

A Ring Polymer Molecular Dynamics Approach to Study the Transition between Statistical and Direct Mechanisms in the $\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ Reaction

Yury V. Suleimanov,^{†,||} Alfredo Aguado,[‡] Susana Gómez-Carrasco,[¶] and Octavio
Roncero^{*,§}

[†]*Computation-based Science and Technology Research Center, Cyprus Institute, 20 Kavafi
Str., Nicosia 2121, Cyprus*

[‡]*Unidad Asociada UAM-CSIC, Departamento de Química Física Aplicada, Facultad de
Ciencias M-14, Universidad Autónoma de Madrid, 28049, Madrid, Spain*

[¶]*Facultad de Química, Universidad de Salamanca, E-37008 Salamanca, Spain*

[§]*Instituto de Física Fundamental (IFF-CSIC), C.S.I.C., Serrano 123, 28006 Madrid, Spain*

^{||}*Department of Chemical Engineering, Massachusetts Institute of Technology, 77
Massachusetts Ave., Cambridge, Massachusetts 02139, United States*

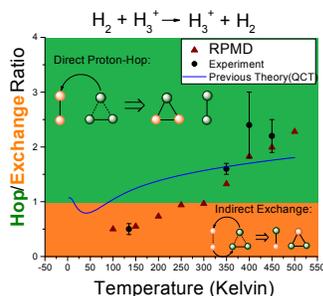
E-mail: octavio.roncero@csic.es

Abstract

Because of fundamental importance in astrochemistry, the $\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ reaction has been studied experimentally in a wide temperature range. Theoretical studies of the title reaction significantly lag primarily due to the challenges associated with the proper treatment of the zero-point energy (ZPE). As a result, all previous theoretical estimates for the ratio between a direct proton-hop and indirect exchange (via the H_5^+ complex) channels deviate from the experiment, in particular, at lower temperatures where the quantum effects dominate. In this work, the Ring Polymer Molecular Dynamics (RPMD) method is applied to study this reaction, providing a very good agreement with the experiment. RPMD is immune to the shortcomings associated to the ZPE leakage and is able to describe the transition from direct to indirect mechanism below the room temperature. We argue that RPMD represents a useful tool for further studies of numerous ZPE-sensitive chemical reactions which are of high interest in astrochemistry.

Graphical TOC Entry

Hop/Exchange Ratio for the Title Reaction Obtained in Experiment and Compared with the Present RPMD results and the Best Previous Calculations.



Keywords

Ring-polymer molecular dynamics, chemical kinetics, astrochemistry, low temperatures, quantum effects

Hydrogen is the most abundant element in the Universe and it is found as ¹ H⁺, H, H₂⁺, H₂, and H₃⁺. The most abundant molecular forms are H₂ and H₃⁺, because H₂⁺ disappears rapidly in the exothermic proton-hop reaction with H₂ to form H₃⁺. H₃⁺ is very reactive and it is considered as the universal protonator of the Universe through the proton-hop reaction ^{1,2}



The HM^+ cations are, in turn, very reactive and trigger many chemical networks giving rise to most of the molecular systems detected in space. ³⁻⁸ In cold environments, M colliders in Eq. (1) deposit on ices and H₃⁺ reacts only with the most abundant molecule, H₂, as



This exchange reaction controls the ortho/para ratio of H₃⁺ and it is constrained by nuclear spin statistics. ⁹⁻¹⁵ In addition, reaction 2 with HD instead of H₂ is responsible for the deuteration of H₃⁺, widely studied experimentally, ^{10,14,16-21} which, in turn, produces the observed high relative abundance of deuterated species, estimated as $\approx 10^4$ times higher than the D/H ratio of the galaxy. ²²⁻²⁵ The efficiency of the deuteration of H₃⁺ is attributed to zero-point energy differences which are important at the low temperatures of the interstellar medium. ^{19,26}

Reaction 2 presents 10 different rearrangements channels, one corresponding to the entrance channel and 9 to the products channels. Three of the products channels are accessible by a direct proton-hop mechanism, in which one of the protons of H₃⁺ “jumps” to the H₂ molecule, forming a new H₃⁺. The other six products channels require a second proton hop back (different from that of the first hop), leading to new H₃⁺ and H₂ products. This last mechanism (exchange mechanism) is indirect and requires the formation of the H₅⁺ complex with a lifetime long enough to enable the second hop. Dealing with fermions, there are nuclear spin symmetry restrictions, different for each of the two mechanisms, hop and exchange.

This allowed the experimental determination of the ratio between the probability of the two mechanisms, $\alpha = P_{\text{hop}}/P_{\text{exc}}$, at different temperatures,^{18,21} where P_{hop} and P_{exc} refer to the hop and exchange reaction probabilities, respectively. A value of $\alpha = 0.5 \pm 0.1$ was found by Crabtree *et al.* at 135 K, while at higher temperatures α increases significantly, being $\alpha = 1.6 \pm 0.1$ at 350 K and 2.4 ± 0.6 at 400K, as reported by Cordonnier *et al.*¹⁸

Statistical approaches^{14,27} including both mechanisms lead to $\alpha = 0.5$, *i.e.* 3/6 corresponding to the number of hop/exchange rearrangement channels. Spin statistic only introduces small deviations from this result. This implies that pure statistical models are not able to reproduce the observed experimental change of the $\alpha = P_{\text{hop}}/P_{\text{exc}}$ ratio with the temperature. The statistical limit is only valid at low temperatures (below ≈ 135 K). To reproduce the $\alpha \approx 2$ values measured at high temperature it is necessary to consider a dominant direct hop mechanism, in which a proton “jumps” from H_3^+ to H_2 as soon as the two reagents collide. This implies that the transient H_5^+ complex is no longer formed, or, if it is formed, it has a much shorter lifetime and lower probability to happen.

A statistical model including a dynamical bias using quasi-classical trajectories (QCT)²⁸ was developed to study the transition between indirect and direct mechanisms. This was done using the scrambling matrix defined in the framework of the statistical model of Park and Light.²⁷ It was found that the α ratio was significantly overestimated within the QCT method used, because of the zero-point energy (ZPE) leakage. In a system with five identical particles, the energy flows among the different modes rather efficiently, leading to products which do not fulfill the zero point energy requirements.

To overcome this problem, a portion of the ZPE was eliminated following a RRKM argument, in order to get a classical density of states approximately equal to the desired quantum one.²⁸ In this way, the artificial flow of energy was avoided, and the α ratio obtained with this ZPE-corrected bias was similar to the experimental one. Nevertheless, this approach is crude and was only intended to show the importance of the ZPE effect. In addition, it is difficult to apply this approach to the deuteration whenever a hydrogen atom is replaced by

a deuterium, since it may introduce artifacts.

In this work, we apply the Ring Polymer Molecular Dynamics (RPMD) method,^{29–34} an *ad hoc* approach to real-time dynamics based on path integrals formalism. Throughout a numerous method assessment using benchmark gas-phase systems, this method has been proven to describe the quantum mechanical effects in chemical dynamics,³³ such as ZPE³⁵ and deep tunneling³⁶ effects, even for very challenging chemical reactions. Partially, the success of the RPMD rate theory can be attributed to its relation to semiclassical instanton theory³⁷ and to a quantum transition-state theory.³⁸ RPMD has also been successful in describing triatomic insertion chemical reactions mediated by long-lived collision complexes.^{33,39–43} In this work, we extend these studies to the title reaction which, as described above, has a complex set of reaction channels and, since all atomic masses are the same, accurate quantum mechanical description of the energy flow between the modes is crucial to avoid the ZPE leakage. Note that RPMD assumes that atoms are distinguishable³⁴ and therefore it does not take into account nuclear spin statistics. Also, RPMD can be used to calculate thermal rate coefficients and, in its original form, it is not able to provide state-to-state quantities.

The full dimensional potential by Aguado *et al*⁴⁴ is used here to study the reaction dynamics. This potential includes analytical derivatives⁴⁵ and it properly describes the permutation symmetry and long range asymptotic behavior. We use the RPMDrate code⁴⁶ developed by one of us (YVS) and modified for direct trajectories approach which consists of two steps, thermalization and real-time dynamics. In the thermalization part, path integral molecular dynamics simulations are performed with a time step of 0.1 fs, using the Andersen thermostat.⁴⁷ The distance between the center-of-mass of the two reagents is kept long, here restricted to be ≈ 45 a.u. The total number of ring polymer beads, n_b , varies inversely with the temperature: it was set to 64 at 400 K and 256 at 100 K. A maximum thermalization time of 2 ps is typically used, for which the average mean energy is approximately constant.

For the real-time part of RPMD simulations, the thermostat is no longer applied. Before starting the dynamics, the coordinates and momenta obtained in the thermalization process

are modified. First, the coordinates of the beads of the two reagents are displaced to locate H_3^+ center of mass at the origin. Second, the velocities of the center of mass of each reagent are rotated to be parallel to the z -axis with opposite sign. A maximum impact parameter, b_{\max} , is set to 20 a.u., selecting b randomly according to a b^2 distribution. $N = 15000$ trajectories are calculated with a maximum propagation time of 20 ns and with a time step of 0.1 fs (for $T < 250$ K these numbers are reduced by reasons which will become clear below). Each trajectory is stopped when the distance between the centroids of any atom pair is longer than 50 a.u. and the rearrangement channel of products is determined from the distances among the centroids. A reaction probability towards a given channel β is determined as $P_\beta(T) = N_\beta/N_{\max}$, where N_β is the number of trajectories leading to arrangement β and N_{\max} are the number of trajectories with impact parameter below b_{\max}^β , where b_{\max}^β is the maximum impact parameter leading to rearrangement β . Finally, the reaction rate coefficient for a particular channel β is determined similar to usual QCT simulations as

$$K_\beta(T) = \sqrt{\frac{8K_B T}{\pi\mu}} \times \pi [b_{\max}^\beta(T)]^2 \times P_\beta(T), \quad (3)$$

with μ being the reduced mass of $\text{H}_2 + \text{H}_3^+$, and K_B is the Boltzmann constant.

For $T > 250$ K, the dynamics of this reaction is essentially direct and all 15000 trajectories finished in less than a few ps. However, at 250 K, the trajectories were extremely long but shorter than 20 ns, and for this reason only 3000 trajectories were propagated in total. On the contrary, at 200 K, 125 trajectories did not finished, exceeding this maximum time of 20 ns, while 109/126 reacted into a hop/exchange channel, of a total of 2000 trajectories. The reason of these long trajectories is the formation of a complex which lives very long time. According to the RRKM theory,⁴⁸⁻⁵¹ the lifetime of these collision complexes is given by the inverse of the unimolecular dissociation rate, *i.e.*,

$$\tau(E) = 2\pi\hbar \frac{\rho(E)}{N_o(E)}, \quad (4)$$

where $\rho(E)$ is the density of states of the complex and $N_o(E)$ is the number of dissociation channels. When the energy decreases, $N_o(E)$ decreases as well, making the complex lifetime longer.

H_2 and H_3^+ have particularly large rotational constants and their first energy levels are listed in Table 1. At 300 K, there are 2 open levels of $\text{H}_2(J = 0 \text{ and } 1)$ and 4 levels of H_3^+ . At 150 K, however, there is only one level for H_2 and three for H_3^+ . This reduction is rather important and produces a rapid increase of the lifetimes of the collision complexes.

Table 1: Lower rotational energies (in Kelvin) of $\text{H}_2(v = 0)$ and $\text{H}_3^+(0, 0^0)$. For H_3^+ the levels marked by an asterisk are non-physical. J is the total rotational angular momentum of each fragments. For H_3^+ , we use the quantum level G and the irreducible representation under permutation described elsewhere.⁵²

H_2		H_3^+		
J	E	J	G Γ	E
0	0	0	0 A'_1	0*
1	174.06	1	0 A'_2	125.13
		1	1 E''	92.27
2	510.59	2	2 E'	243.61
		2	2 E''	341.54

The long lifetimes of the collision complex below 200 K make unaffordable the RPMD simulations of real-time reaction dynamics. However, some simplifications can be done. For long-lived collision complexes, the memory of the initial state is lost and they fragment according to the statistical arguments, *i.e.*, proportionally to the number of rearrangement channels. As an example, the hop and exchange reaction probabilities as a function of time are displayed in Fig. 1. Clearly, for $t > 300$ ps, the hop/exchange probabilities get very close to the 0.3/0.6 statistical limit. This can considerably reduce the computational cost of the RPMD simulations for $T < 200$ K, considering that the hop and exchange probabilities are

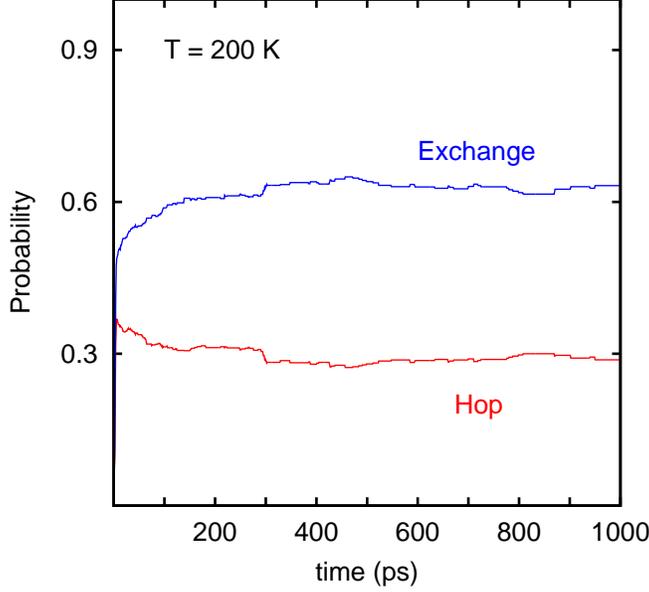


Figure 1: Hop and exchange reaction probabilities obtained for those trajectories finished at a given time for the $\text{H}_2 + \text{H}_3^+$ collision with the RPMD method at 200 K.

obtained as

$$P_{\text{hop}}^* = (N_{\text{hop}} + \frac{3}{10}N_{\text{nf}})/N_{\text{max}}, \quad (5)$$

$$P_{\text{exc}}^* = (N_{\text{exc}} + \frac{6}{10}N_{\text{nf}})/N_{\text{max}},$$

where N_{nf} is the number of non-finished trajectories. Thus, for $T = 100$ and 150 K, we use 2000 trajectories with a maximum time of 600 ps, what is a considerable reduction with respect to the $t_{\text{max}} = 20$ ns used at higher temperatures.

With all these considerations, the $\alpha = \text{hop/exchange}$ ratio was calculated and it is shown in Fig. 2. The RPMD results agree very well with the available experimental data^{18,21} clearly reproducing a switch from the statistical mechanism at low temperatures ($\alpha < 1$) to the direct mechanism at higher temperature ($\alpha > 1$). A pure statistical method leads to a value of $\alpha = 0.5$ clearly not valid in the entire temperature range. The QCT-biased statistical model²⁸ gives too high value of α , because, when the two reagents collide, they

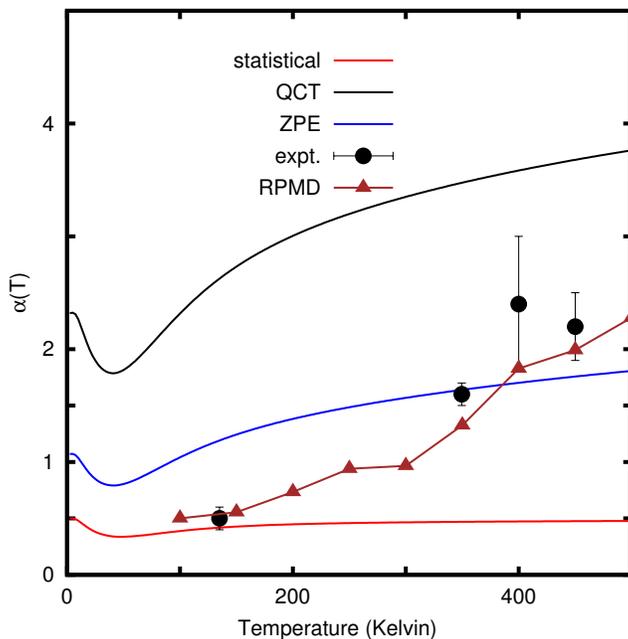


Figure 2: Hop/exchange ratio, α , obtained with different methods. The experimental values are obtained from Refs. ^{18,21} QCT and ZPE refers to results of Ref., ²⁸ as described in the text.

form short-lived complexes artificially favoring the hop mechanism. The high ZPE of the complex flows into translational modes leading to fragments which do not fulfill the ZPE requirements. This artifact was corrected in the ZPE-corrected version of the QCT-biased statistical model²⁸ (called ZPE in Fig. 2) by reducing the ZPE of the reagents in order to get the classical density of states for the complex similar to the quantum one. This crude simple correction leads to results in semiquantitative agreement with the experimental values. The present RPMD results, obtained without any corrections, reproduce much better the experimental evolution of the hop/exchange ratio, showing that this method is able to account for correctly for the quantum effects in the title reaction, especially the ZPE effects. This means that the RPMD method is able to reproduce accurately the density of states and their lifetimes, certainly within a thermally averaged picture given by the method.

The RPMD rate coefficients of the title reaction for the two different rearrangements channels, hop and exchange, are shown in Fig. 3. They are compared with the ZPE re-

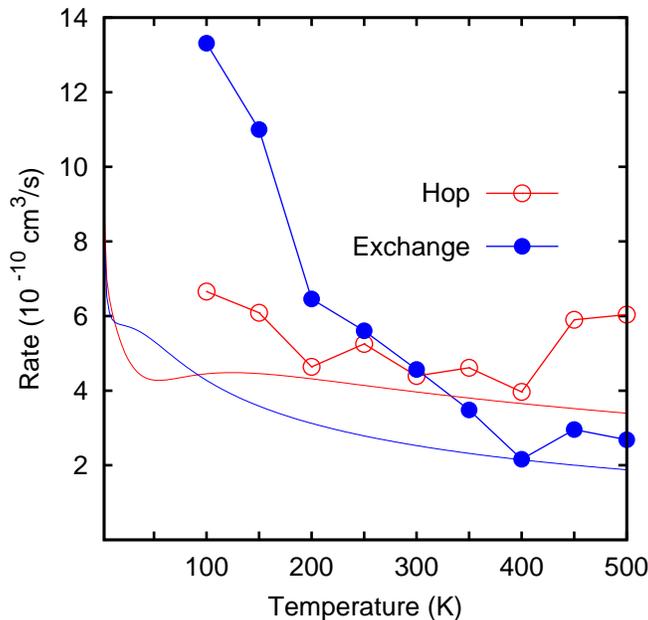


Figure 3: Thermal rate coefficients separated into hop (red) and exchange (blue) rearrangements channels versus the temperature. Line-points correspond to the present RPMD results while lines are the ZPE-corrected results of Ref.²⁸

sults of Ref.²⁸ In the temperature range considered, the hop mechanism presents a nearly constant ring polymer rate coefficient and the corresponding RPMD and ZPE results are pretty similar. However, the exchange ring polymer rate coefficient increases with decreasing the temperature. Exchange involves at least two proton hops and therefore it requires the formation of long-lived complexes. These complexes are formed at all temperatures. However, as temperature decreases the number of open channels dramatically reduces to only a few, and, under these circumstances, the complex lifetimes becomes very large, as supported by the extremely long RPMD trajectories reported here. On the contrary, previous QCT trajectories²⁸ did not yield to such an increase of the complex lifetime simply because the classical phase space is very large, *i.e.*, the classical "number" of open channels is very large, and the products end with any internal energy, without fulfilling ZPE requirements. Thus classical mechanics do not allow the formation of complex that live long enough to produce the exchange mechanism. This problem is partially solved in the ZPE-corrected QCT results of Ref.²⁸ when artificially removing part of the ZPE to reduce the number

of accessible classical states of the products. This allowed to conclude in Ref.²⁸ that one main factor determining the α ratio is the proper account of the ZPE effects. The present RPMD calculations automatically consider quantum effects. Since there is no barrier for the reaction, tunneling can be neglected. Therefore, we may conclude the ZPE is the major quantum effect which is properly accounted for by the RPMD calculations presented in this work. However, note that the statistical error of RPMD rate coefficients obtained from the direct approach is larger as compared to that of the α ratio. This may partially explain the oscillations observed in Fig. 3, where the hop and exchange mechanisms compete.

To summarize, we showed that the RPMD method is able to solve a long-standing problem of theoretical description of statistical complex forming exchange and direct proton hop mechanisms in the $\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ reaction. RPMD correctly describes the transition between these two mechanisms with changing the temperature and provides very good agreement with the available experimental data for the $\alpha = \text{hop/exchange}$ ratio, as compared to the previous theoretical estimates obtained using statistical approaches. The key factor of RPMD success is its ability to correctly treat the ZPE effects in this system which, as described above, are complicated. The RPMD results are obtained directly from the calculations, with no correction parameters like in the ZPE correction of the statistical method. One problem that remains to be solved for this reaction is the nuclear spin statistics. RPMD solves the ZPE leakage problem, leading to a proper description of the α ratio, but treats all atoms as distinguishable. Hence it is not capable to include the ortho/para conversion adequately. One possible way to overcome this difficulty that needs to be analyzed is to use RPMD results to bias statistical approaches accounting for the spin-statistics and therefore calculate state-to-state rate coefficients to include ortho/para conversion of H_2 and H_3^+ .

Generally speaking, the temperature of astrochemical reactions in molecular clouds is very low, from 10 to 100 K. Such processes are strongly affected by quantum mechanical effects and the present work confirms that RPMD is able to include them for complex systems as the title reaction. However, one must note that its application to low-temperature

chemical dynamics is challenging because of complex lifetimes leading to long propagation times. New approaches to address these computational challenges are probably required. We believe that the present results will motivate further RPMD methodology development and studies of reactions of astrochemical importance with complex ZPE structure. In particular, the deuterated variants of the title reaction (such as, $\text{H}_3^+ + \text{HD}$) are of high interest in astrophysics as they can explain the high ratio of deuterated species observed in different astrophysical objects. Until now, only statistical models have been used.^{14,27} This work is currently in progress.

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