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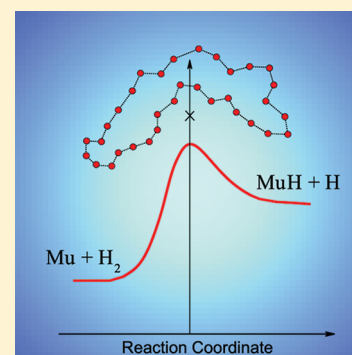
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Chemical Reaction Rates from Ring Polymer Molecular Dynamics:
Zero Point Energy Conservation in $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$ Ricardo Pérez de Tudela,^{†,§} F. J. Aoiz,^{*,†} Yury V. Suleimanov,^{‡,§} and David E. Manolopoulos[‡][†]Departamento de Química Física I, Facultad de CC. Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain[‡]Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

ABSTRACT: A fundamental issue in the field of reaction dynamics is the inclusion of the quantum mechanical (QM) effects such as zero point energy (ZPE) and tunneling in molecular dynamics simulations, and in particular in the calculation of chemical reaction rates. In this work we study the chemical reaction between a muonium atom and a hydrogen molecule. The recently developed ring polymer molecular dynamics (RPMD) technique is used, and the results are compared with those of other methods. For this reaction, the thermal rate coefficients calculated with RPMD are found to be in excellent agreement with the results of an accurate QM calculation. The very minor discrepancies are within the convergence error even at very low temperatures. This exceptionally good agreement can be attributed to the dominant role of ZPE in the reaction, which is accounted for extremely well by RPMD. Tunneling only plays a minor role in the reaction.



SECTION: Dynamics, Clusters, Excited States

The inclusion of quantum effects such as zero point energy (ZPE) and tunneling in simulations of chemical reactions is an important problem in computational chemistry, especially for reactions involving light atoms. In this respect, the hydrogen exchange reaction and its isotopic variants constitute an excellent benchmark for the assessment of approximate quantum and classical methods.¹ The first rigorous full-dimensional quantum mechanical (QM) calculation of the $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction was carried out by Schatz and Kuppermann in 1976,² and since then this reaction and its isotopic variants have been used to test the accuracy of a panoply of theoretical methods that have been developed for the study of reaction dynamics.^{3–8}

Reactions involving a muonium atom (Mu) have attracted special attention, as its light mass of 0.114 u makes it the most quantum atom one can find. In particular, the $\text{Mu} + \text{H}_2$ reaction has recently been highlighted as providing an extreme contrast to the reaction between muonic helium ($\text{He}\mu$) and H_2 . The isotopic mass ratio of 36 between Mu and $\text{He}\mu$ leads to an enormous inverse kinetic isotope effect that has been measured experimentally and reproduced in accurate QM calculations.^{9,10} The origin of this isotope effect is the considerably larger ZPE in the MuH product of $\text{Mu} + \text{H}_2$ than in the $\text{He}\mu\text{H}$ product of $\text{He}\mu + \text{H}_2$, and indeed than in the H_2 reactant of either reaction. It follows from this that the $\text{Mu} + \text{H}_2$ reaction is expected to provide a particularly severe test of how well many approximate reaction dynamics methods—including all those that involve the evolution of classical, quasi-classical, or semiclassical trajectories—account for the conservation of ZPE during the course of a chemical reaction.

In the present Letter, we report a study this reaction using the recently developed ring polymer molecular dynamics

(RPMD) method.^{11–17} This method exploits the isomorphism between the statistical properties of the quantum system and those of a classical ring polymer,¹⁸ using the classical molecular dynamics of the ring polymer to approximate real-time quantum evolution. The application of RPMD to the study of gas-phase bimolecular reactions is a relatively recent development.^{19,20} The gas-phase results that have been obtained so far with the method have been found to be reliable (predictive) at high temperatures, and to be within a factor of 2–3 of accurate QM results even at very low temperatures in the deep quantum tunneling regime.^{19,20} Richardson and Althorpe have explained why the method works so well in deep tunneling by establishing an illuminating connection between RPMD and semiclassical instanton theory.²¹

The present RPMD calculations on the $\text{Mu} + \text{H}_2$ reaction were performed using the methodology developed in refs 19 and 20, which can be summarized very briefly as follows. The method begins by introducing two dividing surfaces: one located in the asymptotic reactant valley ($s_0 = 0$) and the other located in the transition state region ($s_1 = 0$). The reaction coordinate ξ is taken to be an interpolating function that connects these dividing surfaces,⁷

$$\xi(\bar{\mathbf{r}}) = \frac{s_0(\bar{\mathbf{r}})}{s_0(\bar{\mathbf{r}}) - s_1(\bar{\mathbf{r}})} \quad (1)$$

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Table 1. Summary of Classical and RPMD Results for the Mu+H₂ Reaction^a

T/K	classical				RPMD					QM	
	$\xi_{\text{cl}}^{\ddagger}$	κ_{cl}	k_{TST}	k_{cl}	$\xi_{\text{RPMD}}^{\ddagger}$	κ_{RPMD}	k_{QTST}	k_{RPMD}	% dev	k_{QM}	
200	1.000	0.753	3.80(−22)	2.86(−22)	1.044	0.328	2.70(−23)	8.87(−24)	15	7.71(−24)	
300	1.000	0.743	2.44(−18)	1.82(−18)	1.031	0.489	1.79(−19)	8.75(−20)	6	8.24(−20)	
400	1.000	0.733	1.95(−16)	1.43(−16)	1.026	0.513	3.02(−17)	1.55(−17)	1	1.53(−17)	
500	1.000	0.725	3.20(−15)	2.32(−15)	1.023	0.519	7.85(−16)	4.07(−16)	−2	4.17(−16)	
600	1.000	0.717	1.98(−14)	1.42(−14)	1.021	0.530	7.29(−15)	3.86(−15)	−4	4.02(−15)	
700	1.000	0.712	7.77(−14)	5.53(−14)	1.019	0.529	3.76(−14)	1.99(−14)	−5	2.09(−14)	
800	1.000	0.705	2.23(−13)	1.57(−13)	1.018	0.528	1.30(−13)	6.86(−14)	−6	7.34(−14)	
900	1.000	0.699	5.14(−13)	3.59(−13)	1.016	0.534	3.49(−13)	1.86(−13)	−6	1.98(−13)	
1000	1.000	0.698	1.08(−12)	7.50(−13)	1.015	0.537	8.07(−13)	4.34(−13)	−2	4.41(−13)	

^a ξ^{\ddagger} is the position of the maximum of the PMF along the reaction coordinate ξ . κ is the transmission coefficient, and the k 's are various rate coefficients in cm³/s. Exact QM rates (from ref 8) on the BKMP2 PES and the percentage deviations of the RPMD rates from these exact rates are shown in the last two columns.

such that $\xi \rightarrow 0$ as $s_0 \rightarrow 0$ and $\xi \rightarrow 1$ as $s_1 \rightarrow 0$. Here the notation $\bar{\mathbf{r}}$ indicates that we have taken the dividing surfaces $s_0(\bar{\mathbf{r}}) = 0$ and $s_1(\bar{\mathbf{r}}) = 0$ (and hence the reaction coordinate $\xi(\bar{\mathbf{r}})$) to be functions of the centroid coordinate

$$\bar{\mathbf{r}} = \frac{1}{n} \sum_{j=1}^n \mathbf{r}^{(j)} \quad (2)$$

of a ring polymer composed of n beads (i.e., of n classical copies of the system with the corresponding atoms in neighboring copies connected by harmonic springs¹⁸). The analytical formulas for the dividing surfaces are given by^{7,19}

$$s_0(\mathbf{r}) = R_{\infty} - R \quad (3)$$

$$s_1(\mathbf{r}) = \max[s_B(\mathbf{r}), s_C(\mathbf{r})] \quad (4)$$

$$s_B(\mathbf{r}) = (r_{BC} - r_{BC}^{\ddagger}) - (r_{AB} - r_{AB}^{\ddagger}) \quad (5)$$

$$s_C(\mathbf{r}) = (r_{BC} - r_{BC}^{\ddagger}) - (r_{AC} - r_{AC}^{\ddagger}) \quad (6)$$

where R is the distance between the center of mass of H₂ and the Mu atom, and r_{AB} , r_{BC} , and r_{AC} are the interatomic distances.

The rate coefficient is then written in the Bennet–Chandler form^{22,23}

$$k_{\text{RPMD}}(T) = k_{\text{QTST}}(T, \xi^{\ddagger}) \kappa(t \rightarrow \infty, \xi^{\ddagger}) \quad (7)$$

Here the first factor, $k_{\text{QTST}}(T, \xi^{\ddagger})$, is the centroid-density quantum transition state theory (QTST) rate coefficient^{4,5,24} evaluated at the transition state ξ^{\ddagger} along the reaction coordinate $\xi(\bar{\mathbf{r}})$. This can be calculated from the potential of mean force (PMF) (or free energy) along the reaction coordinate, $W(\xi)$, using standard thermodynamic integration techniques.^{19,20} The second factor in eq 7, $\kappa(t \rightarrow \infty, \xi^{\ddagger})$, is the long-time limit of a time-dependent ring polymer transmission coefficient. This is a dynamical correction to centroid density QTST that accounts for recrossing of the dividing surface at $\xi(\bar{\mathbf{r}}) = \xi^{\ddagger}$ and ensures that the resulting RPMD rate coefficient $k_{\text{RPMD}}(T)$ will be independent of this choice of the dividing surface.¹³

All of the present calculations were performed using Cartesian atomic coordinates, thus imposing no restrictions on the rotational and translational motions of the Mu + H₂ system. The potential energy surface (PES) that we employed was BKMP2,²⁵ which has proven to be one of the most accurate adiabatic potentials for the H₃ system.²⁶ In contrast to

the most recent PES,²⁷ the diagonal Born–Oppenheimer correction^{28,29} is not included in the BKMP2 potential, and will not be considered in this work; its effect is relatively minor and including it would not change any of the conclusions we shall reach concerning the conservation of ZPE in RPMD rate theory.

A total of $n = 512$ ring polymer beads were used so as to ensure convergence at all temperatures studied. The remaining parameters used in the RPMD calculations were taken from our previous study of the H + H₂ reaction.¹⁹ We used umbrella integration^{30,31} to calculate the QTST rate. The transmission coefficient was obtained by running recrossing trajectories starting with the centroid pinned to the transition state at time $t = 0$. The RPMD rate coefficients were calculated using eq 7 at nine temperatures ranging from 200 to 1000 K in steps of 100 K. Purely classical rates were also calculated for comparison by setting the number of beads to one.

The resulting classical and RPMD rate coefficients for the Mu + H₂ reaction are summarized in Table 1, along with the accurate QM results from ref 8 computed using the ABC code.³² In order to facilitate the discussion of these results, the two key ingredients in the RPMD calculation—the PMF along the reaction coordinate $W(\xi)$ and the time-dependent transmission coefficient $\kappa(t, \xi^{\ddagger})$ —are shown at two representative temperatures in Figures 1 and 2, together with their counterparts from the classical calculation.

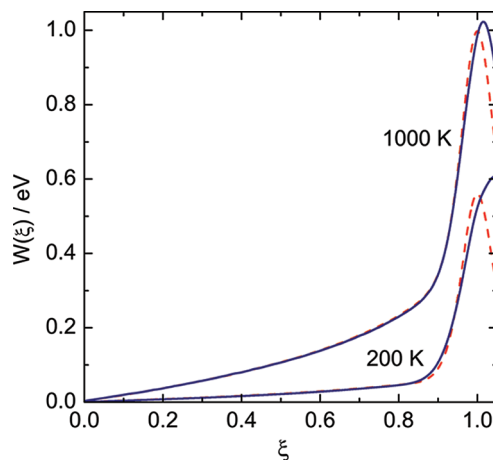


Figure 1. Classical (dashed red line) and RPMD (solid blue line) PMFs for the Mu + H₂ reaction at 1000 and 200 K.

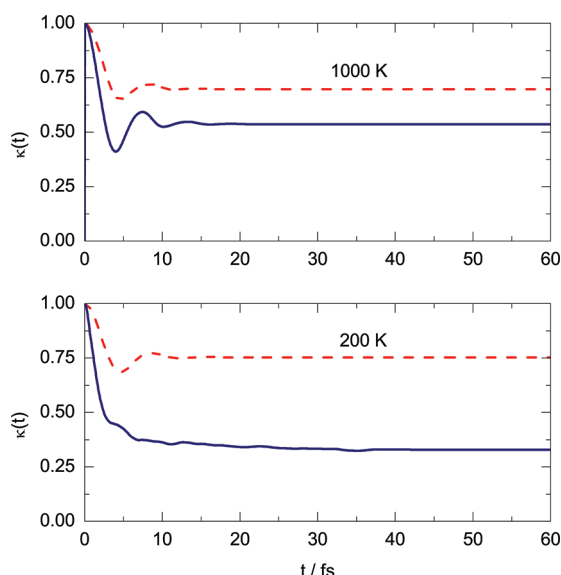


Figure 2. Classical (dashed red line) and RPMD (solid blue line) transmission coefficients for the $\text{Mu} + \text{H}_2$ reaction at 1000 and 200 K.

Consider first the free energy profiles $W(\xi)$ in Figure 1. These profiles exhibit barriers that are related to the barrier in the PES and also include a temperature-dependent entropic contribution, which increases their height with increasing temperature. In all of the other reactions that have been studied using RPMD, the QM free energy barrier has been found to be significantly lower than the classical free energy barrier, and increasingly so at lower temperatures.^{19,20} As a result, the QTST rate has been found to be significantly larger than the classical TST rate, owing primarily to the contribution from QM tunneling. For example, the QTST rate for the $\text{H} + \text{H}_2$ reaction is more than 3 orders of magnitude larger than the classical TST rate at 200 K.¹⁹

From the results in Table 1 and Figure 1, one sees that quite the opposite is found for $\text{Mu} + \text{H}_2$. For this reaction, the QM free energy barrier is actually *higher* than the classical free energy barrier at 1000 K, and even more so at 200 K, and as a result the QTST rate is over an order of magnitude *smaller* than the classical TST rate at 200 K. This clearly shows that the $\text{Mu} + \text{H}_2$ reaction is qualitatively different from the reactions that have been studied previously using RPMD ($\text{H} + \text{H}_2$,¹⁹ $\text{F} + \text{H}_2$,¹⁹ $\text{Cl} + \text{HCl}$,¹⁹ and $\text{H} + \text{CH}_4$ ²⁰), and it provides a strong indication that tunneling in this reaction does not play any major role. The dominant QM effect in $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$ is simply the dramatic increase in ZPE between the H_2 reactant and the MuH product, which we have already mentioned above and shall return to discuss further below.

Figure 2 shows the classical and RPMD time-dependent transmission coefficients at 200 K and 1000 K. Trajectories do recross the dividing surface, especially in the RPMD case, before the transmission coefficient reaches its asymptotic value after around 50 fs. There are also short-time oscillations in the transmission coefficients, except in the case of the RPMD calculation at 200 K. These oscillations have been seen before for asymmetric reactions like $\text{F} + \text{H}_2$, where they were attributed to the stretching of H_2 at the transition state.¹⁹ The asymptotic values of the transmission coefficients are significantly less than 1 (0.7 in the classical case and 0.5 in the RPMD case), even at high temperatures. This indicates that the choice we have made for the dividing surface is not optimal

and explains why classical TST (QTST) overestimates the full classical (RPMD) rate even at 1000 K (see Table 1).

The classical transmission coefficients in Table 1 increase slightly with decreasing temperature, as expected (less recrossing at lower temperatures). However, the RPMD transmission coefficients exhibit the opposite tendency below around 500 K. This has also been seen in previous studies.^{19,20} It is associated with the use of a reaction coordinate based on the ring polymer centroid. Richardson and Althorpe have shown that the internal modes of the ring polymer begin to contribute to the optimum reaction coordinate for an asymmetric reaction as soon as the temperature passes below $T_c = \hbar\nu_b/k_B$, where $i\nu_b$ is the imaginary frequency at the barrier maximum.²¹ For the $\text{Mu} + \text{H}_2$ reaction on the BKMP2 PES, we have $i\tilde{\nu}_b = 1784 \text{ cm}^{-1}$, giving $T_c = 409 \text{ K}$. For comparison, $T_c = 345 \text{ K}$ for the $\text{H} + \text{H}_2$ reaction on the same PES ($i\tilde{\nu}_b = 1506 \text{ cm}^{-1}$), which is not so different from the value for $\text{Mu} + \text{H}_2$. Below this crossover temperature, the centroid-based transition state dividing surface becomes poorer, the centroid-density QTST rate increases in an unphysical fashion, and the RPMD transmission coefficient decreases to compensate for this (in such a way as to give exactly the same rate as one would have obtained using any other dividing surface, including the optimum one¹³).

Figure 3 compares our final classical and RPMD rate coefficients for $\text{Mu} + \text{H}_2$ with the accurate QM results and with

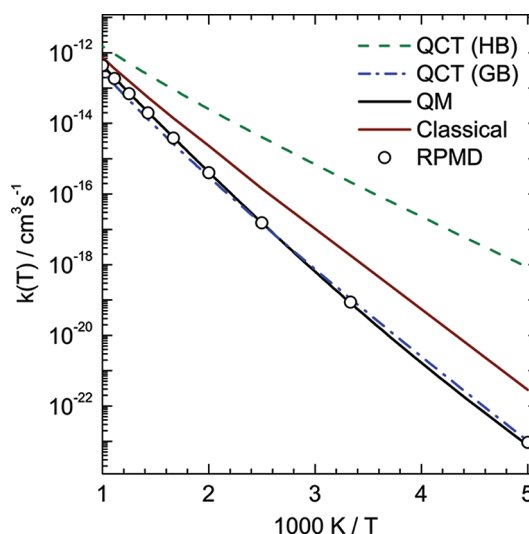


Figure 3. Arrhenius plot of QM, RPMD, classical, and QCT rate coefficients for the $\text{Mu} + \text{H}_2$ reaction between 200 and 1000 K. QM and QCT results are taken from ref 8.

two different implementations of the quasi-classical trajectory (QCT) method.⁸ One sees that the purely classical rates are systematically higher than the exact QM rates, a fact that is clearly consistent with the strong inverse kinetic isotope effect between $\text{Mu} + \text{H}_2$ and $\text{He}\mu + \text{H}_2$ that we mentioned above. QCT calculations with histogram binning (QCT-HB), which are entirely classical except for including the ZPE of the reactants, overestimate even further the exact QM results. The reason for this is that most of the reactive trajectories lead to classical vibrational energies below the ZPE of the MuH product. Gaussian binning (QCT-GB) fares much better because it weighs product trajectories with MuH vibrational actions close to the correctly quantized values much more

heavily than the rest. Nevertheless, differences of up to 35% are found between the QCT-GB and QM results and, in addition, this difference is rather sensitive to the choice of the Gaussian width (see ref 8 for details). Since in QCT-GB only initial and final (reactant and product) quantization effects are included in the description of the reaction, the good agreement between the QCT-GB results and the exact QM results provides another indication that tunneling is not crucial in this reaction.

The agreement between the RPMD rate coefficients and the accurate QM rate coefficients in Figure 3 is truly excellent. The errors are around 5% (which is the order of the statistical error in the umbrella integration method) at all temperatures except for 200 K, where RPMD overestimates the rate by 15% (see Table 1). Interestingly, this is the first time that RPMD has been found to give such accurate results at temperatures below the crossover temperature ($T_c = 409$ K for $\text{Mu} + \text{H}_2$). This is somewhat surprising because in earlier studies^{19,20} it has been found that RPMD overestimates the QM rate coefficients of other asymmetric reactions by a factor of 2–3 in the deep-tunneling regime ($T < T_c$), and Richardson and Althorpe's analysis of the connection between RPMD rate theory and semiclassical instanton theory suggests that this sort of overestimation should be fairly general.²¹ Perhaps the explanation is that this analysis was based on harmonic fluctuations around the instanton, and there are significant anharmonicities in the case of $\text{Mu} + \text{H}_2$.

All of the evidence presented above suggests that there is not any significant tunneling in this reaction at temperatures as low as $T_c/2$ (~ 200 K) or that, at least, its effect is overcompensated by the ZPE of the products. Additionally, above this temperature, the RPMD approximation is seen to provide the same level of accuracy for $\text{Mu} + \text{H}_2$ as that obtained for other reactions^{19,20} at much higher temperatures (≥ 400 K), where tunneling and ZPE effects contribute less to the reaction rate. It is illustrative to perform the simplest canonical TST calculations for comparison. At the highest temperatures, canonical TST overestimates the reactivity due to the lack of recrossing, but at intermediate energies (270–400 K) the agreement is fairly good, certainly better than that obtained in the $\text{H} + \text{H}_2$ reaction. Only at 200 K is the TST rate lower than the QM rate by a factor of ~ 6 , indicating some tunneling. By contrast, the RPMD calculations account for the exact rates very well in the whole range of temperatures.

To shed more light on why tunneling does not seem to contribute very much to the reaction, Figure 4 shows the classical and ground-state vibrationally adiabatic potential energy profiles along the minimum energy path for $\text{Mu} + \text{H}_2$. The inclusion of the (mass-dependent) diagonal Born–Oppenheimer correction¹⁰ would change the profile almost imperceptibly. From this figure, one can see that the inclusion of ZPE leads to a shifting and broadening of the barrier along the reaction coordinate. The shifting implies that ZPE affects the position of the optimal dividing surface, whereas the broadening of the barrier is the reason for the ineffectiveness of tunneling. Note also that the ZPE of the products ($\text{MuH} + \text{H}$) lies well above the classical barrier. This ZPE is what is responsible for the strong inverse kinetic isotope effect of the $\text{Mu} + \text{H}_2$ reaction when compared to the reactions with other isotopologues.^{8–10} It is also the reason why the RPMD approach, which correctly captures the change in ZPE, gives results that are in an unprecedentedly good agreement with accurate QM rate coefficients, even at temperatures below T_c .

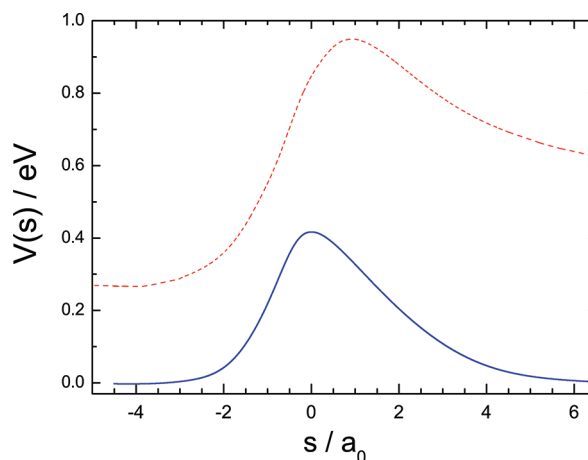


Figure 4. Classical minimum energy path (blue solid line) and vibrationally adiabatic curve for the (00^0) state (red dashed line) for the $\text{Mu} + \text{H}_2$ reaction vs the natural reaction coordinate.

At first glance the small relevance of tunneling in the $\text{Mu} + \text{H}_2$ reaction may seem paradoxical considering the light mass of Mu compared with other isotopologues of hydrogen. However, as shown above, the ZPE effect is the dominant factor and seems to overcome the effect of tunneling to a large extent. It should be noted that the $\text{Mu} + \text{H}_2$ reaction involves the transfer of a H atom; if instead a Mu atom were transferred, as in $\text{H} + \text{MuD} \rightarrow \text{HMu} + \text{D}$, the contribution of tunneling would be decisive.

The correct description of ZPE effects is crucial not only in gas-phase calculations, but also in condensed-phase simulations. In a recent study of liquid water,³³ it was shown that RPMD is immune to the unphysical flow of initially quantized ZPE from the intramolecular to the intermolecular modes of the liquid as the simulation progresses. This unphysical ZPE leakage is a serious concern for most other trajectory-based methods that begin with quantized initial conditions, as illustrated in the present context by the very poor QCT-HB results in Figure 3.

To summarize, we have performed theoretical calculations of the rate coefficient for the $\text{Mu} + \text{H}_2$ reaction over a wide range of temperatures, using the recently developed RPMD methodology. We have found that the RPMD approximation gives highly accurate results for the thermal rate coefficient of the reaction, in excellent agreement with exact QM calculations. This is the first reaction for which such accurate RPMD results have been obtained. We have argued that this is because the dominant QM effect in the reaction is the change in ZPE between the reactants and the products. Our numerical evidence indicates that this effect is captured almost perfectly by RPMD.

AUTHOR INFORMATION

Corresponding Author

*E-mail: aoiz@quim.ucm.es.

Author Contributions

[§]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Aoiz, F. J.; Bañares, L.; Herrero, V. J. The H + H₂ Reactive System. Progress in the Study of the Dynamics of the Simplest Reaction. *Int. Rev. Phys. Chem.* **2005**, *24*, 119–190.
- (2) Schatz, G. C.; Kuppermann, A. Quantum Mechanical Reactive Scattering for Three-Dimensional Atom Plus Diatom Systems. II. Accurate Cross Sections for H + H₂. *J. Chem. Phys.* **1976**, *65*, 4668–4692.
- (3) Truhlar, D. G.; Garrett, B. C. Variational Transition-State Theory. *Acc. Chem. Res.* **1980**, *13*, 440–448.
- (4) Gillan, M. J. Quantum Simulation of Hydrogen in Metals. *Phys. Rev. Lett.* **1987**, *58*, 563–566.
- (5) Voth, G. A.; Chandler, D.; Miller, W. H. Rigorous Formulation of Quantum Transition State Theory and Its Dynamical Corrections. *J. Chem. Phys.* **1989**, *91*, 7749.
- (6) Miller, W. H.; Zhao, Y.; Ceotto, M.; Yang, S. Quantum Instanton Approximation for Thermal Rate Constants of Chemical Reactions. *J. Chem. Phys.* **2003**, *119*, 1329.
- (7) Yamamoto, T.; Miller, W. H. On the Efficient Path Integral Evaluation of Thermal Rate Constants within the Quantum Instanton Approximation. *J. Chem. Phys.* **2004**, *120*, 3086.
- (8) Jambrina, P. G.; Garcia, E.; Herrero, V. J.; Saez-Rabanos, V.; Aoiz, F. J. Can Quasiclassical Trajectory Calculations Reproduce the Extreme Kinetic Isotope Effect Observed in the Muonic Isotopologues of the H + H₂ Reaction? *J. Chem. Phys.* **2011**, *135*, 034310.
- (9) Fleming, D. G.; Arseneau, D. J.; Sukhorukov, O.; Brewer, J. H.; Mielke, S. L.; Schatz, G. C.; Garrett, B. C.; Peterson, K. A.; Truhlar, D. G. Kinetic Isotope Effects for the Reactions of Muonic Helium and Muonium with H₂. *Science* **2011**, *331*, 448–450.
- (10) Fleming, D. G.; Arseneau, D. J.; Sukhorukov, O.; Brewer, J. H.; Mielke, S. L.; Truhlar, D. G.; Schatz, G. C.; Garrett, B. C.; Peterson, K. A. Kinetics of the Reaction of the Heaviest Hydrogen Atom with H₂, the ⁴Heμ + H₂ → ⁴Heμ H + H Reaction: Experiments, Accurate Quantal Calculations, and Variational Transition State Theory, Including Kinetic Isotope Effects for a Factor of 36.1 in Isotopic Mass. *J. Chem. Phys.* **2011**, *135*, 184310.
- (11) 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.
- (12) Craig, I. R.; Manolopoulos, D. E. Chemical Reaction Rates from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2005**, *122*, 084106.
- (13) Craig, I. R.; Manolopoulos, D. E. A Refined Ring Polymer Molecular Dynamics Theory of Chemical Reaction Rates. *J. Chem. Phys.* **2005**, *123*, 034102.
- (14) Collepardo-Guevara, R.; Craig, I. R.; Manolopoulos, D. E. Proton Transfer in a Polar Solvent from Ring Polymer Reaction Rate Theory. *J. Chem. Phys.* **2008**, *128*, 144502.
- (15) Markland, T. E.; Habershon, S.; Manolopoulos, D. E. Quantum Diffusion of Hydrogen and Muonium Atoms in Liquid Water and Hexagonal Ice. *J. Chem. Phys.* **2008**, *128*, 194506.
- (16) Boekelheide, N.; Salomón-Ferrer, R.; Miller, T. F. Dynamics and Dissipation in Enzyme Catalysis. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 16159–16163.
- (17) Menzelev, A. R.; Ananth, N.; Miller, T. F. Direct Simulation of Electron Transfer Using Ring Polymer Molecular Dynamics: Comparison with Semiclassical Instanton Theory and Exact Quantum Methods. *J. Chem. Phys.* **2011**, *135*, 074106-1–074106-17.
- (18) Chandler, D. Exploiting the Isomorphism between Quantum Theory and Classical Statistical Mechanics of Polyatomic Fluids. *J. Chem. Phys.* **1981**, *74*, 4078.
- (19) Collepardo-Guevara, R.; Suleimanov, Y. V.; Manolopoulos, D. E. Bimolecular Reaction Rates from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2009**, *130*, 174713; Erratum: Bimolecular Reaction Rates from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2010**, *133*, 049902.
- (20) Suleimanov, Y. V.; Collepardo-Guevara, R.; Manolopoulos, D. E. Bimolecular Reaction Rates from Ring Polymer Molecular Dynamics: Application to H + CH₄ → H₂ + CH₃. *J. Chem. Phys.* **2011**, *134*, 044131.
- (21) 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.
- (22) Bennett, C. H. Algorithms for Chemical Computations. In *Molecular Dynamics and Transition State Theory: The Simulation of Infrequent Events*; Christoffersen, R. E., Ed.; American Chemical Society: Washington, DC, 1977; Vol.46, Chapter 4, pp 63–97.
- (23) Chandler, D. Statistical Mechanics of Isomerization Dynamics in Liquids and the Transition State Approximation. *J. Chem. Phys.* **1978**, *68*, 2959.
- (24) Gillan, M. J. Quantum-Classical Crossover of the Transition Rate in the Damped Double Well. *J. Phys. C* **1987**, *20*, 3621–3641.
- (25) Boothroyd, A. I.; Keogh, W. J.; Martin, P. G.; Peterson, M. R. A Refined H₃ Potential Energy Surface. *J. Chem. Phys.* **1996**, *104*, 7139.
- (26) Bañares, L.; Aoiz, F. J.; Herrero, V. J.; D'Mello, M. J.; Niederjohann, B.; Seekamp-Rahn, K.; Wrede, E.; Schnieder, L. Experimental and Quantum Mechanical Study of the H + D₂ Reaction near 0.5 eV: The Assessment of the H₃ Potential Energy Surfaces. *J. Chem. Phys.* **1998**, *108*, 6160.
- (27) Mielke, S. L.; Schwenke, D. W.; Schatz, G. C.; Garrett, B. C.; Peterson, K. A. Functional Representation for the Born–Oppenheimer Diagonal Correction and Born–Huang Adiabatic Potential Energy Surfaces for Isotopomers of H₃. *J. Phys. Chem. A* **2009**, *113*, 4479–4488.
- (28) Mielke, S. L.; Garrett, B. C.; Peterson, K. A. A Hierarchical Family of Global Analytic Born–Oppenheimer Potential Energy Surfaces for the H + H₂ Reaction Ranging in Quality from Double-Zeta to the Complete Basis Set Limit. *J. Chem. Phys.* **2002**, *116*, 4142–4161.
- (29) Mielke, S. L.; Schwenke, D. W.; Peterson, K. A. Benchmark Calculations of the Complete Configuration-Interaction Limit of Born–Oppenheimer Diagonal Corrections to the Saddle Points of Isotopomers of the H + H₂ Reaction. *J. Chem. Phys.* **2005**, *122*, 224313.
- (30) Kastner, J.; Thiel, W. Bridging the Gap between Thermodynamic Integration and Umbrella Sampling Provides a Novel Analysis Method: “Umbrella Integration”. *J. Chem. Phys.* **2005**, *123*, 144104.
- (31) Kastner, J.; Thiel, W. Analysis of the Statistical Error in Umbrella Sampling Simulations by Umbrella Integration. *J. Chem. Phys.* **2006**, *124*, 234106.
- (32) Skouteris, D.; Castillo, J.; Manolopoulos, D. ABC: A Quantum Reactive Scattering Program. *Comput. Phys. Commun.* **2000**, *133*, 128–135.
- (33) Habershon, S.; Manolopoulos, D. E. Zero Point Energy Leakage in Condensed Phase Dynamics: An Assessment of Quantum Simulation Methods for Liquid Water. *J. Chem. Phys.* **2009**, *131*, 244518.