

## MIT Open Access Articles

*Full dimensional quantum rate coefficients and kinetic isotope effects from ring polymer molecular dynamics for a seven-atom reaction  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

**Citation:** Allen, Joshua W., William H. Green, Yongle Li, Hua Guo, and Yury V. Suleimanov. "Communication: Full Dimensional Quantum Rate Coefficients and Kinetic Isotope Effects from Ring Polymer Molecular Dynamics for a Seven-Atom Reaction  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ ." The Journal of Chemical Physics 138, no. 22 (2013): 221103.

**As Published:** <http://dx.doi.org/10.1063/1.4811329>

**Publisher:** American Institute of Physics (AIP)

**Persistent URL:** <http://hdl.handle.net/1721.1/92369>

**Version:** Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

**Terms of use:** Creative Commons Attribution-Noncommercial-Share Alike



# Full dimensional quantum rate coefficients and kinetic isotope effects from ring polymer molecular dynamics for a seven-atom reaction $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$

Joshua W. Allen<sup>1</sup>, William H. Green<sup>1</sup>, Yongle Li<sup>2</sup>, Hua Guo<sup>2</sup>, and Yury V. Suleimanov<sup>1,3,a)</sup>

<sup>1</sup>*Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, Massachusetts 02139, United States*

<sup>2</sup>*Department of Chemistry and Chemical Biology, University of New Mexico, 1 University Blvd. NE, Albuquerque, New Mexico 87131, United States*

<sup>3</sup>*Department of Mechanical and Aerospace Engineering, Combustion Energy Frontier Research Center, Princeton University, Olden St., Princeton, New Jersey 08544, United States*

The kinetic isotope effect (KIE) of the seven-atom reactions  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$  and  $\text{OH} + \text{CD}_4 \rightarrow \text{CD}_3 + \text{HDO}$  over the temperature range 200-1000 K is investigated using ring polymer molecular dynamics (RPMD) on a full-dimensional potential energy surface. A comparison of RPMD with previous theoretical results obtained using transition state theory shows that RPMD is a more reliable theoretical approach for systems with more than 6 atoms which provides a predictable level of accuracy. We show that the success of RPMD is a direct result of its independence of the choice of transition state dividing surface, a feature that is not shared by any of the transition state theory-based methods. Our results demonstrate that RPMD is a prospective method for studies of KIEs for polyatomic reactions for which rigorous quantum mechanical calculations are currently impossible.

Many classes of chemical reactions exhibit significant quantum mechanical characters at low temperatures due to the effects of zero-point vibrational energy and/or tunneling through an activation barrier. A rigorous determination of these effects via solution of the quantum reactive scattering Schrödinger equation is currently feasible only for systems containing six or fewer atoms.<sup>1</sup> For this reason, several theoretical methods have been developed in an effort to approximately incorporate these important quantum effects in the calculation of chemical reaction rate coefficients for larger systems. Many previous methods are refinements of

---

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic address: [ysuleyma@mit.edu](mailto:ysuleyma@mit.edu)

transition state theory. Modern implementations of both conventional and variational transition state theory incorporate zero-point energy by utilizing quantum mechanical partition functions for at least the internal degrees of freedom. There are several ways of including a semiclassical tunneling correction, both one-dimensional and multidimensional.<sup>2</sup> There has also been significant effort toward developing a fully quantum transition state theory (QTST),<sup>3-7</sup> such as the quantum instanton (QI) theory of Miller *et al.*,<sup>8</sup> which improves on an earlier semiclassical transition state theory<sup>9</sup> by treating the Boltzmann operator fully quantum mechanically.

Recently, an alternative method of incorporating quantum effects in chemical reaction rates has been developed based on ring polymer molecular dynamics (RPMD).<sup>10-12</sup> RPMD exploits the isomorphism between the statistical properties of the quantum system and those of a classical fictitious ring polymer consisting of many copies of the original system connected by harmonic springs.<sup>13</sup> This isomorphism enables the inclusion of quantum effects via classical molecular dynamics simulations in an extended phase space, an approach with several desirable features for calculating bimolecular gas-phase rate coefficients. First, the RPMD rate coefficient becomes exact in the high temperature limit, where the ring polymer collapses to a single bead. Second, the RPMD rate coefficient has a well-defined short-time limit that acts as an upper bound on the RPMD rate. When the transition state dividing surface is defined in terms of the centroid of the ring polymer, this short-time limit coincides with a well-known (centroid density) version of quantum transition state theory (QTST). Finally, and most importantly, the RPMD rate coefficient is rigorously independent of the choice of the transition state dividing surface used to compute it, a feature that distinguishes it from transition state theory-based methods.

Previous applications of RPMD rate theory have demonstrated that it provides systematic and consistent performance across a wide range of system dimensionalities, including one-dimensional Eckart barriers,<sup>10-11</sup> atom-diatom<sup>14-16</sup> and small polyatomic reactions in the gas phase,<sup>17-19</sup> enzyme-catalyzed reactions,<sup>20</sup> electron transfer reactions,<sup>21</sup> and proton-coupled electron transfer reactions across many different regimes.<sup>22</sup> In all gas phase systems considered so far, the RPMD rate coefficient captures almost perfectly the zero-point energy effect, and is within a factor of 2-3 of the exact rate at low temperatures in the deep tunneling regime, as determined by comparison to rigorous quantum mechanical results available for these systems.<sup>14-19</sup> Furthermore, RPMD rate theory has been shown to consistently underestimate the rates for symmetric reactions and overestimate them for asymmetric reactions.<sup>16,23</sup> The systematic and consistent performance of RPMD rate theory contrasts with the performance of transition state theory-based methods, which are sensitive to the choice of the transition state dividing surface. Proper identification of this dividing surface becomes increasingly difficult as the dimensionality of the problem increases due to the multidimensional nature of tunneling at low temperatures and sometimes large amount of recrossings at high temperatures; as a result, QTST methods are often less accurate in higher dimensionalities. Tailoring the dividing surface for each reaction can significantly improve the accuracy of TST calculations,<sup>24,25</sup> but it requires special expertise, and for some systems even the optimal dividing surface would still have many recrossings. Elaborate quantum implementations of transition state theory have similar sensitivity to the

definition of the dividing surface, and do not necessarily provide improved accuracy when compared to less sophisticated methods, and therefore are not guaranteed to provide a predictable level of error when applied to higher-dimensionality systems. RPMD rate theory has been shown to give better agreement with accurate quantum mechanical (multiconfigurational time-dependent Hartree)<sup>26</sup> calculations than transition state theory methods for the six-atom reactions  $\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2$  and  $\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$ .<sup>17,19</sup> The predictable level of accuracy, which occurs because of the rigorous independence of the method from the choice of transition state dividing surface, is one of the most important and attractive features of RPMD rate theory. The successful application of RPMD to small systems motivated us to develop the open-source software package RPMDrate for computing bimolecular gas-phase reaction rates of arbitrary polyatomic systems where potential energy surfaces are available.<sup>27</sup>

In this Letter, we apply RPMD rate theory to a seven-atom system, for which no exact quantum mechanical results are currently available. The system of interest is the reaction



an important reaction in atmospheric chemistry as the main process by which methane is removed from the atmosphere,<sup>28</sup> and in combustion as a chain-propagating reaction of high-temperature methane flames.<sup>29</sup> This reaction has received considerable experimental attention.<sup>30</sup> In particular, this work focuses on the kinetic isotope effect (KIE) of R1 relative to the reaction



KIE is widely used in experiments to detect quantum mechanical effects; as a ratio of rate coefficients, the KIE depends weakly on the height of the classical reaction barrier, and therefore provides a useful means for comparison to experiment even when the potential energy surface (PES) is less accurate. The KIE of reactions R1 and R2 has been measured in three independent experiments, two of which agree very closely over the temperature range 300-400 K where their experiments overlap.<sup>31-33</sup> However, although there have been several theoretical calculations of the KIE, they generally are not consistent with one another or the experimental result.<sup>34-40</sup> As we will see, the choice of a hydrogen abstraction and a deuterium abstraction reaction will be useful in illustrating the predictable level of accuracy of RPMD rate theory.

RPMD rate theory was used to calculate the rate coefficients of the reactions R1 and R2 at several temperatures over the range 200 to 1000 K. All RPMD calculations were performed using the RPMDrate software; the working equations of RPMD rate theory have been published elsewhere.<sup>27</sup> The RPMD calculations utilized 128 beads at all temperatures below 700 K and 64 beads at the higher temperatures. Although our recent calculations showed that the RPMD rate coefficient could be numerically converged using fewer beads,<sup>19</sup> we nonetheless continued to use additional beads due to the relative computational affordability of the RPMD method. Energies and forces were determined using the global potential energy surface of Espinosa-García and

Corchado.<sup>39</sup> The  ${}^2\Pi_{1/2}$  excited state of OH, which is only  $140\text{ cm}^{-1}$  above the ground state,<sup>41</sup> was included in the electronic partition function. All other parameters, as well as plots of the potential of mean force and transmission coefficient profiles calculated for reaction R1 at 300 K, can be found in the RPMDrate manuscript.<sup>27</sup> Calculations of the crossover temperature, below which the reactions are in the deep tunneling regime, were performed using POLYRATE,<sup>42</sup> with the same parameters as used by Espinosa-García and Corchado.<sup>39</sup> Representative experimental results for the R1 rate coefficient are taken from Vaghjani and Ravishankara,<sup>43</sup> Sharkey and Smith,<sup>44</sup> and Bryukov *et al.*<sup>45</sup>

The RPMD results for the kinetics of reaction R1 are compared against two previously published theoretical results using the same potential energy surface in Table . The canonical unified statistical model with microcanonical optimized multidimensional tunneling (CUS/ $\mu$ OMT) results of Espinosa-García and Corchado<sup>39</sup> show very good agreement with experimental data, even well into the deep tunneling regime (computed by us to be below 387 K, based on the imaginary frequency of  $1703\text{ cm}^{-1}$  used by Espinosa-García and Corchado). This level of accuracy is initially surprising due to the many approximations utilized in the CUS/ $\mu$ OMT method, including a 1D hindered rotor approximation along the minimum energy path and harmonic approximation for all other modes, which are unlikely to accurately describe tunneling at low temperatures. However, we note that the CUS/ $\mu$ OMT method was applied by the same authors who constructed the analytical PES; the authors calibrated this PES so that the CUS/ $\mu$ OMT method reproduced the experimental results.

The quantum instanton (QI) method, as applied by Wang and Zhao,<sup>40</sup> is expected to be more accurate than the CUS/ $\mu$ OMT method since it eliminates several of the latter's approximations. However, the results for reaction R1 are mixed; at 300 K the QI result is more accurate than the CUS/ $\mu$ OMT result, but at 250 K the QI method is less accurate. At 200 K – for which no experimental data was available when the analytical PES was generated – the QI rate is faster than the CUS/ $\mu$ OMT one by a factor of three, a much larger disagreement than at the other temperatures, suggesting that the CUS/ $\mu$ OMT method significantly underestimates the tunneling contribution, and therefore that the analytical PES is inaccurate.

The RPMD results of this work further suggest the inaccuracy of the PES. Table shows the RPMD results with and without the transmission coefficient, with the latter labeled cd-QTST to reflect its coincidence with the centroid-density version of quantum transition state theory. At 1000 K the RPMD rate is 20-30% lower than both the other theoretical methods and the experimental results. Since RPMD rate theory is exact at high temperatures, the deviation of the RPMD result from experiment is likely due to the fitting of the analytical PES with the CUS/ $\mu$ OMT method, i.e. the true reaction barrier is a little lower than that on the fitted PES of Ref. 39. The RPMD transmission coefficient – which can be calculated by dividing the cd-QTST value by the RPMD value – is very small (0.4) at 1000 K, consistent with the expected high-level of recrossing in heavy-light-heavy reactions.

Based on previous experience,<sup>14-19</sup> we expected the RPMD rate coefficient to overestimate the exact rate by about a factor of two to three in the deep tunneling regime. However, the results

show a larger error than expected; for instance, the RPMD rate coefficient at 250 K is about four times larger than that observed experimentally. This discrepancy is also likely due to the fitting of the analytical PES. For this reason we focus our evaluation more on the predicted kinetic isotope effects (KIEs), which are much less dependent on the accuracy of the potential energy surface, and should give a better indication of the relative performance of each method.

Table shows the values of the KIE for R1 to R2 at several temperatures as predicted by the various theoretical methods and measured experimentally. Because KIEs are less sensitive to the PES parameters, we have included two additional theoretical calculations that utilized direct dynamics instead of the analytical PES to compute energies and forces. Melissas and Truhlar applied canonical variational transition state theory with small curvature tunneling (CVT/SCT) at the MP-SAC2//MP2/adj-cc-pVTZ level.<sup>34,35</sup> Masgrau and coworkers also utilized variational transition state theory with interpolated single-point energy corrections and small curvature tunneling (VTST-ISPE/SCT) using the MCCM-CCSD(T)-1sc multicoefficient correlation method.<sup>37-38</sup> The experimental kinetic isotope effects are taken from Gordon and Mulac,<sup>31</sup> Dunlop and Tully,<sup>32</sup> and Gierczak *et al.*<sup>33</sup> The experimental KIE values are larger than two even at 1000 K, and increase as temperature decreases, showing a much smaller tunneling effect for R2 than R1.

The transition state theory-based methods give contradictory estimates of the KIE, with the CVT/SCT and QI methods overpredicting the KIE and the VTST-ISPE/SCT and CUS/ $\mu$ OMT methods underpredicting the KIE. Surprisingly, the oldest and least sophisticated CVT/SCT calculation is the most accurate, though this accuracy is likely a result of error cancellation. The CUS/ $\mu$ OMT method improves on CVT/SCT by accounting for some recrossing of the optimized dividing surface, while the VTST-ISPE/SCT method uses dual level direct dynamics to correct the minimum energy path using interpolated single-point energies. Both refinements cause the calculated KIEs to be much lower than those of the CVT/SCT method, but both are also further from the experimental data. Conversely, the QI method gives KIEs that are much larger than experiment, especially at very low temperatures, where the QI result is four times larger than experiment. This inconsistent, unpredictable performance of the TST-based methods is a direct result of their sensitivity to the choice of transition state dividing surface.

Our cd-QTST results are very similar to the QI results except at very low temperatures, where the cd-QTST result is slightly more accurate. By contrast, in previous investigations of 1D Eckart barrier and gas-phase atom-diatom reactions, the QI method often provided equal or more accurate results than those of CVT, cd-QTST, or RPMD rate theory.<sup>46,47</sup> This system is the second demonstration that the accuracy of the QI method, which depends on the transition state dividing surface, decreases when the method is applied to larger polyatomic reactions where it is harder to draw an accurate dividing surface.<sup>17</sup>

Since the experiments show that the deuterium abstraction reaction R2 has a smaller tunneling contribution than the corresponding hydrogen abstraction R1, we expect the RPMD rate coefficient for R2 to be computed very accurately. As a result, we anticipate that the KIE will be overpredicted by RPMD theory by about factor of two at low temperatures due to the anticipated

overprediction of the rate of R1. Indeed, the results in Table are consistent with our expectations. Within the methods that utilize the same potential energy surface, the RPMD result is consistently closer to the experimental data than the QI result at all temperatures, and is also significantly more accurate than the CUS/ $\mu$ OMT result at high temperatures, where the KIE is even less sensitive to the PES. RPMD gives a more accurate KIE than CUS/ $\mu$ OMT even despite the tuning of the analytical PES to reproduce the experimental KIE data using the latter method.<sup>39</sup> Note that the inclusion of the transmission coefficient, which distinguishes RPMD from the otherwise-identical cd-QTST method, improves the accuracy significantly. The transmission coefficient correction is what makes RPMD theory independent of the choice of transition state dividing surface.

In summary, we have demonstrated that ring polymer molecular dynamics is accurate method of predicting the kinetic isotope effect of  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$  to  $\text{OH} + \text{CD}_4 \rightarrow \text{CD}_3 + \text{HDO}$ . The consistent and predictable accuracy of RPMD rate theory is a direct result of its independence of the choice of transition state dividing surface. This feature is not shared by any of the approximate quantum transition state theory methods, and makes RPMD extremely attractive for further application to polyatomic chemical reactions when the exact quantum mechanical calculations are impossibly expensive.

YVS acknowledges the support of a Combustion Energy Research Fellowship through the Combustion Energy Frontier Research Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0001198. YL, HG, JWA, and WHG were supported by the Department of Energy (DE-FG02-05ER15694 to HG and DE-SC0001198 – to WHG).

## REFERENCES

- <sup>1</sup> S. C. Althorpe, D. C. Clary, *Ann. Rev. Phys. Chem.* **54**, 493 (2003).
- <sup>2</sup> A. Fernández-Ramos, J. A. Miller, S. J. Klippenstein, D. G. Truhlar, *Chem. Rev.* **106**, 4518 (2006).
- <sup>3</sup> M. J. Gillan, *Phys. Rev. Lett.* **58**, 563 (1987).
- <sup>4</sup> M. J. Gillan, *J. Phys. C: Solid State Phys.* **20**, 3621 (1987).
- <sup>5</sup> G. A. Voth, D. Chandler, W. H. Miller, *J. Chem. Phys.* **91**, 7749 (1989).
- <sup>6</sup> N. F. Hansen, H. C. Andersen, *J. Chem. Phys.* **101**, 6032 (1994).
- <sup>7</sup> N. F. Hansen, H. C. Andersen, *J. Phys. Chem.* **100**, 1137 (1996).
- <sup>8</sup> W. H. Miller, Y. Zhao, M. Ceotto, S. Yang, *J. Chem. Phys.* **119**, 1329 (2003).
- <sup>9</sup> W. H. Miller, *J. Chem. Phys.* **62**, 1899 (1975).
- <sup>10</sup> I. R. Craig, D. E. Manolopoulos, *J. Chem. Phys.* **122**, 084106 (2005).
- <sup>11</sup> I. R. Craig, D. E. Manolopoulos, *J. Chem. Phys.* **123**, 034102 (2005).
- <sup>12</sup> S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller, *Ann. Rev. Phys. Chem.* **64**, 387 (2013).
- <sup>13</sup> D. Chandler, P. G. Wolynes, *J. Chem. Phys.* **74**, 4078 (1981).

- <sup>14</sup> R. Collepardo-Guevara, Yu. V. Suleimanov, D. E. Manolopoulos, *J. Chem. Phys.* **130**, 174713 (2009).
- <sup>15</sup> R. Pérez de Tudela, F. J. Aoiz, Y. V. Suleimanov, D. E. Manolopoulos, *J. Phys. Chem. Lett.* **3**, 493 (2012).
- <sup>16</sup> Yu. V. Suleimanov, R. Pérez de Tudela, P. G. Jambrina, J. F. Castillo, V. Sáez-Rábanos, D. E. Manolopoulos, F. J. Aoiz, *Phys. Chem. Chem. Phys.* **15**, 3655 (2013).
- <sup>17</sup> Y. V. Suleimanov, R. Collepardo-Guevara, D. E. Manolopoulos, *J. Chem. Phys.* **134**, 044131 (2011).
- <sup>18</sup> Y. Li, Y. Suleymanov, M.-H. Yang, W. H. Green, H. Guo, *J. Chem. Phys.* **138**, 094307 (2013).
- <sup>19</sup> Y. Li, Y. Suleymanov, M.-H. Yang, W. H. Green, H. Guo, *J. Phys. Chem. Lett.* **4**, 48 (2013).
- <sup>20</sup> N. Boekelheide, R. Salomón-Ferrer, and T. F. Miller III, *Proc. Nat. Acad. Sci. USA*, **108**, 16159 (2011).
- <sup>21</sup> A. R. Menzeleev, N. Ananth, and T. F. Miller III, *J. Chem. Phys.*, **135**, 074106 (2011).
- <sup>22</sup> J. S. Kretchmer and T. F. Miller III, *J. Chem. Phys.*, **138**, 134109 (2013).
- <sup>23</sup> J. O. Richardson, S. C. Althorpe, *J. Chem. Phys.* **131**, 214106 (2009).
- <sup>24</sup> S. J. Klippenstein, W. D. Allen, *Ber. Bunsenges. Phys. Chem.* **101**, 423 (1997).
- <sup>25</sup> S. J. Klippenstein, Y. Georgievskii, L. B. Harding, *J. Phys. Chem. A* **115**, 14370 (2011).
- <sup>26</sup> H. D. Meyer, U. Manthe, L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990).
- <sup>27</sup> Y. V. Suleimanov, J. W. Allen, W. H. Green, *Comp. Phys. Commun.* **184**, 833 (2013).
- <sup>28</sup> R. P. Wayne, *Chemistry of Atmospheres*. Third ed.; Oxford University Press: 2000.
- <sup>29</sup> S. M. Hwang, S.-O. Ryu, K. J. De Witt, M. J. Rabinowitz, *J. Phys. Chem. A* **103**, 5949 (1999).
- <sup>30</sup> D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, T. Just, J. A. Kerr, M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker, J. Warnatz, *J. Phys. Chem. Ref. Data* **34**, 757 (2005).
- <sup>31</sup> S. Gordon, W. A. Mulac, *Proc. Symp. Chem. Kinet. Data Upper Lower Atmos.* **1**, 289 (1975).
- <sup>32</sup> J. R. Dunlop, F. P. Tully, *J. Phys. Chem.* **97**, 11148 (1993).
- <sup>33</sup> T. Gierczak, R. K. Talukdar, S. C. Herndon, G. L. Vaghjiani, A. R. Ravishankara, *J. Phys. Chem. A* **101**, 3125 (1997).
- <sup>34</sup> V. S. Melissas, D. G. Truhlar, *J. Chem. Phys.* **99**, 3542 (1993).
- <sup>35</sup> V. S. Melissas, D. G. Truhlar, *J. Chem. Phys.* **99**, 1013 (1993).
- <sup>36</sup> L. Masgrau, A. Gonzalez-Lafont, J. M. Lluch, *J. Chem. Phys.* **114**, 2154 (2001).
- <sup>37</sup> L. Masgrau, A. Gonzalez-Lafont, J. M. Lluch, *J. Chem. Phys.* **115**, 4515 (2001).
- <sup>38</sup> L. Masgrau, A. González-Lafont, J. M. Lluch, *Theor. Chem. Acc.* **108**, 38 (2002).
- <sup>39</sup> J. Espinosa-Garcia, J. C. Corchado, *J. Chem. Phys.* **112**, 5731 (2000).
- <sup>40</sup> W. Wang, Y. Zhao, *J. Chem. Phys.* **137**, 214306 (2012).
- <sup>41</sup> M. W. Chase Jr., C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, A. N. Syverud, *JANAF Thermochemical Tables*. National Bureau of Standards: Washington, D.C., 1985; Vol. 14.
- <sup>42</sup> J. Zheng, S. Zhang, B. J. Lynch, J. C. Corchado, Y.-Y. Chuang, P. L. Fast, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, A. F. Ramos, B. A. Ellingson, V. S. Melissas, J.



Vilà, I. Rossi, E. L. Coitiño, J. Pu, T. V. Albu, R. Steckler, B. C. Garrett, A. D. Isaacson, D. G. Truhlar, *POLYRATE*, 2010-A; 2010.

<sup>43</sup> G. L. Vaghjiani, A. R. Ravishankara, *Nature* **350**, 406 (1991).

<sup>44</sup> P. Sharkey, I. W. M. Smith, *J. Chem. Soc. Faraday Trans.* **89**, 631 (1993).

<sup>45</sup> M. G. Bryukov, V. D. Knyazev, S. M. Lomnicki, C. A. McFerrin, B. Dellinger, *J. Phys. Chem. A* **108**, 10464 (2004).

<sup>46</sup> C. Venkataraman, W. H. Miller, *J. Phys. Chem. A* **108**, 3035 (2004).

<sup>47</sup> T. Yamamoto, W. H. Miller, *J. Chem. Phys.* **120**, 3086 (2004).

Table I. Comparison of rate coefficients (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$  reaction as calculated using several theoretical methods.

$T$ (K)	Espinosa-García and Corchado PES <sup>b</sup>				Experiment <sup>d</sup>
	cd-QTST <sup>a</sup>	RPMD <sup>a</sup>	CUS/ $\mu$ OMT <sup>b</sup>	QI <sup>c</sup>	
200	$7.08 \times 10^{-15}$	$3.04 \times 10^{-15}$	$5.40 \times 10^{-16}$	$1.53 \times 10^{-15}$	
250	$1.58 \times 10^{-14}$	$8.18 \times 10^{-15}$	$2.20 \times 10^{-15}$	$3.33 \times 10^{-15}$	$2.04 \times 10^{-15}$
298					$6.30 \times 10^{-15}$
					$6.81 \times 10^{-15}$
300	$3.07 \times 10^{-14}$	$1.75 \times 10^{-14}$	$6.40 \times 10^{-15}$	$7.65 \times 10^{-15}$	$7.60 \times 10^{-15}$
400	$9.33 \times 10^{-14}$	$5.83 \times 10^{-14}$	$3.10 \times 10^{-14}$	$2.39 \times 10^{-14}$	$3.48 \times 10^{-14}$
500	$2.20 \times 10^{-13}$	$1.37 \times 10^{-13}$	$9.30 \times 10^{-14}$	$8.08 \times 10^{-14}$	$1.04 \times 10^{-13}$
600	$4.55 \times 10^{-13}$	$2.77 \times 10^{-13}$	$2.10 \times 10^{-13}$	$2.13 \times 10^{-13}$	$2.35 \times 10^{-13}$
700	$8.46 \times 10^{-13}$	$4.86 \times 10^{-13}$		$4.21 \times 10^{-13}$	$4.45 \times 10^{-13}$
800	$1.46 \times 10^{-12}$	$7.24 \times 10^{-13}$	$6.80 \times 10^{-13}$	$8.31 \times 10^{-13}$	$7.49 \times 10^{-13}$
1000	$3.56 \times 10^{-12}$	$1.37 \times 10^{-12}$	$1.60 \times 10^{-12}$	$1.80 \times 10^{-12}$	$1.69 \times 10^{-12}$

<sup>a</sup>From this work.

<sup>b</sup>From Espinosa-García and Corchado.<sup>39</sup>

<sup>c</sup>From Wang and Zhao.<sup>40</sup>

<sup>d</sup>From Vaghjiani and Ravishankara,<sup>43</sup> Sharkey and Smith,<sup>44</sup> and Bryukov *et al.*<sup>45</sup>

Table II. Comparison of kinetic isotope effects for  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$  to  $\text{OH} + \text{CD}_4 \rightarrow \text{CD}_3 + \text{HDO}$  calculated using several theoretical methods.

$T$ (K)	Espinosa-García and Corchado PES <sup>b</sup>				Direct dynamics		Experiment
	cd-QTST <sup>a</sup>	RPMD <sup>a</sup>	CUS/ $\mu$ OMT <sup>b</sup>	QI <sup>c</sup>	CVT/SCT <sup>d</sup>	VTST-ISPE <sup>e</sup>	
200	73.69	48.64	9.79	96.39		7.45	
250	34.15	23.47	5.73	41.11			10.19 <sup>f</sup>
300	19.15	13.78	3.97	16.81	8.27	3.27	7.36 (298 K) <sup>f</sup> 6.75 (293 K) <sup>g</sup>
400	9.00	6.38	2.45	7.54	4.82	2.43	4.31 <sup>f</sup> 4.04 (409 K) <sup>g</sup>
500	5.36	4.14	1.81	4.45		1.85	3.30 (498 K) <sup>g</sup>
600	3.90	3.08	1.49	4.16		1.64	2.63 (602 K) <sup>g</sup>
700	3.07	2.41		3.12		1.52	2.31 (704 K) <sup>g</sup>
800	2.64	2.16	1.45	2.80	2.16		1.96 <sup>g</sup>
1000	2.20	1.46	1.32	2.25		1.34	

<sup>a</sup>From this work.

<sup>b</sup>From Espinosa-García and Corchado.<sup>39</sup>

<sup>c</sup>From Wang and Zhao.<sup>40</sup>

<sup>d</sup>From Melissas and Truhlar, using direct dynamics at the MP-SAC2//MP2/adj-cc-pVTZ level.<sup>34,35</sup>

<sup>e</sup>From Masgrau and coworkers, using direct dynamics at the MCCM-CCSD(T)-1*sc* level.<sup>36-38</sup>

<sup>f</sup>From Gierczak *et al.*<sup>33</sup>

<sup>g</sup>From Dunlop and Tully.<sup>32</sup>