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HD–H⁺ collisions: statistical and quantum state-to-state studies

In the early Universe, the cooling mechanisms of the gas significantly rely on the HD abundance and excitation conditions. A proper modeling of its formation and destruction paths as well as its excitation by both radiative and collisional processes is then required to accurately describe the cooling mechanisms of the pristine gas. In such media, ion-molecule reactions are dominant. Their theoretical study is challenging and state-of-the-art quantum time-independent methods are computationally limited to collisions involving light molecules. Here, we report a state-to-state scattering study of the HD–H⁺ collisional system using two different methods: an exact quantum time-independent approach and a recently developed fast and efficient statistical method. Reactive and inelastic rate coefficients were obtained for temperatures up to 300 K. The statistical method is able to reproduce exact calculations with an accuracy reaching the astrophysical needs while drastically reducing the computational resources requirements. Such results suggest that this new statistical method should be considered to provide the astrophysical community collisional data for which quantum calculations are impossible.

Benjamin Desrousseaux,^a Maarten Konings,^b Jérôme Loreau,^b and François Lique^a

1 Introduction

In the Universe, hydrogen is the most abundant element and its molecular form, H₂, constitutes the dominant molecule in astrophysical environments. It is now well established that H₂ and its isotopic variant HD are key species for the early Universe chemistry^{1–9} and the cooling mechanisms of the low metallicity clouds and during the formation of the very first stars^{10–12}.

The chemical composition of the primordial gas mainly consists of ionized species (e[–], H, H⁺, H[–], D, D⁺, He, He⁺, He²⁺, Li, Li⁺, Li[–], H₂, H₂⁺, HD, HD⁺, HeH⁺, LiH, LiH⁺, H₃⁺, and H₂D⁺), and ion-molecule reactions are known to be the dominant processes in the early Universe chemistry². Due to their inherent practical advantages for preparation, control and detection, ion-molecule collisions have been subject to many experimental studies over the years¹³. However, the long-range attractive potential of these reactions and the common absence of large activation barriers make the theoretical studies challenging.

Quantum time-dependent or approximate semi-classical calculations struggle to reach the accuracy needed for astrophysical applications at low temperatures. Quantum time-independent treatment is therefore the method of choice to study collisions at typical astrophysical temperatures¹⁴. Still, this method requires extremely large amounts of computational resources and is currently limited to reactive systems with a low number of

degrees of freedom and light collisional partners. As an alternative, a wide variety of statistical methods was developed to study chemical reactions and inelastic collisions (see for example the seminal work of Pechukas *et al.*¹⁵, Miller¹⁶, Quack and Troe^{17,18}, Troe¹⁹). Among them, the recently developed approach of Loreau *et al.*^{20,21} inspired by the simple statistical adiabatic channel model (SACM)^{17,18}, seems to offer a great alternative for the study of ion-molecule scattering. While overcoming the computational obstacles, this new statistical approach is believed to produce results that are sufficiently accurate for astrophysical applications and therefore needs to be benchmarked on relatively simple reactive systems, for which quantum-time independent calculations are feasible. Technical details on this improved SACM can be found in Refs^{21,22}

The H⁺ + H₂ prototypical collisions have been extensively studied over many years. Indeed, the relative simplicity of the H⁺–H₂ collisional system and its isotopic variants represents a serious advantage for theoretical studies²³. While the isotopic reaction D⁺ + H₂ → HD + H⁺ has been intensively studied, both experimentally^{24–26} and theoretically^{27–33}, only a few data is available for the reverse reaction HD + H⁺ → D⁺ + H₂^{24,34–38}.

The HD + H⁺ → D⁺ + H₂ reaction is slightly endothermic by ~ 320 cm^{–1} for the HD molecule in its ground rovibrational level but proceeds without activation barrier and becomes exothermic for HD in rotational states $j \geq 3$. In the early Universe, the destruction of HD molecules through collisions with H⁺ atoms is known to be effective as the temperatures generally allow overcoming the activation barrier of the reaction but also because HD

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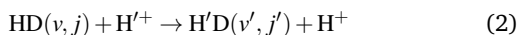
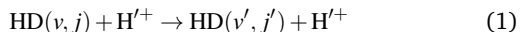
rotational levels higher than $j = 3$ are found to be significantly populated. Moreover, the collisional excitation of HD plays an important role in the cooling mechanism of pristine gas where H^+ ions are present and even dominant colliders. It is then crucial to obtain accurate HD– H^+ collisional data for both the excitation and reactive processes.

Lepers *et al.*^{37,38} recently reported exact quantum time-independent close-coupling (CC) calculations of the state-to-state rate coefficients for the HD– H^+ collisional system. In this work, however, they only focused on the reactive process, providing no rate coefficients for the excitation of HD through collisions with H^+ whereas such data are also very useful for astrophysical applications¹⁴.

In this paper, we present a new theoretical state-to-state scattering study of the HD– H^+ collisional system where the calculations we carried out using two different methods: an exact quantum (CC) approach and a recently developed statistical method. Our goal was (i) to provide new collisional data for this system, and (ii) to evaluate the accuracy of the SACM approach when studying reactive systems. A description of the methods can be found in Section 2. Results from both sets of calculations are presented and compared in Section 3. Concluding remarks and discussions are drawn in Section 4

2 Methods

During collisions between HD and H^+ , the inelastic (1), exchange (2), and reactive (3) processes compete:



where v and j denotes the vibrational and rotational level of the diatomic molecules. In our study of the scattering dynamics, this competition is taken into account and all three processes are considered. The VLABP H_3^+ global potential energy surface (PES) of Velilla *et al.*³⁹, properly describing the interaction energy in the reactants and reaction products channels, was employed in both our CC and statistical calculations. This PES represents an improvement of the long-range interactions from the ARTSM PES of Aguado *et al.*⁴⁰, computed at the full configuration interaction (FCI) *ab initio* level and using an extended basis set. Figure 1 shows the HD– H^+ VLABP PES as a function of the Jacobi coordinates R and θ for a fixed internuclear r_{HD} distance of 1.442 bohr, corresponding to the equilibrium distance of the ground vibrational state. In the Jacobi coordinate system, the centre of coordinates is placed in the HD centre of mass, and the vector R connects the HD centre of mass with the H^+ proton. The rotation of HD molecule is defined by the θ angle ($\theta = 0^\circ$ corresponds to the $\text{H}^+ \cdots \text{D}-\text{H}$ configuration). As could be inferred from previous study on the $\text{H}^+ + \text{H}_2$ system (see Rao *et al.*⁴¹), the VLABP PES is attractive for near T-shaped geometries while a barrier of almost 25 cm^{-1} is present for collinear geometries. The minimum configuration corresponds to $\theta = 100^\circ$ with a well depth of $\sim 35,600 \text{ cm}^{-1}$.

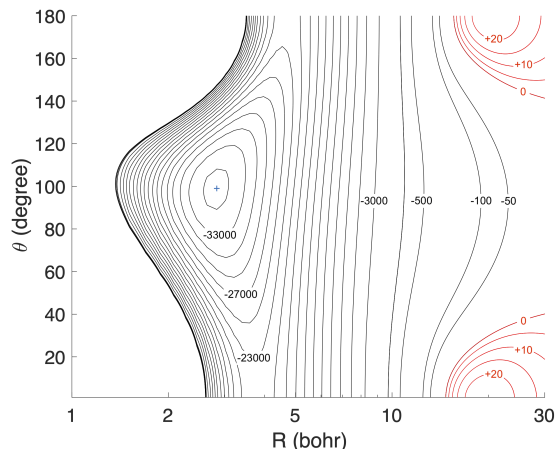


Fig. 1 Contour plot of the HD– H^+ VLABP PES (in cm^{-1}) as a function of the Jacobi coordinates for a fixed internuclear r_{HD} distance of 1.442 bohr.

In the following, the vibrational level of the molecules is omitted as we considered here low collisional energies implying that HD and H_2 remain in their ground vibrational level.

2.1 Close Coupling (CC) calculations

We used the ABC quantum reactive scattering program⁴² to carry out CC calculations of reactive, exchange, and inelastic cross sections of the HD– H^+ collisional system. It is computationally efficient to choose basis functions that are eigenfunctions of the operator corresponding to interchange of the two hydrogens. Hence, since the Hamiltonian is symmetric with respect to interchange of the two hydrogens, there will be no coupling between odd (ortho) and even (para) rotational states of H_2 , so that the number of coupled channels is reduced. We then obtained inelastic, reactive and exchange integral cross sections following the approach described by Tao and Alexander⁴³ and recently used to study the rotational excitation of several hydrides in collision with H ^{44–47}. Excited vibrational states up to $v = 17$ and up to $j = 6$ ($E_{\text{max}} = 4.4 \text{ eV}$) are included in the basis to ensure convergence of the cross sections. The log-derivative method of Manolopoulos⁴⁸ was used to solve the coupled equations for hyperradii up to $\rho_{\text{max}} = 44 \text{ a}_0$. Calculations were done for all values of the total angular momentum J leading to a non-zero contribution in the cross sections (~ 60 at 1500 cm^{-1} , the highest considered energy).

Such calculations are in principle very similar to those performed by Lepers *et al.*^{37,38}. However, the comparison between our results and those of Lepers *et al.*^{37,38} shows a systematic difference in the reactive rate coefficients of a factor of ~ 2 . This systematic difference arises from the consideration of the two H atoms as either distinguishable or indistinguishable particles⁴⁹. In this work, the two H atoms were considered as distinguishable particles as can be seen in Equations 1, 2, and 3.

2.2 Statistical approach

We used a new quantum statistical method inspired by the statistical adiabatic channel model (SACM) of Quack and Troe^{17,18}.

This method, described for the first time by Loreau *et al.*²¹, was successfully benchmarked on inelastic collisions involving several strongly-bound non-reactive systems (OH⁺-H, OH⁺-He, and CN⁻-H₂), showing a very good agreement with CC calculations at low temperatures.

While for CC calculations the set of coupled differential radial equations:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \chi_\alpha}{dR^2} + \sum_{\alpha'} \left\langle \alpha' \left| \mathcal{H}_{\text{int}} + V + \frac{L^2}{2\mu R^2} \right| \alpha \right\rangle \chi_\alpha = E \chi_\alpha \quad (4)$$

has to be solved for a given energy E and each value of the total angular momentum J , the so-called adiabatic curves of the reactants and reaction products channels are alternatively (there is no coupling between the different arrangements) obtained by excluding the nuclear kinetic term and diagonalizing only the W coupling matrix:

$$\left\langle \alpha' \left| \mathcal{H}_{\text{int}} + V + \frac{L^2}{2\mu R^2} \right| \alpha \right\rangle \quad (5)$$

where μ is the reduced mass of the system, R is the distance between the center of mass of the molecule and the atom, and L is the angular momentum describing the relative motion of the two colliding partners. \mathcal{H}_{int} is the Hamiltonian describing the internal rotational motion of the molecule, V denotes the potential energy surface of the system, and $|\alpha\rangle$ corresponds to the angular basis set.

In our case, the molecules were considered as rigid rotors. We fixed the internuclear distances of the molecules at 1.401 and 1.442 a₀ for HD and H₂, respectively. We used the molecular constants $B_e = 45.655$ cm⁻¹, $\alpha_e = 1.986$ cm⁻¹ and $D_e = 0.0260$ cm⁻¹ for the HD molecule, and $B_e = 60.853$ cm⁻¹, $\alpha_e = 3.062$ cm⁻¹ and $D_e = 0.0471$ cm⁻¹ for the H₂ molecule⁵⁰. For both molecules, rotational states up to $j = 20$ were considered. From the generated adiabatic curves, we construct the S matrix by assuming that all energetically open adiabatic channels (adiabatic curve for a given state) have the same probability:

$$|S_{\alpha\beta}(E, J)|^2 = \begin{cases} \frac{1}{N(E, J)} & \text{for open channels} \\ 0 & \text{for closed channels} \end{cases} \quad (6)$$

where α and β represent the initial and final rotational levels of the molecule (HD or H₂) and $N(E, J)$ is the total number of open channels for a given collision energy E and total angular momentum J . All open adiabatic channels at a given energy are included in the calculations so that the S matrix is converged with respect to the rotational basis. In our calculations, the ortho and para rotational states of the H₂ molecule were treated separately, meaning that ortho-H₂ channels were not taken in account when considering para-H₂ as a product of the reaction and *vice versa*. Given this separate treatment, one has to divide the reactive S elements by a factor of two, thereby conserving both symmetry and unitarity properties of the S matrix. The cross sections were then obtained from the constructed S matrix as:

$$\sigma_{\alpha \rightarrow \beta} = \frac{\pi}{g_\alpha k^2} \sum_{J=0}^{\infty} (2J+1) |S_{\alpha\beta}(E, J)|^2 \quad (7)$$

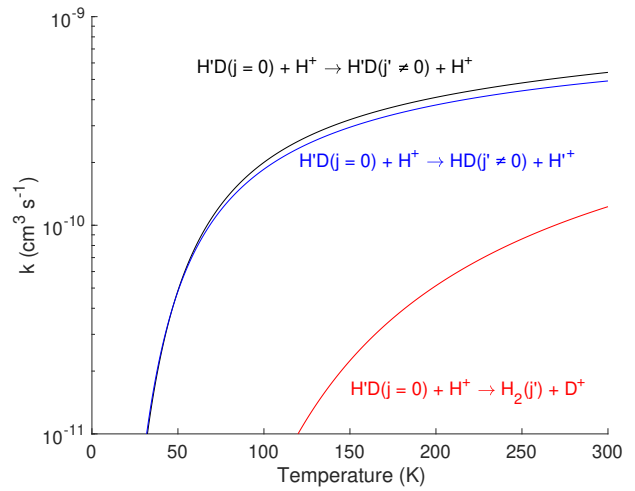


Fig. 2 Temperature variation of the rate coefficients for the inelastic, reactive, and exchange processes (summed over all final states) for collisions of HD($j = 0$) with H⁺.

where g_α is the degeneracy of the considered α state and $k = \sqrt{2\mu E}$.

2.3 Rate coefficients

The determination of the temperature-dependent rate coefficients was achieved by averaging the cross sections $\sigma_{\alpha \rightarrow \beta}$ over the collisional energy E :

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

Where k_B is the Boltzmann constant. For both methods, collisional energies up to 1500 cm⁻¹ were explored in order to allow the determination of rate coefficients for collisions between HD in its first 6 rotational levels ($0 \leq j \leq 5$) and H⁺ for, temperatures up to 300 K.

3 Results

Figure 2 displays the temperature variation of the rate coefficients obtained using pure CC approach for the inelastic, exchange and reactive processes for collisions of HD($j = 0$) with H⁺, summed over all the possible final rotational states. As can be seen, exchange and inelastic rate coefficients are very similar in magnitude over all the temperature range explored in this work, reflecting the large well depth ($\sim 35,600$ cm⁻¹) in the PES and the statistical character of the reaction. The reactive process is negligible at very low temperature and only starts to compete with the excitation of the HD molecule for temperatures higher than ~ 150 K, where the reactive rate coefficients become less than an order of magnitude lower than exchange and inelastic ones. This behavior is explained by the endothermicity of the HD + H⁺ \rightarrow H₂ + D⁺ reaction (~ 320 cm⁻¹), resulting in reactive channels only opening at relatively high collisional energy.

From the astrophysical point of view, excitation through inelastic or exchange process cannot be distinguished. Hence, in the following, inelastic and exchange cross sections have been summed

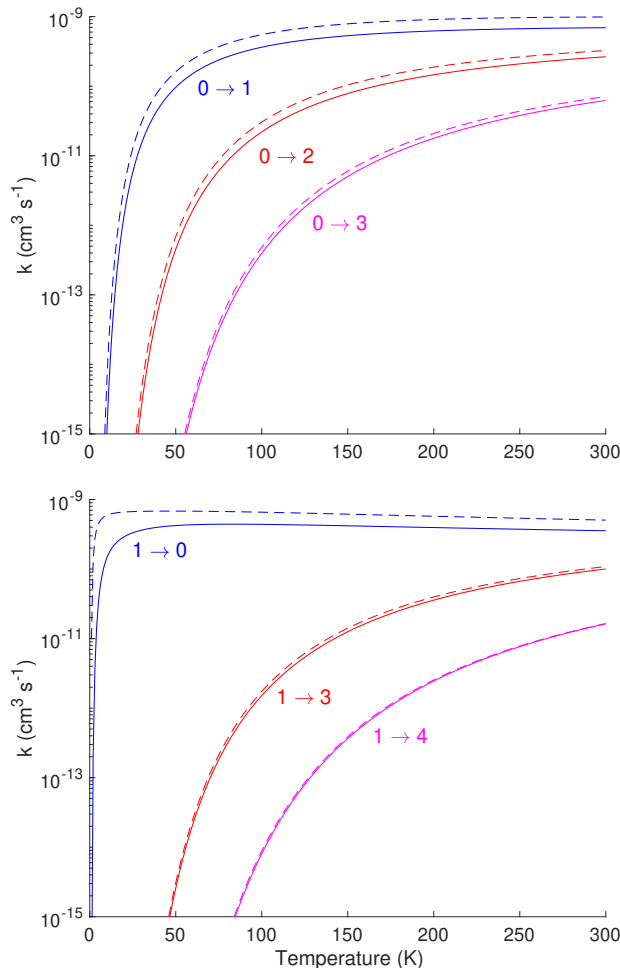


Fig. 3 Temperature variation of the rate coefficients for the rotational (de)excitation of $\text{HD}(j=0) \rightarrow \text{HD}(j')$ (upper panel) and $\text{HD}(j=1) \rightarrow \text{HD}(j')$ (lower panel) induced by collisions with H^+ . Solid and dashed lines represent results obtained using the CC method and the SACM, respectively.

before computing the rate coefficients, denoted in the following as excitation rate coefficients. It is also worth mentioning that, because of its intrinsic nature, the method used in this work assumes the same rate coefficients for the exchange and inelastic processes (see Refs. 21,22).

In Figure 3, we show the temperature variation of the rate coefficients for the rotational (de)excitation of $\text{HD}(j=0) \rightarrow \text{HD}(j')$ and $\text{HD}(j=1) \rightarrow \text{HD}(j')$ induced by collisions with H^+ . Results obtained using the CC method and the SACM are presented. The strongest transitions are those with $\Delta j = 1$, the magnitude of the rate coefficients increasing with decreasing Δj . Rate coefficients for the collisional excitation ($j < j'$) of HD by H^+ are increasing with the temperature. For collisional (de)excitation ($j > j'$), after a rapid increase, rate coefficients are slowly decreasing with increasing temperature. As can be seen, the two sets of data, obtained using whether the CC method or the SACM, are globally in very good agreement, with differences lower than a factor of 2.

A more systematic comparison of the two sets of data is presented Figure 4. In this Figure, we represent the rate coefficients obtained using the SACM as a function of the ones obtained us-

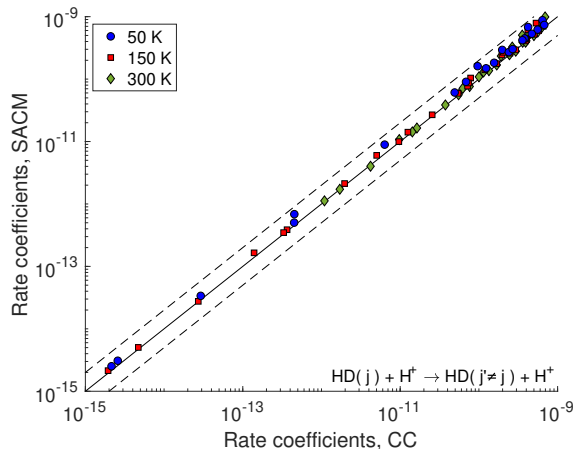


Fig. 4 Systematic comparison between rate coefficients (in units of $\text{cm}^3 \text{s}^{-1}$) obtained using the CC method and the SACM for the rotational excitation HD induced by collisions with H^+ . Rotational transitions between the first 6 levels of HD are taken into account at three different temperatures: 50, 150 and 300K. The dashed lines delimit the region where the rate coefficients differ by less than a factor of 2.

ing the CC method for three different temperatures: 50, 150 and 300 K. All the possible transitions between the 6 first rotational levels of HD ($0 \leq j \leq 5$) are included in the comparison. As one can see, the agreement is very good, better than a factor of 2 at all presented temperatures and for all the transitions. These results demonstrate the ability of the computationally efficient SACM to properly describe state-to-state rate coefficients for the collisional excitation of the HD- H^+ reactive system.

We then focus on the reactive process of the HD- H^+ collisions. In Figure 5, we present the temperature dependence of the rate coefficients for the $\text{HD}(j) + \text{H}^+ \rightarrow \text{H}_2 + \text{D}^+$ reaction, summed over all the final rotational states of the H_2 molecule. As expected, rate coefficients increase with increasing temperature. Rate coefficients for collisions involving higher initial rotational levels of the HD molecule are the largest in magnitude. The agreement between reactive rate coefficients obtained using the two different methods is again very good, the differences being of less than 30% and even almost zero for the reaction involving HD in its ground rotational level.

In order to further investigate the accuracy of the SACM at the state-to-state level, we present in Figure 6 a systematic comparison between state-to-state rate coefficients obtained using the CC method and the ones obtained using the SACM for the $\text{HD}(j) + \text{H}^+ \rightarrow \text{H}_2(j') + \text{D}^+$ reaction. Transitions between the first 6 rotational states of HD and H_2 are taken into account at three different temperatures: 50, 150 and 300K. As can be seen, the SACM is able to reproduce CC calculations to better than a factor of 2 for all the transitions and all represented temperatures, the maximum difference between the two sets of rate coefficients being of $\sim 40\%$.

Finally, we show in Figure 7 the thermal rate coefficient k_{th} as a function of the temperature for the $\text{HD} + \text{H}^+ \rightarrow \text{H}_2 + \text{D}^+$ reaction. The thermal rate coefficient was obtained assuming a Maxwell-Boltzmann distribution of the rotational levels of the HD

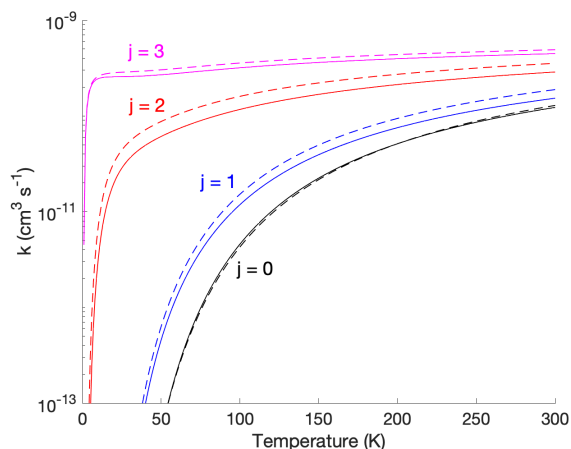


Fig. 5 Temperature dependence of the $\text{HD}(j) + \text{H}^+ \rightarrow \text{H}_2 + \text{D}^+$ reaction rate coefficients (summed over all the product rotational states). The solid and dashed lines correspond to results obtained using the CC method or the SACM, respectively.

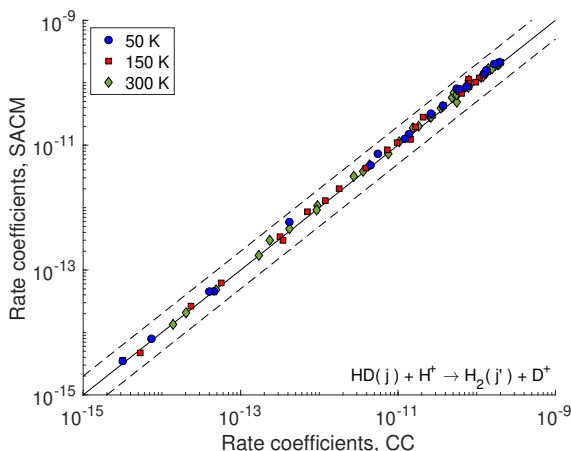


Fig. 6 Systematic comparison between rate coefficients (in units of $\text{cm}^3 \text{s}^{-1}$) obtained using the CC method and the SACM for the $\text{HD}(j) + \text{H}^+ \rightarrow \text{H}_2(j') + \text{D}^+$ reaction. Transitions between the first 6 rotational states of HD and H_2 are taken into account at three different temperatures: 50, 150 and 300K. The dashed lines delimit the region where the rate coefficients differ by less than a factor of 2.

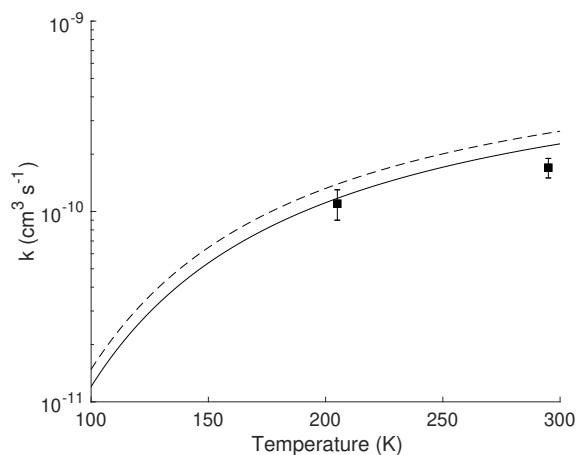


Fig. 7 Comparison of the thermal rate coefficient as a function of the temperature, for the $\text{HD} + \text{H}^+ \rightarrow \text{H}_2 + \text{D}^+$ reaction. Solid and dashed lines represent results obtained using the CC method and the SACM, respectively. Experimental results obtained by Henchman *et al.*²⁴ are also represented.

molecule:

$$k_{\text{th}}(T) = \frac{1}{Z_{\text{rot}}} \sum_{j=0}^5 (2j+1) e^{-\frac{E_j}{k_B T}} \sum_{j'=0}^9 k_{j \rightarrow j'}(T) \quad (9)$$

where E_j is the energy of the $\text{HD}(j)$ rotational level and $Z_{\text{rot}} = \sum_{j=0}^5 (2j+1) e^{-\frac{E_j}{k_B T}}$ is the rotational partition function. We restricted the summations over the HD rotational level to $j=5$ as higher levels are very weakly populated at the temperatures explored in this work and will not significantly affect the final result.

It should be noted that in order to compare to experimental results, one may take into account the nuclear-spin statistics for the two identical nuclei⁴⁹. This is achieved by applying multiplying factors of $\frac{1}{2}$ and $\frac{3}{2}$ to rate coefficients corresponding to *para* and *ortho* states of the H_2 molecule, respectively:

$$k_{\text{th}}(T) = \frac{1}{Z_{\text{rot}}} \sum_{j=0}^5 (2j+1) e^{-\frac{E_j}{k_B T}} \left(\sum_{j'=0,2,\dots}^8 \frac{1}{2} k_{j \rightarrow j'}(T) + \sum_{j'=1,3,\dots}^9 \frac{3}{2} k_{j \rightarrow j'}(T) \right) \quad (10)$$

However, applying such multiplying factors in the present case has no noticeable effect over all the temperature range explored Figure 7 so that using Equation 9 or 10 will give very similar results with differences of less than 2% at 205 K and less than 0.3% at 295 K.

As can be expected from the results presented above, thermal rate coefficients obtained using one or the other method are in very good agreement, the SACM only overestimating the rate coefficients by less than 20% over all the temperature range. Experimental results at 205 and 295 K from Henchman *et al.*²⁴ are also represented on Figure 7. Our theoretical results compare very well with the experiments, the CC thermal rate coefficient lying within the error bars at 205 K and being less than 30% larger at 305 K.

4 Conclusions

In this work, we presented statistical and close-coupling calculations for the scattering study of the HD–H⁺ collisional system. From both methods, state-to-state excitation and reactive rate coefficients were obtained for temperatures up to 300 K. We showed that the SACM approach is able to reproduce CC results with a very good accuracy, the maximum differences being of less than 65% and 40% for the excitation and reactive processes, respectively.

We also computed the thermal rate coefficient for the HD + H⁺ → D⁺ + H₂ reaction and compared it to experimental results, which were available at 205 and 295 K. Our theoretical results are in very good agreement with experimental ones: At 205 K, the CC thermal rate coefficient is within the error bars and less than 30% higher than the experiments at 295 K. Again, the SACM gives very similar result, with less than 20% of differences compared to the CC thermal rate. Such findings strongly suggest that the the new HD–H⁺ collisional data should be used for future applications.

It should be stressed that, because of its need in computational resources, CC calculations are very challenging to carry out for systems for which a large number of channels have to be considered. On the other hand, in the SACM approach, the diagonalization of the *W* coupling matrix is independent of the energy and the convergence of the cross sections with respect to the ro-vibrational basis is much faster than the convergence of CC cross sections: Unlike in the CC approach, it is indeed not necessary to include many closed channels in the ro-vibrational basis in the SACM as they will not account in the construction of the *S* matrix. While the present CC calculations for the HD–H⁺ required a total of 470,000 CPU hours, the SACM was able to produce the rate coefficients using only 0.16 CPU hours. Hence, this new statistical approach should be considered as a great alternative to provide the astrophysical community collisional data for systems for which CC calculations are prohibitive nay impossible, such as interstellar reactive ions (H₃⁺, H₂O⁺, H₃O⁺) in collisions with H/H₂.

Conflicts of interest

There are no conflicts to declare.

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