

Ring Polymer Molecular Dynamics Calculations of Thermal Rate Constants for the $O(^3P) + CH_4 \rightarrow OH + CH_3$ Reaction: Contributions of Quantum Effects

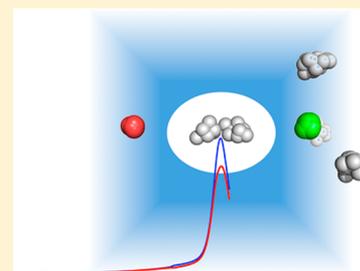
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ABSTRACT: The thermal rate constant of the $O(^3P) + CH_4 \rightarrow OH + CH_3$ reaction is investigated with ring polymer molecular dynamics on a full-dimensional potential energy surface. Good agreement with experimental and full-dimensional quantum multi-configuration time-dependent Hartree results between 300 and 1500 K was obtained. It is shown that quantum effects, for example, tunneling and zero-point energy, can be effectively and efficiently included in this path-integral based approach implemented with classical trajectories. Convergence with respect to the number of beads is rapid, suggesting wide applicability for other reactions involving polyatomic molecules.



SECTION: Kinetics and Dynamics

Accurate determination of rate constants of gas-phase bimolecular reactions is of central importance in modeling kinetics of atmospheric¹ and combustion systems.² While accurate rate constants can often be measured,³ theoretical approaches are complementary with many additional benefits. For instance, experimental measurements of certain reactions might not always be possible or reliable at the temperatures of interest. In addition, an accurate determination of the rate constant provides insights into the dynamics and mechanism of the reaction and offers a stringent test of the underlining potential energy surface (PES), particularly in the transition-state region.

Many bimolecular reactions, especially those in combustion, involve the transfer of a hydrogen atom. As a result, these reactions are affected by many quantum effects, such as zero-point energy (ZPE) and tunneling, particularly at relatively low temperatures. Ideally, the rate constant of such a reaction should be determined using an exact quantum mechanical method on an accurate PES.^{4,5} However, these methods are only amenable to reactions involving a few atoms because of their steep scaling laws with the number of degrees of freedom, even when the most efficient variant, namely, the multi-configuration time-dependent Hartree (MCTDH) method, is used.⁶

Several approximate methods have thus been developed to take into consideration these quantum effects within the framework of transition-state theory.⁷ Whereas ZPE can often be included in the theoretical treatment with relative ease, tunneling remains a difficult issue. The approximate models for treating tunneling through the reaction barrier include not only

the well-established small-curvature tunneling (SCT), large-curvature tunneling (LCT), and the microcanonical optimized multidimensional tunneling (μ OMT) methods⁷ but also the recently implemented⁸ semiclassical transition-state theory.^{9,10} However, these semiclassical models are often unreliable in the deep tunneling regime due to the multidimensional nature of quantum tunneling.

A different approach is based on the so-called ring polymer molecular dynamics (RPMD) method,¹¹ which is an approximate quantum mechanical method based on the isomorphism between the statistical properties of a quantum system and a fictitious ring polymer consisting of a number of classical beads connected by harmonic potentials.¹² Its path integral nature allows the inclusion of quantum effects, while its classical implementation endows it with favorable scaling laws. Recently, it has been formulated by Manolopoulos and coworkers to compute rate constants for chemical reactions.^{13,14} Specifically, for gas-phase bimolecular reactions, the Bennett–Chandler factorization^{15,16} was adapted for computing the RPMD rate constants:^{17,18}

$$k_{\text{RPMD}}(T) = f(T)\kappa(\xi^\ddagger)k_{\text{QTST}}(T, \xi^\ddagger) \quad (1)$$

where $k_{\text{QTST}}(T, \xi^\ddagger)$ is the rate constant computed from the centroid-density quantum transition-state theory at ξ^\ddagger , namely, the peak position along the reaction coordinate ξ . This static

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component is obtained from the potential of mean force (PMF) along the reaction coordinate, which is calculated by umbrella integration¹⁹ of the RPMD distributions in windows along the reaction coordinate biased with harmonic potentials. $\kappa(\xi^\ddagger)$ is the long-time ($t \rightarrow \infty$) limit of the ring polymer transmission coefficient, which represents the dynamic correction. It can be determined from recrossing trajectories with their initial centroids placed at the transition state. Finally, $f(T)$ is the electronic degeneracy factor. For the title reaction, it includes the electronic and spin-orbit partition functions with the following form:^{20,21}

$$f(T) = \frac{3k(1^3A) + 3k(2^3A)}{5 + 3e^{-E(^3P_1)/RT} + e^{-E(^3P_0)/RT}} \quad (2)$$

where $E(^3P_1)$ and $E(^3P_0)$ are the energies of the upper spin-orbit levels of $O(^3P)$ relative to that of 3P_2 , with the values 158.29 and 226.99 cm^{-1} , respectively. In addition, the numerator in eq 2 was approximated by $6k(1^3A)$ as both triplet Jahn-Teller states have similar transition states, but only one (1^3A) was included in the calculation.

The RPMD approach has a number of distinct advantages. First, it gives the exact rate constant in the high-temperature limit as the ring polymer collapses to a single classical bead. Second, it treats all degrees of freedom on an equal footing and as a result is truly full dimensional. In addition, it does not depend on the choice of the dividing surfaces, which is important for large systems where the optimum dividing surface is hard to locate. The PMF approach is also numerically advantageous for large systems because no partition function needs to be explicitly calculated. Finally, because it is implemented with classical trajectories, it scales much more slowly with the degrees of freedom than any quantum mechanical methods and is thus applicable for much larger systems. In fact, an RPMD calculation is roughly n times more expensive than the conventional classical trajectory method, where n is the number of beads in the ring polymer. The RPMD approach has recently been applied to several bimolecular reactions with impressive success.^{17,18,22–24} In particular, it performed quite well in the deep tunneling regime, a surprising phenomenon explained by the recent analysis of Richardson and Althorpe.²⁵ However, most previous work has focused on atom-diatom reactions with only one exception: $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$.^{18,26} To establish the applicability and accuracy of the RPMD approach, we need tests on other more challenging systems.

In this letter, we report the application of RPMD to a hydrogen abstraction reaction involving six atoms. The $\text{O}(^3P) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ reaction represents an important initial step in hydrocarbon combustion.²⁷ Technically, this reaction differs from $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$, which has recently been studied using RPMD,¹⁸ in that the small skew angle for this “heavy-light-heavy” system poses a significant challenge for characterizing the tunneling and barrier recrossing effects.²⁸ Several full-dimensional PESs of this important combustion reaction have been developed,^{20,29} including a recent one based on a large number of ab initio points.³⁰ The thermal rate constant has been determined using canonical variational transition-state theory with tunneling corrections,^{20,21,29} quasi-classical trajectory (QCT),^{31,32} reduced-dimensional quantum dynamics (QD) methods,^{33–37} as well a full-dimensional MCTDH method.³⁸ In this work, we choose to use the analytical PES of Espinosa-García and García-Bernáldez²⁹ because it has been

used in the previous 7D QD study of Yang et al.,³⁶ the MCTDH work of Huarte-Larrañaga and Manthe,³⁸ and transition-state theory calculations.²⁹ Two important features of this PES are noteworthy: It is symmetric with respect to the permutation of the four hydrogen atoms and the first energy derivatives are analytical, which allows accurate and efficient propagation of classical trajectories. We will report in a future work the RPMD rate constants on the more recent ab initio-based PES of Czako and Bowman.³⁰

The RPMD calculations were performed using the RPMDrate code.²⁶ The RPMD procedure for calculating rate constants of bimolecular reactions has been discussed in detail in ref 26, so only the specifics are given here. Different from previous studies,^{17,18,22} the PMF was calculated with different window sizes. In the relatively flat region, namely, the entrance channel ($\xi < 0.75$), larger windows ($d\xi = 0.08$) with a small harmonic bias force constant $k = 0.34$ (T/K) eV were used. The transition-state region, where the free energy changes drastically with the reaction coordinate, was covered with smaller windows with a larger bias force constant ($d\xi = 0.01$ and $k = 2.72$ (T/K) eV). In each window, the sampling was performed for 5 ns, and longer propagation does not change the results. In calculating the transmission coefficient, 100 000 unconstrained child trajectories were propagated for 0.05 ps with initial conditions sampled from a mother trajectory with its centroid constrained at the transition-state geometry. All calculations were performed with a time step of 0.1 fs.

Figure 1 displays the PMFs at 600 K obtained with one and eight beads. It is clear that the PMFs are reasonably flat in the

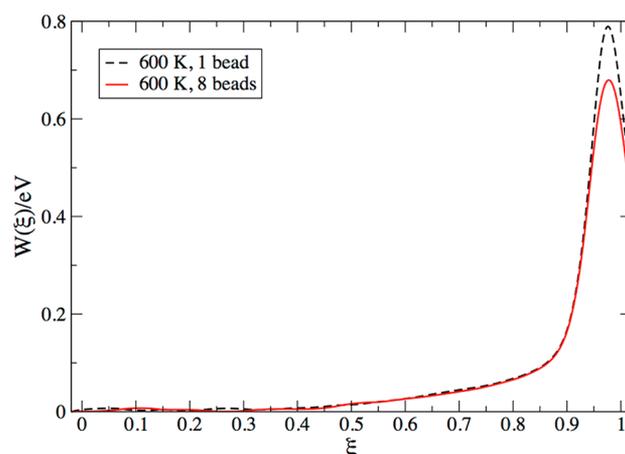


Figure 1. Potentials of mean force (PMFs) for the title reaction at 600 K with one (dashed line) and eight beads (solid line).

entrance channel and rise quickly when the system approaches the transition state. The RPMD activation free energy (ΔG^\ddagger) is 15.7 kcal/mol, which is significantly lower than the classical free-energy barrier of 18.2 kcal/mol obtained with a single bead. This difference apparently stems from the quantum effects, including both ZPE and tunneling. A similar lowering of the activation free energy was observed at other temperatures.

In this work, we consider five different temperatures, 300, 400, 600, 900, and 1500 K. To establish convergence with respect to the number of beads, we first carried out the RPMD simulations with one bead per atom, which represents the classical limit. Larger numbers, namely, 4, 8, 16, and 32, were used until the rate constant converged. The rate constants obtained with different beads at different temperatures are

collected in Figure 2. The classical rate constants form a perfect straight line in the Arrhenius plot. As temperature decreases,

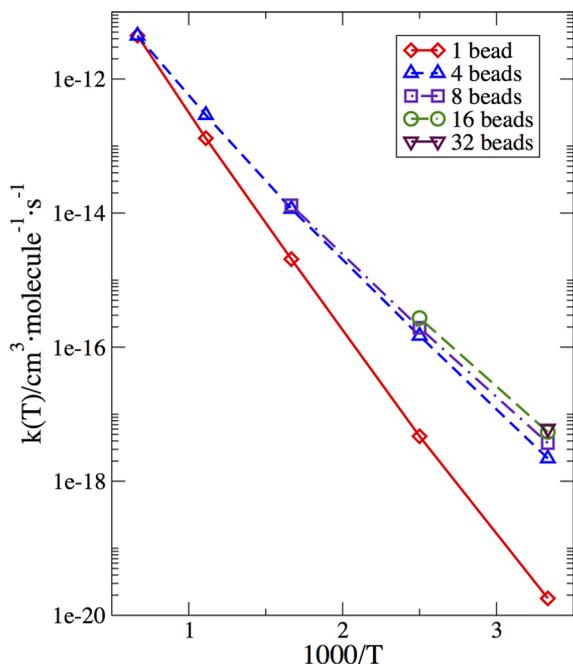


Figure 2. Convergence of RPMD rate constants with respect to the number of beads.

quantum mechanical effects become important, and a larger number of beads is needed to converge the results.

It is well established that the number of ring polymer beads for converged path integral calculations should satisfy the following relationship:³⁹

$$n > n_{\min} \equiv \frac{\hbar\omega_{\max}}{k_{\text{B}}T} \quad (3)$$

where ω_{\max} is the largest frequency of the system. For the title reaction, ω_{\max} corresponds to the OH vibration in the product region and is equal to 3725 cm^{-1} .²⁹ Interestingly, we found that our results converge quickly with only a small number of beads, which satisfies the criterion in eq 3. At the lowest temperature studied here (300 K), for example, 32 beads were sufficient to capture most of the quantum mechanical contributions while $n_{\min} \approx 18$. At the highest temperature (1500 K), four beads

were sufficient with $n_{\min} \approx 4$, underscoring the fact that quantum mechanical effects become less important at high temperatures.

It is also interesting to note that the quantum mechanical effects are captured mostly by the first few beads. Indeed, the rate constant at 300 K increases approximately 122 times when the number of beads increases from 1 to 4, whereas it changes only about three times from 4 to 32 beads. This is quite important as it shows that the RPMD approach should scale quite well with the size of the system.

In Table 1, additional information of the RPMD rate constants is listed. As expected, the activation free-energy (ΔG^\ddagger) increases monotonically with the temperature, underscoring the contribution from tunneling at low temperatures. Interestingly, the position of the free-energy barrier (ξ^\ddagger) is slightly less than 1.0, which indicates that initial dividing surface defined in terms of the breaking and forming bond lengths²⁶ is not optimum. However, barrier recrossing at the barrier top (ξ^\ddagger) is still quite prevalent at all temperatures, as evidenced by nonunity transmission coefficients. Interestingly, κ decreases with decreasing temperature, a phenomenon observed in previous RPMD studies.^{17,18}

The RPMD rate constants are compared in Figure 3 and Table 1 with both experimental data and previous theoretical

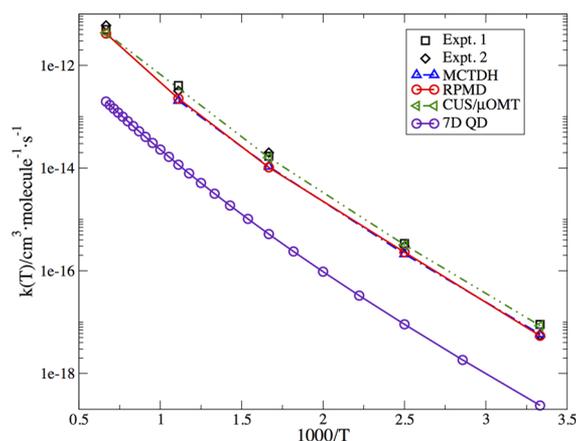


Figure 3. Comparison of the rate constants with experimental and previous theoretical results. Expt. 1 and 2 are from refs 40 and 3.

results. It is quite interesting to note that the RPMD results agree almost perfectly with the MCTDH values at all

Table 1. Calculated Rate Constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) from RPMD with Different Temperatures and Comparison with Both Experimental and Previous Theoretical Data

T (K)	300	400	600	900	1500
N_{bead}	32	16	8	4	4
ΔG (eV)	0.526	0.579	0.679	0.801	0.807
ξ^\ddagger	0.984	0.981	0.978	0.976	0.974
k_{QTST}	1.04×10^{-17}	4.44×10^{-16}	1.98×10^{-14}	4.05×10^{-13}	8.00×10^{-12}
κ	0.584	0.615	0.663	0.719	0.728
k_{RPMD}	5.42×10^{-18}	2.29×10^{-16}	1.03×10^{-14}	2.26×10^{-13}	4.17×10^{-12}
MCTDH	5.81×10^{-18}	2.12×10^{-16}	1.07×10^{-14}	2.06×10^{-13}	--
7D QD	2.38×10^{-19}	9.05×10^{-18}	5.17×10^{-16}	1.16×10^{-14}	1.97×10^{-13}
CUS/ μ OMT	8.50×10^{-18}	3.20×10^{-16}	1.60×10^{-14}	--	4.30×10^{-12}
expt. 1 ^a	9.00×10^{-18}	3.40×10^{-16}	1.70×10^{-14}	4.06×10^{-13}	5.00×10^{-12}
expt. 2 ^a	5.50×10^{-18}	3.00×10^{-16}	2.00×10^{-14}	3.18×10^{-13}	6.00×10^{-12}

^aExperimental data were taken from refs 40 and 3.

temperatures. Although it is expected that the two different implementations of the same quantum dynamical theory should yield similar results, the perfect agreement between the two might be fortuitous due to error cancellation because both approaches contain some approximations. It is evident that the 7D QD results are significantly smaller. Because contributions from the lowest few vibrational states were included in the 7D QD rate constant, the difference may be attributed to the excited rotational states of the methane reactant, which were not included in the scattering calculations.

From Figure 3 and Table 1, we note that the agreement between the RPMD and the canonical unified statistical model with the μ OMT tunneling correction (CUS- μ OMT) of Espinosa-García and García-Bernáldez²⁹ is reasonably good. Quantitatively, however, the CUS- μ OMT rate constants are higher than both the MCTDH and RPMD counterparts, except for 1500 K, where they are quite similar. There are several possible reasons for the deviations. At high temperatures, for example, recrossing in this heavy–light–heavy system may be prevalent, which is only partially taken into account in the variational transition-state theory. However, the good agreement between the RPMD/MCTDH and CUS- μ OMT results at 1500 K seems to suggest that recrossing is a minor problem. Below the crossover temperature (356 K for the title reaction), the deep tunneling nature of the reaction rules out an accurate account of the tunneling contribution by a semiclassical model. Between the two limits, the overestimation of the rate constants by the CUS- μ OMT model is probably due to a combination of errors in describing barrier recrossing and tunneling.

From the same Figure, it is clear that the RPMD results are in reasonably good agreement with the experimental rate constants.^{3,40} While reproducing the curvature of the temperature dependence of the rate constant at low temperatures, the RPMD rate constants consistently underestimate the experiment. Because the PES was adjusted to give the best fit to experimental rate constant using the tunneling-corrected transition-state theory,²⁹ it is possible that this PES is still not sufficiently accurate. For example, the PES has an imaginary frequency of 1549 cm⁻¹ at the transition state, which is significantly smaller than the ab initio values of more than 2100 cm⁻¹.²⁹ A thinner barrier might facilitate more facile tunneling.

To summarize, thermal rate constants for an important combustion reaction have been computed using the RPMD method over a large temperature range. The agreement with experimental results is reasonably good. In particular, it reproduces the curvature in the temperature dependence of the rate constant at low temperatures, apparently due to tunneling. The agreement with previous MCTDH results on the same PES is quite impressive but may be fictitious. The agreement with MCTDH results in this system, and the agreement with exact quantum rate constants in other systems,^{17,18,22,26} offer strong evidence of the accuracy of the RPMD approach. The variational transition-state theory with semiclassical tunneling corrections seems to overestimate the rate constants, presumably due to barrier recrossing and inaccurate description of tunneling. Perhaps most importantly, it is shown that only a small number of beads in the RPMD simulations is sufficient to capture the quantum effects in reactions involving the transfer of a light atom, suggesting that RPMD calculations are feasible on much larger systems.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Barker, J. R.; Golden, D. M. Master Equation Analysis of Pressure-Dependent Atmospheric Reactions. *Chem. Rev.* **2003**, *103*, 4577–4591.
- (2) Fernandez-Ramos, A.; Miller, J. A.; Klippenstein, S. J.; Truhlar, D. G. Modeling the Kinetics of Bimolecular Reactions. *Chem. Rev.* **2006**, *106*, 4518–4584.
- (3) Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, T.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. Evaluated Kinetic Data for Combustion Modeling: Supplement II. *J. Phys. Chem. Ref. Data* **2005**, *34*, 757.
- (4) Althorpe, S. C.; Clary, D. C. Quantum Scattering Calculations on Chemical Reactions. *Annu. Rev. Phys. Chem.* **2003**, *54*, 493–529.
- (5) Guo, H. Quantum Dynamics of Complex-Forming Bimolecular Reactions. *Int. Rev. Phys. Chem.* **2012**, *31*, 1–68.
- (6) Manthe, U. Accurate Calculations of Reaction Rates: Predictive Theory Based on a Rigorous Quantum Transition State Concept. *Mol. Phys.* **2011**, *109*, 1415–1426.
- (7) Truhlar, D. G.; Issacson, A. D.; Garrett, B. C. Generalized Transition State Theory. In *Theory of Chemical Reaction Dynamics*; Bear, M., Ed.; CRC: Boca Raton, FL, 1985; pp 65–137.
- (8) Nguyen, T. L.; Stanton, J. F.; Barker, J. R. A Practical Implementation of Semi-Classical Transition State Theory for Polyatomics. *Chem. Phys. Lett.* **2010**, *499*, 9–15.
- (9) Miller, W. H. Semi-Classical Theory for Non-Separable Systems: Construction of “Good” Action-Angle Variables for Reaction Rate Constants. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 40–46.
- (10) Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D.; Willetts, A. Ab Initio Calculation of Anharmonic Constants for a Transition State, with Application to Semiclassical Transition State Tunneling Probabilities. *Chem. Phys. Lett.* **1990**, *172*, 62–68.
- (11) Craig, I. R.; Manolopoulos, D. E. Quantum Statistics and Classical Mechanics: Real Time Correlation Function from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2004**, *121*, 3368–3373.
- (12) Chandler, D.; Wolynes, P. G. Exploiting the Isomorphism between Quantum Theory and Classical Statistical Mechanics of Polyatomic Fluids. *J. Chem. Phys.* **1981**, *74*, 4078–4095.
- (13) Craig, I. R.; Manolopoulos, D. E. Chemical Reaction Rates from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2005**, *122*, 084106.
- (14) Craig, I. R.; Manolopoulos, D. E. A Refined Ring Polymer Molecular Dynamics Theory of Chemical Reaction Rates. *J. Chem. Phys.* **2005**, *123*, 034102.
- (15) Bennett, C. H. Molecular Dynamics and Transition State Theory: The Simulation of Infrequent Events. In *Algorithms for*

Chemical Computations; Christofferson, R. E., Ed.; ACS Symposium Series 46; ACS: Washington, DC, 1977.

(16) Chandler, D. Statistical Mechanics of Isomerization Dynamics in Liquids and the Transition State Approximation. *J. Chem. Phys.* **1978**, *68*, 2959–2970.

(17) Collepardo-Guevara, R.; Suleimanov, Y. V.; Manolopoulos, D. E. Bimolecular Reaction Rates from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2009**, *130*, 174713.

(18) Suleimanov, Y. V.; Collepardo-Guevara, R.; Manolopoulos, D. E. Bimolecular Reaction Rates from Ring Polymer Molecular Dynamics: Application to $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$. *J. Chem. Phys.* **2011**, *134*, 044131.

(19) Kästner, 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.

(20) Corchado, J. C.; Espinosa-García, J.; Roberto-Neto, O.; Chuang, Y.-Y.; Truhlar, D. G. Dual-Level Direct Dynamics Calculations of the Reaction Rates for a Jahn-Teller Reaction: Hydrogen Abstraction from CH_4 or CD_4 by $\text{O}(^3\text{P})$. *J. Phys. Chem. A* **1998**, *102*, 4899–4910.

(21) González, M.; Hernando, J.; Millán, J.; Sayós, R. Ab Initio Ground Potential Energy Surface, VTST and QCT Study of the $\text{O}(^3\text{P}) + \text{CH}_4(\text{X}^1\text{A}_1) \rightarrow \text{OH}(\text{X}^2\Pi) + \text{CH}_3(\text{X}^2\text{A}_2'')$ Reaction. *J. Chem. Phys.* **1999**, *110*, 7326–7338.

(22) 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 $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$. *J. Phys. Chem. Lett.* **2012**, *3*, 493–497.

(23) Stecher, T.; Althorpe, S. C. Improved Free Energy Interpolation Scheme for Obtaining Gas Phase Reaction Rates from Ring Polymer Molecular Dynamics. *Mol. Phys.* **2012**, *110*, 875–883.

(24) Suleimanov, Y. V.; Pérez de Tudela, R.; Jambrina, P. G.; Castillo, J. F.; Sáez-Rábanos, V.; Manolopoulos, D. E.; Aoiz, F. J. A Ring Polymer Molecular Dynamics Study of the Isotopologues of the $\text{H} + \text{H}_2$ Reaction. *Phys. Chem. Chem. Phys.* **2012**, submitted.

(25) 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.

(26) Suleimanov, Y. V.; Allen, J. W.; Green, W. H. RPMDrate: Bimolecular Chemical Reaction Rates from Ring Polymer Molecular Dynamics. *Comput. Phys. Commun.* **2012**, in press. <http://dx.doi.org/10.1016/j.cpc.2012.10.017>,

(27) Gardiner, W. C. *Combustion Chemistry*; Springer: Berlin, 1984.

(28) Truhlar, D. G.; Gordon, M. S. From Force Fields to Dynamics: Classical and Quantal Paths. *Science* **1990**, *249*, 491–498.

(29) Espinosa-García, J.; García-Bernáldez, J. C. Analytical Potential Energy Surface for the $\text{CH}_4 + \text{O}(^3\text{P}) \rightarrow \text{CH}_3 + \text{OH}$ Reaction. Thermal Rate Constants and Kinetic Isotope Effects. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2345–2351.

(30) Czako, G.; Bowman, J. M. Dynamics of the $\text{O}(^3\text{P}) + \text{CHD}_3(\nu_{\text{CH}}=0,1)$ Reactions on an Accurate Ab Initio Potential Energy Surface. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 7997–8001.

(31) Troya, D.; García-Molina, E. Quasiclassical Trajectory Study of the $\text{O}(^3\text{P}) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ Reaction with a Specific Reaction Parameters Semiempirical Hamiltonian. *J. Phys. Chem. A* **2005**, *109*, 3015–3023.

(32) Varandas, A. J. C.; Caridade, P. J. S. B.; Zhang, J. Z. H.; Cui, Q.; Han, K. L. Dynamics of $\text{X} + \text{CH}_4$ ($\text{X} = \text{H}, \text{O}, \text{Cl}$) Reactions: How Reliable Is Transition State Theory for Fine-Tuning Potential Energy Surfaces? *J. Chem. Phys.* **2006**, *125*, 064312.

(33) Clary, D. C. Quantum Dynamics of the $\text{O}(^3\text{P}) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ Reaction. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1173–1179.

(34) Yu, H.-G.; Nyman, G. Quantum Dynamics of the $\text{O}(^3\text{P}) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ Reaction: An Application of the Rotating Bond Umbrella Model and Spectral Transform Subspace Iteration. *J. Chem. Phys.* **2000**, *112*, 238–247.

(35) Wang, M.-L.; Li, Y.-M.; Zhang, J. Z. H. Application of Semirigid Vibrating Rotor Target Model to the Reaction of $\text{O}(^3\text{P}) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$ Reaction. *J. Phys. Chem. A* **2001**, *105*, 2530–2534.

(36) Yang, M.; Lee, S.-Y.; Zhang, D. H. Seven-Dimensional Quantum Dynamics Study of the $\text{O}(^3\text{P}) + \text{CH}_4$ Reaction. *J. Chem. Phys.* **2007**, *126*, 064303.

(37) Liu, R.; Yang, M.; Czako, G.; Bowman, C. T.; Li, J.; Guo, H. Mode Selectivity for a “Central” Barrier Reaction: Eight-Dimensional Quantum Studies of the $\text{O}(^3\text{P}) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ Reaction on an Ab Initio Potential Energy Surface. *J. Phys. Chem. Lett.* **2012**, *3*, 3776–3780.

(38) Huarte-Larrañaga, F.; Manthe, U. Accurate Quantum Dynamics of a Combustion Reaction: Thermal Rate Constants of $\text{O}(^3\text{P}) + \text{CH}_4(\text{X}^1\text{A}_1) \rightarrow \text{OH}(\text{X}^2\Pi) + \text{CH}_3(\text{X}^2\text{A}_2'')$. *J. Chem. Phys.* **2002**, *117*, 4635–4638.

(39) Markland, T. E.; Manolopoulos, D. E. An Efficient Ring Polymer Contraction Scheme for Imaginary Time Path Integral Simulations. *J. Chem. Phys.* **2008**, *129*, 024105.

(40) Cohen, N. A Reevaluation of Low Temperature Experimental Rate Data for the Reactions of O Atoms with Methane, Ethane, and Neopentane. *Int. J. Chem. Kinet.* **1986**, *18*, 59–82.