Rovibrational transitions of H₂ by collision with H⁺ at high temperature

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Accepted XXX. Received YYY; in original form ZZZ

ABSTRACT

The H⁺+H₂ reaction is studied by means of both exact and statistical quantum methods. Integral cross sections for processes initiated with rotationally excited H₂(*v*, *j* = 1) to produce molecular hydrogen in its rotational ground state are reported up to a value of the collision energy of 3 eV. Rate constants for state-to-state transitions between different H₂ rovibrational states are calculated up to 3000 K. Special emphasis is made on ortho/para conversion processes in which the parity *j* of the H₂(*j*) states changes.

Key words: Scattering – Molecular data – Molecular processes

1 INTRODUCTION

Most of the kinetic models employed in Astrochemistry assume molecular populations in thermodynamic equilibrium. However, recent investigations have shown that deviations from these equilibrium conditions are relevant in the primordial Universe (Coppola *et al.* 2013, 2011). Therefore a precise knowledge of the rovibrational structure and the state-to-state chemistry of first molecules, namely H₂ or HeH⁺ and deuterated versions, is crucial. In addition, the relative abundance of the two nuclear-spin isomers of H₂, ortho (o-H₂) with odd values of the rotational *j* states and para (p-H₂) with even values, plays a crucial role both in the cooling of primordial gas in early structure formation (Glover *et al.* 2008) and in the deuterium enrichment of the molecular gas forming prestellar cores (Dalgarno *et al.* 1973; Flower *et al.* 1984; Pineau des Forêts *et al.* 1991; Pagani *et al.* 1992, 2012). Numerous attempts to calculate the age of these molecular clouds have been based on the conversion of H₃⁺ into H₂D⁺, a process which is directly affected by the corresponding ortho-para ratio of H₂ (Pagani *et al.* 2012). The spin-scrambling mechanisms to convert o-H₂ into p-H₂ require the reactive collision of the molecular hydrogen with H, H₂, H⁺ or H₃⁺. Due to the existence of noticeable barriers in those reactions with the neutral species, at low temperature the ortho-para conversion is mainly mediated by the H⁺+H₂(*j* odd) → H₂(*j* even) + H⁺ and H₃⁺ + H₂(*j* odd) → H₂(*j* even) + H₃⁺ processes (Lique *et al.* 2014). Although in principle radiative processes and rotational excitation collisions should preserve the para/ortho character of molec-

ular hydrogen according to total parity conservation considerations, the complex-forming dynamics of the H⁺+H₂ reaction at low energies have been invoked to explain the redistribution of the H₂(*j*) rotational states (Roueff *et al.* 1988). Detailed investigations on the H⁺+H₂ reaction and corresponding isotopic variants certainly suggest that mechanisms involving the formation of an intermediate complex during the course of the reaction play a significant role on the overall dynamics (González-Lezana *et al.* 2006; GH14 2014; González-Lezana *et al.* 2005; Carmona-Novillo *et al.* 2008; González-Lezana *et al.* 2013; GSH14 2014; González-Lezana *et al.* 2014). In particular the application of statistical techniques has revealed that most of the significant dynamical features such as rotational distributions and differential cross sections can be reproduced by means of a statistical quantum mechanical (SQM) method which produces results in a fairly good agreement with both exact quantum mechanical (EQM) values and experimental measurements (Carmona-Novillo *et al.* 2008). The importance of this complex-forming mechanisms extends to the low energy regime with statistical predictions for rate coefficients down to 10^{−3} eV which reproduce well both EQM and experimental results for the D⁺+H₂ reaction (GSH14 2014).

These studies on the dynamics of the H⁺+H₂ reaction were completed with the calculation of rate constants for the ortho/para conversion of H₂ after the collision with H⁺ (Honvault *et al.* 2011, 2012). The good performance of the SQM approach to reproduce the thermal behaviour of the EQM rates for different state-to-state processes was remarkable. Results up to 100 K were recently reported and employed to design chemical clocks to describe the contraction of cold gas and dust material which yield to prestellar cores (Pagani *et al.* 2012, 2013).

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At high temperature, neutral hydrogen exchange is also a possible way to convert o-H₂ into p-H₂. In this sense, and due to its relevance in astrophysical media, the temperature dependence of rate constants for ro-vibrational excitation of molecular hydrogen from different initial H₂(*v*, *j*) states have been analysed (Lique *et al.* 2012; Lique 2015; Lique *et al.* 2014). New results ranging from 100 to 5000 K suggest a possible review of the commonly assumed cooling mechanism for several astrophysical media (Lique 2015). Motivated by these new findings we have extended our previous investigations of the ortho-para H⁺+H₂ reactions reported for the low temperature regime ($T \leq 100$ K) (Honvault *et al.* 2011, 2012) to much larger values ($T = 3000$ K). Both EQM and SQM methods are applied to calculate cross sections and rate constants for a series of state-to-state reactions between different H₂(*v*, *j*) rovibrational states.

This paper is organised as follows: Section 2 presents theoretical details of the methods employed in the scattering calculations, Section 3 show the present results and finally in Section 4 conclusions are shown.

2 SCATTERING CALCULATIONS

Scattering calculations with both the EQM and SQM approaches have been performed on the potential energy surface (PES) of Velilla *et al.* (2008), the same used in our previous studies on the ortho-para conversion H⁺+H₂ reaction at low temperature (Honvault *et al.* 2011; HJGFP 2011) and recent investigations on D⁺+H₂ (GSH14 2014; González-Lezana *et al.* 2013).

2.1 Exact quantum method

Despite the numerical difficulties introduced by the presence of a deep well of about 4.6 eV in the PES, we have performed three-dimensional reactive scattering calculations for $J \geq 0$ using a fully Coriolis-coupled time independent quantum method (TIQM) based on the body-frame hyperspherical democratic coordinates approach. By means of this method, it is possible to obtain the entire *S* matrix at a given energy and therefore state-to-state scattering attributes, such as cross sections and rate coefficients for a large number of ro-vibrational transitions, can be easily extracted using standard equations. TIQM methods have been proved appropriate for an accurate study of complex-forming reactions, avoiding the difficulties found for time dependent wave packet approaches to tackle dynamics involving long-lived resonances.

Details of the hyperspherical method used here have been already presented before (Honvault *et al.* 2011, 2012; HJGFP 2011; Rajagopala *et al.* 2014) and only a brief description is given here. The main change concerns convergence to be ensured up to the highest collision energies (3 eV) and temperatures (3000 K) considered in the present work.

Previous applications of the TIQM approach reveal its validity for abstraction reactions, such as F + D₂ → DF + D (Martínez-Haya *et al.* 1999), complex-forming reactions, such as the OH + O (Jorfi *et al.* 2009), H + O₂ (Lin *et al.* 2008), and also ultracold alkali-dialkali collisions (Quemener, *et al.* 2007). Within this method, the scattering wave function

is expanded at each value of the hyper-radius on a set of hyperspherical adiabatic states of the Hamiltonian $H = T + V$, where *T* is the kinetic energy and *V* the potential energy. The corresponding expansion coefficients are obtained via the solution of a set of coupled second-order differential equations using the Johnson-Manolopoulos log-derivative propagator (Manolopoulos 1986). In this work, for $J = 0$, 450 states dissociate at large hyper-radius into the H₂(*v*, *j*) rovibrational levels, from ($v = 0, j = 0$) to ($v = 18, j = 8$), with the largest rotational level $j = 34$ for $v = 0$. So a large number of closed channel needed for convergence has been included in the present study. Propagation goes from 0.5 a₀ up to the asymptotic matching distance of 17.5 a₀ with a step of 0.1 a₀, where the *S* matrix is extracted. When computing $J > 0$ partial waves up to 165, we have considered the Ω components from 0 to 35 in the close-coupling expansion to obtain accurate state-to-state ICS and rate constants. Thus, the number of coupled equations increases from 450 for $J = 0$ to 6004 for $J > 34$.

For collision systems with identical nuclei, as the H⁺ + H₂(*v*, *j*) → H₂(*v'*, *j'*) + H⁺ reaction, care should be taken such that the physical observable magnitudes such as the ICSs obey proper spin statistics as described in Honvault *et al.* (2011); Lique (2015).

Additionally, thermal rate constant for a (*v*, *j*) → (*v'*, *j'*) state-to-state transition is calculated as follows:

$$k_{vj,v'j'}(T) = \sqrt{\frac{8}{\pi\mu(k_B T)^3}} \int_0^\infty \sigma_{vj,v'j'}(E_c) e^{-E_c/k_B T} E_c dE_c, \quad (1)$$

where μ is the reduced mass of the corresponding atom-diatom system and the $\sigma_{vj,v'j'}(E_c)$ state-to-state cross sections are calculated as:

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

with $k_{vj}^2 = 2\mu(E - E_{vj})/\hbar^2$, E_{vj} being the energy of the initial rovibrational state *vj* of the reactant diatom, and *g* the electronic degeneracy.

2.2 Statistical quantum method

The complex-forming character of the dynamics found for the H⁺+H₂ reaction justifies the use of statistical techniques for the present investigation. In particular we have employed the SQM approach of Rackham *et al.* (2003); González-Lezana (2007). The method was successfully used before in previous studies on reactions which proceed via the formation of an intermediate complex (Carmona-Novillo *et al.* 2008; Bargaño *et al.* 2008). Under such an assumption capture probabilities of formation and fragmentation from reactants and products rovibrational states, p_{vj}^J and $p_{v'j'}^J$, respectively, for a specific value of the total angular momentum *J*, are calculated by means of a TIQM (Rackham *et al.* 2003). The state-to-state reaction probability at the energy *E* is then approximated as follows:

$$|S_{vj,v'j'}^J(E)|^2 \approx \frac{p_{vj}^J(E) \cdot p_{v'j'}^J(E)}{\sum_{v''j''} p_{v''j''}^J(E)}. \quad (3)$$

Figure 1. Cross sections in a_0^2 for the $\text{H}^+ + \text{H}_2(v=0, j=1) \rightarrow \text{H}^+ + \text{H}_2(v'=0-3, j'=0)$ reaction. Solid lines are for EQM results and dashed lines are SQM predictions. Y axis is plotted with log scale.

Those probabilities are then used in the standard way shown in Eq. 2 to calculate the ICSs. The corresponding coupled equations are solved by means of a log-derivative propagation (Rackham *et al* 2003) in the region defined between the asymptotic distance of $R_{\text{max}} = 15a_0$ and $R_c = 3a_0$, the capture radius at which the complex is assumed to form (Honvault *et al.* 2011; HJGFP 2011). The method employs the same *ab initio* PES as the EQM calculation and no scaling factors are applied for reaction probabilities, cross sections or rate constants.

3 RESULTS

ICSs for ortho-para conversions from the vibrational ground state of $\text{H}_2(v=0, j=1)$ to produce $\text{H}_2(v', j=0)$ in different final vibrational states v' are calculated in this work for collision energies up to 3 eV. Results obtained with the EQM and SQM of Sections 2.1 and 2.2, respectively, are compared in Figure 1. The ICSs for the rotational relaxation to $\text{H}_2(v'=0-1, j'=0)$ responds to the prototype case of barrierless reaction, whereas the production of $\text{H}_2(v'=2-3, j'=0)$ exhibit the corresponding reaction threshold.

The statistical predictions are found to overestimate the EQM cross sections at the larger energies, specially for $v' < 3$, but thresholds for the $\text{H}^+ + \text{H}_2(v=0, j=1) \rightarrow \text{H}^+ + \text{H}_2(v'=2, 3, j'=0)$ transitions are well described. The same comparison for the corresponding transitions when the reactant molecular hydrogen is also vibrationally excited $\text{H}_2(v=1, j=1)$ shown in Figure 2 reveals a similar overestimation of the SQM cross sections with respect to the exact results at large energies. The cross sections for the $v'=2$ and 3 cases obtained with both methods are however in a fairly good agreement. These deviations between the statistical results with respect the EQM values as the energy increases are consistent with previous investigations on different isotopic variants of the title collisions where cumulative reaction probabilities (Jambrina *et al.* 2009), cross

Figure 2. Same as Fig. 1 for $\text{H}^+ + \text{H}_2(v=1, j=1) \rightarrow \text{H}^+ + \text{H}_2(v'=0-3, j'=0)$ reactions .

sections (Jambrina *et al.* 2010; JAAHS 2010) and rate coefficients (Jambrina *et al.* 2012) were reported.

Rate constants for the $\text{H}^+ + \text{H}_2(v=0, j=1) \rightarrow \text{H}^+ + \text{H}_2(v'=0-3, j'=0)$ reactions up to $T = 3000$ K obtained with the ICSs presented above are shown in Figure 3 and in Table 1. The production of molecular hydrogen in its ground rovibrational state is clearly the fastest process with values of $k(T) \sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at almost the entire temperature range under study. Transitions to vibrationally excited $\text{H}_2(v' > 0, j'=0)$ are however much smaller (between one, in the case of $v'=1$, and four orders of magnitude for $v'=3$) and with a more pronounced dependence with the temperature. The SQM approach reproduces remarkably well the EQM $k(T)$ for $v'=0$ and 2, but differences between both results are observed for $v'=1$ and 3. Interestingly these discrepancies seem to decrease as the temperature increases, and thus, the $k^{\text{EQM}}(T)/k^{\text{SQM}}(T)$ ratio at $T = 3000$ K, the largest value of the temperature considered in the present study, is $\sim 1.61, 0.97$ and 0.48 for the $v'=1, 2$ and 3 cases, respectively.

We have also investigated purely rotational relaxations $j=1 \rightarrow j'=0$ in which the vibrational state remains fixed, $v=v'$. The corresponding rate constants are shown in Figure 4. EQM results for $v=v'=1$ and 2 are quite similar, tending to a constant value slightly larger than $\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at $T \sim 3000$ K, whereas the process with $v=v'=3$ exhibits a markedly different dependence with T . The statistical predictions for $k(T)$ corresponding to vibrationally excited processes, $v' > 0$, are far to accurately describe the EQM values, and show almost the same behaviour at low temperature ($T < 500$ K) with slight deviations of the constant for $v'=3$.

The $j=1 \rightarrow j'=0$ conversion is also investigated when the process is initiated from the first excited vibrational state of the molecular hydrogen $\text{H}_2(v=1, j=1)$ and the corresponding rate constants are shown in Figure 5 and in Table 2. The formation of $\text{H}_2(v'=2-3; j'=0)$ are the only processes with rate constants still showing some dependence with the temperature when $T \sim 300$ K. For the $(v=1, j=1) \rightarrow (v'=0-1, j'=0)$ transitions however the corresponding $k(T)$ values are almost independent of T . The

Table 1. Rate constants for the $\text{H}^+ + \text{H}_2(\nu = 0, j = 1) \rightarrow \text{H}^+ + \text{H}_2(\nu', j' = 0)$ transitions. Units are K for T and $10^x \text{ cm}^3 \text{ s}^{-1}$, where x is the number in parenthesis. Numerical data are provided as supplementary material.

T	$\nu' = 0$		$\nu' = 1$		$\nu' = 2$		$\nu' = 3$	
	EQM	SQM	EQM	SQM	EQM	SQM	EQM	SQM
500	1.27(-10)	1.08(-10)	1.35(-16)	2.01(-17)	3.61(-22)	2.64(-22)	2.04(-29)	1.83(-26)
1000	1.03(-10)	8.74(-11)	4.29(-14)	1.48(-14)	3.89(-17)	4.78(-17)	9.94(-21)	2.02(-19)
1500	8.66(-11)	7.42(-11)	2.76(-13)	1.23(-13)	1.88(-15)	2.08(-15)	7.23(-18)	4.27(-17)
2000	7.45(-11)	6.49(-11)	6.68(-13)	3.46(-13)	1.28(-14)	1.35(-14)	1.86(-16)	6.27(-16)
2500	6.54(-11)	5.77(-11)	1.10(-12)	6.28(-13)	3.97(-14)	4.10(-14)	1.26(-15)	3.14(-15)
3000	5.78(-11)	5.20(-11)	1.48(-12)	9.20(-13)	8.26(-14)	8.48(-14)	4.41(-15)	9.10(-15)

Figure 3. Rate constants obtained by means of the EQM (solid lines) and SQM approaches (dashed lines) for the $\text{H}^+ + \text{H}_2(\nu = 0, j = 1) \rightarrow \text{H}^+ + \text{H}_2(\nu' = 0 - 3, j' = 0)$ transitions. Units are $\text{cm}^3 \text{ s}^{-1}$. Numerical data are provided as supplementary material. **Figure 4.** Same as 2 for the $\text{H}^+ + \text{H}_2(\nu, j = 1) \rightarrow \text{H}^+ + \text{H}_2(\nu' = \nu, j' = 0)$ transitions with $\nu = \nu' = 0 - 3$. Units are $\text{cm}^3 \text{ s}^{-1}$. Numerical data are provided as supplementary material.

comparison between EQM and SQM results is much more favourable with fairly good agreements in the cases of $\nu' = 2$ and 3.

Processes initiated from the rotational ground state $\text{H}_2(\nu, j = 0)$ have been here investigated only with the statistical method. Rate constants for the rotational $\text{H}^+ + \text{H}_2(\nu =$

Figure 5. Same as 4 for $\text{H}^+ + \text{H}_2(\nu = 1, j = 1) \rightarrow \text{H}^+ + \text{H}_2(\nu' = 0 - 3, j' = 0)$. Numerical data are provided as supplementary material.

$0, j = 0) \rightarrow \text{H}^+ + \text{H}_2(\nu' = 0, j' > 0)$ transitions are shown in Figure 6. One of the most remarkable features of those results regards the different behaviour of the $k_{00,0j'}(T)$ under study for the temperature range $T < 2500$ K. Both the rapid increase up to a maximum value which differs for each transition, and the temperature range required to stabilize and tend to a pseudo-plateau with almost no dependence on T differ depending on the final rotational state $\text{H}_2(\nu' = 0, j')$. Despite these differences, all transitions are quite fast with values of the thermal rate constant around $\sim 5 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ as soon as the temperature exceeds 500 K.

Collisions with $\text{H}_2(\nu = 1, j = 0)$ in its first vibrational excited state are ruled by rate constants which exhibit a similar behaviour with respect to the temperature. The results corresponding to the $\text{H}^+ + \text{H}_2(\nu = 1, j = 0) \rightarrow \text{H}^+ + \text{H}_2(\nu' = 0 - 3, j' > 0)$ reactions obtained by means of the SQM approach are shown in Figure 7. The statistical predictions for the different rotational transitions for each vibrational case ν' display a quite uniform dependence with the temperature with few differences on the overall behaviour. The transitions to $\nu' = 0$ and 1 manage to stabilize the value of the corresponding $k(T)$ for almost the entire temperature range beyond $T = 1000$ K. In particular, $k_{10,0j'}(T)$ oscillate between $\sim 6 \cdot 10^{-11}$, $\sim 10^{-10}$ and $\sim 1.2 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, for $j' = 1, 2$ and 3, respectively, for $T = 3000$ K, whereas values for $k_{10,1j'}(T)$ are $\sim 6 \cdot 10^{-11}$, $\sim 8 \cdot 10^{-11}$ and $\sim 9 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Rate constants for the formation of molecular hydrogen vibrationally excited to the $\nu' = 2$ and 3 states tend to values of $\sim 10^{-11}$ and $10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively.

Table 2. Same as Table 1 for reactions starting from $\text{H}^+ + \text{H}_2(\nu = 1, j = 1)$.

T	$\nu' = 0$		$\nu' = 1$		$\nu' = 2$		$\nu' = 3$	
	EQM	SQM	EQM	SQM	EQM	SQM	EQM	SQM
500	2.41(-11)	5.68(-12)	1.14(-11)	1.86(-12)	2.60(-16)	1.98(-16)	2.63(-21)	2.01(-21)
1000	3.00(-11)	1.40(-11)	1.34(-11)	4.58(-12)	7.54(-14)	4.48(-14)	1.42(-16)	1.43(-16)
1500	2.98(-11)	1.78(-11)	1.31(-11)	5.82(-12)	4.90(-13)	2.79(-13)	5.63(-15)	5.65(-15)
2000	2.82(-11)	1.95(-11)	1.25(-11)	6.35(-12)	1.21(-12)	6.97(-13)	3.57(-14)	3.44(-14)
2500	2.62(-11)	2.01(-11)	1.17(-11)	6.52(-12)	2.02(-12)	1.19(-12)	1.07(-13)	9.94(-14)
3000	2.42(-11)	2.01(-11)	1.10(-11)	6.51(-12)	2.79(-12)	1.69(-12)	2.19(-13)	1.98(-13)

Figure 6. Rate constants for the rotational $\text{H}^+ + \text{H}_2(\nu = 0, j = 0) \rightarrow \text{H}^+ + \text{H}_2(\nu' = 0, j' = 1 - 3)$ transitions obtained with the SQM approach. Units are $\text{cm}^3 \text{s}^{-1}$. Numerical data are provided as supplementary material.

Rotational excitations in processes in which the vibrational state of $\text{H}_2(\nu, j = 0)$ remains unchanged are considered for the $\nu = \nu' = 2$ and 3 cases. The corresponding rate constants are shown in Figures 8 and 9, respectively for the temperature range under consideration in the present study. As in the cases shown in Figure 7 values of $k(T)$ for the $j = 0 \rightarrow j' = 1$ conversion are slightly smaller at the largest temperature, once the rate already exhibits a stabilized independence with respect to T . The $j = 0 \rightarrow j' = 3$ transition is about ~ 1.5 and ~ 1.6 times larger in comparison.

4 CONCLUSIONS

Transitions between rovibrational $\text{H}_2(\nu, j)$ states after collisions with H^+ have been investigated by means of an EQM and a SQM approach. Cross sections up to a value of the collision energy of 3 eV have been calculated and rate constants for a number of possible $\text{H}^+ + \text{H}_2(\nu, j) \rightarrow \text{H}_2(\nu', j') + \text{H}^+$ processes, including ortho-para conversions of H_2 for temperatures up to 3000 K have been investigated. The comparison of the QM results with the statistical predictions provides an useful insight on the relevance of complex-forming mechanisms on the overall dynamics of the reactions. Present state-to-state rate constants are expected to provide essential data, currently unavailable, for astrochemical modeling.

Figure 7. SQM predictions for the rate constants corresponding to reactions initiated with $\text{H}_2(\nu = 1, j = 0)$ to produce $\text{H}_2(\nu', j' = 1 - 3)$ with ν' from 0 (top panel) up to 3 (bottom panel). Numerical data are provided as supplementary material.

ACKNOWLEDGEMENTS

The authors would like to acknowledge F. Lique and E. Roueff for useful discussions to motivate this work. Support from MICINN with Grant No. FIS2014-51933-P and from the French national program PCMI (Physique et Chimie du Milieu Interstellaire) is also acknowledged. All the EQM calculations have been done on the cluster of the Centre de Calcul de l' Université de Bourgogne (CCUB, Dijon, France).

Figure 8. Rate constants for rotational transitions from $\text{H}_2(\nu=2, j=0)$ obtained by means of the SQM method. Numerical data are provided as supplementary material.

Figure 9. Same as Fig. 8 for reaction from $\text{H}_2(\nu=3, j=0)$. Numerical data are provided as supplementary material.

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