Validation of Variational Transition State Theory with Multidimensional Tunneling Contributions Against Accurate Quantum Mechanical Dynamics for H + CH$_4$ $\rightarrow$ H$_2$ + CH$_3$ in an Extended Temperature Interval

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Model chemistries for electronic structure calculations are consistent levels of theory that can be applied to a variety of systems.[1,2] An advantage of model chemistries is that they can be tested and validated on systems for which accurate results are available so that their level of reliability can be assessed; such validation and reliability estimates are very useful when computational methods are applied to practical applications.

For dynamics computations, there are two sources of error – the potential energy surface or surfaces and the dynamical method itself. In order to disentangle these sources of error, it is desirable to compare approximate dynamics calculations to accurate quantum mechanical dynamics for given realistic potential energy surfaces.[3] This enables one to estimate how much error is due to the dynamical method itself, and in principle this information can be combined with a separate estimate of the reliability of the potential surface to gauge the overall credibility of dynamical prediction.

Variational transition state theory with multidimensional tunneling corrections[4-9] (VTST/MT) has bee extensively validated against accurate quantum mechanical dynamics, especially for atom-diatom reaction.[10] Recently, well converged quantum dynamical calculations for a realistic potential energy surface became available for the title reaction over the 200–500 K interval,[11] and these were used[12] to test VTST/MT. In an even more recent paper[13] the results at 400–500 K were revised, and the temperature

interval was extended up to 1000 K. This extension is very important because now the upper temperature limit includes the lower range of interest for combustion[14] and because the rate constant at higher temperatures includes much greater contributions from excited vibrational states. This provides an opportunity to extend the previous critical test of VTST/MT for a polyatomic reaction, and this extension is presented in the present note.

The potential energy surface used for the previous[11-13] and present studies is Jordan-Gilbert surface,[15] which is a modified version of an older surface by Joseph *et. al.*[16]

The quantum dynamics calculations[13,33] are well converged for total angular momentum zero, and contributions of higher total angular momenta are added by separable rotation approximation.

The versions of VTST used here are canonical variational theory (CVT[3,4,17]) and improved canonical variational theory (ICVT[4,18]). Tunneling contributions are included by the microcanonically optimized multidimensional tunneling (μOMT) algorithm[8,9] which involves the ground-state transmission coefficient approximation,[4] semiclassical methods for calculating tunneling probabilities in terms of multidimensional imaginary action integrals,[5-9] and choosing at each total energy between the small-curvature tunneling[7] (SCT) approximation, and the large-curvature tunneling[6,8,9] (LCT) approximation. The version of the LCT approximation used here is the most recent one,[9] called version 4; this represents a modification of the version-3 algorithm[8] that was used for many years in order to take better account of anharmonicity along low-energy

tunneling paths. All generalized normal mode analyses required for the calculation were carried out in redundant curvilinear coordinates with the harmonic approximation.[19,20]

Although anharmonicity is known to be important,[21-23] one can rely on a certain amount of cancellation between anharmonic corrections for the reactant and for the generalized transition states,[10,23] and testing the validity of this and other assumptions of the standard VTST/MT approach is the goal of the present work. VTST/MT also involves the separable rotation approximation,[24] but that is not really tested here because it is also used in the quantum dynamics calculations; however, tests of the separable rotation approximation on simpler systems indicate that it is very accurate when applied using accurate dynamical data from a high enough value of J.[25-27]

The comparison of the new calculations to quantum dynamical[11,13] rate constants is given in Table I. For convenience the ratios of approximate rate constants of both Ref. 12 and here to the quantum dynamical ones are given in Table II for selected temperatures. In addition to ICVT/μOMT (our most accurate model) and CVT/μOMT (a slightly simpler model that is easier to apply to condensed-phase systems), we also present the results of conventional[24] transition state theory without tunneling (denoted TST) and CVT without tunneling. Conventional TST and CVT without tunneling lead to significant errors at low T. Both CVT/μOMT and ICVT/μOMT are accurate within 22% over the full factor of 5 in temperature. This is quite gratifying, especially when one considers that the quantum rate constant increases by more than eight order of magnitude over this temperature range. The approximate methods employed here are available as standard options in POLYRATE computer program,[28] which is available on the Internet.[29]

The computer time for the calculations in Table I is 63 seconds on one processor of an IBM SP computer.

The fact that the error in CVT/µOMT is only 21% at 200 K is very encouraging in that temperature of 200–300 K are very important for atmospheric modeling. The fact that the error in CVT/µOMT is only 21% at 300 K is very encouraging since ensemble-averaged CVT/µOMT has recently been developed as a general method for enzyme kinetics at physiological temperature.[34] The fact that the approximate theories remain accurate at the highest temperature studied, 1000 K, is very encouraging for combustion applications. The ability of the flux correlation function method[30-33] employed by Huarte-Larrañaga to provide benchmark calculations for testing dynamical theories is very encouraging for the future progress of computational science in addressing the fundamental problems of chemical kinetics.

References

(1)   Pople, J. A. in *Energy, Structure, and Reactivity*, edited by D. W. Smith (Wiley, New York, 1973), p. 51.

(2)   Pople, J. A. *Rev. Mod. Phys.* **1999**, *71*, 1267.

(3)   Truhlar, D. G.; Kuppermann, A. *Chem. Phys. Lett.* **1971**, *9*, 269.

(4)   Truhlar, D. G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, *13*, 440.

(5)   Truhlar, D. G.; Isaacson, A. D.; Skodje, R. T.; Garrett, B. C. *J. Phys. Chem.* **1982**, *86*, 2252. **1983**, *87*, 4554(E).

(6)   Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. In *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, FL, 1985), Vol. 4, p. 65.

(7)   Liu, Y.-P.; Lynch, G. C.; Truong, T. N.; Lu, D.-h.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 2408.

(8)   Liu, Y.-P.; Lu, D.-h.; Gonzalez-Lafont, A.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 7806.

(9)   Fernandez-Ramos, A.; Truhlar, D. G. *J. Chem. Phys.* **2001**, *114*, 1491.

(10)   Allison, T. C.; Truhlar, D. G. In *Modern Methods for Multidimensional Dynamics Computations in Chemistry* (World Scientific, Singapore, 1998), p. 618.

(11)   Bowman, J.; Wang, D.; Huang, X.; Huarte-Larrañaga, F.; Manthe, U. *J. Chem. Phys.* **2001**, *114*, 9683.

(12)   Pu, J.; Corchado, J. C.; Truhlar, D. G. *J. Chem. Phys.* **2001**, *115*, 6266.

(13)   Huarte-Larrañaga, F.; Manthe, U. *J. Chem. Phys.* **2002**, **116**, 2863.

(14)   Glassman, I. *Combustion*, 2nd ed. (Academic Orlando, 1987)

(15)   Jordan, M.; Gilbert, R. *J. Chem. Phys.* **1995**, *102*, 5669.

(16)   Joseph, T.; Steckler, R.; Truhlar, D. G. *J. Chem. Phys.* **1987**, *87*, 7036.

(17)   Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1979**, *70*, 1593.

(18)   Garrett, B. C.; Truhlar, D. G.; Grev, R. S.; Magnuson, A. W. *J. Phys. Chem.* **1980**, *84*, 1730.

(19)   Jackels, C. F.; Gu, Z.; Truhlar, D. G. *J. Chem. Phys.* **1995**, *102*, 3188.

(20)   Chuang, Y.-Y.; Truhlar, D. G. *J. Phys. Chem. A* **1998**, *102*, 242.

(21)   Garrett, B. C.; Truhlar, D. G. *J. Phys. Chem.* **1979**, *83*, 1915.

(22)   Isaacson, A. D.; Truhlar, D. G. *J. Chem. Phys.* **1982**, *76*, 1380.

(23)   Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1984**, *81*, 309.

(24)   Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

(25)   Mielke, S. L.; Lynch, G. C.; Truhlar, D. G.; Schwenke, D. W. *Chem. Phys. Lett.* **1993**, *216*, 441.

(26)   Mielke, S. L.; Lynch, G. C.; Truhlar, D. G.; Schwenke, D. W. *J. Phys. Chem.* **1994**, *98*, 8000.

(27)   Mielke, S. L.; Allison, T. C.; Truhlar, D. G.; Schwenke, D. W. *J. Phys. Chem.* **1996**, *100*, 13588.

(28)   Corchado, J. C.; Chuang, Y.-Y.; Fast, P. L. *et al*. POLYRATE-version 8.7.2, University of Minnesota, Minneapolis, 2002.

(29)   http://comp.chem.umn.edu/polyrate

(30)   Yamamoto, T. *J. Chem. Phys.* **1974**, *61*, 1823.

(31)   Miller, W. H.; Schwartz, S. D.; Tromp, J. W. *J. Chem. Phys.* **1983**, *79*, 4889.

(32)   Matzkies, F.; Manthe, U. *J. Chem. Phys.* **1999**, *110*, 88.

(33)   Huarte-Larrañaga, F.; Manthe, U. *J. Chem. Phys.* **2000**, *113*, 5115.

(34)   Alhambra, C. A.; Corchado, J. C.; Sanchez, M. L.; Garcia-Viloca, M.;

Gao, J.; Truhlar, D. G. *J. Phys. Chem. B* **2001**, *105*, 11326.

Table I. Generalized transition state theory and benchmark rate constants

(cm^{3}molecule^{-1}s^{-1})

T(K)	TST	CVT	CVT/μOMT	ICVT/μOMT	accurate[a]
400	2.50(−16)	1.78(−16)	3.58(−16)	3.60(−16)	4.20(−16)
500	3.38(−15)	2.65(−15)	4.11(−15)	4.15(−15)	4.67(−15)
600	2.02(−14)	1.68(−14)	2.26(−14)	2.30(−14)	2.50(−14)
700	7.53(−14)	6.53(−14)	8.03(−14)	8.22(−14)	8.70(−14)
800	2.09(−13)	1.86(−13)	2.16(−13)	2.22(−13)	2.31(−13)
900	4.74(−13)	4.31(−13)	4.80(−13)	4.95(−13)	5.09(−13)
1000	9.32(−13)	8.60(−13)	9.31(−13)	9.62(−13)	9.74(−13)

[a]Reference 13.

Table II. Ratios of generalized transition state theory rate constants[a] to quantum

mechanical[b] ones at selected temperatures.

T(K)	1000/T	TST	CVT	CVT/μOMT	ICVT/μOMT
200	5.00	0.09	0.04	0.79	0.80
250	4.00	0.23	0.12	0.77	0.77
300	3.33	0.37	0.22	0.79	0.79
400	2.50	0.60	0.42	0.85	0.86
500	2.00	0.72	0.57	0.88	0.89
600	1.67	0.81	0.67	0.90	0.92
800	1.25	0.90	0.81	0.94	0.96
1000	1.00	0.96	0.88	0.96	0.99

[a]Reference 12 and present

[b]Reference 11 for $T = 200 - 300$ K and Ref. 13 for $T = 400 - 1000$ K