3.095	14	324.848
2	9.285	15	371.234
3	18.570	16	420.706
4	30.949	17	473.264
5	46.423	18	528.906
6	64.990	19	587.631
7	86.651	20	649.437
8	111.406	21	714.324
9	139.252	22	782.290
10	170.191	23	853.333
11	204.220	24	927.451
12	241.340	25	1004.645

The equilibrium structure was found for a T-shape configuration with the H atom of N_2H^+ pointing towards the centre of mass of H_2 . The corresponding distance between the centres of mass is $5.8 a_0$ and the well depth is -2530.86 cm^{-1} .

The spherical harmonic expansion of the PES required by quantum calculations is given by the following expansion ([Green 1975](#)):

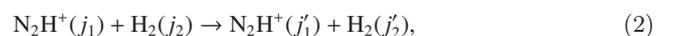
$$V(R, \theta_1, \theta_2, \varphi) = \sum_{l_1=0}^{16} \sum_{l_2=0}^6 \sum_{l=|l_1-l_2|}^{l_1+l_2} v_{l_1, l_2, l}(R) A_{l_1, l_2, l}(\theta_1, \theta_2, \varphi) \quad (1)$$

A set of radial functions (238 terms) were needed to represent correctly the anisotropy of the PES with respect to the θ_1 and θ_2 Jacobi angles.

2.2 Scattering calculations

2.2.1 Methods

This study focuses on the following collisional excitation process:



where j_1 (j'_1) and j_2 (j'_2) are the rotational angular momenta of N_2H^+ and H_2 , respectively.

The Close-Coupling (CC) method is the most accurate approach to describe inelastic collisions. For all

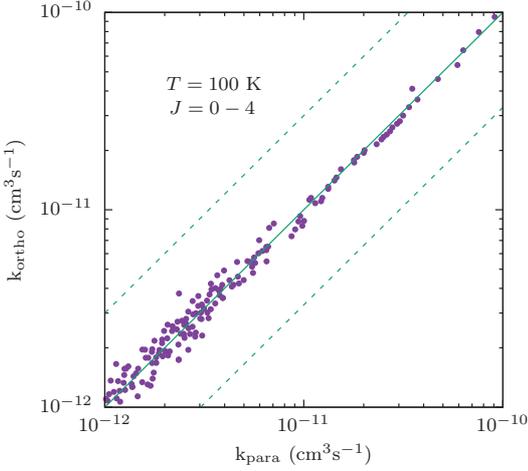


Figure 2. Comparison of the ortho and para- H_2 rate coefficients, computed with the full 4D-CC method, summed over $J = 0 - 4$ for $T = 100$ K. The dashed lines represent an error by a factor of 3.

calculations, we used the full quantum CC approach of Green (1975) to obtain the state-to-state cross sections for transitions between N_2H^+ rotational levels. The S -matrix elements were calculated using the MOLSCAT program (Hutson & Green 1994). The modified log-derivative Airy propagator of Alexander & Manolopoulos (1987) was employed with a variable step size to solve the CC equations from $R = 4$ to $R = 100$ bohr. The N_2H^+ energy levels (see Table 1) were computed using the rotational constants of Sastry et al. (1981). 4D-calculations were carried out for total energies up to 1000 cm^{-1} . Parameters of integrator were adjusted in order to insure a typical precision of 0.05 \AA^2 for the calculated cross sections from which, one can obtain the corresponding thermal rate coefficients at temperature T by an average over the collision energy (E_c):

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

where $\sigma_{\alpha \rightarrow \beta}$ is the cross section from initial level α to final level β , $\mu = 1.8847$ amu is the reduced mass of the system and k_B is Boltzmann's constant.

In the case of $N_2H^+ - H_2$ collisions, preliminary CC calculations, for the partial wave $J = 0$ of the total angular momentum and at a collision energy of 100 cm^{-1} , showed that the convergence of the cross sections requires to include all N_2H^+ rotational states up on $j_1 = 28$ (Spielfiedel et al. 2015). However, the dependence of the rate coefficients (found for the partial wave $J = 0$) with the H_2 rotational basis set is rather moderate with differences lower than a few percent between $j_2 = 4$ and $j_2 = 6$ para- H_2 rate coefficients and less than 10 per cent between $j_2 = 3$ and $j_2 = 5$ ortho- H_2 rate coefficients.

It is important to notice that due to the large N_2H^+ basis set needed for convergence of the scattering calculations combined to the large number of terms in the PES expansion (see Eq. 1), complete converged CC calculations become prohibitive. Thus, we have explored two approximate approaches to overcome this problem: the Adiabatic Hindered Rotor approach (AHR)(Li et al. 2010)

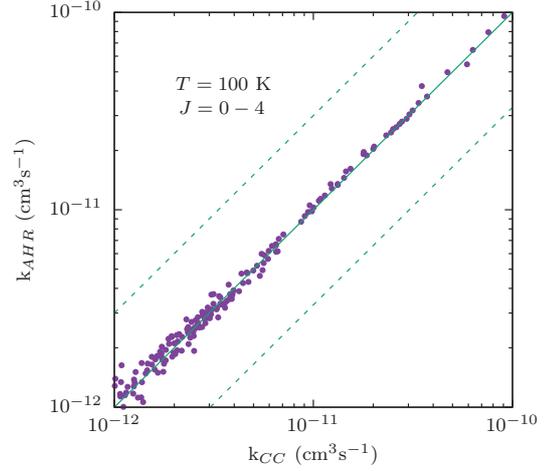


Figure 3. Comparison of the rate coefficients, summed over $J = 0 - 4$, obtained with the 2D adiabatically reduced dimensionally (AHR) and the full 4D-CC method for $T = 100$ K. The dashed lines represent an error by a factor of 3.

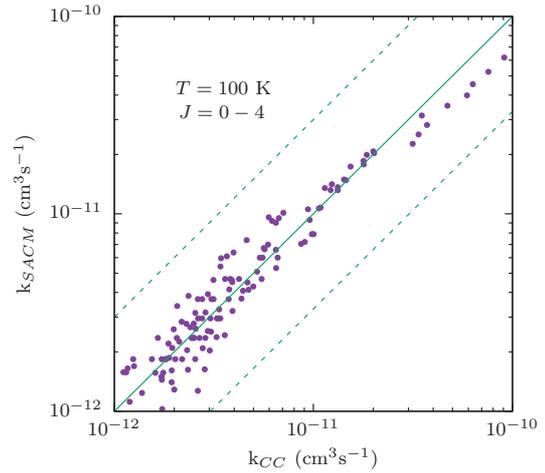


Figure 4. Adiabatic SACM rate coefficients, compared to full 4D-CC rate coefficients, summed over $J = 0 - 4$. The dashed lines represent an error by a factor of 3.

and the Statistical Adiabatic Channel Model (SACM) (Quack & Troe 1974, 1975). The applicability and accuracy of these two methods to the $N_2H^+ - H_2$ collisional system are discussed in the following section.

The Adiabatic Hindered Rotor approach (AHR), proposed by Li et al. (2010) was used successfully by Zeng et al. (2011) for bound states calculations and by Scribano et al. (2012) for scattering calculations. In this approximation, the rotation of the H_2 molecule is adiabatically decoupled to the other intermolecular degrees of freedom. This approximation results in a reduced 2D inter-molecular PES adapted to rotational excitation of N_2H^+ by para- H_2 . It is important to specify that the resulting 2D PES is not computed by averaging the 4D PES over a single rotational state of H_2 (as it is frequently done in the literature using the ground rotational state $j_2 = 0$). The AHR 2D PES is obtained from an adiabatic eigenvalue problem solved in a para-symmetrized

rotational basis of H_2 (with $j_{2\max}=4$) and thus takes into account the angular anisotropy as well as the rotational energy contribution of the para- H_2 state (see [Scribano et al. \(2012\)](#); [Spielfiedel et al. \(2015\)](#) for details). The resulting PES was fitted by means of the procedure described by [Werner et al. \(1989\)](#). As shown in [Spielfiedel et al. \(2015\)](#), an excellent agreement between cross sections computed for a total angular momentum $J = 0$ using 4D and 2D-AHR PESs was found with differences less than a few percent between the data and a remarkable description of the resonances present at low temperatures, while the agreement is not as good using a 2D-spherical averaged PES. The same conclusion was found for the corresponding rate coefficients.

The statistical adiabatic channel model (SACM) was introduced by [Quack & Troe \(1974, 1975\)](#) to describe reactive processes and applied for the first time to a study of rotationally inelastic collision for benchmark systems ([Loreau et al. 2018a](#)) and more recently to scattering of CO with H_2O ([Loreau et al. \(2018b\)](#), [Faure et al. \(2020\)](#)). It was shown ([Loreau et al. 2018a](#)) that the statistical method gives the best results for collisions in the cases where the depth of the interaction PES is large so that a long-lived intermediate molecular complex is formed during the collision resulting in a statistical distribution of the population of the internal molecular levels. It is then found that the SACM method is able to reproduce CC results with an error smaller than a factor of 2 at low temperatures. Considering the large well depth (-2530.86 cm^{-1}) found in the $\text{N}_2\text{H}^+\text{-H}_2$ 4D PES, we anticipate that the SACM approach is a competitive alternative to describe rotational excitation of N_2H^+ by H_2 at relatively low energy.

2.2.2 Discussion on the accuracy of approximate scattering treatment

First of all, it is important to compare para- and ortho- H_2 CC-rate coefficients. For this comparison, we have considered partial rate coefficients summed over the first five total angular momenta J in order to minimize the role of the large resonances found in the cross sections at low collision energy. Taking as a "reference" calculations with $j_{1\max} = 24$ and $j_{2\max} = 4$ for para- H_2 and $j_{2\max} = 3$ for ortho- H_2 , we compare in [Fig. 2](#) the two sets of $J = 0-4$ rate coefficients at temperature $T = 100 \text{ K}$, for all transitions with an initial state up to $j_1 = 20$. It appears clearly that the two sets of data agree well, within a few percent for the largest ones. The same agreement is found for other temperatures. This comparison confirms that both the para- and ortho-data exhibit similar values. The relatively small difference between para- and ortho- H_2 rate coefficients, also found for other ionic systems (HCO^+ ([Massó & Wiesenfeld 2014](#)), CN^- ([Kłos & Lique 2011](#)), C_6H^- ([Walker et al. 2017](#)), CF^+ ([Desrousseaux et al. 2019](#))), indicates that, at the temperatures considered, the inelastic process is mostly governed by the long range interactions. Accordingly, the use of para- H_2 values to estimate ortho- H_2 rate coefficients could be considered as a realistic approach for astrophysical modelling. Thus in what follows, we focus the paper on the study of rotational excitation of N_2H^+ by para- H_2 .

Concerning rotational excitation of N_2H^+ by para- H_2 , we have considered the two approximate methods detailed

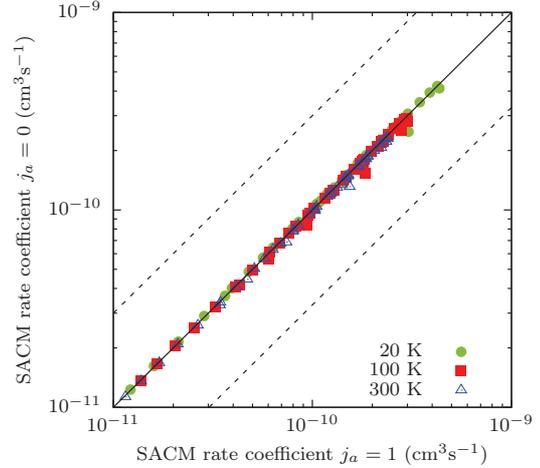


Figure 5. Comparison of the ortho and para- H_2 rate coefficients for all N_2H^+ transitions up to $j_1 = 9$, computed with the SACM approach. The dashed lines represent an error by a factor of 3.

in [Sec. 2.2.1](#). To ascertain the accuracy of the AHR approach, already mentioned previously ([Spielfiedel et al. 2015](#)), we compare in [Fig. 3](#) the 4D-CC "reference" data ($j_{1\max} = 24$, $j_{2\max} = 4$) with the 2D-AHR para- H_2 rate coefficients at 100 K, for all N_2H^+ rotational transitions up to $j_1 = 20$. The horizontal axis represents the 4D-CC rate coefficients and the vertical axis those obtained within the AHR approach. For this comparison, the 2D AHR results were also obtained using $j_{1\max} = 24$. As can be seen, the agreement between the two sets of data is extremely good, with differences within a factor of 2 and better than 20 per cent for the dominant transitions.

[Fig. 4](#) shows a comparison between the 4D-CC and the SACM partial rate coefficients (summed over $J = 0-4$) for collisions with para- H_2 at 100 K and for all N_2H^+ transitions up to $j_1 = 12$. For this comparison, the SACM calculations were performed with basis sets up to $j_{1\max} = 20$ and $j_{2\max} = 2$, which are enough for full convergence of the rate coefficients. We observe that the statistical method predicts the rate coefficients with a good accuracy, better than a factor of 2 over several orders of magnitude and within 10-20 per cent for the largest one. It is the same at all temperatures up to 300 K. We also observe a good agreement between full J -converged AHR and SACM rate coefficients. However, this agreement is not as good when considering rotational excitation involving higher rotational levels of N_2H^+ . For values of $j_1 > 15$ the statistical approach strongly underestimates the rate coefficients and a method to correct for this discrepancy will require further investigation. Finally, we also want to notice that J -converged para- and ortho- H_2 rate coefficients, calculated within the SACM approach are very close together (see [Fig. 5](#)) which confirms the results found using the $J = 0-4$ 4D-CC approach.

Since our purpose is to provide rate coefficients for transitions involving N_2H^+ rotational states up to $j_1 = 25$, and temperatures up to 500 K, we consider that the 2D-AHR approach is a real alternative to the full 4D treatment of rotational excitation by para- H_2 . The results are given in the following section.

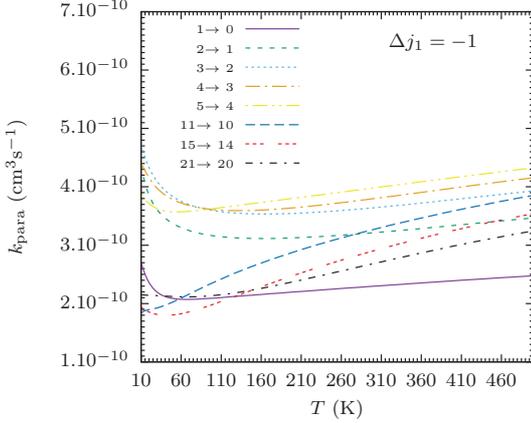


Figure 6. Rate coefficients for collisions for the rotational excitation of N_2H^+ by para- H_2 ($j_2 = 0$) for transitions $\Delta j_1 = 1$ as a function of temperature. The rate coefficients are labelled according to the related transition $j_1 \rightarrow j'_1$.

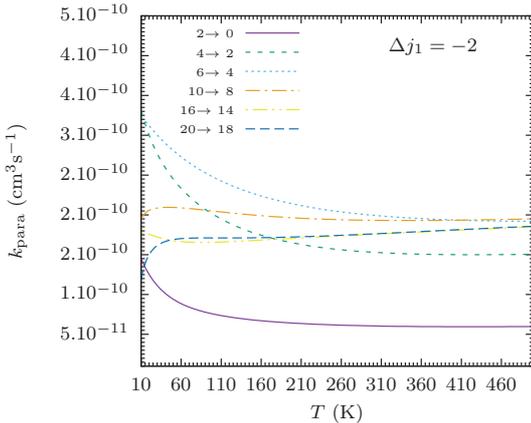


Figure 7. Same as figure 6 for transitions $\Delta j_1 = 2$

3 RESULTS

We present in this section state-to-state rate coefficients calculated within the 2D-AHR approach. These calculations were carried out for total energies ranging from 3.2 to 3000 cm^{-1} with energy grid steps of 0.2 cm^{-1} for $E \leq 300$ cm^{-1} , 1 cm^{-1} for $300 \leq E \leq 500$ cm^{-1} , 2 cm^{-1} for $300 \leq E \leq 1000$ cm^{-1} and 5 cm^{-1} for $1000 \leq E \leq 3000$ cm^{-1} . 28 N_2H^+ rotational states were included in the basis set for energies ≤ 1000 cm^{-1} and 30 levels for larger energies. Rate coefficients for transitions involving N_2H^+ rotational states up to $j_1 = 25$ were determined for temperatures ranging from 5 to 500 K.

The rotational de-excitation rate coefficients are displayed as a function of temperature in Figs. 6 and 7 for selected $\Delta j_1 = 1$ and $\Delta j_1 = 2$ transitions, respectively. At the temperatures considered in the present work, the rate coefficients exhibit rather constant values. This is in agreement with the Langevin capture model for ion-neutral interac-

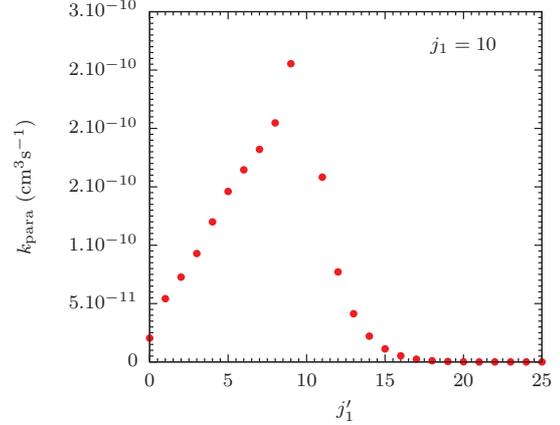


Figure 8. Propensity rules for transitions out of initial state $j_1 = 10$ for collision of N_2H^+ with para- H_2 at $T = 100$ K.

tions. For a given Δj_1 , the rate coefficients values increase with j_1 for the lowest rotational states and then become slightly decreasing at the largest temperatures. This could be explained by the increasing energy distance between the rotational states.

The propensity rules of these rate constants are also interesting to discuss. The excitation and de-excitation rate coefficients at 100 K out of initial state $j_1 = 10$ are shown in Fig. 8. The rate coefficients decrease with increasing Δj_1 with a propensity in favour of $\Delta j_1 = 1$ transitions. The decrease is however relatively slow with only a factor 10 from $\Delta j_1 = 1$ to $\Delta j_1 = 10$. Similar results were found for other ionic systems in collision with H_2 (Walker et al. (2017); Senent et al. (2019)).

The complete sets of (de-)excitation rate coefficients will be made available through the LAMDA (Schöier et al. 2005) and BASECOL (Dubernet, M.-L. et al. 2013) databases.

4 HYPERFINE EXCITATION OF N_2H^+ BY H_2

As mentioned in the introduction, the hyperfine structure of N_2H^+ is frequently resolved in the astronomical spectra. Hence, it is important to provide collisional data considering the hyperfine structure. Lique et al. (2015) computed rate coefficients between the first hyperfine structure levels using a recoupling technique (Alexander & Dagdighian 1985; Faure & Lique 2012). However, the calculations were limited to temperatures up to 70 K and to energy levels with $j_1 \leq 7$. It is then of high interest to provide hyperfine resolved $N_2H^+-H_2$ for higher temperatures.

Almost exact recoupling approaches are very challenging to use both in terms of CPU times and storage of the S-matrices. Hence, we have decided to determine $N_2H^+-H_2$ rate coefficients from the present CC rate coefficients ($k_{j_1 \rightarrow j'_1}^{CC}(T)$) using the Infinite order sudden (IOS) approximation described in Faure & Lique (2012).

Since the nitrogen atoms possess a non-zero nuclear spin ($I = 1$), the N_2H^+ rotational energy levels are split in hyperfine levels which are characterized by the quantum numbers j_1 , F_1 and F . Here, F_1 results from the coupling of \vec{j}_1 with

\vec{I}_1 ($\vec{F}_1 = \vec{j}_1 + \vec{I}_1$, I_1 being the nuclear spin of the first nitrogen atom) and F results from the coupling of \vec{F}_1 with \vec{I}_2 ($\vec{F} = \vec{F}_1 + \vec{I}_2$, I_2 being the nuclear spin of the second nitrogen atom).

Within the IOS approximation, inelastic rotational rate coefficients $k_{j_1 \rightarrow j'_1}^{IOS}(T)$ can be calculated from the “fundamental” rates (those out of the lowest $j = 0$ level) as follows (e.g. [Corey & McCourt 1983](#)):

$$k_{j_1 \rightarrow j'_1}^{IOS}(T) = (2j'_1 + 1) \sum_L \begin{pmatrix} j'_1 & j_1 & L \\ 0 & 0 & 0 \end{pmatrix}^2 k_{0 \rightarrow L}^{IOS}(T). \quad (4)$$

Similarly, IOS rate coefficients among hyperfine structure levels can be obtained from the $k_{0 \rightarrow L}^{IOS}(T)$ rate coefficients using the following formula (e.g. [Corey & McCourt 1983](#); [Daniel et al. 2005](#)):

$$\begin{aligned} k_{j_1 F_1 F \rightarrow j'_1 F'_1 F'}^{IOS}(T) &= (2j_1 + 1)(2j'_1 + 1)(2F_1 + 1)(2F'_1 + 1)(2F + 1) \\ &\times \sum_L \begin{pmatrix} j'_1 & j_1 & L \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_1 & j'_1 & L \\ F_1 & F_1 & I_1 \end{Bmatrix}^2 \\ &\times \begin{Bmatrix} F_1 & F'_1 & L \\ F & F & I_1 \end{Bmatrix}^2 k_{0 \rightarrow L}^{IOS}(T) \end{aligned} \quad (5)$$

where $()$ and $\{ \}$ are respectively the “3-j” and “6-j” Wigner symbols.

Then, in order to improve the accuracy of the IOS data, we follow [Neufeld & Green \(1994\)](#) who have suggested to compute the hyperfine rate coefficients as:

$$k_{j_1 F_1 F \rightarrow j'_1 F'_1 F'}^{NG}(T) = \frac{k_{j_1 F_1 F \rightarrow j'_1 F'_1 F'}^{IOS}(T)}{k_{j_1 \rightarrow j'_1}^{IOS}(T)} k_{j_1 \rightarrow j'_1}^{CC}(T), \quad (6)$$

using the CC rate coefficients $k^{CC}(0 \rightarrow L)$ for the IOS “fundamental” rates ($k_{j_1 \rightarrow j'_1}^{IOS}(T)$) in Eqs. 4-5.

In addition, we note that the fundamental excitation rates $k_{0 \rightarrow L}^{CC}$ were replaced by the de-excitation fundamental rates using the detailed balance relation:

$$k_{0 \rightarrow L}^{CC} = (2L + 1)k_{L \rightarrow 0}^{CC} \quad (7)$$

This procedure is found to significantly improve the results at low temperature due to important threshold effects.

Hence, from the calculated N_2H^+ - H_2 rotational rate coefficients, we were able to determine the state-to-state hyperfine rate coefficients, for transitions involving the 15 lowest N_2H^+ rotational levels, using the computational scheme described above in Eqs. 5-7. In order to check the accuracy of the present data, we report in Fig. 9 the N_2H^+ - H_2 rate coefficients of [Lique et al. \(2015\)](#) (k^{RE}) at 70 K as a function of the present ones, for all hyperfine resolved transitions $j_1 F_1 F \rightarrow j'_1 F'_1 F'$ with $j_1, j'_1 \leq 7$.

As one can see, the global agreement between the two sets of data is good, the agreement being better than a factor of 3 for most of the rate coefficients. The agreement is expected to increase with increasing temperature so that the present set of collisional rate coefficients can be used for modelling warm regions with temperatures above 100 K. We also notice that, already found by [Lique et al. \(2015\)](#), the $\Delta F = \Delta F_1 = \Delta j_1$ propensity rule is observed whatever the rotational levels considered.

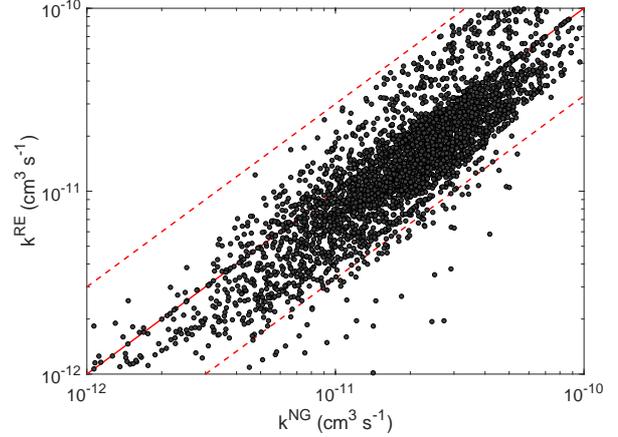


Figure 9. Comparison between present (k^{NG}) and [Lique et al. \(2015\)](#) (k^{RE}) N_2H^+ - H_2 rate coefficients at 70 K. The dashed lines represent an error by a factor of 3.

5 SUMMARY AND CONCLUSION

We have used the quantum Close-Coupling approach to investigate rotational excitation of N_2H^+ by the H_2 molecule. The rate coefficients were computed using a PES obtained from highly correlated ab initio calculations. From test calculations, we have shown that the rate coefficients for collisions with para- and ortho- H_2 agree well within a few percent for the largest ones. Accordingly, the use of para- H_2 rate coefficients for collisions with ortho- H_2 could be considered as a realistic approach for astrophysical modelling.

Considering rotational excitation of N_2H^+ by para- H_2 , it is found that 4D-CC calculations are very difficult to carry out due to the very large N_2H^+ basis set needed for full convergence. So, we have checked two approximations to overcome this difficulty, the statistical SACM method and the AHR approximation which reduces the 4D PES into a 2D PES. Both approaches give results which compare well to full Close-Coupling calculations. However, the SACM approach leads to some discrepancy for high N_2H^+ rotational levels while the agreement between the AHR and the 4D-CC rate coefficients is very good at all temperatures for all j_1 levels, better than 20 per cent for the largest values. Thus, the resulting rate coefficients presented in this paper were computed using the 2D-AHR PES. We would like to note that an even better agreement of the scattering application of the AHR model could come from the recent Diagonal Born Oppenheimer Correction (DBOC) proposed by [Scribano & Faure \(2017\)](#) in the bound state study of the $\text{H}_2\text{O}-\text{H}_2$ complex. This correction has shown a quantitative improvement of the original AHR results and work is in progress for scattering applications.

The state-to-state rate coefficients display almost constant values for temperatures above 100 K, in agreement with the prediction of the Langevin capture model. Whatever the temperature range, the rate coefficients exhibit propensity rules in favour of $\Delta j_1 = -1$ rotational transitions and a slow decrease with increasing $|\Delta j_1|$ values. Similar trends were observed for rotational excitation of other ionic systems (e.g. [Walker et al. 2017](#); [Kłos & Lique 2011](#); [Senent et al. 2019](#)). From the N_2H^+ - H_2 rotational rate coef-

ficients, state-to-state hyperfine rate coefficients were computed using a recoupling technique based on the IOS approximation. The $\Delta F = \Delta F_1 = \Delta j_1$ propensity rule is found for these hyperfine transitions. A comparison with the exact recoupling rate coefficients (Lique et al. 2015) shows a global good agreement between the two sets of data. The present rate coefficients for collisions of N_2H^+ with H_2 will contribute to help to accurately model astrophysical observations of N_2H^+ emission lines in various environments.

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