THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

Cite This: J. Phys. Chem. Lett. 2018, 9, 2133−2137

pubs.acs.org/JPCL

A Ring Polymer Molecular Dynamics Approach to Study the Transition between Statistical and Direct Mechanisms in the $H_2 + H_3^+ \rightarrow H_3^+ + H_2$ 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

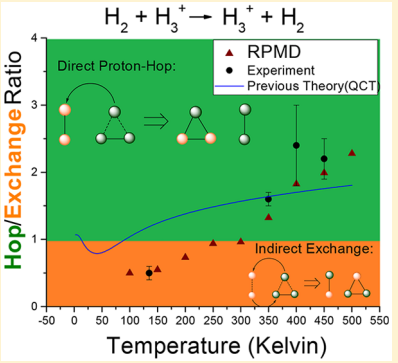
[‡]Unidad Asociada UAM-CSIC, Departamento de Química Física Aplicada, Facultad de Ciencias M-14, Universidad Autónoma de Madrid, 28049 Madrid, Spain

[¶]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 Avenue, Cambridge, Massachusetts 02139, United States

ABSTRACT: Because of its fundamental importance in astrochemistry, the $H_2 + H_3^+ \rightarrow H_3^+ + H_2$ reaction has been studied experimentally in a wide temperature range. Theoretical studies of the title reaction significantly lag primarily because of 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 very good agreement with the experiment. RPMD is immune to the shortcomings associated with the ZPE leakage and is able to describe the transition from direct to indirect mechanisms below room temperature. We argue that RPMD represents a useful tool for further studies of numerous ZPE-sensitive chemical reactions that are of high interest in astrochemistry.



Hydrogen is the most abundant element in the universe, and it is found as[1] H^+, H, H_2^+, H_2, and H_3^+. The most abundant molecular forms are H_2 and H_3^+, because H_2^+ disappears rapidly in the exothermic proton-hop reaction with H_2 to form H_3^+. H_3^+ is very reactive, and it is considered as the universal protonator of the universe through the proton-hop reaction[1,2]

$$H_3^+ + M \rightarrow HM^+ + H_2 \quad (1)$$

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 H_3^+ reacts only with the most abundant molecule, H_2, as

$$H_2 + H_3^+ \rightarrow H_3^+ + H_2 \quad (2)$$

This exchange reaction controls the ortho/para ratio of H_3^+, and it is constrained by nuclear spin statistics.[9−15] In addition, reaction 2 with HD instead of H_2 is responsible for the deuteration of H_3^+, which is widely studied experimentally.[10,14,16−21] This is considered to be responsible for the observed high relative abundance of deuterated species, estimated as $\approx 10^4$ times greater than the D/H ratio of the galaxy.[22−25] The efficiency of the deuteration of H_3^+ 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 rearrangement channels, one corresponding to the entrance channel and nine to the product channels. Three of the product channels are accessible by a direct proton-hop mechanism, in which one of the protons of H_3^+ "jumps" to the H_2 molecule, forming a new H_3^+. The other six product channels require a second proton hop back (different from that of the first hop), leading to new H_3^+ and H_2 products. This last mechanism (exchange mechanism) is indirect and requires the formation of the H_5^+ complex with a lifetime long enough to enable the second hop. Dealing with fermions, there are nuclear spin symmetry restrictions, which are 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, $\alpha = P_{hop}/P_{exc}$, 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 $\alpha =$

Received: March 13, 2018
Accepted: April 10, 2018
Published: April 10, 2018

DOI: 10.1021/acs.jpclett.8b00783
J. Phys. Chem. Lett. 2018, 9, 2133−2137

1.6 ± 0.1 at 350 K and 2.4 ± 0.6 at 400 K, 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 statistics introduces only small deviations from this result. This implies that pure statistical models are not able to reproduce the observed experimental change of the $\alpha = P_{hop}/P_{exc}$ ratio with the temperature. The statistical limit is valid only 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 of occurrence.

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 Rice−Ramsperger−Kassel−Marcus (RRKM) argument 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, because 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 integral formalism. Throughout numerous method assessments using benchmark gas-phase systems, this method has been proven to describe the quantum mechanical effects in chemical dynamics,[33] such as ZPE[35] and deep tunneling[36] effects, even for very challenging chemical reactions. In part, the success of the RPMD rate theory can be attributed to its relation to semiclassical instanton theory[37] 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 because 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 distinguishable;[34] 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 derivatives,[45] and it properly describes the permutation symmetry and long-range asymptotic behavior. We use the RPMDrate code[46] developed by one of us (Y.V.S.) and modified it for the 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 au. 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 the 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 au, selecting b randomly according to a b^2 distribution. N = 15 000 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 for reasons which will become clear below). Each trajectory is stopped when the distance between the centroids of any atom pair is longer than 50 au, and the rearrangement channel of products is determined from the distances among the centroids. A reaction probability toward 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} is 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 in a manner similar to usual QCT simulations as

$$K_\beta(T) = \sqrt{\frac{8K_BT}{\pi\mu}} \cdot \pi[b_{max}^\beta(T)]^2 \cdot P_\beta(T) \tag{3}$$

with μ being the reduced mass of $H_2 + H_3^+$ and K_B is the Boltzmann constant.

For $T > 250$ K, the dynamics of this reaction is essentially direct and all 15 000 trajectories finished in less than a few picoseconds. 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. In contrast, at 200 K, 125 trajectories did not finish, exceeding this maximum time of 20 ns, while 109/126 reacted into a hop/exchange channel, of a total of 2000 trajectories. The reason for these long trajectories is the formation of a complex which lives for a 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, that is

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

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 two open levels of H_2 (J = 0 and 1) and four 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.

DOI: 10.1021/acs.jpclett.8b00783
J. Phys. Chem. Lett. 2018, 9, 2133−2137

Table 1. Lower Rotational Energies (in Kelvin) of $H_2(v = 0)$ and $H_3^+(0, 0°)$[a]

H_2		H_3^+	
J	E	$J\ G\ \Gamma$	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

[a]For H_3^+, the levels marked by an asterisk are non-physical. J is the total rotational angular momentum of each fragment. For H_3^+, we use the quantum level G and the irreducible representation, Γ, under permutation described elsewhere.[52]

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 Figure 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 obtained as

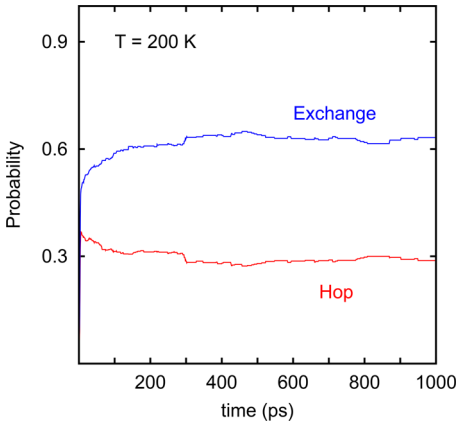


Figure 1. Hop and exchange reaction probabilities obtained for those trajectories finished at a given time for the $H_2 + H_3^+$ collision with the RPMD method at 200 K.

$$P_{hop} = \left(N_{hop} + \frac{3}{10}N_{nf}\right)/N_{max}$$

$$P_{exc} = \left(N_{exc} + \frac{6}{10}N_{nf}\right)/N_{max} \quad (5)$$

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

With all these considerations, the α = hop/exchange ratio was calculated, and it is shown in Figure 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

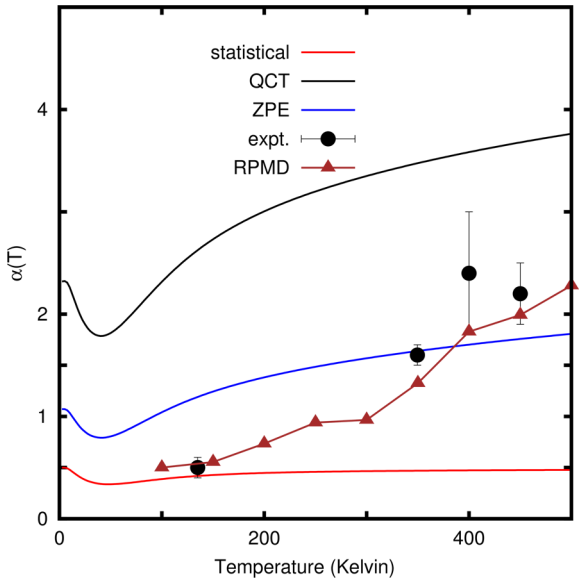


Figure 2. Hop/exchange ratio, α, obtained with different methods. The experimental values are obtained from refs 18 and 21. QCT and ZPE refer to results of ref 28, as described in the text.

of $\alpha = 0.5$, which is clearly not valid in the entire temperature range. The QCT-biased statistical model[28] gives too high a value of α, because, when the two reagents collide, they 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 model[28] (called ZPE in Figure 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 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 Figure 3. They are compared with the ZPE results 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 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 become very large, as supported by the extremely long RPMD trajectories reported here. In contrast, previous QCT trajectories[28] did not yield 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 does not allow the

DOI: 10.1021/acs.jpclett.8b00783
J. Phys. Chem. Lett. 2018, 9, 2133−2137

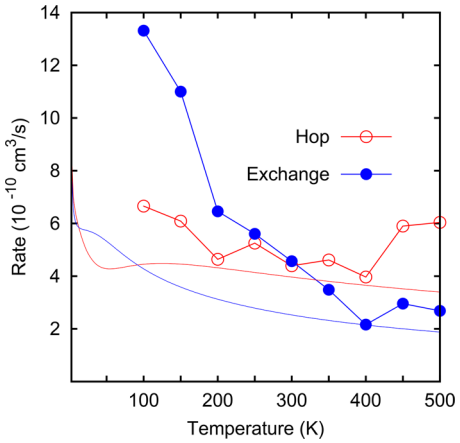


Figure 3. Thermal rate coefficients separated into hop (red) and exchange (blue) rearrangements channels versus the temperature. Line-points correspond to the present RPMD results, while lines are the ZPE-corrected results of ref 28.

formation of complexes that live long enough to produce the exchange mechanism. This problem is partially solved in the ZPE-corrected QCT results of ref 28 when part of the ZPE is artificially removed to reduce the number of accessible classical states of the products. This allowed the conclusion in ref 28 that one main factor determining the α ratio is the proper accounting of the ZPE effects. The present RPMD calculations automatically consider quantum effects. Because 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 greater as compared to that of the α ratio. This may partially explain the oscillations observed in Figure 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 the theoretical description of the statistical complex forming exchange and direct proton hop mechanisms in the $H_2 + H_3^+ \rightarrow H_3^+ + H_2$ reaction. RPMD correctly describes the transition between these two mechanisms with changing temperature and provides very good agreement with the available experimental data for the α = 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 of including 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, such 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, $H_3^+ + HD$) 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: octavio.roncero@csic.es.

ORCID

Yury V. Suleimanov: 0000-0001-9978-2791

Alfredo Aguado: 0000-0002-4270-1046

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Y.V.S. thanks the European Regional Development Fund and the Republic of Cyprus for support through the Research Promotion Foundation (Project Cy-Tera NEA ΥΠΟΔΟΜΗ/ΣΤΡΑΤΗ/0308/31). S.G.-C., A.A., and O.R. acknowledge the support of the Ministerio de Economía y Competitividad (SPAIN) under Grants FIS2014-52172-C2 and FIS2017-83473-C2 and the support from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. 610256 (NANOCOSMOS). We also acknowledge the financial support of the European COST program, CM1401, "Our Astrochemical History". The calculations have been performed at the CyI (Cy-Tera), CESGA (finisterrae2), UAM (CCC), and CSIC (trueno) supercomputer centers.

REFERENCES

(1) Oka, T. Interstellar H_3^+. *Chem. Rev.* **2013**, *113*, 8738−8761.

(2) Oka, T. Chemistry astronomy and physics of H_3^+. *Philos. Trans. R. Soc., A* **2012**, *370*, 4991−5000.

(3) Watson, W. D. The Rate of Formation of Interstellar Molecules by Ion−Molecule Reactions. *Astrophys. J.* **1973**, *183*, L17−L20.

(4) Herbst, E.; Klemperer, W. The Formation and Depletion of Molecules in Dense Interstellar Clouds. *Astrophys. J.* **1973**, *185*, 505−533.

(5) Millar, T. J.; Bennett, A.; Herbst, E. Deuterium fractionation in dense interstellar clouds. *Astrophys. J.* **1989**, *340*, 906−920.

(6) Pagani, L.; Salez, M.; Wannier, P. The chemistry of H_2D^+ in cold clouds. *Astron. Astrophys.* **1992**, *258*, 479−488.

(7) Tennyson, J. Spectroscopy of H_3^+: planets, chaos and the Universe. *Rep. Prog. Phys.* **1995**, *58*, 421−476.

(8) McCall, B. J.; Oka, T. H3+-an Ion with Many Talents. *Science* **2000**, *287*, 1941−1942.

(9) Quack, M. Detailed symmetry selection rules for reactive collisions. *Mol. Phys.* **1977**, *34*, 477−504.

(10) Uy, D.; Cordonnier, M.; Oka, T. Observation of Ortho-Para H_3^+ Selection Rules in Plasma Chemistry. *Phys. Rev. Lett.* **1997**, *78*, 3844−3847.

(11) Oka, T. Nuclear spin selection rules in chemical reactions by angular momentum algebra. *J. Mol. Spectrosc.* **2004**, *228*, 635−639.

DOI: 10.1021/acs.jpclett.8b00783
J. Phys. Chem. Lett. 2018, 9, 2133−2137

(12) Gerlich, D.; Windisch, F.; Hlavenka, P.; Plasil, R.; Glosik, J. Dynamical constrains and nuclear spin caused restrictions in $H_mD_n^+$ collision systems. *Philos. Trans. R. Soc., A* **2006**, *364*, 3007−3034.
(13) Park, K.; Light, J. C. Nuclear spin selection rules for reactive collision systems by the spin-modification probability method. *J. Chem. Phys.* **2007**, *127*, 224101.
(14) Hugo, E.; Asvany, O.; Schlemmer, S. $H_3^+ + H_2$ isotopic system at low temperatures: microcanonical model and experimental study. *J. Chem. Phys.* **2009**, *130*, 164302.
(15) Crabtree, K. N.; Tom, B. A.; McCall, B. J. Nuclear spin dependence of the reaction of H_3^+ with H_2. I. Kinetics and modelling. *J. Chem. Phys.* **2011**, *134*, 194310.
(16) Smith, D.; Adams, N. G.; Alge, E. Some H/D exchange reactions involved in the deuteration of interstellar molecules. *Astrophys. J.* **1982**, *263*, 123−129.
(17) Giles, K.; Adams, N. G.; Smith, D. A study of the reactions of H_3^+, H_2D^+,HD_2^+ and D_3^+ with H_2, HD and D_2 using a variable-temperature selected ion flow tube. *J. Phys. Chem.* **1992**, *96*, 7645−7650.
(18) Cordonnier, M.; Uy, D.; Dickson, R. M.; Kerr, K. E.; Zhang, Y.; Oka, T. Selection rules for nuclear spin modifications in ion-neutral reactions involving H_3^+. *J. Chem. Phys.* **2000**, *113*, 3181−3193.
(19) Gerlich, D.; Schlemmer, S. Deuterium fractionation in gas-phase reactions measured in the laboratory. *Planet. Space Sci.* **2002**, *50*, 1287−1297.
(20) Gerlich, D.; Herbst, E.; Roueff, E. $H_3^+ + HD \rightarrow H_2D^+ + H_2$: low-temperature laboratory measurements and interstellar implications. *Planet. Space Sci.* **2002**, *50*, 1275−1285.
(21) Crabtree, K. N.; Kauffman, C. A.; Tom, B. A.; Becka, E.; McGuire, B. A.; McCall, B. J. Nuclear spin dependence of the reaction of H_3^+ with H_2. II. Experimental measurements. *J. Chem. Phys.* **2011**, *134*, 194311.
(22) Millar, T. J. Modelling Deuterium Fractionation in Interstellar Clouds. *Planet. Space Sci.* **2002**, *50*, 1189−1195.
(23) Pagani, L.; Vastel, C.; Hugo, E.; Kokoouline, V.; Greene, C. H.; Bacmann, A.; Bayet, E.; Ceccarelli, C.; Peng, R.; Schlemmer, S. Chemical modeling of L183 (L134MN): an estimate of the ortho/para H_2 ratio. *Astron. Astrophys.* **2009**, *494*, 623−636.
(24) Bell, T. A.; Willacy, K.; Phillips, T. G.; Allen, M.; Lis, D. The influence of deuteration and turbulent diffusion on the observed D/H ratio. *Astrophys. J.* **2011**, *731*, 48.
(25) Fontani, F.; Palau, A.; Caselli, P.; Sánchez-Monge, A.; Butler, M. J.; Tan, J. C.; Jiménez-Serra, I.; Busquet, G.; Leurini, S.; Audard, M. Deuteration as an evolutionary tracer in massive-star formation. *Astron. Astrophys.* **2011**, *529*, L7.
(26) Gerlich, D. Ortho-para transitions in reactive $H^+ + H_2$ collisions. *J. Chem. Phys.* **1990**, *92*, 2377−2388.
(27) Park, K.; Light, J. C. Microcanonical statistical study of ortho-para conversion in the reaction $H_3^+ + H_2 \rightarrow H_3^+ + H_2$ at very low energies. *J. Chem. Phys.* **2007**, *126*, 044305.
(28) Gómez-Carrasco, S.; González-Sánchez, L.; Aguado, A.; Zanchet, A.; Roncero, O. Dynamically biased statistical model for the ortho/para conversion in the $H_2 + H_3^+ \rightarrow H_3^+ + H_2$ reaction. *J. Chem. Phys.* **2012**, *137*, 094303.
(29) Craig, I. R.; Manolopoulos, D. E. Quantum statistics and classical mechanics: Real time correlation functions from ring polymer molecular dynamics. *J. Chem. Phys.* **2004**, *121*, 3368−3373.
(30) Craig, I. R.; Manolopoulos, D. E. Chemical reaction rates from ring polymer molecular dynamics. *J. Chem. Phys.* **2005**, *122*, 084106.
(31) Craig, I. R.; Manolopoulos, D. E. A refined ring polymer molecular dynamics theory of chemical reaction rates. *J. Chem. Phys.* **2005**, *123*, 034102.
(32) Suleimanov, Y. V.; Collepardo-Guevara, R.; Manolopoulos, D. E. Bimolecular reaction rates from ring polymer molecular dynamics: application to $H + CH_4 \rightarrow H_2 + CH_3$. *J. Chem. Phys.* **2011**, *134*, 044131.
(33) Suleimanov, Y. V.; Aoiz, F. J.; Guo, H. Chemical Reaction Rate Coefficients from Ring Polymer Molecular Dynamics: Theory and Practical Applications. *J. Phys. Chem. A* **2016**, *120*, 8488−8502.
(34) Habershon, S.; Manolopoulos, D. E.; Markland, T. E.; Miller, T. F., III Ring-Polymer Molecular Dynamics: Quantum Effects in Chemical Dynamics from Classical Trajectories in an Extended Phase Space. *Annu. Rev. Phys. Chem.* **2013**, *64*, 387−413.
(35) Pérez de Tudela, R.; Aoiz, F. J.; Suleimanov, Y. V.; Manolopoulos, D. E. Chemical Reaction Rates from Ring Polymer Molecular Dynamics: Zero Point Energy Conservation in $Mu + H_2 \rightarrow MuH + H$. *J. Phys. Chem. Lett.* **2012**, *3*, 493−497.
(36) Pérez de Tudela, R.; Suleimanov, Y. V.; Richardson, J. O.; Sáez Rábanos, V.; Green, W. H.; Aoiz, F. J. Stress Test for Quantum Dynamics Approximations: Deep Tunneling in the Muonium Exchange Reaction $D + HMu \rightarrow DMu + H$. *J. Phys. Chem. Lett.* **2014**, *5*, 4219−4224.
(37) Richardson, J. O.; Althorpe, S. C. Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory. *J. Chem. Phys.* **2009**, *131*, 214106.
(38) Althorpe, S. C.; Hele, T. J. H. Derivation of a true $(t \rightarrow 0_+)$ quantum transition-state theory. II. Recovery of the exact quantum rate in the absence of recrossing. *J. Chem. Phys.* **2013**, *139*, 084115.
(39) Hickson, K. M.; Loison, J.-C.; Guo, H.; Suleimanov, Y. V. Ring-Polymer Molecular Dynamics for the Prediction of Low-Temperature Rates: An Investigation of the $C(^1D) + H_2$ Reaction. *J. Phys. Chem. Lett.* **2015**, *6*, 4194−4199.
(40) Rampino, S.; Suleimanov, Y. V. Thermal Rate Coefficients for the Astrochemical Process $C + CH^+ \rightarrow C_2^+ + H$ by Ring Polymer Molecular Dynamics. *J. Phys. Chem. A* **2016**, *120*, 9887−9893.
(41) Hickson, K. M.; Suleimanov, Y. V. An experimental and theoretical investigation of the $C(^1D) + D_2$ reaction. *Phys. Chem. Chem. Phys.* **2017**, *19*, 480−486.
(42) Hickson, K. M.; Suleimanov, Y. V. Low-Temperature Experimental and Theoretical Rate Constants for the $O(^1D) + H_2$ Reaction. *J. Phys. Chem. A* **2017**, *121*, 1916−1923.
(43) Nunez-Reyes, D.; Hickson, K. M.; Larregaray, P.; Bonnet, L.; Gonzalez-Lezana, T.; Suleimanov, Y. V. A combined theoretical and experimental investigation of the kinetics and dynamics of the $O(^1D) + D_2$ reaction at low temperature. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4404−4414.
(44) Aguado, A.; Barragan, P.; Prosmiti, R.; Delgado-Barrio, G.; Villarreal, P.; Roncero, O. A new accurate full dimensional potential energy surface of H_5^+ based on triatomics-in-molecule analytical functional form. *J. Chem. Phys.* **2010**, *133*, 024306.
(45) Sanz-Sanz, C.; Aguado, A.; Roncero, O.; Naumkin, F. Non-adiabatic couplings and dynamics in proton transfer reactions of H_n^+ systems: Application to $H_2+H_2^+ \rightarrow H + H_3^+$ collision. *J. Chem. Phys.* **2015**, *143*, 234303.
(46) Suleimanov, Y.; Allen, J.; Green, W. RPMDrate: Bimolecular chemical reaction rates from ring polymer molecular dynamics. *Comput. Phys. Commun.* **2013**, *184*, 833−840.
(47) Andersen, H. C. Molecular dynamics simulations at constant pressure and/or temperature. *J. Chem. Phys.* **1980**, *72*, 2384−2393.
(48) Marcus, R. A. Lifetimes of Active Molecules. I. *J. Chem. Phys.* **1952**, *20*, 352−354.
(49) Marcus, R. A. Lifetimes of Active Molecules. II. *J. Chem. Phys.* **1952**, *20*, 355−359.
(50) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, U.K., 2005.
(51) Croft, J. F. E.; Bohn, J. L. Long-lived complexes and chaos in ultracold molecular collisions. *Phys. Rev. A: At., Mol., Opt. Phys.* **2014**, *89*, 012714.
(52) Aguado, A.; Roncero, O.; Tablero, C.; Sanz, C.; Paniagua, M. Global potential energy surface for the H_3^+ system: Analytical representation of the adiabatic ground state $1^1A'$ potential. *J. Chem. Phys.* **2000**, *112*, 1240−1254.

DOI: 10.1021/acs.jpclett.8b00783
J. Phys. Chem. Lett. 2018, 9, 2133−2137