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## ***Ortho-Para* H<sub>2</sub> Conversion by Proton Exchange at Low Temperature: An Accurate Quantum Mechanical Study**

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We report extensive, accurate fully quantum, time-independent calculations of cross sections at low collision energies, and rate coefficients at low temperatures for the  $\text{H}^+ + \text{H}_2(v=0, j) \rightarrow \text{H}^+ + \text{H}_2(v=0, j')$  reaction. Different transitions are considered, especially the *ortho-para* conversion ( $j=1 \rightarrow j'=0$ ) which is of key importance in astrophysics. This conversion process appears to be very efficient and dominant at low temperature, with a rate coefficient of  $4.15 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 10 K. The quantum mechanical results are also compared with statistical quantum predictions and the reaction is found to be statistical in the low temperature regime ( $T < 100 \text{ K}$ ).

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Hydrogen is by far the most abundant baryon in the Universe and molecular hydrogen, H<sub>2</sub>, is the primary molecule. In the interstellar medium, H<sub>2</sub> forms efficiently via the recombination of hydrogen atoms on the surface of submicron size dust grains (see [1] and references therein). In the early Universe, where dust grains were absent, it is believed that the dominant source of H<sub>2</sub> was the associative detachment between H and H<sup>−</sup> and, with increasing density, the three body recombination  $\text{H} + \text{H} + \text{H}$  [2]. Owing to its identical hydrogen nuclei, H<sub>2</sub> exists in *ortho* and *para* forms. In the ground electronic state, the rotational levels of *ortho*-H<sub>2</sub> have odd values of the angular momentum  $j$  while the levels of *para*-H<sub>2</sub> have even  $j$  values. The internal energy of the newly formed H<sub>2</sub> molecules is not known but it is generally assumed that, whatever the formation mechanism, H<sub>2</sub> is initially highly excited. The initial *ortho*-to-*para* ratio (OPR) of H<sub>2</sub> is therefore usually taken as its limiting (high temperature) statistical value of 3, which is the ratio of the degeneracies of the *ortho* ( $I=1$ ) and *para* ( $I=0$ ) nuclear spin states.

The OPR of H<sub>2</sub> is expected to decrease slowly with temperature below  $\sim 300 \text{ K}$  and to play a crucial role in both the physical and chemical evolution of astronomical environments. For instance, the very first stars are believed to have formed within small protogalactic objects, cooled mainly by molecular hydrogen whose cooling rates depend on the OPR of H<sub>2</sub> [3,4]. In cold ( $\sim 10 \text{ K}$ ) dark interstellar clouds, where stars form at the present epoch, H<sub>2</sub> cannot emit radiation but it is the dominant colliding partner and the OPR can be important to determine the excitation of other molecular species (e.g., [5]). The OPR value is also

of utmost importance to understand the deuterium chemistry in star forming regions: Pagani *et al.* [6] have thus shown that an  $\text{OPR} \lesssim 0.01$  is a necessary condition to explain the large deuterium enrichment observed in some prestellar cores (see also [7]). The fact that H<sub>2</sub> lies mostly in its *para* ( $j=0$ ) form in cold interstellar clouds is also suggested by the low OPR values estimated from pure H<sub>2</sub> rotational emission detected near shock-heated regions (see [8] and references therein). Chemical models have also shown that the OPR should not reach the thermal equilibrium in the coldest clouds [7,9]. The OPR of a given interstellar cloud is therefore expected to depend on its chemical history and lifetime.

Radiative transitions between the *ortho* and *para* forms of H<sub>2</sub> are known to be very slow, with an interconversion lifetime greater than the age of the Universe for the  $j=1 \rightarrow 0$  transition [10]. As a result, *ortho-para* transitions may occur only in reactive collision with H and H<sup>+</sup> (or H<sub>3</sub><sup>+</sup> in some environments [6,7]). The reaction with H has a substantial activation energy ( $\sim 5000 \text{ K}$ ) and it is thus efficient only at high temperatures. Collisions with protons are therefore expected to drive the OPR of H<sub>2</sub> in most astrophysical environments, from the primordial to the interstellar gas. The knowledge of the collision rate for proton exchange between H<sup>+</sup> and H<sub>2</sub> is therefore of fundamental astrophysical interest.

Although the  $\text{H}^+ + \text{H}_2$  reaction is one of the most elementary ones, there exist only approximate estimates for the *ortho-para* conversion (OPC) rate coefficients. The current values employed in most astrophysical models were computed 20 years ago using a statistical model

[11]. In this Letter, we compute the first accurate rate coefficients for the OPC of  $H_2$  by proton exchange at low temperature ( $T < 100$  K). We employ a fully quantum, time-independent approach combined with a high accuracy *ab initio* potential energy surface (PES). New statistical calculations are also performed in order to test the possible statistical behavior of the  $H^+ + H_2$  reaction.

First, accurate three-dimensional quantum dynamics calculations have been performed on a recently published *ab initio* PES [12] that is rigorously symmetric under any permutation of the three identical atoms. It presents a deep well (4.6 eV relative to the  $H^+ + H_2$  asymptote) and no barrier in the entrance channel. All approaches are therefore possible and both abstraction and insertion mechanisms can occur. We use a time-independent quantum mechanical (TIQM) method that employs body-frame democratic hyperspherical coordinates. It was presented in detail in Ref. [13], and thus, a brief summary will suffice here. This method is robust and accurate and has already proved successful in describing atom-diatom insertion reactions [14–16], OH + atom reactions [17], and ultracold collisions [18,19]. At each hyperradius, the scattering wave function is expanded on a set of hyperspherical adiabatic states of a reference Hamiltonian. The adiabatic states are obtained by a variational expansion on a basis of hyperspherical harmonics, and span a large fraction of configuration space and allow for atom exchange. The expansion coefficients are the solution of a set of coupled second-order differential equations which are solved using the Johnson-Manolopoulos log-derivative propagator [20]. The number of coupled equations increases from 100 for  $J = 0$  to 864 for  $J = 21$  (where  $J$  is the total angular momentum) and the asymptotic matching distance is  $35.5 a_0$ . They are the important parameters for convergence and we carefully checked it with respect to these two parameters. The time-independent approaches are suitable to treat dynamics of complex-forming reactions at low temperatures. At low collision energies the time dependent wave packet methods are less accurate because of the inherent problems of the wave packet approach at reaction threshold stemming from the incomplete absorption of the long de Broglie wavelength components in the wave packet. Finally, it should be noted that, though the charge transfer channel leading to  $H_2^+ + H$  is not accessible at the energies involved in the present study (much lower than 1.8 eV where it becomes open), non-adiabatic interaction with the charge transfer channel will modify the energy level spectrum of  $H_3^+$  and it may influence the dynamics.

The  $H_3^+$  system is composed of three identical nuclei that are undistinguishable. It therefore belongs to the  $P_3$  nuclear permutation symmetry group and the nuclear wave function, nuclear spin excluded, belongs to the  $\Gamma = A_2$  or  $E$  irreducible representations. The specific symmetry properties of the nuclear wave function can be incorporated in a simple manner, through an appropriate choice of the

hyperspherical harmonics that are built from products of simple analytical functions [21,22].

When the three-particle system under consideration has  $P_3$  permutation symmetry, the nuclear spin of the identical particles (here, each nucleus is a fermion with  $1/2$  nuclear spin) must be taken into account. The Hamiltonian which was described before does not have spin-dependent terms (all spin-orbit and spin-spin interactions are neglected). The total nuclear wave function can be written as a direct product of the spatial wave function which satisfies the spin-independent Schrödinger equation and a nuclear spin wave function. For bosons, the total nuclear wave function is symmetric, whereas, for fermions, it is antisymmetric with respect to interchange of the identical nuclei. Accordingly, for the  $H^+ + H_2(v = 0, j) \rightarrow H^+ + H_2(v = 0, j')$  transitions, the physically observable integral cross sections (ICSs),  $\sigma_{vj}^{v'j'}$ , which must obey the proper spin statistics, can therefore be derived by weighting the calculated ICSs [23]:

$$\begin{aligned} \sigma_{vj}^{E,v'j'} & \quad j \text{ and } j' \text{ even (para} \rightarrow \text{para)}, \\ \frac{2}{3} \sigma_{vj}^{A_2,v'j'} + \frac{1}{3} \sigma_{vj}^{E,v'j'} & \quad j \text{ and } j' \text{ odd (ortho} \rightarrow \text{ortho)}, \\ \frac{1}{3} \sigma_{vj}^{E,v'j'} & \quad j \text{ odd, } j' \text{ even (ortho} \rightarrow \text{para)}, \\ \sigma_{vj}^{E,v'j'} & \quad j \text{ even, } j' \text{ odd (para} \rightarrow \text{ortho)}. \end{aligned}$$

It is worth mentioning that, if a full quantum method is used to treat the dynamics of three identical nuclei, as in this Letter, the reactive and inelastic scattering processes cannot be distinguished.

The title reaction has been also studied by means of a statistical quantum method (SQM) [24,25] based on the assumption that the process takes place via a complex-forming mechanism. Applications of this model to study different reactions such as atom +  $H_2$  [25,26],  $H + O_2$  [27], or  $O(^1D) + HCl$  [28] have been previously reported. Within the framework of this approach, the state-to-state reaction probability is obtained as the product of the capture probability for the complex to be formed from the initial rovibrational state of the reactants channel and the fraction of complexes which decay via the final state of the products. Those individual capture probabilities are calculated by solving the corresponding coupled equations with a time-independent log-derivative propagation between  $R_c = 3a_0$  (the capture radius which defines the region where the intermediate complex is supposed to exist) and  $R_{\max} = 15a_0$  (which defines the asymptotic region). These values are identical to those employed in previous studies of the  $H^+ + H_2$  reaction performed with the SQM approach [29,30]. The considerations mentioned above for symmetries and nuclear spin also apply to the SQM method.

TIQM ICSs for the  $H^+ + H_2(v = 0, j = 1) \rightarrow H^+ + H_2(v = 0, j')$  reaction are presented in Fig. 1(a). Only the vibrational quantum number  $v = 0$  is considered

in this study and therefore we will not mention it anymore. For the OPC process,  $j = 1 \rightarrow j' = 0$ , the ICS decreases relatively smoothly with the collision energy, as expected for a barrierless entrance channel. In contrast, the ICSs for  $j = 1 \rightarrow j' = 2$  and  $j = 1 \rightarrow j' = 3$  have an energy threshold of 0.029 eV and 0.073 eV, respectively, corresponding to the energy difference between the rotational levels. It is clear that at the lowest collision energies, only the OPC process,  $j = 1 \rightarrow j' = 0$ , is possible. TIQM ICSs show a structure of narrow peaks, indicating a large number of pronounced resonances existing in the reaction probabilities. These resonances are associated with a long-lived intermediate complex formed in the deep  $\text{H}_3^+$  well (4.6 eV) of the PES which supports many quasibound states. It is interesting to note that, in the present case, the resonant structure has survived to the partial wave  $J$  summation. While no resonances are obtained using the SQM method as expected, a fairly good average description is obtained by the SQM results for all processes, with the largest difference found for the transition  $j = 1 \rightarrow j' = 3$ .

TIQM ICSs for the  $\text{H}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}^+ + \text{H}_2(v = 0, j')$  reaction are presented in Fig. 1(b). An energy threshold is found for all processes, because the reaction is endothermic in all cases. Again, a good agreement is observed between the SQM and TIQM results, showing that the  $\text{H}^+ + \text{H}_2$  reaction is statistical at low collision energies. Comparing these two figures, it is clear that, below 0.015 eV, the only possible process is the

OPC process,  $j = 1 \rightarrow j' = 0$ . Above this collision energy, a second process appears, the reverse transition *para-ortho*  $j = 0 \rightarrow j' = 1$ .

The TIQM rate coefficients corresponding to the TIQM ICSs displayed in Fig. 1(a) are shown in Fig. 2(a) for temperatures up to 100 K. The highest rate coefficient is obtained for the OPC process,  $j = 1 \rightarrow j' = 0$ . It slightly depends on temperature and keeps an almost constant value around  $4.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is about 1/6 of the (temperature independent) Langevin rate value ( $2.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Then, we find in order of importance rate coefficients for the  $j = 1 \rightarrow j' = 2$  and  $j = 1 \rightarrow j' = 3$  transitions, which increase steadily with temperature. These rate coefficients differ from the  $j = 1 \rightarrow j' = 0$  rate coefficient by several orders of magnitude for the considered temperature range. For instance, at 20 K the  $j = 1 \rightarrow j' = 2$  rate coefficient is 6 orders of magnitude lower than the  $j = 1 \rightarrow j' = 0$  rate coefficient. The OPC process,  $j = 1 \rightarrow j' = 0$ , appears to be the dominant process at low temperature. The SQM rate coefficients are also plotted in Fig. 2(a). They are in good agreement with the TIQM result. This accord confirms the statistical nature of the reaction. We also plotted the rate coefficients obtained by D. Gerlich using a statistical model (SM) down to 10 K [11]. Although an overall view seems to give a fairly good qualitative agreement, some important differences exist. First, at very low temperature for the  $j = 1 \rightarrow j' = 0$  transition, the SM

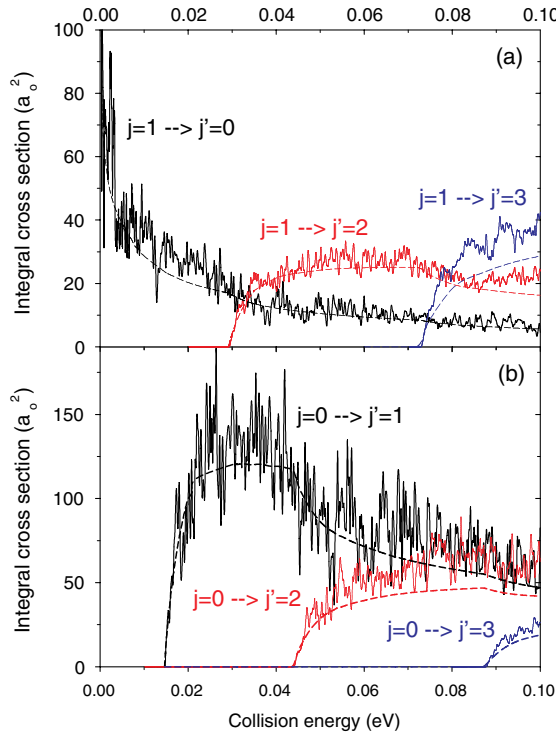


FIG. 1 (color online). TIQM (solid line) and SQM (dashed line) integral cross sections as a function of the collision energy for  $\text{H}^+ + \text{H}_2(v = 0, j = 1) \rightarrow \text{H}^+ + \text{H}_2(v = 0, j')$  (a) and  $\text{H}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}^+ + \text{H}_2(v = 0, j')$  (b).

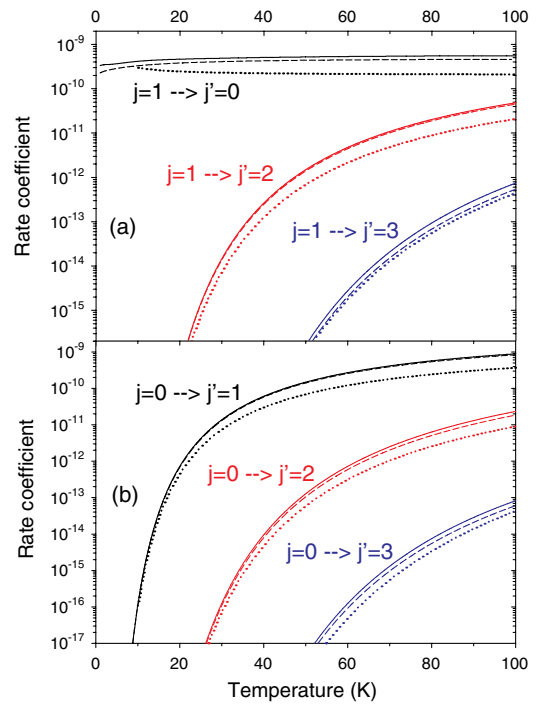


FIG. 2 (color online). TIQM (solid line), SQM (dashed line), and SM (dotted line) rate coefficients (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) as a function of the temperature for  $\text{H}^+ + \text{H}_2(v = 0, j = 1) \rightarrow \text{H}^+ + \text{H}_2(v = 0, j')$  (a) and  $\text{H}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}^+ + \text{H}_2(v = 0, j')$  (b).



rate coefficient increases as the temperature decreases, while it is the reverse for the TIQM or SQM rate coefficient. Moreover, the SM rate coefficients differ quantitatively with the TIQM rate coefficients, and the disagreement increases with temperature. For example, at 10 K, the TIQM rate coefficient is  $4.15 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  while the SM value is  $2.97 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , yielding an increase of 40%. Similarly, at 100 K, we have, respectively,  $5.54 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $2.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The new rate is thus 2.6 times higher at that temperature. These differences may have significant effects in astrophysical models. Therefore, the TIQM rate coefficients presented in this Letter constitute a valid benchmark and they should be used in future models. The TIQM rate coefficients corresponding to the TIQM ICSs displayed in Fig. 1(b) are shown in Fig. 2(b) for temperatures up to 100 K. The comments mentioned above apply here again. The comparison between Figs. 2(a) and 2(b) confirms that the OPC process,  $j = 1 \rightarrow j' = 0$ , is dominant at low temperature, the rate coefficient of the reverse process reaching the same order of magnitude above 70 K only, as expected from the detailed balance principle.

For practical purposes, fits of the TIQM rate coefficients to the analytical Kooij formula,  $k(T) = \alpha(T/300)^\beta \times \exp(-\gamma/T)$ , have been performed. The  $\alpha$ ,  $\beta$ ,  $\gamma$  parameters, for all the transitions involved in the present study, are available upon request to the authors.

This Letter gives the values of rate coefficients as accurately as possible, obtained using an exact quantum method, for the OPC process,  $j = 1 \rightarrow j' = 0$ , which plays a key role in astrophysics. Rate coefficients were also calculated by the same method for all other processes, *ortho-para*, *para-ortho*, *ortho-ortho*, and *para-para*, occurring below 100 K for the  $\text{H}^+ + \text{H}_2(v = 0, j = 0, 1)$  reaction. The rate coefficients obtained with the presently employed SQM constitute a noticeable improvement with respect to those reported by Gerlich [11]. The comparison with the corresponding TIQM results enables us to unambiguously establish the statistical nature of the reaction at low temperature.

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