Low-energy $\text{H}^+ + \text{H}_2$ reactive collisions

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Abstract. An overview of the results of theoretical treatments of the reactive $\text{H}^+ + \text{H}_2$ system in the interval of collision energies $E_c = (1 - 500) \text{ meV}$ is presented. The inelastic and reactive processes occur via scrambling of protons and formation of a long-lived collision complex, allowing for the application of various statistical theories. The first systematic theoretical treatment has been based on the “most dynamically biased” (MDB) statistical theory. Recently, the numerically exact (converged) time-independent quantum mechanical (TIQM) calculations have been compared with the statistical quantum mechanical (SQM) model. Our recent results have demonstrated, within the mean-potential statistical (MPS) model, the importance of a proper incorporation of the permutation symmetry of equivalent protons taking part in the collision. We present detailed comparisons of the calculated cross sections and thermal rate coefficients obtained by using our MPS model with MDB, SQM and TIQM results.

1. Introduction
Hydrogen atoms, molecules and molecular ions represent the most abundant element in our universe and collision processes with their participation occur in variety of physical environments ranging from laboratory plasmas to interstellar media. The simplicity of their structure makes the processes describing their interaction with photons, electrons and heavy particles the benchmark systems for testing various theoretical methods and making comparisons with experiments. In the present report we consider the low-energy, complex-forming, scattering process:

$$\text{H}^+ + \text{H}_2(v, j) \rightarrow (\text{H}_3^+)^* \rightarrow \text{H}^+ + \text{H}_2(v', j'),$$

where $(v, j)$ and $(v', j')$ are the vibrational and rotational quantum numbers of the diatom in the reactant and product arrangements. The ground electronic state potential energy surface (PES) of $\text{H}_3^+$ has a deep (4.6 eV) potential well at small reactant (product) separations and can support a large number of bound states and resonances of the collision complex. As a consequence, the full quantum mechanical treatment of the above reaction involves a very large number of coupled channels and represents a challenging problem. However, if the lifetime of the complex is long enough to allow for randomization of the energy amongst the internal degrees of freedom, than the decay of the complex into the accessible product channels can be expected to proceed according to their statistical weights.

The formulation of the statistical theory of reactive collisions originates from nuclear physics but it’s application to chemical reactions can be traced back to the works of Light [1] and Miller [2]. It turns out that the only required input for the implementation of the statistical theory is a knowledge of the complex formation (or capture) probabilities from reactant and product channels (the decay probabilities being related to the formation probabilities through the
microreversibility principle [1, 2]). Among the simplest is the mean potential statistical (MPS) model, that is the Langevin-type classical model, obtained by assuming an isotropic interaction potential between the fragments which in combination with the centrifugal potential determines, for a given collision energy, the maximum orbital angular momentum (or impact parameter) for which a capture, namely, a complex formation can occur. Mean isotropic potentials can be obtained either by angle-averaging of the anisotropic asymptotic interactions (for low collision energies) or by angle-averaging of (if available) the \textit{ab initio} PES [3]. These models can be improved by taking into account the quantum tunnelling through a potential barrier [4]. The next level of sophistication is obtained by taking into account the anisotropy of the interaction explicitly. For example, the capture probabilities can be determined by solving the single-arrangement close-coupled equations in the limited parts of configuration space but employing the \textit{ab initio} PES (the so called statistical quantum mechanical (SQM) model [5]). Interestingly, the same quality of the results has been obtained by using the capture probabilities obtained by running batches of classical trajectories on the limited part of the PES [6].

The process (1) involves identical nuclei and therefore requires the incorporation into the theory of the quantum mechanical symmetrization postulate [7, 8]. This also means that in a full quantum mechanical treatment the inelastic and reactive processes cannot be distinguished. It is, however, possible to formally treat the protons as distinguishable and define two rearrangement mechanisms:

\begin{align*}
\mathrm{H}^+ + \tilde{\mathrm{H}}_2 &\rightarrow \mathrm{H}^+ + \mathrm{H}_2 \quad \text{identity} \\
&\rightarrow \mathrm{H}^+ + \tilde{\mathrm{H}} \quad \text{exchange}
\end{align*}

and even build up the corresponding statistical models [8]. In addition, by neglecting the hyperfine interaction the conservation of the total nuclear spin should also be taken into account [8]. Some time ago, in his work on \textit{ortho-para} (that is, \(j = \text{odd} \rightarrow j' = \text{even}\) conversion of \(\mathrm{H}_2\) in the process (1), Gerlich [9] used the ”most dynamically biased” (MDB) statistical model which incorporates the indistinguishability of the protons in an approximate way. More recently, the process (1) (actually the \textit{exchange} mechanism from Eq.(2)) has been studied by Gonzalez-Lezana et al [10] in the context of a comparison between the classical trajectory based, statistical (SQM) and the time independent quantum mechanical (TIQM) methods. Very recently, Honvault et al [11, 12] have studied extensively the process (1), comparing the SQM and TIQM methods over a wide range of low energies \(E_c = (10^{-6} - 0.1)\) eV and using the VLABP-PES [13] with correct long-range asymptotic behavior.

Here we report on our recent study [14] of the process (1) by using the MPS model, based on the isotropic mean potential derived from the global VLABP-PES and with full implementation of the permutation symmetry.

2. Theoretical method
The state-to-state integral cross section for the process (1) is given by:

\[
\sigma_{v,j,v',j'}(E) = \frac{\pi \hbar^2}{(2j+1)2\mu E_c} \sum_{J,\Pi} (2J+1)P_{v,j,v',j'}(E, J, \Pi),
\]

where \(J\) is the total motional angular momentum quantum number, \(\Pi = \pm 1\) is the total parity quantum number and \(\mu \simeq 2m_p/3\) is the reduced mass, where \(m_p\) is the proton mass. The total energy is \(E = E_c + E_{v,j} = E'_c + E_{v',j'}\), where \(E_c(E'_c)\) and \(E_{v,j}(E_{v',j'})\) are respectively the collision and rovibrational energies of the reactants(products). The state-to-state partial cumulative reaction probability (CRP), within the microcanonical statistical method of Park and Light [8],
is given by

\[ P_{v_j,v'_j}(E, J, \Pi) = \begin{cases} \frac{2}{3} P^{(1)}_{v_j,v'_j}(E, J, \Pi) + \frac{1}{3} P^{(2)}_{v_j,v'_j}(E, J, \Pi) & \text{for } j \text{- odd and } j' \text{- odd} \\ \frac{1}{3} P^{(2)}_{v_j,v'_j}(E, J, \Pi) & \text{for } j \text{- odd and } j' \text{- even} \\ P^{(2)}_{v_j,v'_j}(E, J, \Pi) & \text{otherwise.} \end{cases} \] (4)

where

\[ P^{(1)}_{v_j,v'_j}(E, J, \Pi) = \frac{p_{v_j}(E, J, \Pi)p_{v'_j}(E, J, \Pi)}{\sum_{v''j''} p_{v''j''}(E, J, \Pi)}, \] (5)

\[ P^{(2)}_{v_j,v'_j}(E, J, \Pi) = \frac{p_{v_j}(E, J, \Pi)p_{v'_j}(E, J, \Pi)}{\sum_{v''j''} p_{v''j''}(E, J, \Pi)}, \] (6)

and the summations in the denominators are restricted to states that are energetically accessible. The cumulative complex formation probabilities (CCFPs) \( p_{v_j}(E, J, \Pi) \), can be calculated in a number of different ways depending on the method used to describe the collision dynamics. The general form of (4)-(6) is, however, independent on that and is the consequence of the indistinguishability of the protons in the quantum mechanical treatment of the reaction (1) and the assumption of the conservation of the total nuclear spin during the collision [8].

In our approach, we calculate the CCFPs \( p_{v_j}(E, J, \Pi) \), by summing over all possible quantum numbers \( l \) of relative orbital angular momenta:

\[ p_{v_j}(E, J, \Pi) = \sum_{l=|J-j|}^{J+j} \left\{ \begin{array}{ll} \delta_{\Pi,(-1)^j} 1 & l \leq l_m(E_c) \\ 0 & l > l_m(E_c) \end{array} \right., \] (7)

where the Kronecker delta stands for the conservation of parity. The above expression corresponds to a simple classical Langevin model which assumes that capture (namely, complex formation) occurs whenever the collision energy is larger than the maximum of an effective isotropic potential. Therefore, the \( l_m(E_c) \) is defined as the maximum integer \( l \) that satisfies:

\[ E_c > \max_R \left\{ \frac{\hbar^2 l(l+1)}{2\mu R^2} + \tilde{V}(R) \right\}. \] (8)

In our calculations we have used as an isotropic interaction potential \( \tilde{V}(R) \), the mean potential obtained from angle averaging [3]:

\[ \tilde{V}(R) = \frac{1}{2} \int_0^\pi V(R, r = r_e, \theta) \sin \theta d\theta \] (9)

where \( V(R, r, \theta) \) is a PES of the \( \text{H}_3^+ \) molecule, \( R \) is the distance between the \( \text{H}^+ \) and the center of mass of \( \text{H}_2 \), \( r \) is the bond distance of \( \text{H}_2 \) (\( r_e = 1.40104 \) a.u. is its equilibrium value) and \( \theta \) is the angle between the vectors \( \vec{R} \) and \( \vec{r} \). The zero of the potential is taken at \( R \to \infty \).

3. Results

3.1. Cross sections

Previously, Gerlich [9] has considered the ortho-para transitions in \( \text{H}_2 \) in the process (1) by using the MDB statistical model and, relying on the results of Quack [7], took (approximately) into account the permutation symmetry of protons and conservation of total nuclear spin. The corresponding state-to-state partial CRP has been taken in the form [9]:

\[ P^{G}_{v_j,v'_j}(E, J, \Pi) = \frac{p_{v_j}(E, J, \Pi)g_{jj'}p_{v'_j}(E, J, \Pi)}{\sum_{v''j''} g_{jj''}p_{v''j''}(E, J, \Pi)}, \] (10)
with

$$g_{jj'} = \begin{cases} 5 & \text{for } j - \text{odd and } j' - \text{odd} \\ 1 & \text{otherwise}. \end{cases} \quad (11)$$

The CCFPs $p_{v_j}(E, J, \Pi)$, have been obtained from empirical analytic formulas established by combining the classical trajectory calculations using the correct long range potential for low-energy collisions and a diatomic-in-molecule PES for higher energies [9].

The dependence on the CCFPs in (4)-(6) and (10)-(11) is different only if an initial $ortho-H_2$ (reactant with odd $j$) is involved, although even in these cases at higher energies (when subsums over even and odd $j''$ become practically the same) the two expressions merge. Actually, it is easy to see that in this limit, CRPs that correspond to $ortho \rightarrow ortho$, $ortho \rightarrow para$, $para \rightarrow ortho$ and $para \rightarrow para$ transitions are all proportional to $P_{v_j'v_j'}^{(2)}(E, J, \Pi)$, Eq.(6), with respective pre-factors: 5/3, 1/3, 1 and 1. The latter are exactly the “average statistical correction factors”, derived by Quack [7]. Specific comparisons between the results of MPS and MDB statistical models, given in Ref. [14], show that they are generally in good agreement.

Recently, Honvault et al [11, 12] studied the process (1) in the wide range of low energies $E_c = (10^{-6} - 0.1)$ eV, by employing the SQM and TIQM methods and the VLBP-PES [13]. While both methods require solutions of coupled-states quantum mechanical equations, the SQM method employs solutions in the limited regions of PES in order to define channel-dependent capture probabilities and applies them in the corresponding statistical model. The TIQM method has been formulated using the hyperspherical coordinates and provides a full quantum mechanical solution. Assuming the convergence requirements are fulfilled, it gives in principle the “exact” results.

The SQM and TIQM state-to-state integral cross sections are compared in Fig.1 with our MPS and Gerlich’s (where available) MDB results. In all cases $H_2$ molecules are initially and finally in ground vibrational states. Fig.1(a) shows rotational transitions from the first excited state $j = 1$ to $j' = 0, 2$ and 3. The MPS and MDB integral cross sections are in reasonable agreement. The TIQM results exhibit a highly oscillatory and irregular structure, located between MPS (and MDB) results which are higher and the SQM results which are lower. The irregular oscillations of the TIQM results are presumably due to the large number of scattering resonances, localized in the complex formation region (that is above the deep potential well) which take part in the reactive scattering process. It is interesting to note that the largest differences between MPS, TIQM and SQM results appear for the only $ortho-ortho$, $j = 1$ to $j' = 3$ transition. Fig.1(b) shows cross sections for transitions starting from the ground state $j = 0$ to $j' = 1, 2$ and 3. One can see that the same ordering in magnitudes of the cross sections obtained by different methods persists in these cases too.

The most striking fact in Fig.1 is that the SQM predictions are considerably lower than those of the MPS and MDB models. Honvault et al [11, 12] do not give explicit SQM expressions for the partial CRPs which correspond to our Eqs. (5) and (6). However, from the text in Honvault et al [12] it seems that these authors have been using instead of our Eq.(6) the expression:

$$\tilde{P}_{v_j,v_j'}^{(2)}(E, J, \Pi) = \frac{p_{v_j}(E, J, \Pi)p_{v_j'}(E, J, \Pi)}{\sum_{v_j} p_{v_j}(E, J, \Pi) + \sum_{v_j'} p_{v_j'}(E, J, \Pi)}.$$

where $j$ and $j'$ are of the same parity. The above expression, however, is related to exchange reactions of the form $A^+ + B_2 \rightarrow B^+ + AB$ and does not fully incorporate the permutation symmetry of all three protons in reaction (1). In order to clarify the relationship between the expressions (6) and (12), it is useful to adopt the high-energy approximation where the sub-sums over even and odd $j''$s in denominators of Eqs.(6) and (12) are assumed to be equal, so that one finds

$$\tilde{P}_{v_j,v_j'}^{(2)}(E, J, \Pi) \approx \frac{2}{3} P_{v_j,v_j'}^{(2)}(E, J, \Pi). \quad (13)$$
Indeed, in many comparisons (especially at higher energies) the SQM results are roughly 2/3 of the MPS results. The additional differences are, of course, due to the fact that CCFPs $p_{vj}(E, J, \Pi)$ are computed by two different methods. The relationship between Eq.(12) and the exchange rearrangement mechanism from Eq.(2) is further discussed in subsection 3.3.
3.2. Thermal rate coefficients

Once the integral cross sections are known the state-to-state thermal rate coefficients can be calculated from:

\[
k_{vj,v'j'}(T) = \left[ \frac{8}{\pi \mu (k_B T)^{3/2}} \right]^{1/2} \int_0^\infty \sigma_{vj,v'j'}(E_c) e^{-E_c/k_B T} E_c dE_c,
\]

where \( T \) is the temperature and \( k_B \) is the Bolzmann constant.

![Figure 2. Calculated thermal rate coefficients for the reaction (1) corresponding to \((v = 0, j = 1) \rightarrow (v' = 0, j' = 0)\) and \((v = 0, j = 0) \rightarrow (v' = 0, j' = 1)\) transitions as functions of the temperature \( T \). The MPS [14] results are represented as thick red lines and the MDB [9] results as dashed lines. The TIQM (thin blue lines) and SQM (dot-dashed lines) results from Honvault et al [11, 12] are corrected by factor of \((0.52918)^2\) due to an error in original data [15].](image)

In Fig.2 we compare our MPS [14] thermal rate coefficients for the two dominant low-temperature transitions \( j = 1 \rightarrow j' = 0 \) and \( j = 0 \rightarrow j' = 1 \) with Gerlich’s MDB [9] and TIQM and SQM results of Honvault et al [11, 12, 15]. As can be seen the MPS rates (just like the cross sections) for \( j = 1 \rightarrow j' = 0 \) and \( j = 0 \rightarrow j' = 1 \) transitions are somewhat lower than those of the MDB model, but higher than TIQM and SQM results. It is also noticeable that in the case of the \( j = 1 \rightarrow j' = 0 \) transitions, MPS and MDB rates slightly decrease while TIQM and SQM rates slightly increase with temperature.

3.3. Rearrangement mechanisms

As already mentioned in the Introduction, one can formally consider the two rearrangement mechanisms related to the process (1): identity and exchange, defined in Eq.(2). In the formulation of our MPS model [14], in Gerlich’s MDB model [9], as well as in the TIQM method used by Honvault et al [11, 12, 15], the total contribution of both mechanisms has been included, as it should be due to the indistinguishability of the protons. On the other hand, as discussed in subsection 3.1, it seems that the SQM method employed in Honvault et al [11, 12] as well as the SQM and TIQM methods in the previous work of Gonzalez-Lezana et al [10] correspond to the description of the exchange mechanism only, but treating it as a reaction of the form \( A^+ + B_2 \rightarrow B^+ + AB \). It is however possible, by using the “spin modification probability” method of Park and Light [8], to derive the precise expressions for the partial CRPs corresponding to each of the rearrangement mechanisms. For the identity mechanism one finds:

\[
P_{vj,v'j'}^{(id)}(E, J, \Pi) = \begin{cases} 
\frac{2}{5} P_{vj,v'j'}^{(1)}(E, J, \Pi) + \frac{2}{5} P_{vj,v'j'}^{(2)}(E, J, \Pi) & \text{for } j - \text{odd and } j' - \text{odd} \\
\frac{2}{5} P_{vj,v'j'}^{(2)}(E, J, \Pi) & \text{for } j - \text{even and } j' - \text{even} \\
0 & \text{otherwise},
\end{cases}
\]
while for the *exchange* mechanism one finds:

$$P_{v_jv'_j}(E, J, \Pi) = \begin{cases} 
\frac{4}{9}P^{(1)}_{v_jv'_j}(E, J, \Pi) + \frac{1}{9}P^{(2)}_{v_jv'_j}(E, J, \Pi) & \text{for } j \text{ - odd and } j' \text{ - odd} \\
\frac{1}{3}P^{(2)}_{v_jv'_j}(E, J, \Pi) & \text{for } j \text{ - even and } j' \text{ - odd} \\
\text{otherwise} & 
\end{cases}$$  \hspace{1cm} (16)

The relations (5) and (6) still hold. Of course, by summing up (15) and (16) we arrive at (4).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Calculated integral cross-section distributions over the final rotational quantum numbers at collision energy $E_c = 0.44$ eV for the *exchange* rearrangement mechanism Eq.(17). Squares - MPS [14] results obtained using Eq.(16), triangles - SQM [10] results, circles - TIQM [10] results.}
\end{figure}

If we use now our MPS model with Eq.(16) instead of Eq.(4), the calculated rotational distribution of the integral cross sections at $E_c = 0.44$ eV, for the *exchange* process

$$\text{H}^+ + \text{H}_2(v=0, j=0) \rightarrow \text{H}^+ + \text{HH}(v'=0, j'),$$  \hspace{1cm} (17)

is represented in Fig.3 by squares. As seen from Fig.3 these results oscillate around the predictions of the SQM and TIQM methods from Ref.[10], where the process (17) has been treated as reaction $A^+ + B_2 \rightarrow B^+ + AB$, that is the SQM results, for example, have been
obtained by identifying $P_{v_j, v'_j}(E, J, \Pi)$ with expression given in Eq.(12). All methods, however, predict similar values of the total (summed over $j'$s) cross sections at $E_c = 0.44$ eV: MPS $\sigma_{00}^{(ex)} = 22.42$ Å²; SQM $\sigma_{00}^{(ex)} = 23.70$ Å² and TIQM $\sigma_{00}^{(ex)} = 23.13$ Å².

4. Conclusions

We have shown that studying the process (1) within the framework of our MPS model [14], fair agreement is obtained with previous MDB statistical calculations of Gerlich [9]. The use of expressions that exactly account for the permutation symmetry as opposed to approximate expressions of Gerlich [9], introduces only small differences at low collision energies for reactions involving initial ortho-H$_2$ molecules.

The comparisons of our MPS calculations with the recent TIQM calculations of Honvault et al [11, 12], which also properly account for the permutation symmetry of the protons, show that in the wide range of collision energies $E_c = (10^{-3} - 0.1)$ eV our results predict somewhat higher cross sections and can be typically considered as an upper limit of the otherwise highly oscillating quantum mechanical results.

On the other hand, the SQM calculations of Honvault et al [11, 12], as well as SQM and TIQM calculations of Gonzalez-Lezana et al [10] do not fully account for the permutation symmetry of the protons and predict lower cross sections which could be related to the exchange rearrangement mechanism in Eq. (2).

The MPS model has also been applied to reaction (1) with the reactant H$_2$ replaced by D$_2$ [16]. The existing theoretical and experimental results for "deuterated" variants of reaction (1), where one or two protons are substituted by deuterons, have been summarized recently by Jambrina et al [17].

We expect that the proposed mean-potential statistical method with proper account of the symmetrization postulate might be useful in more complicated reactions, in particular for those involving polyatomic molecules, providing that they proceed via the complex-forming mechanism.

Acknowledgments

This work has been supported by Ministry of Education and Science of the Republic of Serbia through the project No. 171020.

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