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Ro-vibrational excitation of H_2 by H extended to high temperatures

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ABSTRACT
Collisions between H_2 and H are crucial to the thermal balance of astrophysical media, especially that of the early Universe. We report quasi-classical trajectory (QCT) calculations of rate coefficients for the collisional (de-)excitation of H_2 by H—including the three-body collisional dissociation—on a highly accurate H_3 potential energy surface (PES). Translational temperatures ranging from 100 to 15 000 K, and ro-vibrational energy levels of H_2 up to ≈ 50 000 K are considered. Our QCT rate coefficients agree well with those obtained from previous quantum calculations on the same PES. This good agreement supports our claim that, in order to study the 5000-to-15 000 K temperature range, typical of the early Universe, inexpensive QCT calculations should be preferred to extrapolation of costly quantum calculations run at lower temperatures. The new collisional rate coefficients should enhance our ability to model the cooling and heating budget of the primordial gas.

Key words: Molecular data – Molecular processes – scattering – early Universe

1 INTRODUCTION

In astrophysical media, collisional excitation processes followed by radiative decay lead to the conversion of thermal energy into photons, which can escape from the medium. Hence, they contribute significantly to the thermal balance of astrophysical media. Since atomic hydrogen and helium, the two most abundant species in space, have no fine structure in their ground electronic state, the cooling in the interstellar gas takes place mostly through collision with heavier atoms. Hence, cooling in the interstellar medium is dominated by collisions with the next most abundant elements, carbon and oxygen (Wolfire et al. 1995).

In the early Universe, the situation is different since such atoms are absent. Such kind of cooling takes place thanks to the first molecules that have been formed. Even if H_2 is on small abundance (Galli & Palla 2013), the cooling by infrared emission of H_2 following its collisional excitation is the dominant cooling mechanism. Indeed, collisions between H_2 and H provide the cooling essential to the formation of protogalaxies and of the first stars (Flower & Pineau des Forêts 2001). Modeling of collisions between H_2 and H are then crucial in order to qualitatively and quantitatively model the thermal balance of the early Universe.

Because of their astrophysical interest, and especially because of their experimental and theoretical accessibility, collisions between H_2 and H have been the object of constant and detailed investigations (See Aoiz et al. 2005, for a review). Collisional rate coefficients computed using either quasiclassical trajectory (QCT) (see Mandy & Martin 1993, and references therein) or time independent quantum mechanical (TIQM) (Wrathmall & Flower 2007, and references therein) approaches have been provided to the astrophysical community during the last three decades. Current models of the early Universe (Wrathmall et al. 2007; Glover & Abel 2008) generally rely on the later TIQM collisional data. Indeed, the data of Wrathmall & Flower (2007) were obtained using the state-of-the-art potential energy surface (PES) of Mielke et al. (2002) that has been shown to reproduce all the main experimental features (Mielke et al. 2003).

However, these TIQM rate coefficients were obtained using pure inelastic approaches assuming that the reactive cross sections are negligible and hence neglecting the possible ortho-to-para-H_2[1] nuclear spin conversion process during hydrogen exchange reactive collisions. Whereas such an approximation may be valid at low temperature, it is much

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[1] Owing to its identical hydrogen nuclei (with nuclear spin 1/2), H_2 exists in ortho (o-H_2) and para (p-H_2) forms, also called nuclear-spin isomers. In the electronic ground state, the rotational levels of o-H_2 have odd values of the angular momentum j while the levels of p-H_2 have even j values

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more questionable at temperatures above 1000 K and/or when dealing with ro-vibrational (de-)excitation.

Hence, in order to provide the astrophysical community with highly accurate data including the possible ortho-to-para-H_2 conversion process, one of the authors contributed new TIQM results (Lique et al. 2012, 2014; Lique 2015) for the ro-vibrational excitation of H_2 by H at low to moderate temperatures ($T < 5000$ K), using the PES of Mielke et al. (2002). Ro-vibrational energy levels of H_2 with internal energies up to $\simeq 22\,000$ K were considered. The computed data are in very good agreement with the available experimental data. Significant differences were found with previous TIQM calculations by Wrathmall & Flower (2007), mainly due to the neglect of reactive channels in the latter. These new data were used to derive an updated temperature and density-dependent cooling function for H_2 colliding with atomic hydrogen (Coppola et al. 2018). The inclusion of reactive channels in the calculation results in a larger ortho-to-para ratio, which in turn gives rise to a stronger cooling effect at low temperature.

For high temperature applications ($T > 5000$ K), the only available data (Mandy & Martin 1993) are based on QCT calculations on the Liu-Siegbahn-Truhlar-Horowitz (LSTH) PES of Truhlar & Horowitz (1978). Clearly, rate coefficients for the H + H_2 collision on the recent PES of Mielke et al. (2002) are desirable and would be very useful to the astrophysical community. In this paper, we present QCT calculations of rate coefficients for the ro-vibrational (de-)excitation of H_2 by H—including the ortho–para conversion and the three-body collisional dissociation—for temperatures up to 15 000 K, and for ro-vibrational energy levels of H_2 up to $\simeq 50\,000$ K. Our QCT data are benchmarked against the recent TIQM calculations of Lique (2015) in order to assess the accuracy of our QCT calculations, normally expected to improve with increasing temperature. 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 QUASI-CLASSICAL TRAJECTORY METHOD

Standard methods for performing quasi-classical trajectory calculations have been reviewed by Karplus et al. (1965) and Truhlar & Muckerman (1979). Here we simply give a short overview of the QCT method with, however, some details relative to the trajectory analysis. The following processes are considered:

$$\mathrm{H}_A + \mathrm{H}_B\mathrm{H}_C(v,j) \rightarrow \begin{cases} \mathrm{H}_A + \mathrm{H}_B\mathrm{H}_C(v',j') & \text{inelastic,} \\ \mathrm{H}_B + \mathrm{H}_A\mathrm{H}_C(v',j') & \text{reactive,} \\ \mathrm{H}_C + \mathrm{H}_A\mathrm{H}_B(v',j') & \text{reactive,} \\ \mathrm{H}_A + \mathrm{H}_B + \mathrm{H}_C & \text{dissociative,} \end{cases}$$

where v and j are the vibrational and rotational quantum numbers, respectively, of the H_2 target molecule. We assume that the Born-Oppenheimer approximation (Messiah (1995)) is valid, so that only the ground state PES of H_3 is considered in the present calculations. The twelve coupled Hamilton equations of motion in Jacobi coordinates are propagated by means of a standard Runge–Kutta integrator with adaptive time stepsize (Press et al. (1992)). Space derivatives are computed numerically by means of a finite difference formula of order three. The local truncation error on the coordinates and momenta is monitored to achieve a relative precision better than 10^{-6} in the conservation of the total energy, and the total angular momentum.

Preliminary to the trajectory propagation, the quantum bound vibrational states of the free H_2 molecule are computed by means of the Fourier-Grid-Hamiltonian (FGH) method of Balint-Kurti (Marston & Balint-Kurti (1989)). Note that this has to be done for each rotational state j of H_2, since the *effective* potential interaction of H_2, V_{eff}, includes a centrifugal term due to the rotational motion of the molecule:

$$V_{\mathrm{eff}}(r) = V(r) + j(j+1)\hbar^2/2mr^2, \tag{1}$$

where r is the H–H internuclear distance, $V(r)$ is the potential energy curve of H_2, and m is its reduced mass.

In the trajectory calculation, the initial ro-vibrational energy $\epsilon_{v,j}$ obtained from the FGH calculation, as well as the initial collision energy, are fixed. All other collision parameters are selected at random according to their probability distributions (Truhlar & Muckerman (1979)). In particular, the impact parameter b is ascribed the usual b^2 distribution between zero and a maximum value, which is sufficiently large that no reaction takes place beyond it. Moreover, the maximum value of b was found to be strongly dependent on the collision energy E_c, so that the maximum impact parameter function $b_{max}(E_c)$ had to be determined, prior to the trajectory calculation, by running small batches of trajectories at selected collision energies. Values of b_{max} for a particular value of E_c are then obtained by linear interpolation of $b_{max}(E_c)$.

We ran batches of 80 000 to 110 000 trajectories per energy for 20 collision energies between $E_{thresh} = 0.1$ eV (equivalent to 1160 K) and $E_{max} = 2.7$ eV (equivalent to 31 330 K) for each initial ro-vibrational state (v,j) with internal energies up to 4.3 eV (equivalent to 50 000 K). The highest internal energy levels (v,j) are: (0,30), (1,29), (2,26), (3,25), (4,24), (5,22), (6,20), (7,18), (8,16), (9,14), (10,11), (11,8), (12,4), with internal energies less than or equal to 50 000K. A total of 260 initial states were taken into account in the calculations. Each individual trajectory is propagated in time until any two of the three internuclear distances get larger than a "collision shell" distance $\rho_0 = 25a_0$. The remaining H–H fragment with the smallest internuclear separation may be a stable molecule (resulting from an inelastic or reactive collision), a quasibound molecule (trapped behind its centrifugal barrier), or an unbound molecule still evolving toward dissociation; analysis of this fragment's internal energy and angular momentum allows a definitive assignment. In the present calculations, quasibound H_2 molecules are counted as pertaining to the three-body dissociative channel. Around 5000 K they contribute up to 50% of the dissociative channel, and their contribution decreases with temperature to reach 30% at 15 000 K. The above assumption remains valid as long as the quasibound molecules have a life-time lower than the typical collision time. In high density media, collisions are more frequent and a part of the quasibound molecules may interact before dissociating.

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Once a trajectory has met the above end-of-trajectory criterion that corresponds to a bound H–H fragment, *continuous* "pseudo" quantum numbers for this diatom, which will be marked with a tilde sign, are derived from the trajectory's final positions and momenta. The rotational quantum number $\tilde{j'}$ is taken as the root of the equation:

$$J'^2_{int} = \hbar^2 \tilde{j'}(\tilde{j'}+1), \tag{2}$$

where J'_{int} is the internal angular momentum of the H_2 product. The vibrational quantum number $\tilde{v'}$ is obtained through the semiclassical Wentzel-Kramers-Brillouin (WKB) quantization condition (Berry & Mount (1972)):

$$2\int_{r_-}^{r_+} \left\{ 2\mu \left[\epsilon'_{int} - V(r) - \frac{J'^2_{int}}{2mr^2} \right] \right\}^{1/2} dr = \left(\tilde{v'} + \frac{1}{2} \right) 2\pi\hbar, \tag{3}$$

where r_- and r_+ are the left and right turning points, respectively, relative to the classical internal energy of the relevant H_2 fragment, noted ϵ'_{int} (Truhlar & Muckerman (1979)).

Once the above continuous pseudo-quantum numbers $(\tilde{v'}, \tilde{j'})$ have been determined, they are rounded to the nearest integers through a "binning" procedure (histogram method) (Truhlar & Muckerman (1979)), and the corresponding trajectory is attributed to the bin labeled by the couple of *discrete* quantum numbers (v', j'). Notice that this method has to be adapted to account for the fact that ortho–para conversion of H_2 is forbidden in purely inelastic collisions. Then, a $\Delta j = 2$ parity rule is enforced through the binning procedure, i.e., the continuous $\tilde{j'}$ is rounded to the nearest integer j' of same parity as j. In H + H_2 reactive collisions, ortho–para conversion is allowed, and the regular binning process described above is applied.

Finally, after being analysed as described above, all trajectories are accumulated in the histogram. The trajectory count in the histogram bin labeled (v', j'), denoted $N_r(v', j'; E_c)$, allows us to determine the state-to-state cross section for the reaction:

$$\sigma_{v',j' \leftarrow v,j}(E_c) = \pi b^2_{max}(E_c) \frac{N_r(v', j'; E_c)}{N_{tot}(v, j; E_c)}, \tag{4}$$

where $N_{tot}(v, j; E_c)$ is the total number of trajectories started in the ro-vibrational state (v, j) and propagated with the collision energy E_c. The estimated statistical error on this cross section is given by (Truhlar & Muckerman (1979)):

$$\Delta\sigma_{v',j' \leftarrow v,j}(E_c) = \sigma_{v',j' \leftarrow v,j}(E_c) \sqrt{\frac{N_{tot} - N_r}{N_{tot} \times N_r}} \tag{5}$$

In this study, the average error on the cross section is about 10% for the less populated states and it is below 3% for the most populated states.

The state-to-state rate constant is given by:

$$k_{v',j' \leftarrow v,j}(T) = \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} \frac{1}{(k_B T)^2} \times \int_0^\infty \sigma_{v',j' \leftarrow v,j}(E_c) E_c e^{-\frac{E_c}{k_B T}} dE_c \tag{6}$$

where k_B is Boltzmann's constant, μ is the reduced mass for the H–H_2 motion, and where the integration was carried out numerically.

3 RESULTS

3.1 Comparison with previous quantum results

It is first important to estimate the accuracy and validity domain of the QCT results. To this aim, we compare the new QCT rate coefficients with the TIQM one of Lique (2015).

We compare QCT and TIQM results for collisional (de-)excitation of H_2 by H. The upper panels of Fig. 1 shows the QCT and TIQM results of the pure rotational de-excitation of $H_2(v, j)$ induced by collisions with H. The ro-vibrational (de-)excitation is studied on the lower panels of Fig. 1. As anticipated, significant deviations occur at low temperatures because of the inability of QCT treatments to conserve the vibrational zero-point energy that renders this method unreliable near reaction thresholds. However, at higher temperatures, above a few hundreds of Kelvins, the QCT approach is relatively accurate for both rotational and ro-vibrational transitions, the mean deviations being of the order of a factor 3 and tend to decrease with increasing temperatures, as expected.

Fig. 2 presents a comparison between the QCT and TIQM results of Lique (2015) at 5000 K for all (de-)excitation transitions between levels with internal energy lower than 22 000 K. One can observe a global agreement within a factor of 3 between the two sets of data. It is interesting to note that the agreement improves with increasing magnitude of the data. It means that the accuracy of the rate coefficients for the dominant transitions will be relatively high. The QCT rate coefficients are then closed to the values computed by Lique (2015), and with a better agreement for the inelastic channel than for the reactive one where quantum effects are not negligible, especially at low and intermediate collisional energy.

The good agreement between the previous quantum and the new QCT rate coefficients allows us to be confident in the accuracy of the new data that will be provided for high temperatures and highly excited ro-vibrational levels.

3.2 Collisional dissociation process vs. inelastic and reactive processes

As mentioned above, the three body collisional dissociation process has been included in the calculations. Such process is usually neglected in TIQM calculations and in some of the previous QCT calculations whereas it is expected to be the dominant channel at high temperature and for ro-vibrational levels highly excited. The respective importance of inelastic and reactive collisions and of the dissociation process is investigated on Fig. 3.

As can be seen, pure rotational excitations[2] are principally induced by the purely inelastic process, the effect being even enhanced with increasing temperature. For ro-vibrational excitation, the behavior is relatively similar. However, the inelastic process is less dominant than for pure rotational transition. As expected while temperature increases above a thousand of Kelvins, the excitation process due to reactive collisions decreases because of the dissociative process that becomes dominant. For temperature above

[2] Pure rotational ortho-to-para-H_2 transitions occurs only through the reactive process

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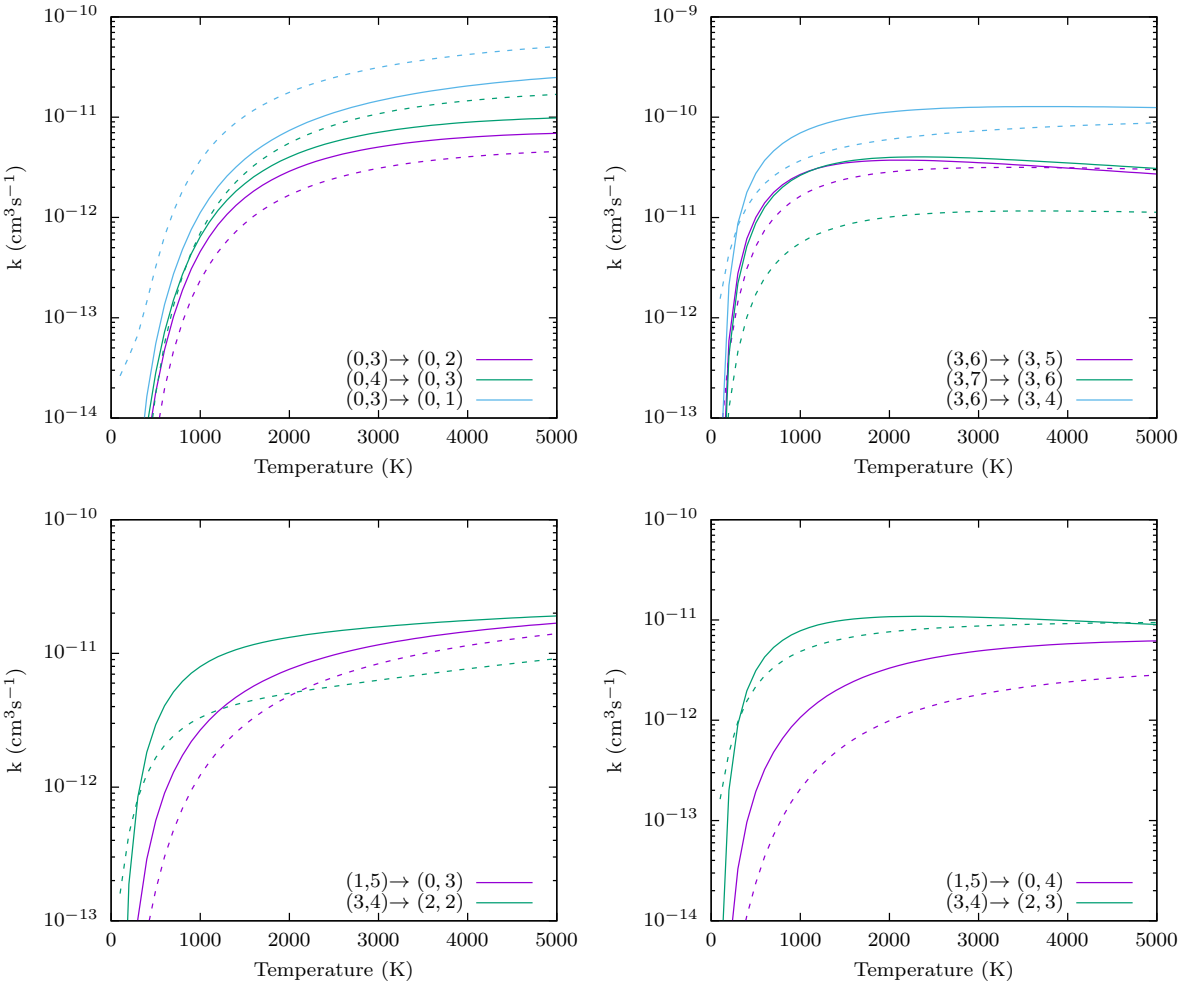

Figure 1. Temperature dependence of the QCT (solid lines) and TIQM (dashed lines) rate coefficients for pure rotational (upper row) and ro-vibrational (lower row) de-excitation of H_2 by H. From initial (v, j) to final (v', j') level.

~ 3000 K, there is a clear competition between collisional excitation through the reactive process and dissociation and for temperature above ~ 5000 K, the collisional dissociation becomes the dominant process. Hence, collisional data obtained neglecting such process may be doubtful for high temperature application. It is worth mentioning that the importance of dissociation process increases with increasing energy of the H_2 ro-vibrational level, with differences up to 4 orders of magnitude for the rate coefficients between the lowest and the highest ro-vibrational state.

3.3 Pure rotational (de-)excitation

Fig. 4 shows the temperature variation of pure rotational de-excitation rate coefficients within the ground and excited vibrational states.

For the lowest vibrational level $v = 0$, the rate coefficients for both nuclear spin conversion and conversion transitions increase rapidly with increasing temperatures up to 5000 K and then reach a plateau up to 15 000 K. As noticed by Lique (2015), nuclear spin conversion transitions are slower than those corresponding to nuclear spin conservation because of a significant activation barrier in the PES that inhibit the hydrogen exchange process that lead to nuclear spin conversion process.

While increasing the vibrational level, there is an increase of the pure rotational rate coefficients (for both nuclear spin conservation and conversion transitions) as already found in previous TIQM calculations (Wrathmall & Flower 2007; Lique 2015) and can be explained by the anisotropy of the PES that is is strongly dependent on the vibration of the diatomic molecule (Lique et al. 2014). However, for a given rotational transition, we note that the rotational rate coefficients for the different vibrational levels tend to converge at high temperatures. The rate coefficients for nuclear spin conservation transitions reach a plateau at lower temperatures than for the vibrational level $v = 0$ as can be easily seen in Fig. 4.

The noticeable point is the decrease of the rate coefficients for p-o-H_2 and o-p-H_2 conversion process for high

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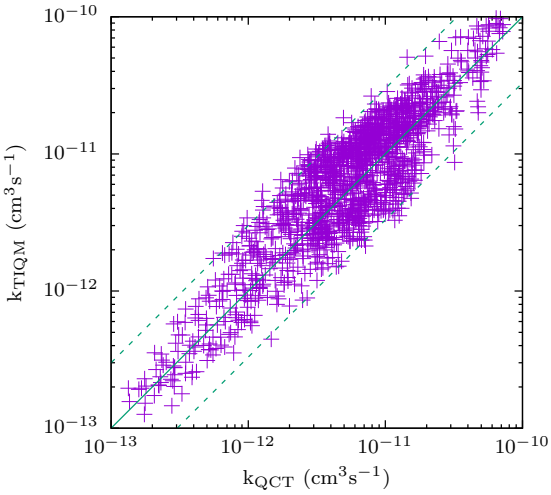

Figure 2. Comparison between QCT and TIQM rate coefficients at 5000 K for all (de-)excitation transitions for internal energies lower than 22 000 K. Dashed-lines represent a deviation of a factor 3.

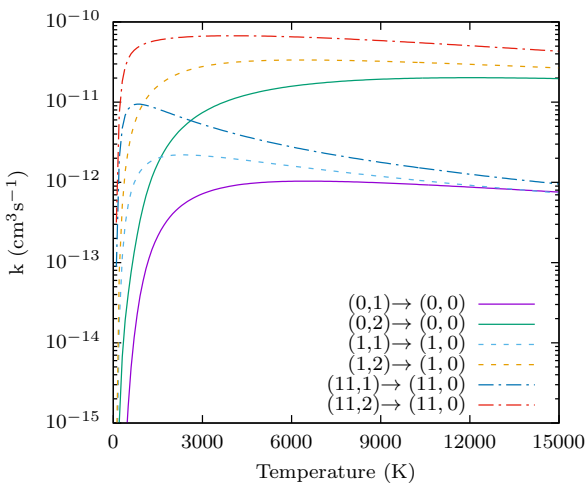

Figure 4. Temperature dependence of the QCT rate coefficients for ro-vibrational (de-)excitation of H_2 by H, p-o-H_2 and o-p-H_2 transitions for low and high initial vibrational level. From initial (v, j) to final (v', j') state.

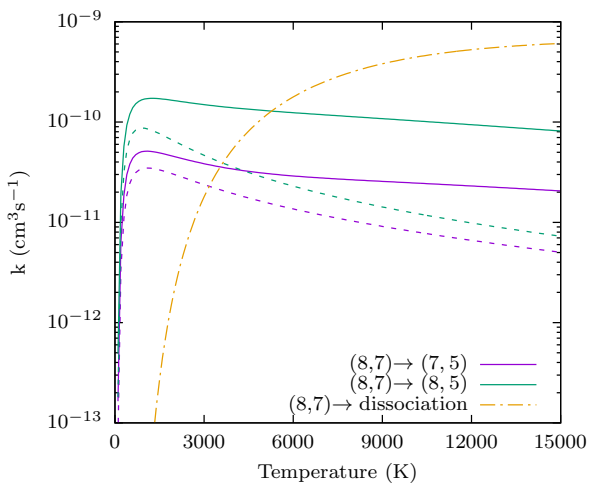

Figure 3. Temperature dependence of the QCT rate coefficients for ro-vibrational (de-)excitation of H_2 by H (solid lines), for the reactive channel (dashed lines) and for the dissociation (dotted-dashed line). From initial (v, j) to final (v', j') state.

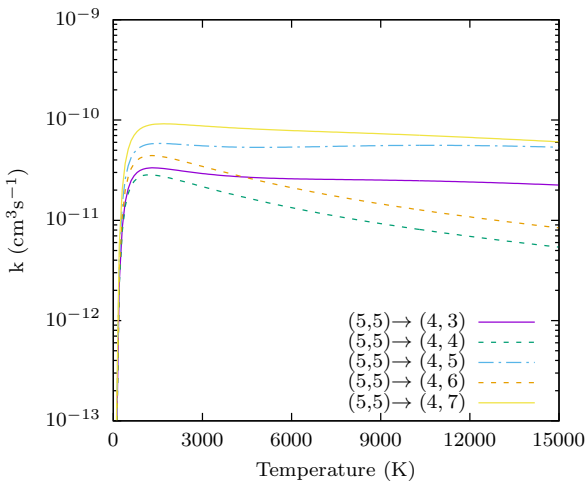

Figure 5. Temperature dependence of the QCT rate coefficients for ro-vibrational (de-)excitation of H_2 by H with $\Delta v = 1$. From initial (v, j) to final (v', j') state.

temperatures. Such effect can be explained by the fact that the only reactive collisions contribute at such process and that at high temperature, and the kinetic energy of the reaction starts to be exchanged for internal rotational energy leading to formation of H_2 in various highly excited states. Such effect is not or weakly seen in the temperature variation of the rate coefficients for spin conservation process as the dominant contribution come from non-reactive process that favor a weak change in internal energy. As noticed by Lique et al. (2012) the o-p-H_2 conversion process is slower than the inverse conversion process.

3.4 Ro-vibrational (de-)excitation

Fig. 5 presents the temperature dependence of the rate coefficients for a given Δv transition and rotational (de-)excitations. For both the spin conservation and conversion processes, the rate coefficients increase with increasing final rotational state, and rotational excitation is faster than rotational de-excitation. This can be explained by a propensity rules in conserving, as much as possible, the internal energy. For the spin conversion process corresponding to reactive collisions there is a steep increase at low temperature and a slow regular decrease over temperature as seen and explained on Fig. 4. For the spin conservation process, where both inelastic and reactive collisions are involved, the rate

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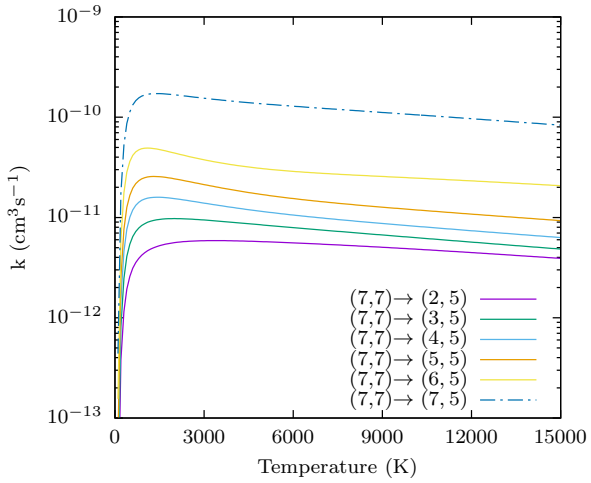

Figure 6. Temperature dependence of the QCT rate coefficients for ro-vibrational (de-)excitation of H_2 by H with $\Delta j = 2$. From initial (v, j) to final (v', j') state.

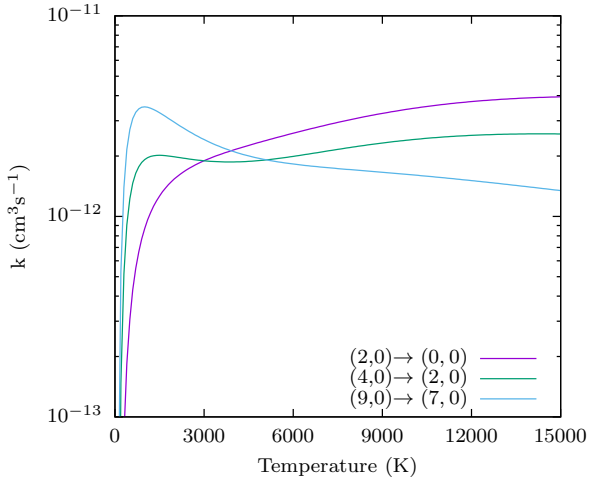

Figure 7. Temperature dependence of the QCT rate coefficients for vibrational de-excitation of H_2 by H. From initial (v, j) to final (v', j') state.

coefficients tend to be quite constant above few hundreds of Kelvins.

Fig. 6 shows, for a fixed Δj, the temperature dependence of the rate coefficients for ro-vibrational (de-)excitations conserving the rotational momentum of H_2. The temperature variation of these rate coefficients is similar to that seen in Fig. 5, with an increase of the rate coefficient with decreasing Δv transitions. It is interesting to note that the ro-vibrational rate coefficients are smaller in magnitude than that of the pure rotational excitation ones. However, the differences are less than or about an order of magnitude even for large $\Delta v > 1$ transitions and decrease with increasing v. As discussed by Lique (2015), the strong coupling between H_2 vibrational states induced by hydrogen collisions explains this behavior.

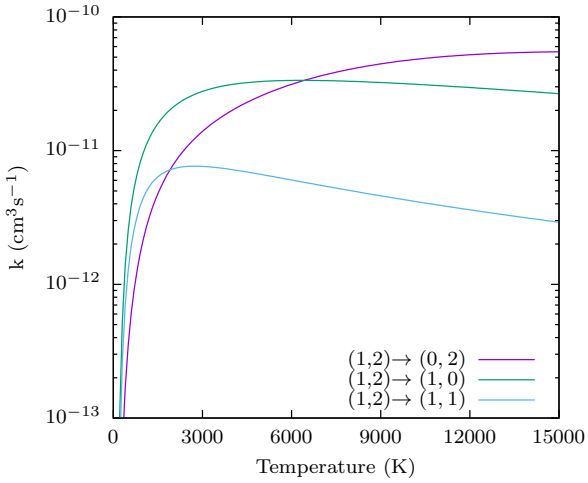

Figure 8. Temperature dependence of the QCT rate coefficients for ro-vibrational and pure rotational de-excitation of H_2 by H. From initial (v, j) to final (v', j') state.

Fig. 7 shows the rate coefficients for nuclear spin conservation transitions with different $\Delta v = 2$. At temperatures below 1000–1500 K, the rate coefficients increase with the initial vibrational level. At the opposite, at higher temperatures, the effect is totally reversed, and the lowest initial vibrational level is having the faster rate coefficients. At high temperatures, the kinetic energy starts to be exchanged for internal energy leading to formation of H_2 in various excited states. As the number of open final ro-vibrational levels increases with increasing vibrational levels, there is a decrease of the magnitude of the rate coefficients with increasing initial vibrational levels.

The unusual behavior of the rate coefficients (i.e. a decrease and then an increase of the magnitude of the rate coefficients) for the (4,0) → (2,0) (also seen for other transitions) can be understood on the basis of the respective contribution of the inelastic and reactive processes. At low temperature, as discussed in Lique (2015), the ro-vibrational transitions mainly proceed through the reactive exchange process leading to a decrease of the rate coefficients with increasing temperature. At higher temperature above ~ 5000 K, the ro-vibrational relaxation process (for nuclear spin conservation transitions) is again dominated by the non reactive collisions and increase again with increasing temperatures.

We also found that, at high temperatures, the rate coefficients for ro-vibrational de-excitation cross the pure rotational de-excitation rate coefficients which is visible on Fig. 8. It happens above 6000 K for an initial vibrational level $v = 1$, and the crossing moves toward higher temperatures while increasing the initial vibrational level. Contrarily to the o-p-H_2 and p-o-H_2 conversion processes which decrease while temperature increases because of suffering of the increase of channels opening, the rate coefficients of the vibrational de-excitation do not show any evolution going in that sense and there is still a smooth slope while temperature increases.

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Table 1. Room temperature thermal rate coefficients for $H_2(v = 1)$+H→ $H_2(v' = 0)$+H process from experimental and theoretical calculations. Thermal rate coefficients are in units of 10^{-13}cm^{3}s^{-1}.

Reference	$\bar{k}_{1\to0}(T)$
Experimental data: Heidner & Kasper (1972)	3.0±1.5
TIQM calculation: Lique (2015)	1.8
QCT calculation: Martin & Mandy (1995)	0.8
QCT calculation: Garcia & Laganà (1986)	1.1
QCT calculation: this work	1.28

3.5 Comparison with experiments

Experimental rate coefficients at room temperature for the relaxation of $H_2(v = 1) \to H_2(v = 0)$ due to H collisions were provided by Heidner & Kasper (1972). Hence, we compared the thermal rate coefficients at room temperature of our QCT calculations with these data. The thermal rate coefficient for the $v = 1 \to v' = 0$ is computed as follow:

$$\bar{k}_{1\to0}(T) = \frac{\sum_{j=0}^{29}\sum_{j'=0}^{31} w_j(2j+1)e^{-\epsilon_{1,j}/kT}k_{1,j\to0,j'}(T)}{Q(T)}$$
$$Q(T) = \sum_j w_j(2j+1)e^{-\epsilon_{1,j}/kT}, \quad (7)$$

where $\epsilon_{1,j}$ 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-H_2 rotational states, respectively.

Results are shown in Tab. 1 together with the rate coefficients computed previously by Lique (2015) using TIQM approach and by Martin & Mandy (1995) and Garcia & Laganà (1986) that both used QCT method.

As could have been anticipated, the present rate coefficients for the relaxation of $H_2(v = 1)$ to $H_2(v = 0)$ fail at reproducing the experimental data. The temperature of the experiments (300 K) is out of the accuracy domain of the QCT calculations. However, the agreement between the new QCT results using the state of the art H_3 PES of Mielke et al. (2002) and both the experimental and TIQM data is much better than what was found with previous QCT calculations of Martin & Mandy (1995) and Garcia & Laganà (1986).

4 DISCUSSIONS AND CONCLUSIONS

We have presented the calculations of new high temperature state specific rate coefficients for the collisional excitation of H_2 by H using QCT method. The accuracy of the present results have been validated through a detailed comparison with TIQM calculations and experiments. In particular, the new collisional data are closer to experimental data than the previous QCT calculations due to the high accuracy of the PES used in this work.

We have found that, because of the competition between inelastic, reaction and dissociative processes, the temperature variation of the rate coefficients is not smooth and strongly dependent of the ro-vibrational level of H_2. Such findings show the evidence that actual calculations at high temperatures are preferable than extrapolations of low to moderate temperatures data for astrophysical applications where the temperature domain is around 5000 K to 15 000 K as in the early Universe.

As discussed in the introduction, in the early universe, the H_2 cooling function is computed from H_2 radiative and collisional data, the main colliding partner being generally H atoms (Galli & Palla 1998). Hence, H_2–H collisions dominate the cooling so that the cooling function is almost proportional to the H_2–H rate coefficients. The new rate coefficients, the first one computed for such high temperatures, will allow accurate modeling the cooling of the warm primordial gas and allow a significant revision of the cooling of the gas at temperature between 5000 and 15 000 K. As the very first stars are believed to have formed thanks to H_2 cooling, our knowledge of star formation should be enhanced by the use of these new data.

Apart from in the early Universe, H_2 is also an important coolant in shocks and photon dominated regions of the interstellar medium because of its high abundance. In photon dominated regions, evidence of highly excited H_2 have been found and the new data will be crucial for modelling the kinetic and thermal evolution of these regions.

Finally, this high temperature study showed some interesting results, making obvious that a collisional excitation study induced by hydrogen atoms in this temperature range for the other dominant molecules in the early Universe such as HD or H_2^+ is required in order to update the present data used.

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