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Tomás González-Lezana,^{1,a)} Pierre Hily-Blant,² and Alexandre Faure²

AFFILIATIONS

¹Instituto de Física Fundamental, IFF-CSIC, Serrano 123, 28006 Madrid, Spain

²Université Grenoble Alpes, CNRS, IPAG, F-38000 Grenoble, France

^{a)}Author to whom correspondence should be addressed: t.gonzalez.lezana@csic.es

ABSTRACT

The $\text{H}^+ + \text{HD}(v, j)$ reaction has been investigated in detail by means of a statistical quantum method. State-to-state cross sections and rate constants for transitions between reactants and rovibrational states $\text{HD}(v', j')$ of the product arrangement with energies below 0.9 eV collision energy [that is, $\text{HD}(v = 0, j = 0-11)$ and $\text{HD}(v = 1, j = 0-6)$] have been calculated. For the other product channel, $\text{D}^+ + \text{H}_2(v', j')$, rovibrational states up to $(v' = 0, j' = 9)$ have been considered for the calculation of the corresponding thermal rate. Present predictions are compared with previously reported theoretical and experimental rates. Finally, cooling functions for HD due to proton and atomic hydrogen collisions are computed in the low-density regime. We find that the much larger HD- H^+ cooling function, as compared with that of HD-H, does not compensate for the low H^+/H abundance ratio in astrophysical media so that HD cooling is dominated by HD-H (or HD- H_2) collisions.

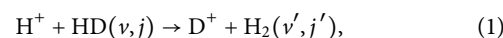
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I. INTRODUCTION

The first structures appearing in the Universe mark both the end of the cosmic dark ages and the beginning of states of increasing complexity, such as galaxies, planets, and life. The so-called Population III (Pop III) stars are likely the first objects to form out of metal-free (no atoms heavier than helium) baryonic matter, at cosmological redshifts $z \approx 10-30$. One of the major questions is the mass distribution of the Pop III, the so-called primordial initial mass function (IMF).^{1,2} Although the James Webb Space Telescope will probe the Universe up to $z \approx 15$, observational constraints on Pop III stars will remain indirect, through their imprint on the generation of stars immediately after or more directly as a transient highly energetic supernova at high redshifts.^{2,3} Among the various parameters that determine the IMF, one is the temperature of the primordial gas that eventually collapses within the potential well of dark-matter halos. Indeed, the typical mass of the gravitationally unstable unit is $\propto T^{3/2}$. However, if dark matter dynamics is governed solely by gravity, that of the primordial gas involves an array of microscopic processes, such as inelastic or reactive collisions. Actually, H_2 molecules

forming at particle density above $\sim 1 \text{ cm}^{-3}$ are the main coolants at temperatures below $\sim 1000 \text{ K}$.⁴ Furthermore, below $\sim 200 \text{ K}$ and density above $\sim 10^8 \text{ cm}^{-3}$, the HD molecule becomes an important coolant,^{5,6} despite its lower abundance. This is essentially because its rotational levels are more compact than those of H_2 , with a $j = 1$ level lying 128 K above ground state, while the quadrupolar H_2 $j = 2-0$ transition has an energy of 510 K. Computing the cooling by HD is therefore of central importance for precise cosmological simulations of the formation of Pop III stars. In this context, it is crucial to provide state-to-state rate coefficients for collisions between HD and the dominant colliders, namely, hydrogen, helium, electrons, and protons. In particular, this paper focuses on HD- H^+ collisions.

The reactive collision between H^+ and HD can lead to two different product channels,



Early measurements⁷ of the rate coefficient of reaction (1) at 205 and 295 K led values of (1.1 ± 0.2) and $(1.7 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively. Millar *et al.*⁸ suggested an Arrhenius fit for those measured values. In their study of H/D exchange reactions in deuteration processes for interstellar molecules, Smith *et al.*⁹ estimated the rate constant for reaction (1) to be $\sim 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ at 20 K, and therefore concluded that this process that converts HD to H₂ is totally unimportant in cold interstellar clouds. This might explain the relatively scarce literature on this reaction in comparison with some other isotopic variants of the corresponding atom–diatom collisions for the H₃⁺ species. In most of the cases, the information on the title reaction is provided completing studies devoted to the reverse reaction $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$.^{10,11} Gerlich and Schlemmer¹¹ reported values of the rate coefficient between 100 and 500 K obtained by means of a dynamically biased statistical theory. A possible fit to an Arrhenius expression for the temperature range 30–130 K was also suggested. Jambriña *et al.*¹⁰ performed theoretical calculations of the rate constant between 100 and 500 K by means of quasiclassical trajectory (QCT), a statistical QCT^{12,13} and time independent quantum mechanical (TIQM) methods that lead to a reasonable agreement with the two experimental values of Ref. 7.

More recently, Lepers *et al.*¹⁴ performed TIQM calculations on the collision yielding $\text{D}^+ + \text{H}_2$, reaction (1), to produce rate coefficients as a function of the temperature below 4000 K. The investigation was limited to the ground vibrational state, $v = 0$, considering up to $j = 9$ rotational states of the reactant HD. Desrousseaux *et al.*¹⁵ tested a statistical adiabatic channel model (SACM)¹⁶ for both product channels [Eqs. (1) and (2)] and compared rate constants with results obtained by means of the ABC code of Ref. 17. The calculations were restricted to processes in which both HD and H₂ species remain in their vibrational ground state.

The presence of a deep potential well (about 4.3 eV depth) in the intermediate region, H₂D⁺, between reactants and products favors complex-forming mechanisms to govern the overall dynamics of the process at collision energies below 3 eV.^{18–21} The statistical quantum mechanical (SQM) method of Refs. 22–24 has been applied several times before to the title reaction and isotopic alternatives interchanging hydrogen and deuterium atoms.^{24–30} Thus, for example, simulations of differential cross sections and kinetic energy spectra were found to reproduce fairly well both exact quantum mechanical (EQM) results and experimental results for the H⁺ + D₂ reaction.³¹ The method also provides an average description of the reaction probabilities, usually characterized for this type of insertion processes by numerous resonances, and of the rotational distributions, which show a preference to populate high rotational states of the resulting diatom formed at the product arrangement.

The information about the reaction so obtained can then be employed in astrochemical models to estimate the age of molecular clouds and prestellar cores of the interstellar medium.^{32,33} In a recent investigation on the H⁺ + H₂ reaction³⁴ with the SQM method, integral cross sections (ICSSs) for the transitions between a series of rovibrational states of H₂ and then the corresponding state-to-state rate constants between $T = 5 \text{ K}$ and 3000 K. Cooling rate coefficient of molecular hydrogen excited by protons was calculated and compared with previous estimates. Those results were ultimately applied on the investigation on the cooling of primordial and interstellar media by H₂.³⁵

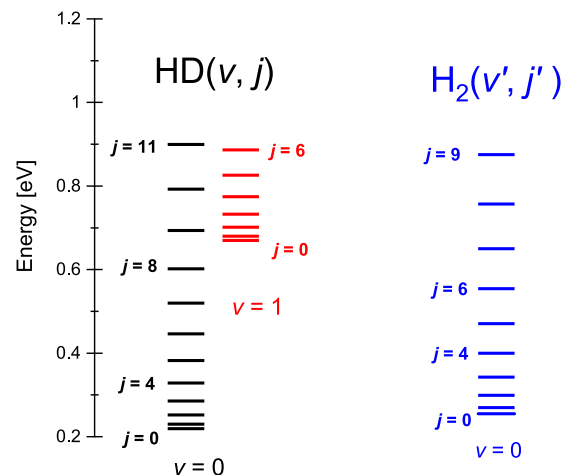


FIG. 1. Total energy levels for the rovibrational states of HD(v, j) and H₂(v', j') considered in this study measured in eV.

In the same spirit, here, we have extended those calculations to reactions (1) and (2). First, ICSSs up to a collision energy of 2.3 eV have been calculated by means of the SQM method for both product arrangements of the title reaction and, second, we obtain the corresponding rate coefficients for a temperature range between 5 and 3000 K. For reaction (1), transitions between HD($v = 0, j = 0–8$) and H₂($v' = 0, j' = 9$) have been considered, whereas, for reaction (2), we have investigated transitions involving states with total energy below 0.9 eV, that is, HD($v = 0, j = 0–11$) and HD($v = 1, j = 6$). All these involved rovibrational states for HD and H₂ are shown in the levels scheme as a function of the total energy of Fig. 1.

The structure of this paper is as follows: In Sec. II, we briefly describe the theoretical details of the calculation; in Sec. III, we show the results for both reactions (A) and (B); in Sec. IV, we present the cooling rate coefficient; and in Sec. V, conclusions are drawn.

II. THEORY

Given that the title reaction, and other isotopic variants where at least one H atom is substituted by a D atom, seems to be governed at not too large energies by complex-forming mechanisms, the application of the above-mentioned SQM approach^{22–24} usually provides useful information. The technical details about this method have been amply discussed and explained in previous occasions, and so, in order to avoid repetitions, here we restrict ourselves to the essential aspects.

The ICSSs are calculated following the standard expression:

$$\sigma_{vj, v'j'}(E) = \frac{\pi}{k_{vj}^2 (2j+1)} \sum_J (2J+1) P_{vj, v'j'}^J(E), \quad (3)$$

where $k_{vj}^2 = 2\mu(E - E_{vj})/\hbar^2$, with E_{vj} the energy of the initial rovibrational state of the reactant diatom and μ the reduced mass of the system. However, in Eq. (3), the state-to-state probability between the initial rovibrational HD(v, j) and the product species (either HD or H₂) in its rovibrational state (v', j') at the energy E and the total

angular momentum J , $P_{v'j',v''j''}^J(E)$ is approximated by the product of the individual probability of the intermediate complex to be formed from the initial HD(v, j) state, $p_{vj}^J(E)$, and $p_{v'j'}^J(E)/\sum_{v''j''} p_{v''j''}^J(E)$, the fraction of fragmenting complexes into the final rovibrational state (v', j'), where the sum of the denominator runs over all accessible (v'', j'') channels at the energy E . This assumption implies that no information regarding the phase of the scattering matrix can be obtained, and therefore, resonances cannot be reproduced. As explained before,³⁴ those individual probabilities, $p_{vj}^J(E)$ and $p_{v'j'}^J(E)$, are obtained by separate calculations on each arrangement solving the corresponding coupled-channel equations by means of a time independent approach with a log-derivative propagation between a capture radius of about 1.5 Å and an asymptotic distance of about 36 Å. This calculation is performed by means of completely quantum mechanical (QM) techniques and using the *ab initio* full PES. In turn, the neglect of the intermediate region in the log-derivative propagation implies the assumption that the formation of the intermediate complex leads to reaction up to products. That means that no recrossing effects back to the reactants arrangement is taken into account. The calculation of the capture probabilities based on purely QM considerations distinguishes the SQM approach from other statistical techniques where a classical or semiclassical framework is considered or where, as in the case of the SACM,³⁶ the square of the scattering matrix elements is approximated by counting the energetically open adiabatic channels at specific values of the total angular momentum and energy.

ICSSs are calculated for collision energies between 10^{-4} and 1.8–2.3 eV. With the ICSSs from Eq. (3), we then calculate the state-to-state rate constants as a function of the temperature as follows:

$$k_{v'j',v''j''}(T) = \sqrt{\frac{8\beta^3}{\pi\mu}} \int_0^\infty \sigma_{v'j',v''j''}(E) E e^{-\beta E} dE, \quad (4)$$

where $\beta = (k_B T)^{-1}$ and k_B is the Boltzmann constant.

All SQM calculations have been performed using the *ab initio* potential energy surface (PES) by Velilla *et al.*³⁷ for the ground electronic state $1^1A'$. This surface was developed by means of refinements of the ARTSPthe global potential of Refs. 38 and 39. About 5230 *ab initio* additional full configuration interaction calculations were calculated in the C_s symmetry group, with the aug-cc-pV6Z basis set. A total of 381 functions with the (11s6p5d4f3g2h)/(7s6p5d4f3g2h) extended basis were employed to reproduce the short, medium, and long range potentials. One of these improvements concerns the description of the long range interactions, including a functional form, both for the three-body terms and for the atom–diatom terms, which in the case of the reactive non-transfer channel under consideration in this work, is expressed as a two-term Legendre series with R^{-3} and R^{-4} terms for the anisotropic charge-quadrupole dispersion energy and the charge-induced dipole dispersion energy, respectively.

III. RESULTS

A. The $H^+ + HD \rightarrow D^+ + H_2$ reaction

ICSSs for reaction (1) have been calculated for transitions starting from HD($v = 0, j = 0-8$) leading to the formation of $H_2(v' = 0, j' = 0-9)$. In Fig. 2, we compare present SQM results with those

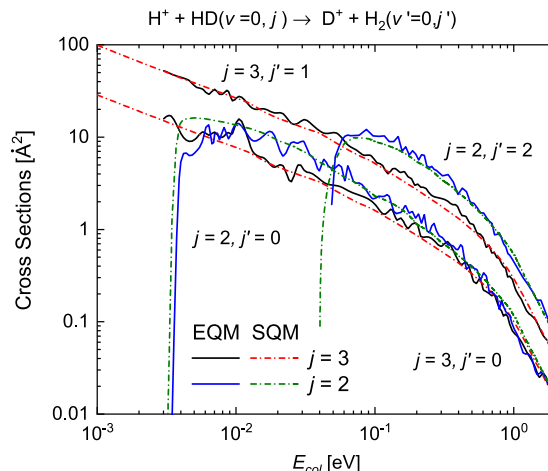


FIG. 2. Integral cross sections for the $H^+ + HD(v = 0, j) \rightarrow D^+ + H_2(v' = 0, j')$ reaction measured in Å^2 as a function of the collisional energy (in eV). Present SQM results (dashed lines) are compared with those obtained in the EQM calculation of Ref. 14 (solid lines). In black (red), EQM (SQM) ICSSs for transitions from the HD($j = 3$) rotational state; in blue (green) for the EQM (SQM) transitions from HD($j = 2$).

obtained by Lepers *et al.* with an exact quantum mechanical (EQM) calculation employing a time independent method.¹⁴ In particular, we show some rotational transitions between the vibrational ground states of HD($v = 0, j$) and $H_2(v' = 0, j')$: $2 \rightarrow 0$, $2 \rightarrow 2$, $3 \rightarrow 0$, and $3 \rightarrow 1$. The agreement found between the exact cross sections and the present statistical estimations is fairly good. As already mentioned,²⁴ the SQM method provides an average description of the oscillations displayed by the profile of the EQM cross sections due to the existing resonances.

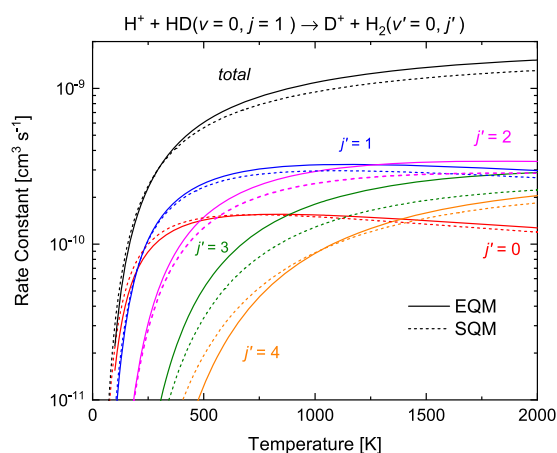


FIG. 3. State-to-state rate constants for the $H^+ + HD(v = 0, j = 1) \rightarrow D^+ + H_2(v' = 0, j' = 0-4)$ reaction as a function of the temperature obtained with the present SQM calculation (dotted lines) in comparison with the EQM calculation (solid lines) by Lepers *et al.* from Ref. 14. Total rate constants summing all contributions of transitions to $H_2(v' = 0, j' = 0-9)$ are also added in the comparison.

Those ICSs are used to obtain the corresponding rate constants following Eq. (4). In Fig. 3, we show the $k(T)$ values for the $\text{H}^+ + \text{HD}(v=0, j=1) \rightarrow \text{D}^+ + \text{H}_2(v'=0)$ reaction obtained with the present SQM approach in comparison with those reported in Ref. 14 for temperatures up to 2000 K. The total rate constant, $k_{v=0, j=1; v'=0}$, has been obtained summing up those corresponding to the reactions leading to $\text{H}_2(v'=0, j'=0-9)$. Also included in the figure are some of those state-to-state rate constants (those up to $j'=4$). The accord between the both sets of results, EQM and SQM, is certainly remarkable (the ratio $\tau = k_{\text{EQM}}/k_{\text{SQM}}$ between the EQM and SQM rates is 2.7 and 1.004 at $T = 250$ and 2000 K, respectively), thus supporting the importance of the complex-forming mechanism on the overall dynamics of the title reaction.

A similar test is carried out for the reaction initiated from the $\text{HD}(v=0, j=2)$. The SQM results are compared in Fig. 4 with those reported by Lepers *et al.* between $T = 5$ and 3000 K. State-to-state values of $k(T)$ for rotational transitions between the ground vibrational states of both $\text{HD}(v=0, j=2)$ and $\text{H}_2(v'=0, j'=0-6)$ and the total rate constant for the process $\text{H}^+ + \text{HD}(v=0, j=2) \rightarrow \text{D}^+ + \text{H}_2(v'=0)$ obtained summing contributions from transitions to the first ten rotational states $\text{H}_2(v'=0, j'=0-9)$ are shown in Fig. 4. Again, the agreement between the EQM rate constants and the statistical predictions is certainly good, with values of the above-mentioned ratio τ of 0.98 and 1.15, at 250 and 2000 K, respectively. In the [supplementary material](#), we have also included examples of the performance of the SQM approach for the case of $\text{H}^+ + \text{HD}(v=0, j=0) \rightarrow \text{D}^+ + \text{H}_2(v'=1, j'=0-2)$. The comparison of both ICSs and rate constants for such transitions with the results of the EQM calculation by Lepers *et al.*⁴⁰ reveals that the statistical predictions also describe well the formation of vibrationally excited H_2 .

A direct comparison with the above-mentioned measurements of the rate coefficients reported by Henschman *et al.*⁷ requires the calculation of the thermal rate constant following the procedure described in Ref. 40, which involves the Boltzmann average of the first $\text{HD}(v=0, j \leq 8)$ rotational states and the corresponding

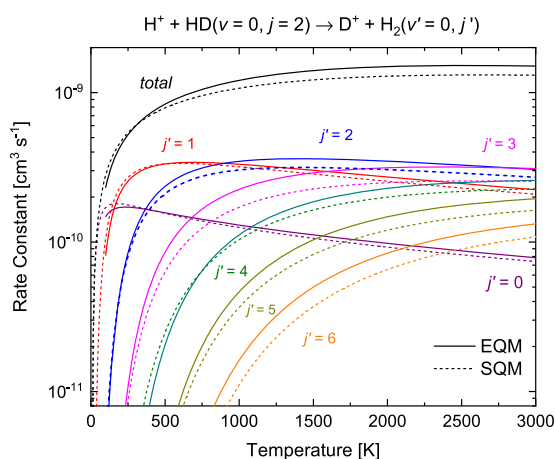


FIG. 4. Same as Fig. 3 for the $\text{H}^+ + \text{HD}(v=0, j=2) \rightarrow \text{D}^+ + \text{H}_2(v'=0, j'=0-4)$ reaction.

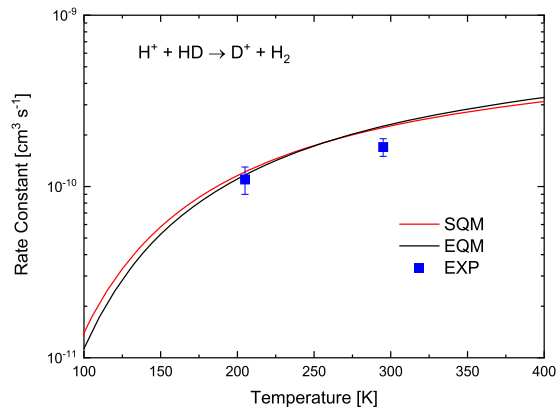


FIG. 5. Thermal rate constants for the $\text{H}^+ + \text{HD} \rightarrow \text{D}^+ + \text{H}_2$ reaction. See text for details of calculation of the two theoretical results shown in the figure: present SQM result (red line) and the EQM calculation from Ref. 40 (black line). Experimental values are from Ref. 7.

nuclear-spin multiplicity factors for the first $\text{H}_2(v'=0, j'=0-9)$ rotational states,

$$k(T) = \frac{1}{Z_{\text{rot}}} \sum_{j=0}^8 (2j+1) e^{-E_{0j}/k_B T} \left(k_{0j}^{\text{even}}(T) + k_{0j}^{\text{odd}}(T) \right), \quad (5)$$

where $Z_{\text{rot}} = \sum_{j=0}^8 (2j+1) e^{-E_{0j}/k_B T}$, and

$$k_{0j}^{\text{even}}(T) = \frac{1}{4} \sum_{j'=0,2,\dots} k_{0j,0j'}(T), \quad (6)$$

$$k_{0j}^{\text{odd}}(T) = \frac{3}{4} \sum_{j'=1,3,\dots} k_{0j,0j'}(T). \quad (7)$$

In Fig. 5, we show the comparison of our present results with those obtained with the EQM calculation by Lepers *et al.*⁴⁰ and the early measurements reported in Ref. 7. The accord of the SQM rates with the EQM values is fairly good: $k_{\text{SQM}} = 1.21 \times 10^{-10}$ and $2.21 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at $T = 205$ and 295 K, respectively, in comparison with the EQM values $k_{\text{EQM}} = 1.16 \times 10^{-10}$ and $2.20 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively. On the other hand, both sets of theoretical results match nicely the measurement at $T = 205$ K ($1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and slightly overestimate the experiment at 295 K ($1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). The so obtained thermal rate constant can be fitted by means of the Arrhenius expression $k(T) = \alpha e^{-\gamma/T}$ with values $\alpha = 8.57 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $\gamma = 405$ K. It is worth noticing that this value of γ (~ 0.035 eV) is close to the difference between the rovibrational ground state energies of H_2 and HD .

The full set of state-to-state rate coefficients for reaction 1 is available in the [supplementary material](#).

B. The $\text{H}^+ + \text{HD} \rightarrow \text{H}^+ + \text{HD}$ process

The present investigation also comprises the case of process (2) that also lead to the formation of HD . Transitions between the reactants $\text{HD}(v, j)$ and products $\text{HD}(v', j')$ rovibrational states with total energy below 0.9 eV shown in Fig. 1 have been considered,

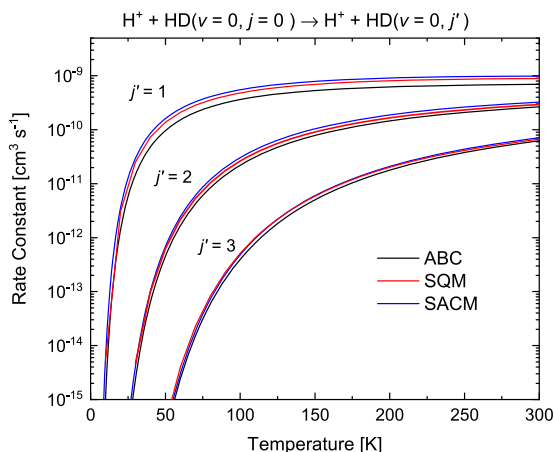


FIG. 6. State-to-state rate constants for the $\text{H}^+ + \text{HD}(v=0, j=0) \rightarrow \text{H}^+ + \text{HD}(v=0, j'=1-3)$ transitions calculated with the present SQM method (red) and the ABC (black) and SACM (blue) approaches of Ref. 15.

that is, $(v=0, j=0-11)$ for the ground vibrational state and $(v'=1, j'=0-6)$ for the first vibrational state.

Once the ICSs are calculated, we obtain the rate constants between $T=5$ and 3000 K. In Figs. 6 and 7, we compare in a more reduced temperature range (T up to 300 K) present SQM results with rate coefficients recently obtained by Desrousseaux *et al.*¹⁵ for the transitions from $\text{HD}(v=0, j=0)$ and $\text{HD}(v=0, j=1)$, respectively, to different rotational states of the vibrational ground state $\text{HD}(v'=0, j')$. Rate constants from Ref. 15 were calculated by means of the SACM and the TIQM ABC methods. The comparison for the transitions from the ground rovibrational state $\text{HD}(v=0, j=0)$ (in Fig. 6) reveals that the SQM provides a good description of the ABC rates: At $T=300$ K, the ratios $\tau = k_{\text{ABC}}/k_{\text{SQM}}$ for the production of $\text{HD}(v'=0, j')$ are 0.78 (for $j'=1$), 0.90 (for $j'=2$), and 0.93 (for $j'=3$), which, in fact, are somewhat better than the corresponding ratio found

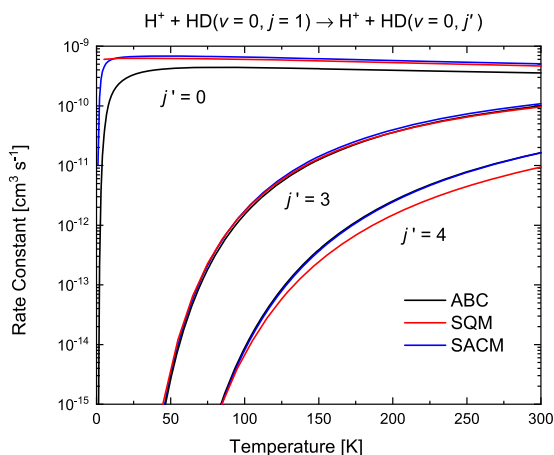


FIG. 7. Same as Fig. 6 for the $\text{H}^+ + \text{HD}(v=0, j=1) \rightarrow \text{H}^+ + \text{HD}(v=0, j'=0, 3, 4)$.

between the ABC and SACM rate coefficients, 0.7, 0.81, and 0.88. Some deviations are seen, on the contrary, for the case of $\text{H}^+ + \text{HD}(v=0, j=1) \rightarrow \text{H}^+ + \text{HD}(v'=0, j'=4)$ (see Fig. 7). On the one hand, both statistical approaches overestimate the ABC result for the $\text{HD}(j=1) \rightarrow \text{HD}(j'=0)$ transition at the very low temperature ($T < 20$ K), also shown in Fig. 7. On the other hand, at $T=300$ K, the SQM predictions for $j'=0$ and $j'=3$ (4.67×10^{-10} and 9.30×10^{-11}) are closer to the ABC rates (3.57×10^{-10} and 9.68×10^{-11}) than the SACM values (5.08×10^{-10} and 1.05×10^{-10}), but exhibit some noticeable deviations with respect to the other theoretical results for $j'=4$.

Due to computational limitations, calculations with the ABC approach in Ref. 15 are restricted to transitions involving some few rotational states of $\text{HD}(v=0, j)$ in its vibrational ground state. In this work, however, we have obtained rate coefficients for transitions among rovibrational states at higher energies. Examples of the present SQM rates as a function of the final rotational state j' at $T=705$ K can be seen in Fig. 8 for different excited reactant rovibrational states. Values of the rate constant increase as the rotational excitation j of the reactant $\text{HD}(v=0, j)$ decreases. Thus, the comparison for transitions forming $\text{HD}(v'=0, j'=5)$ reveals that the rate constant decreases from $3.95 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $(v=0, j=6)$, to $2.76 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $(v=0, j=8)$, and down to $1.41 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $(v=0, j=11)$. Figure 8 also shows that rate constants for transitions from a specific initial rovibrational state $\text{HD}(v, j)$ increase with the final rotational state j' . Thus, the transition $(v=0, j=11) \rightarrow (v'=0, j')$ has a rate constant with values that ranges from $1.34 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for $j'=0$ up to $2.17 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $j'=10$. The comparison shown in the figure between rates for transitions from vibrationless $\text{HD}(v=0)$ or from excited $\text{HD}(v=1)$ at $T=705$ K reveals that the former case is a faster process: the value of the rate for $(v=0, j=6) \rightarrow (v'=0, j'=5)$ is $3.95 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, whereas for $(v=1, j=6) \rightarrow (v'=0, j'=5)$, the

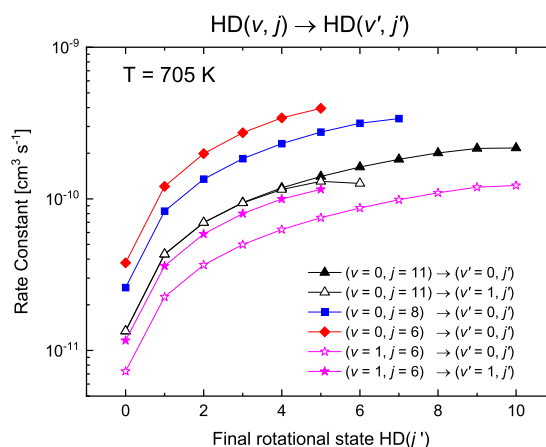


FIG. 8. State-to-state rate constants for different de-excitation transitions $\text{H}^+ + \text{HD}(v, j) \rightarrow \text{H}^+ + \text{HD}(v', j')$ as a function of the final rotational state j' at $T=705$ K calculated by means of the present SQM approach. In particular, the figure shows rate constants for $(v=0, j=11) \rightarrow (v'=0/1, j')$ in black full/empty triangles; $(v=0, j=8) \rightarrow (v'=0, j')$ in blue squares; $(v=0, j=6) \rightarrow (v'=0, j')$ in red diamonds; and $(v=1, j=6) \rightarrow (v'=0/1, j')$ in pink empty/full stars.

value is $7.51 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Rate constants for transitions from $\text{HD}(v=0, j=11)$ to rotational states of both the ground $\text{HD}(v'=0, j')$ and first excited vibrational state $\text{HD}(v'=1, j')$ are almost identical up to $j'=5$, a feature also observed for the $\text{H}^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{H}_2$ reaction.³⁴ This is, however, not the case for the $\text{H}^+ + \text{HD}(v=1, j=6) \rightarrow \text{H}^+ + \text{HD}(v'=0, 1, j')$, also shown in Fig. 8. The trend followed by the rate constants as a function of the final product rotational state j' shown in Fig. 8 resembles the tendency seen in rotational distributions obtained by statistical means to populate the largest rotational states²⁴ (see Fig. 3 of the supplementary material). Most of the similarities and differences observed among rate constants mentioned earlier could also be explained in terms of the existing energy difference between the corresponding reactant $\text{HD}(v, j)$ and product $\text{HD}(v', j')$. Thus, it seems reasonable to see that rate constants for the process $\text{HD}(v=1, j=6) \rightarrow \text{HD}(v'=1, j')$ are closer to those for $\text{HD}(v=0, j=11) \rightarrow \text{HD}(v'=0, j')$ than to rates for $\text{HD}(v=1, j=6) \rightarrow \text{HD}(v'=0, j')$. As for the case of Sec. III A, the full set of state-to-state rate coefficients for reaction 2 are included in the supplementary material and will be made available in the EMAA database at <https://emaa.osug.fr/>.

The good performance of the SQM method observed in the present investigation for the $\text{H}^+ + \text{HD} \rightarrow \text{H}^+ + \text{HD}$ and $\text{H}^+ + \text{HD} \rightarrow \text{D}^+ + \text{H}_2$ reactions reaction is as good as the results seen for the $\text{H}^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{H}_2$.³⁴ The comparison of the statistical predictions with the EQM results, when available, shows the complex-forming character of the overall dynamics of both processes. The SQM thus constitutes a useful approach to provide reliable rate constants for the title reaction and isotopic variants. On the other hand, values of the rate constant $k(T)$ obtained with the SQM approach at $T = 1005 \text{ K}$ for the three processes reveal that the reactive collision of HD with a proton is a more effective process than the collision with H_2 : For $\text{H}^+ + \text{H}_2(v=0, j=1) \rightarrow \text{H}^+ + \text{H}_2(v'=0, j'=0)$, $k(T)$ is $9.02 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; for $\text{H}^+ + \text{HD}(v=0, j=1) \rightarrow \text{D}^+ + \text{H}_2(v'=0, j'=0)$, $k(T)$ is $1.50 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and for $\text{H}^+ + \text{HD}(v=0, j=1) \rightarrow \text{H}^+ + \text{HD}(v'=0, j'=0)$, $k(T)$ is $2.48 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

IV. ASTROPHYSICAL APPLICATION: THE COOLING RATE COEFFICIENT

As already mentioned in the Introduction, HD plays a crucial role in the cooling of primordial condensations below $\approx 200 \text{ K}$ because its $\text{HD}(j=1)$ rotational level lies only 128 K above ground state, compared to 510 K for the $\text{HD}(j=2)$ level. In primordial gas condensations, the dominant colliders are atomic and molecular hydrogen, helium, protons, and electrons. The first accurate calculations for the cooling of HD were performed by Flower *et al.*,⁵ who considered collisional excitation by H, He, and para- and ortho- H_2 , but not protons and electrons. We provide below the first quantitative estimate of the $\text{HD}-\text{H}^+$ cooling function, which is compared to a new cooling function for $\text{HD}-\text{H}$ based on recent scattering calculations.⁴¹

Assuming no radiation field and optically thin transitions, the total HD cooling rate is the sum of the power radiated by each rovibrational transition,

$$\Lambda = \sum_u \sum_{l < u} n_u A_{ul} (E_u - E_l), \quad (8)$$

where n_u is the population of the upper level $u = (v, j)$ relative to the total HD number density; $l = (v', j')$ is the level with the lower energy; A_{ul} is the Einstein coefficient for spontaneous emission, and $(E_u - E_l)$ is the energy of the transition between the upper and lower energies. In what follows, protons and atomic hydrogen are considered separately, with a fixed density at $n(\text{H}^+) = n(\text{H}) = 10^{-2} \text{ cm}^{-3}$. This range corresponds to the “low-density regime” where HD is predominantly in the ground and first rotational states $j=0$ and $j=1$, respectively. The kinetic temperature, T , was varied in the range 5–3000 K for protons and 5–5000 K for atomic hydrogen. The normalized HD level populations, n_j , were computed at steady-state with the public code RADEX⁴² using our SQM collisional rate constants for $\text{HD}-\text{H}^+$, the recent TIQM rate constants of Desrousseaux *et al.*⁴¹ for $\text{HD}-\text{H}$, and spectroscopic data (including both dipole and quadrupole transitions) from the HITRAN database.⁴³ The statistical equilibrium equations were solved for HD levels up to $(v, j) = (0, 11)$ for collisions with H^+ (see Fig. 1) and up to $(v, j) = (2, 11)$ for collisions with H. The resulting cooling rate coefficient L (in $\text{erg cm}^3 \text{ s}^{-1}$)

$$Ln_c = \Lambda, \quad (9)$$

where $n_c = n(\text{H}^+)$ or $n_c = n(\text{H})$, is plotted in Fig. 9.

For atomic hydrogen, we find very good agreement with the fit of Lipovka *et al.*,⁴⁴ with only a slight departure (up to $\sim 20\%$) above 2000 K, which is most likely due to their use of old H_2-H rovibrational rate coefficients.⁴⁵ The cooling rate coefficient due to H^+ collisions is found to be significantly larger than that by collisions with H, by up to two orders of magnitude, as expected from the larger H_2-H^+ collisional rate coefficients. This means that proton collisions will compete with atomic hydrogen for abundance ratio $[\text{H}^+]/[\text{H}]$ larger than ~ 0.01 . Such high fractional ionization is however unusual in astrophysical environments where molecules

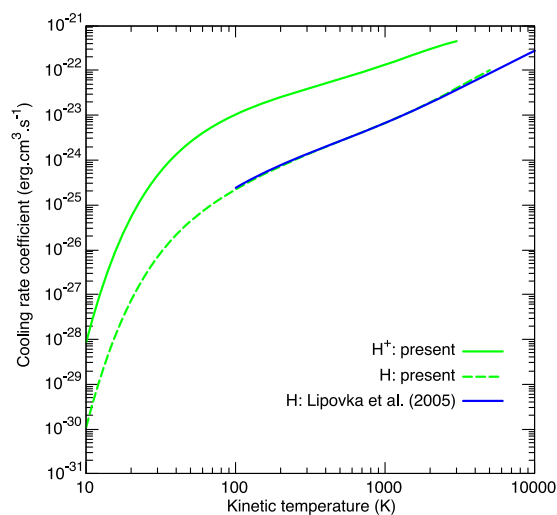


FIG. 9. Total cooling rate coefficient L for HD in a thermal bath of H^+ or H. The green solid and dashed lines denote our results based on the present SQM rate constants for H^+ and the TIQM rate constants of Desrousseaux *et al.*⁴¹ for H, respectively. The solid blue line shows the fit of Lipovka *et al.*⁴⁴

are present. For example, in the primordial Universe, $[H^+]/[H] > 0.01$ is only found at redshifts $z > 1000$ where molecular cooling/heating plays a negligible role.⁴⁶ The much larger HD–H⁺ cooling function therefore does not compensate for the low relative abundance of H⁺ so that the HD cooling in astrophysical media will be dominated by collisions with atomic (or molecular) hydrogen. This result was anticipated by Flower *et al.*⁵ based on the much larger HD–H rate coefficients compared with those for H₂–H. Indeed, in the case of H₂, H⁺ collisions are crucial in allowing proton exchanges and ortho ↔ para (i.e., odd Δj) transitions.³⁴

Finally, it should be noted that when the density increases, H is progressively converted into H₂ so that HD–H₂ collisions also become important. Flower *et al.*⁵ have shown that HD cooling is only weakly sensitive to the H/H₂ abundance ratio so that the HD–H cooling function plotted in Fig. 9 is actually also a good approximation for the HD–H₂ cooling function.

For a general use in hydrodynamic models, it can be useful to fit the HD cooling rate to a simple function of density and temperature, as in the recent work of Flower *et al.*³⁵ on H₂. This will be performed in a future work where all colliders (H, He, ortho- and para-H₂, H⁺, and electrons) will be considered. We note in this context the recent scattering calculations by Wan *et al.*⁴⁷ on HD–H₂.

V. CONCLUSIONS

Rate constants for the H⁺ + HD reaction have been calculated by means of a statistical quantum mechanical (SQM) method for the temperature range between 5 and 3000 K. Both possible product arrangements (HD + H⁺ and D⁺ + H₂) have been considered, and comparisons with previous exact quantum mechanical and statistical adiabatic channel model methods reveal the good performance of the SQM approach. Present findings are then consistent with a previous investigation on the isotopic variant H⁺ + H₂ reaction. These rate constants are then employed to calculate the cooling rate coefficient, which is compared with that corresponding to the collision between HD and atomic hydrogen. Our results reveal that although the HD cooling rate coefficients are considerably larger for H⁺ than for H, the overwhelming abundance of hydrogen atoms (or molecules) makes that cooling with H (or H₂) will prevail in most of the astronomical environments.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for examples of cross sections and rate constants to form vibrationally excited H₂; the final state rotational distribution for H⁺ + HD($v = 0, j = 10$) → HD(v', j') + H⁺ and numerical values of the state-to-state rate constants evaluated in this work with the SQM approach for both processes in Eqs. (1) and (2).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tomás González-Lezana: Conceptualization (equal); Investigation (equal); Project administration (lead); Supervision (lead); Validation (lead); Writing – original draft (lead); Writing – review & editing (lead). **Pierre Hily-Blant:** Writing – review & editing (supporting). **Alexandre Faure:** Conceptualization (equal); Project administration (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

REFERENCES

- 1 T. Hartwig, V. Bromm, R. S. Klessen, and S. C. O. Glover, *Mon. Not. R. Astron. Soc.* **447**, 3892 (2015).
- 2 A. Lazar and V. Bromm, *Mon. Not. R. Astron. Soc.* **511**, 2505 (2022).
- 3 J. Tumlinson, *Astrophys. J.* **641**, 1 (2006).
- 4 D. Hollenbach and C. F. McKee, *Astrophys. J., Suppl. Ser.* **41**, 555 (1979).
- 5 D. R. Flower, J. Le Bourlot, G. Pineau des Forêts, and E. Roueff, *Mon. Not. R. Astron. Soc.* **314**, 753 (2000).
- 6 N. Yoshida, K. Omukai, L. Hernquist, and T. Abel, *Astrophys. J.* **652**, 6 (2006).
- 7 M. J. Henchman, N. G. Adams, and D. Smith, *J. Chem. Phys.* **75**, 1201 (1981).
- 8 T. J. Millar, A. Bennett, and E. Herbst, *Astrophys. J.* **340**, 906 (1989).
- 9 D. Smith, N. G. Adams, and E. Alge, *Astrophys. J.* **263**, 123 (1982).
- 10 P. G. Jambrina, J. M. Alvaríño, D. Gerlich, M. Hankel, V. J. Herrero, V. Sáez-Rábanos, and F. J. Aoiz, *Phys. Chem. Chem. Phys.* **14**, 3346 (2012).
- 11 D. Gerlich and S. Schlemmer, *Planet. Space Sci.* **50**, 1287 (2002).
- 12 F. J. Aoiz, T. González-Lezana, and V. Sáez Rábanos, *J. Chem. Phys.* **127**, 174109 (2007).
- 13 F. J. Aoiz, T. González-Lezana, and V. Sáez Rábanos, *J. Chem. Phys.* **129**, 094305 (2008).
- 14 M. Lepers, G. Guillon, and P. Honvault, *Mon. Not. R. Astron. Soc.* **488**, 4732 (2019).
- 15 B. Desrousseaux, M. Konings, J. Loreau, and F. Lique, *Phys. Chem. Chem. Phys.* **23**, 19202 (2021).
- 16 M. Konings, B. Desrousseaux, F. Lique, and J. Loreau, *J. Chem. Phys.* **155**, 104302 (2021).
- 17 D. Skouteris, J. F. Castillo, and D. E. Manolopoulos, *Comput. Phys. Commun.* **133**, 128 (2000).
- 18 I. G. Csizmadia, J. C. Polanyi, A. C. Roach, and W. H. Wong, *Can. J. Chem.* **47**, 4097 (1969).
- 19 J. R. Krenos, R. K. Preston, R. Wolfgang, and J. C. Tully, *J. Chem. Phys.* **60**, 1634 (1974).
- 20 D. Gerlich, U. Nowotny, C. Schlier, and E. Teloy, *Chem. Phys.* **47**, 245 (1980).
- 21 A. Ichihara, T. Shirai, and K. Yokoyama, *J. Chem. Phys.* **105**, 1857 (1996).
- 22 E. J. Rackham, F. Huarte-Larrañaga, and D. E. Manolopoulos, *Chem. Phys. Lett.* **343**, 356 (2001).
- 23 E. J. Rackham, T. González-Lezana, and D. E. Manolopoulos, *J. Chem. Phys.* **119**, 12895 (2003).
- 24 T. González-Lezana, *Int. Rev. Phys. Chem.* **26**, 29 (2007).
- 25 T. González-Lezana, A. Aguado, M. Paniagua, and O. Roncero, *J. Chem. Phys.* **123**, 194309 (2005).

- ²⁶T. González-Lezana, O. Roncero, P. Honvault, J.-M. Launay, N. Bulut, F. Javier Aoz, and L. Bañares, *J. Chem. Phys.* **125**, 094314 (2006).
- ²⁷P. Honvault, M. Jorfi, T. González-Lezana, A. Faure, and L. Pagani, *Phys. Chem. Chem. Phys.* **13**, 19089 (2011).
- ²⁸T. González-Lezana, P. Honvault, and Y. Scribano, *J. Chem. Phys.* **139**, 054301 (2013).
- ²⁹T. González-Lezana, Y. Scribano, and P. Honvault, *J. Phys. Chem. A* **118**, 6416 (2014).
- ³⁰T. González-Lezana and P. Honvault, *Int. Rev. Phys. Chem.* **33**, 371 (2014).
- ³¹E. Carmona-Novillo, T. González-Lezana, O. Roncero, P. Honvault, J.-M. Launay, N. Bulut, F. J. Aoz, L. Bañares, A. Trottier, and E. Wrede, *J. Chem. Phys.* **128**, 014304 (2008).
- ³²L. Pagani, P. Lesaffre, E. Roueff, M. Jorfi, P. Honvault, T. González-Lezana, and A. Faure, *Philos. Trans. Royal Soc. A* **370**, 5200 (2012).
- ³³L. Pagani, P. Lesaffre, M. Jorfi, P. Honvault, T. González-Lezana, and A. Faure, *Astron. Astrophys.* **551**, A38 (2013).
- ³⁴T. González-Lezana, P. Hily-Blant, and A. Faure, *J. Chem. Phys.* **154**, 054310 (2021).
- ³⁵D. R. Flower, G. Pineau des Forêts, P. Hily-Blant, A. Faure, F. Lique, and T. González-Lezana, *Mon. Not. R. Astron. Soc.* **507**, 3564 (2021).
- ³⁶J. Loreau, F. Lique, and A. Faure, *Astrophys. J.* **853**, L5 (2018).
- ³⁷L. Velilla, B. Lepetit, A. Aguado, J. A. Beswick, and M. Paniagua, *J. Chem. Phys.* **129**, 084307 (2008).
- ³⁸A. Aguado, O. Roncero, C. Tablero, C. Sanz, and M. Paniagua, *J. Chem. Phys.* **112**, 1240 (2000).
- ³⁹C. Sanz, O. Roncero, C. Tablero, A. Aguado, and M. Paniagua, *J. Chem. Phys.* **114**, 2182 (2001).
- ⁴⁰M. Lepers, G. Guillon, and P. Honvault, *Mon. Not. R. Astron. Soc.* **500**, 430 (2021).
- ⁴¹B. Desrousseaux, C. M. Coppola, and F. Lique, *Mon. Not. R. Astron. Soc.* **513**, 900 (2022).
- ⁴²F. F. S. van der Tak, J. H. Black, F. L. Schöier, D. J. Jansen, and E. F. van Dishoeck, *Astron. Astrophys.* **468**, 627 (2007).
- ⁴³I. Gordon, L. Rothman, R. Hargreaves, R. Hashemi, E. Karlovets, F. Skinner, E. Conway, C. Hill, R. Kochanov, Y. Tan *et al.*, *J. Quant. Spectrosc. Radiat. Transfer* **277**, 107949 (2022).
- ⁴⁴A. Lipovka, R. Núñez-López, and V. Avila-Reese, *Mon. Not. R. Astron. Soc.* **361**, 850 (2005).
- ⁴⁵S. Tiné, S. Lepp, and A. Dalgarno, *Mem. S.A.It* **69**, 345 (1998).
- ⁴⁶D. Puy, G. Alecian, J. Le Bourlot, J. Leorat, and G. Pineau Des Forets, *Astron. Astrophys.* **267**, 337 (1993).
- ⁴⁷Y. Wan, N. Balakrishnan, B. H. Yang, R. C. Forrey, and P. C. Stancil, *Mon. Not. R. Astron. Soc.* **488**, 381 (2019).