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# Revisited study of the ro-vibrational excitation of H<sub>2</sub> by H: towards a revision of the cooling of astrophysical media

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## ABSTRACT

We report nearly exact quantum time-independent calculations of rate coefficients for the collisional (de-)excitation of H<sub>2</sub> by H, from low to high temperatures. Our calculations are based on a highly accurate global potential energy surface. The reactive hydrogen exchange channels are taken into account rigorously. New collisional data are obtained for the ro-vibrational relaxation of highly excited H<sub>2</sub> (with internal excitation up to  $\simeq 22\,000$  K) for temperatures ranging from 100 to 5000 K. We also provide a comparison with the available experimental rate coefficients at room temperature. The good agreement between theory and experiment is an illustration of the accuracy of the present calculations. The new results significantly differ from previous data presently used in astrophysical models, especially at low temperatures, the difference being essentially due to the inclusion of the reactive channels. The impact of these new data in astrophysics is discussed. In particular, the cooling mechanism will have to be reviewed for several astrophysical media.

**Key words:** Molecular data – Molecular processes – scattering.

## 1 INTRODUCTION

Modelling of astrophysical media relies on modelling microscopic processes that may lead to (de-)excitation of atomic and molecular constituents. In the Universe, the most abundant element is hydrogen and collisions involving H<sub>2</sub> molecules and H atoms are crucial to the thermal balance and chemistry of astrophysical media.

In the early Universe, the infrared emission of H<sub>2</sub> following its collisional excitation is an important cooling mechanism at the end of the post-recombination era after the first molecules have been formed and after the primordial clouds have begun to collapse (roughly a red shift of  $\simeq 20$ ). Even if H<sub>2</sub> has a low abundance (Galli & Palla 2013), it dominates the cooling so that collisions between H<sub>2</sub> and H provide the cooling essential to the gravitational collapse of inhomogeneities in the primordial gas and to the formation of the first stars (Flower & Pineau des Forêts 2001). This is because the others usual coolants (metals, grains, C<sup>+</sup>, ...) are absent in the early Universe. Prior to that red shift, Puy et al. (1993) show that adiabatic expansion dominates the cooling and H<sub>2</sub>–H collisions are the dominant heating mechanism as long as the temperature of matter is less than the radiation temperature as shown by Flower (2000).

Moreover, in photon-dominated regions of the interstellar medium, there exists a region of overlap of atomic and molecular hydrogen and the kinetic temperature in this region is also controlled by inelastic H<sub>2</sub>–H collisions (Le Boulart, Pineau des Forêts & Flower 1999).

Finally, in astrophysical media, the distribution of molecular hydrogen between its ortho (nuclear spin  $I = 1$ ) (hereafter o-H<sub>2</sub>) and para (nuclear spin  $I = 0$ ) (hereafter p-H<sub>2</sub>) forms is a key parameter for the physical chemistry of interstellar molecular clouds and of the early Universe. Radiative transitions are inefficient in converting o-H<sub>2</sub> into p-H<sub>2</sub> or the reverse. o–p-H<sub>2</sub> (ortho–para-H<sub>2</sub>) transitions are forbidden during inelastic collisions so that conversion between ortho- and para-H<sub>2</sub> only occurs through reactive collisions leading to hydrogen or proton exchange (Lique, Honvault & Faure 2014).

Accurate studies of the collisions between H<sub>2</sub> and H are then crucial for qualitatively and quantitatively modelling many astrophysical media. The collision/reaction of H with H<sub>2</sub> and its isotopologues has become a prototype because of its experimental and theoretical accessibility (see Aoiz, Bañares & Herrero 2005, for a review). Thus, theoretical and experimental thermal rate constants have now converged within 10 per cent and the H+H<sub>2</sub> reaction can be considered as an almost solved problem. Surprisingly, despite its crucial importance in astrophysics, accurate rotational and ro-vibrational rate coefficients for the H<sub>2</sub>–H collisions (including o–p-H<sub>2</sub> conversion due to H collisions and considering highly excited ro-vibrational levels of H<sub>2</sub>) were not available until very recently. Indeed, to the best of our knowledge, the

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latest and most accurate theoretical study is the work of Sun & Dalgarno (1994). However, their calculations were restricted to p-H<sub>2</sub> ( $v = 0$ ,  $j = 0$ ) and o-H<sub>2</sub> ( $v = 0$ ,  $j = 1$ ) so that it is not possible to use them in astrophysical modelling of warm media.

Recently, Lique, Honvault & Faure (2012) (hereafter Paper I) provided new quantum results for pure rotational excitation of H<sub>2</sub> by H at low to moderate temperatures ( $T < 1500$  K). Their results are in very good agreement with the available experimental data. However, in these calculations, the ro-vibrational excitation was not considered whereas H<sub>2</sub> can be found in vibrationally excited states in astrophysical media (Donahue et al. 2000). For high temperatures and ro-vibrational relaxation of H<sub>2</sub> by H, most of the available data have been based on quasi-classical trajectory calculations (Mandy & Martin 1993, and references therein). Unfortunately, the inability of quasi-classical trajectory treatments to conserve the vibrational zero-point energy renders this method unreliable near reaction thresholds. In addition, H<sub>2</sub>–H rate coefficients are very sensitive to the choice of the interaction potential (Wrathmall & Flower 2007), so that additional uncertainties can even be added to these calculations performed using interaction potentials from the previous century.

This certainly explains why, for astrophysical modelling of warm media and of the early Universe, current models (Wrathmall, GUSDORF & Flower 2007, hereafter WGF07; Glover & Abel 2008) generally employ the collisional data of Flower and co-workers (Wrathmall & Flower 2006, 2007; WGF07). These data were obtained from an accurate H<sub>3</sub> interaction potential using pure inelastic approaches and assuming that the reactive cross-sections are negligible, the barrier height being estimated to be around 5000 K (Mielke, Garrett & Peterson 2002). Whereas such an approach may be used at low temperature, it is much more questionable at temperatures above 1000 K and/or when dealing with ro-vibrational (de-)excitation. Indeed, vibrational excitation of the reagent molecule lowers the reaction threshold and leads to a great enhancement of the reactive rate constants (Aoiz et al. 2005).

In this paper, following the work of Paper I, we compute purely quantum rate coefficients for the ro-vibrational (de-)excitation of H<sub>2</sub> by H, including the ortho–para conversion, for temperatures up to 5000 K. We employ a full-dimensional quantum time-independent approach combined with a high-accuracy *ab initio* potential energy surface. The paper is organized as follows. Section 2 provides a brief description of the scattering calculations. In Section 3, we present the results. Possible astrophysical consequences are drawn in Section 4.

## 2 SCATTERING CALCULATIONS

In our calculations, we use the H<sub>3</sub> global potential energy surface (PES) of Mielke et al. (2002). The PES was calculated using highly correlated *ab initio* methods and proved to be very successful in the calculation of H+D<sub>2</sub> and D+H<sub>2</sub> thermal rate coefficients for both the inelastic and reactive processes (see for example Mielke et al. 2003).

Despite its simple appearance, exact quantum mechanical calculations of the cross-sections for H<sub>2</sub>–H collisions are not trivial since the cross-sections must be obtained from wavefunctions that are properly antisymmetrized with respect to interchange of the protons (Miller 1969). They can also be calculated from wavefunctions that treat the protons as distinguishable by adding the appropriate S-matrix elements for inelastic (e.g.  $A + BC \rightarrow A + BC$ ) and reactive (e.g.  $A + BC \rightarrow AB + C$  or  $AC + B$ ) processes obtained from such wavefunctions (Truhlar 1976). In the present study, we used the second approach. However, in Paper I, we checked that results obtained from the two approaches were equivalent.

In the following, the H<sub>2</sub> states are described by the quantum numbers  $j$ ,  $k$  (the rotational angular momentum of the H<sub>2</sub> molecule and its projection along the reactant Jacobi vector), and  $v$  (the vibrational quantum number of the H<sub>2</sub> molecule). The H+H<sub>2</sub> ( $v, j$ ) → H+H<sub>2</sub> ( $v', j'$ ) integral cross-section, summed over final projection quantum numbers and averaged over initial projection quantum numbers, is given by (Truhlar 1976; Miller 1969):

$$\sigma_{vj \rightarrow v'j'}(E_c) = \frac{\pi}{k_{vj}^2(2j+1)} \times \sum_{Jkk'} (2J+1) |\delta_{vv'} \delta_{jj'} - S^J(E, vjk \rightarrow v'j'k')|^2 \quad (1)$$

where the S-matrix for the H+H<sub>2</sub> collision is given by:

$$|S^J(E, vjk \rightarrow v'j'k')|^2 = \begin{cases} |S_n^J(E, vjk \rightarrow v'j'k') - S_r^J(E, vjk \rightarrow v'j'k')|^2, & \text{if } j, j' \text{ even,} \\ |S_n^J(E, vjk \rightarrow v'j'k') + S_r^J(E, vjk \rightarrow v'j'k')|^2 + 2|S_r^J(E, vjk \rightarrow v'j'k')|^2, & \text{if } j, j' \text{ odd,} \\ 3|S_r^J(E, vjk \rightarrow v'j'k')|^2, & \text{if } j \text{ even, } j' \text{ odd,} \\ |S_r^J(E, vjk \rightarrow v'j'k')|^2, & \text{if } j \text{ odd, } j' \text{ even,} \end{cases} \quad (2)$$

where  $S_n^J$  and  $S_r^J$  are the nonreactive and reactive S-matrix elements, respectively.

In equation (1),  $k_{vj}$  denotes the initial wavevector. The calculations were carried out on a grid of total energies  $E$ :

$$E = E_c + \epsilon_{vj}, \quad (3)$$

where  $E_c$  is the initial collisional energy and  $\epsilon_{vj}$  is the ro-vibrational energy of the H<sub>2</sub> reactant.

The ground electronic state of H<sub>3</sub> conically intersects the first excited state (Bouakline et al. 2009) and, as a consequence, there is a sign change of the electronic wavefunction as one follows a closed path in nuclear configuration space around the line of the conical intersection. This sign change is usually referred to as the geometric phase effect. In Paper I, it was concluded that the geometric phase effect can be neglected in calculations of integral cross-sections at low and moderate collisional energies (up to  $\simeq 15\,000$  K). This effect can

be more important for differential cross-sections and at very high collisional energies. Hence, the accuracy of our calculations may slightly decrease with increasing energy because we consider only the ground electronic state PES. Nevertheless, we believe that the corresponding rate coefficients will remain accurate for the temperature range considered in this work.

We used the ABC reactive scattering code (Skouteris, Castillo & Manolopoulos 2000) to carry out inelastic and reactive calculations for all values of the total angular momentum that made a non-zero contribution to inelastic and reactive processes. We computed cross-sections for all the ro-vibrational levels with internal energies  $\epsilon_{vj} < 22\,000$  K. A large number of closed ro-vibrational channels of the diatomic moiety were included in the scattering calculations subject to the exclusion of (a) levels with internal energy greater than  $\simeq 45\,000$  K and (b) levels in which the angular momentum  $j$  of the diatomic moiety is greater than 24. Converged integral reactive cross-sections could be obtained by restricting the projection quantum number of the total angular momentum to  $K \leq 7$ . Calculations were performed for collisional energies up to at least  $\simeq 36\,000$  K.

From the calculated cross-sections  $\sigma_{vj \rightarrow v'j'}(E_c)$ , one can obtain the corresponding thermal rate coefficients for temperatures ranging from 100 to 5000 K as follows:

$$k_{vj \rightarrow v'j'}(T) = \left( \frac{8}{\pi \mu k_B^3 T^3} \right)^{\frac{1}{2}} \times \int_0^{\infty} \sigma_{vj \rightarrow v'j'}(E_c) E_c e^{-E_c/k_B T} dE_c \quad (4)$$

where  $\mu$  is the reduced mass of  $\text{H}_2\text{-H}$  and  $k_B$  is Boltzmann's constant. The complete set of (de-)excitation rate coefficients are given as supplementary data to this article.

### 3 RESULTS

#### 3.1 Pure rotational (de-)excitation

We first present the results for the pure rotational excitation. Fig. 1 displays rate coefficients for the pure rotational de-excitation of  $\text{H}_2$  in its ground vibrational state induced by collisions with H.

For rotational transitions within the ground vibrational states, p-o- $\text{H}_2$  and o-p- $\text{H}_2$  transitions are slower than those corresponding to spin conservation as already noticed in Paper I and by Sun & Dalgarno (1994). Indeed, at these temperatures, the reaction (which leads to o-p- $\text{H}_2$  conversion) proceeds mainly by the tunnelling effect and the magnitude of the cross-sections is then expected to be small. However, the spin conversion process is only one order of magnitude slower than the spin conserving process, showing nevertheless a clear competition between inelastic and reactive processes even for  $\text{H}_2$  in its ground vibrational states. A similar result was found by Lique & Faure (2012) for the isotopologue  $\text{H}+\text{D}_2$  reaction.

We note that o-p- $\text{H}_2$  transitions are slower than p-o- $\text{H}_2$  transitions as already noticed in Paper I. In contrast, rotational relaxation of o- $\text{H}_2$  is faster than that of p- $\text{H}_2$ .

Fig. 2 shows rate coefficients for pure rotational de-excitation of vibrationally excited  $\text{H}_2$  induced by H.

The magnitude of the rate coefficients increases with increasing initial vibrational state. Such findings are in agreement with the results of Wrathmall & Flower (2007). Such behaviour seems to be specific to the  $\text{H}_2\text{-H}$  collisional system (or at least to light collisional systems) where the anisotropy of the PES is strongly influenced by the vibration of the diatomic molecule (Lique et al. 2014), since the magnitude of pure rotational transitions is generally weakly dependent on the vibrational state (Roueff & Lique 2013). The propensity rules in favour of nuclear spin conservation transitions are again observed for all vibrational states.

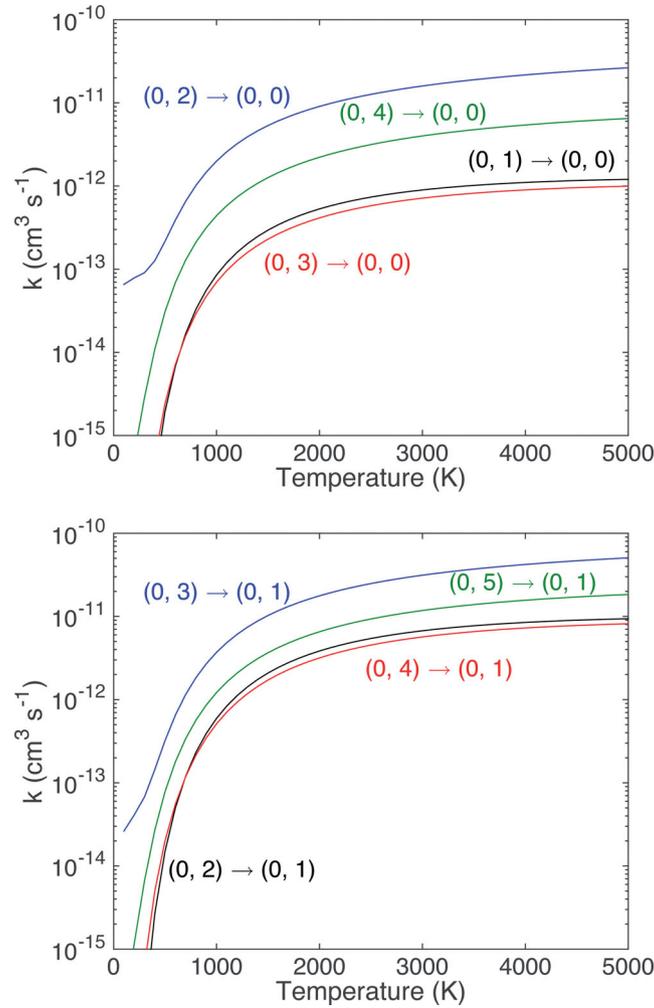
#### 3.2 Ro-vibrational (de-)excitation

Fig. 3 presents the state-to-state rate coefficients for the ro-vibrational de-excitation of  $\text{H}_2$  by H.

For a given  $\Delta v$  transition, the rate coefficients slightly increase with increasing vibrational states. This result is consistent with previous ro-vibrational excitation studies that found that the vibrational relaxation rate coefficients increase with increasing initial vibrational states (Roueff & Lique 2013). However, in the present case, the increase is very moderate and mainly seen at low temperatures.

The most unusual result concerns the magnitude of the rate coefficients at low and intermediate temperatures. Indeed, the ro-vibrational rate coefficients are less than an order of magnitude lower than the pure rotational rate coefficients even for large  $\Delta v$  transitions. This is in contradiction with previous ro-vibrational rate coefficients determined for most of the astrophysical systems. Indeed, generally, in collisional excitation studies with rare gas or a  $\text{H}_2$  collisional partner, the ro-vibrational rate coefficients are several orders of magnitude lower than pure rotational rate coefficients (Roueff & Lique 2013). However, Millikan & White (1963) and Millikan (1964) found that the vibrational relaxation rate coefficients increase with decreasing mass of the colliding partner so that we could expect that ro-vibrational quenching of  $\text{H}_2$  due to H collisions would be efficient. Hence, such behaviour can be explained by the strong coupling between  $\text{H}_2$  vibrational states induced by hydrogen collisions (Wrathmall & Flower 2007). Vibrational de-excitation of CO (Balakrishnan, Yan & Dalgarno 2002; Song et al. 2015) and HF (Tao & Alexander 2007) due to H collisions has also been found to be relatively fast even at moderate temperatures.

Nevertheless, the fact that the hydrogen is the collisional partner may not only be explanation to these large rate coefficients. Indeed, this behaviour also originates from the reactive pathways that compete with the inelastic pathways during the collisions. During their study



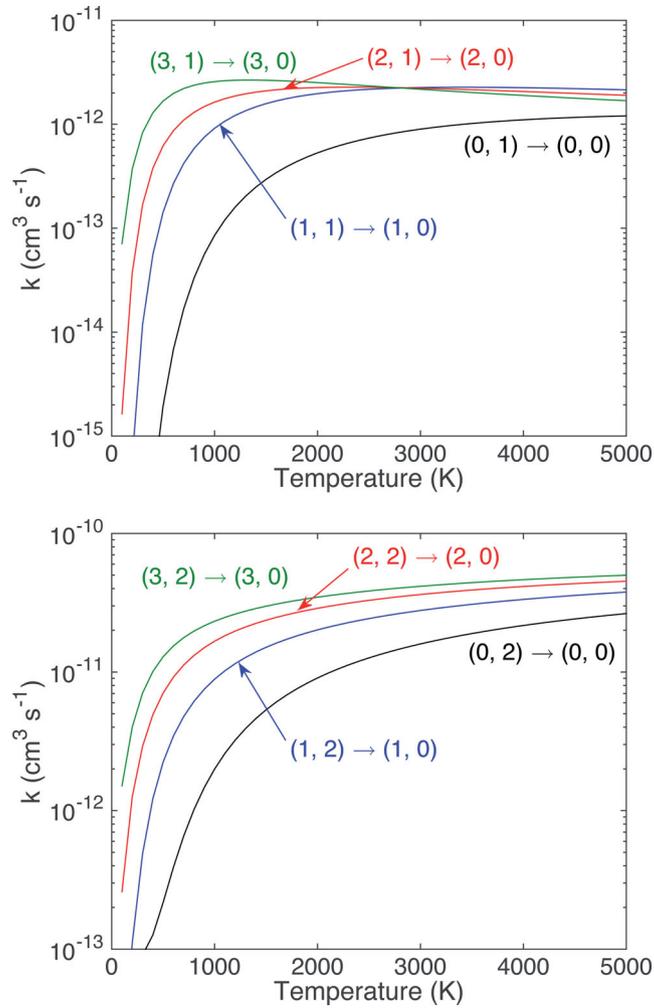
**Figure 1.** Temperature dependence of the rate coefficients for the rotational de-excitation of  $H_2$  in its ground vibrational state induced by collisions with  $H$ . From initial level  $(v, j)$  to final level  $(v', j')$ .

on the effect of initial vibration and rotation on  $H+H_2$  reactivity, Barg, Mayne & Toennies (1981) found that vibrational excitation of the reagent molecule lowers the reaction threshold and leads to a great enhancement of the reactive rate constants. Hence, the reaction barrier can become as low as 1000 K for vibrationally excited  $H_2$  in collisions with  $H$ . Then, the reactive nature of the system (and the fact that reactive channels become rapidly classically open) favours the vibrational relaxation that could take place during reactive collisions. The fact that *o-p*- $H_2$  transitions during vibrational relaxation are almost as fast as nuclear spin conservation transitions attests to the efficiency of the process. In addition, Barg et al. (1981) found that all vibrational states of the newly formed  $H_2$  are significantly populated. Such an effect also clearly shows that ro-vibrational relaxation competes with the rotational relaxation even if the temperature is low to moderate. As a consequence, vibrational quenching is almost as probable as rotational quenching for  $H_2$  ( $v \geq 1$ ).

It is also interesting to analyse the rotational distribution after vibrational relaxation. The final rotational state of the  $H_2$  molecule is generally higher than the initial rotational state of  $H_2$  whatever the initial vibrational state is. In Fig. 3, we can clearly see that the vibrational relaxation of a *p*- $H_2$  ( $v, j = 0$ ) molecule will preferentially form a  $H_2$  molecule in rotationally excited states. The effect is even more pronounced at high temperatures where transitions with  $\Delta j \geq 8$  can be efficient. Such an effect has already been found by Wrathmall & Flower (2007) and can be explained by a propensity in conserving the collisional energy (i.e. conserving the internal energy of the  $H_2$  molecule). We have then an efficient way to produce  $H_2$  molecules that are rotationally hot.

### 3.3 Comparison with previous experimental and theoretical results

It is then interesting to compare our new collisional data with those previously computed. As mentioned in the introduction, the most commonly used data are those of Flower and co-workers (Wrathmall & Flower 2007; WGF07) and we focus here on a comparison with their results. These authors computed ro-vibrational rate coefficients for temperatures ranging from 100 to 6000 K also using the PES of Mielke et al. (2003). In their scattering calculations, they also used a close coupling approach but did not consider the reactive channels, arguing that reactivity is negligible for temperatures up to 6000 K. This hypothesis may be valid for collisions with  $H_2$  in its ground vibrational state but, as we discussed above, cannot be applied for collisions with  $H_2$  in vibrationally excited states.



**Figure 2.** Temperature dependence of the rate coefficients for rotational de-excitation of  $\text{H}_2$  by  $\text{H}$  within excited vibrational states. From initial level  $(v, j)$  to final level  $(v', j')$ .

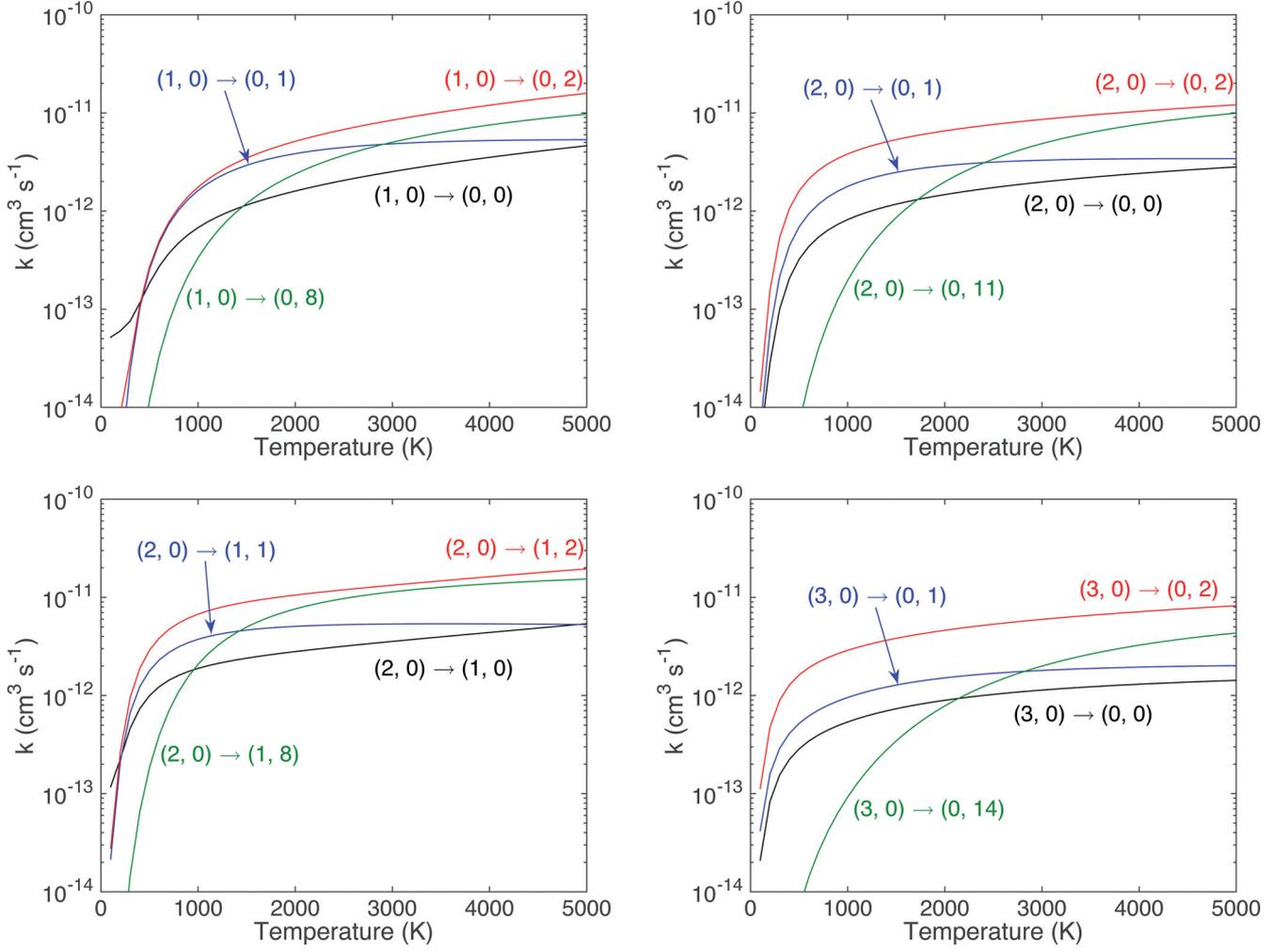
In Table 1, we show a comparison of our rate coefficients for pure rotational de-excitation of  $\text{H}_2$  in its ground vibrational state induced by collisions with  $\text{H}$  versus those of WGF07. The transitions with  $\Delta j = 2$  are mainly responsible for the cooling of the early Universe.

As expected, very good global agreement is found at low and intermediate temperatures. At these temperatures, the reaction is very inefficient and it is not surprising to see such a good agreement. At higher temperatures, deviations appear between the two sets of data, which can simply be explained by the non-inclusion of the reactive channels in the calculations by WGF07. Indeed, WGF07's results generally slightly overestimate the present results at high temperature since their calculations did not consider the possibility of o-p- $\text{H}_2$  transitions during the collisions that are only an order of magnitude lower than the nuclear spin conversion transitions at high temperatures. The maximum deviations are less than 20–30 per cent but these differences can impact the cooling process of the Universe.

For pure rotational transitions within an excited vibrational state of  $\text{H}_2$  (not shown here), the difference between the present and WGF07's results are of the same order of magnitude even if the difference slightly increases with increasing vibrational state because of the increasing impact of the reactive channels.

In Fig. 4, we show a comparison of our ro-vibrational rate coefficients versus those of WGF07. The differences are much more significant than for the pure rotational excitation. In addition, unlike pure rotational excitation, the maximum deviation is at low temperatures. The difference can be as high as an order of magnitude. As discussed above, the ro-vibrational relaxation of  $\text{H}_2$  by  $\text{H}$  is significantly due to reactive channels that were not considered in WGF07 and it is not surprising to see that the rate coefficients of WGF07 significantly underestimate the ro-vibrational relaxation rate coefficients at low temperatures. When  $\Delta v$  of the ro-vibrational transition increases (not shown here), the differences decrease so that the rate coefficients of WGF07 may be higher than the present rate coefficients for specific transitions.

At high temperatures, the rate coefficients of WGF07 are generally larger than the present rate coefficients. These differences can be understood because the o-p- $\text{H}_2$  conversion competes with the nuclear spin conservation process since the  $\text{H}$  and  $\text{H}_2$  reactants have enough energy to pass the barrier as can be seen in Fig. 3. This simply shows that the pure inelastic approach, which neglects the reactive pathway, overestimates the inelastic process.



**Figure 3.** Temperature dependence of the state-to-state rate coefficients for the ro-vibrational de-excitation of p- $H_2$  ( $j = 0$ ) induced by collisions with H. From initial level  $(v, j)$  to final level  $(v', j')$ .

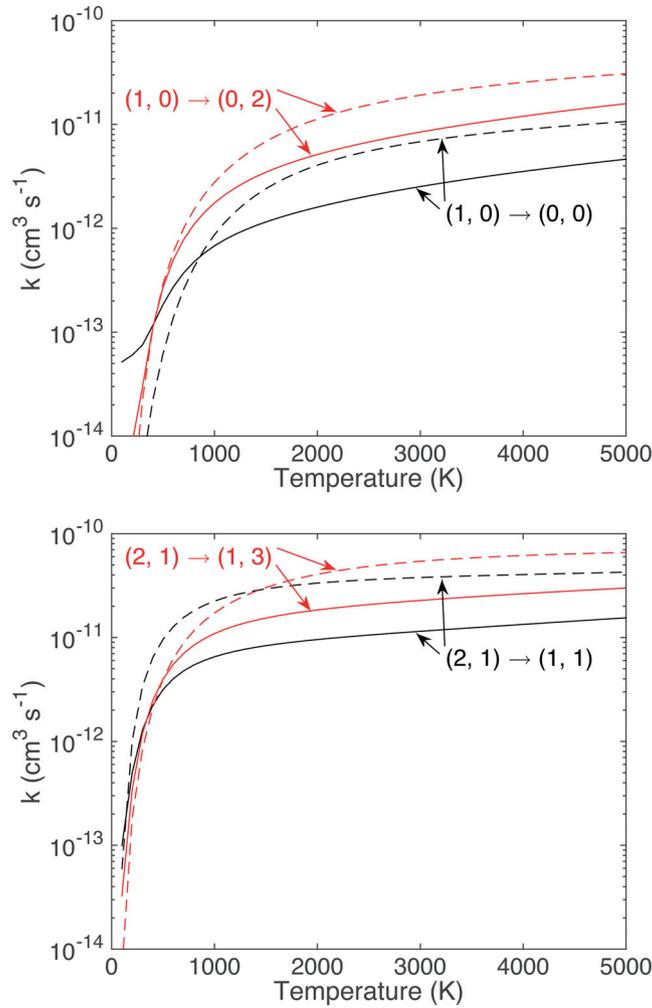
**Table 1.** Comparison between present rate coefficients and those of WGF07 for vibrationally elastic ( $v = 0 \rightarrow v' = 0$ ) to rotationally inelastic transitions. The rates are in units of  $\text{cm}^3 \text{s}^{-1}$ .

$T$ (K)	$j = 2 \rightarrow j' = 0$		$j = 4 \rightarrow j' = 0$		$j = 3 \rightarrow j' = 1$		$j = 5 \rightarrow j' = 1$	
	WGF07	This work						
100	7.2(-14)	6.6(-14)	8.7(-17)	1.0(-16)	2.5(-14)	2.6(-14)	1.3(-16)	1.7(-16)
200	8.1(-14)	7.9(-14)	4.5(-16)	6.0(-16)	3.7(-14)	4.1(-14)	6.5(-16)	1.2(-15)
300	8.9(-14)	9.1(-14)	1.9(-15)	2.9(-15)	5.8(-14)	6.8(-14)	3.2(-15)	6.6(-15)
500	2.0(-13)	2.2(-13)	2.2(-14)	3.1(-14)	2.5(-13)	3.2(-13)	3.5(-14)	7.9(-14)
1000	2.1(-12)	2.0(-12)	3.8(-13)	4.4(-13)	3.2(-12)	3.7(-12)	6.6(-13)	1.2(-12)
2000	1.1(-11)	9.1(-12)	2.4(-12)	2.2(-12)	1.8(-11)	1.8(-11)	4.8(-12)	6.5(-12)
3000	2.0(-11)	1.6(-11)	4.8(-12)	4.0(-12)	3.3(-11)	3.1(-11)	9.9(-12)	1.2(-11)
5000	3.2(-11)	2.6(-11)	8.1(-12)	6.5(-12)	5.4(-11)	5.1(-11)	1.6(-11)	1.8(-11)

Finally, we compare our theoretical results with the available experimental data. To the best of our knowledge, the only state-to-state data for the ro-vibrational relaxation are provided by Heidner & Kasper (1972). These authors measured rate coefficients for the  $H+H_2$  ( $v = 1$ )  $\rightarrow$   $H+H_2$  ( $v' = 0$ ) process at room temperature. The rotational structure of  $H_2$  was not resolved. To compare with the experimental results, we determined the thermal rate coefficients for the  $v = 1 \rightarrow v' = 0$  vibrational relaxation. Boltzmann averaging was done using partition function  $Q$  of the first nine rotational states ( $j = 0-8$ ) of the  $H_2$  ( $v = 1$ ) molecule:

$$\bar{k}_{v=1 \rightarrow v=0} = \frac{\sum_{j=0}^8 \sum_{j'=0}^{12} w_j (2j+1) e^{-\epsilon_{v=1,j}/kT} k_{v=1,j \rightarrow v'=0,j'}}{Q}$$

$$Q = \sum_j w_j (2j+1) e^{-\epsilon_{v=1,j}/kT}, \quad (5)$$



**Figure 4.** Comparison between present (solid lines) and WGF07 (dashed lines) inelastic rate coefficients for the ro-vibrational de-excitation of  $\text{H}_2$  by H. From initial level  $(v, j)$  to final level  $(v', j')$ .

**Table 2.** Room temperature rate coefficients for  $\text{H}_2$  ( $v = 1$ ) + H  $\rightarrow$   $\text{H}_2$  ( $v' = 0$ ) + H process.

Reference	Rate coefficients (in units of $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ )
Heidner & Kasper (1972)	$3.0 \pm 1.5$
This work	1.8
WGF07	0.7
Martin & Mandy (1995)	0.8
Garcia & Laganà (1986)	1.1

where  $\epsilon_{v=1j}$  is the energy of the  $v = 1, j$  rotational levels and  $w_j$  is a degeneracy weight, which is equal to 1 and 3 for para- and ortho- $\text{H}_2$  rotational states, respectively.

A comparison between present and experimental results is presented in Table 2. We also show in Table 2 the results of previous theoretical calculations.

The agreement between present results and the experiments of Heidner & Kasper (1972) is very good. This agreement confirms the accuracy of the PES and of the scattering approach used in this work. We also note that previous calculations fail to reproduce the experimental data because of the use of (i) a non-reactive approach (WGF07) and (ii) quasi-classical trajectory methods that are inaccurate at low to moderate temperature (Garcia & Laganà 1986; Martin & Mandy 1995). Taking into account the very high accuracy of our calculations (confirmed by the agreement with the available experimental data), we recommend the use of our new rate coefficients in astrophysical applications.

#### 4 DISCUSSIONS AND CONCLUSIONS

We have presented accurate calculations of rate coefficients for the ro-vibrational (de-)excitation of  $H_2$  by  $H$ , including the hydrogen exchange channels. These new data are, to the best of our knowledge, the first computed for the o-p- $H_2$  conversion at high temperature and using a purely quantum approach. Together with other molecular data for the other o-p- $H_2$  converter, the o-p- $H_2$  ratio can then be determined more accurately for warm media.

The new rate coefficients were compared to experimental data and to those presently used in astrophysical modelling. Whereas the agreement with experiment was good, we found significant differences with previous theoretical calculations, mainly due to the inclusion of reactive channels in the calculations. These differences imply that the cooling mechanism in astrophysical media has to be reviewed.

The  $H_2$  cooling function in astrophysical media is computed from  $H_2$  radiative and collisional data (Le Bourlot et al. 1999), the collisional partners being generally  $H$ ,  $He$  and  $H_2$  particles. Among them, the collisional data for  $H$  are of crucial importance for the computation of the cooling function (Galli & Palla 1998). They even dominate the cooling in the early Universe so that the cooling function is almost proportional to the  $H_2$ - $H$  rate coefficients. Then, we anticipate that our new data will significantly impact the magnitude of the  $H_2$  cooling function and then change the cooling mechanism in astrophysical media. In particular, we have seen that the  $H_2$ - $H$  rate coefficients are generally lower than those of WGF07 at temperatures above 1000 K, so that the cooling will probably be less efficient via these transitions. In contrast, in colder media, we can anticipate that the cooling may increase. Recall that in the early Universe, the very first stars are believed to have formed thanks to  $H_2$  cooling. Our knowledge of star formation may then be enhanced by the use of these new data.

Apart from in the early Universe,  $H_2$  formation is an important process in post-shock regions ( $H_2$  starts to reform again on the surfaces of dust grains) and in these regions,  $H_2$  is an active participant in the cooling because of its high abundance.  $H_2$  cooling is more efficient than atomic oxygen cooling in low-density and high-temperature regions (Neufeld, Lepp & Melnick 1995) and it cools the gas phase to roughly 100 K when cooling by  $H_2O$  takes over. The new data will be crucial for modelling the evolution of shock regions. As mentioned in the introduction, modelling of photon-dominated regions will also be impacted by these new data.

Collisional rate coefficients can also be used to model  $H_2$  emission from media where atomic hydrogen is abundant. Indeed, due to the low density of the interstellar medium, the ro-vibrational levels of molecules are generally not in local thermodynamic equilibrium and to model the observed interstellar spectra accurately, one must consider the processes of spectral line formation and this requires an accurate knowledge of rates for radiative and collisional excitation.

Finally, the new results probably imply that new collisional data have also to be obtained for the other main coolant in the Universe, the HD molecule. Indeed, the most recent HD- $H$  collisional data (WGF07) were obtained by neglecting the reactive channels. In the light of this study, it seems obvious that the accuracy of HD- $H$  rate coefficients can be improved.

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## SUPPORTING INFORMATION

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