

Test of Variational Transition State Theory with Multidimensional Tunneling Contributions Against an Accurate Full-Dimensional Rate Constant Calculation for a Six-Atom System

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Abstract. We present calculations of the $\text{H} + \text{CH}_4$ reaction rate on the Jordan-Gilbert surface using canonical variational transition state theory with minocanonical optimized multidimensional tunneling contributions (CVT/ μ OMT). The purpose of the calculation is to compare the results to the recent accurate dynamical calculations of Bowman, Wang, Huang, Huarte-Larrañaga, and Manthe for this potential energy surface. Over the full 200–500 K range for which accurate results are available we find a mean absolute deviation of only 17% and a maximum absolute deviation of 23%. This provides a rigorous validation of this popular method for a larger system than has previously been possible and indicates that previous validations for atom-diatom reactions were indeed indicative of the kind of accuracy one can obtain for larger systems.

Benchmark dynamics calculations have played a critical role in assessing the validity of approximation schemes. A benchmark dynamics calculation is one in which the nuclear-motion Schrödinger equation is solved accurately (to within some specific numerical tolerance) for a given potential energy surface (or surfaces, if non-Born-Oppenheimer effects are involved). The potential energy surface should be realistic, although it need not be quantitatively accurate. By carrying out calculations employing an approximate dynamical scheme with the same potential energy surface, one can test the dynamical scheme itself more definitively than by comparison to experiment, where uncertainties in the potential energy surface usually cloud the interpretation.

One dynamical scheme that has been widely tested¹⁻³ against benchmark rate constants is variational transition state theory with multidimensional tunneling (VTST/MT) contributions. VTST has its origins in classical mechanics,^{4,5} but when applied with quantized vibrations⁶ and optimized multidimensional tunneling contributions,⁷ it has been shown to be capable of high accuracy, although there is always a question of whether anharmonicity^{8,9}, and mode-mode coupling effects^{9,10} are handled adequately in actual practical applications. Some, but not all, inadequacies in the treatment of these effects at transition states may be cancelled by a consistent treatment of transition states and reactants, and it is important to gauge how successful this can be in quantitative terms (just as, in an analogous situation for comparison, one wants to test how well electronic structure calculations can predict energies without treating the correlation energy of core electrons, which largely cancels out). Furthermore, there is also some question of how well multidimensional tunneling calculations will perform as one increases the number of dimensions.¹¹ VTST/OMT has been well tested for atom-diatom reactions,³ which involve six degrees of freedom in a center-of-mass coordinate system, but a recent report of benchmark dynamics calculations¹² for $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$, a six-body system with 15 degrees of freedom in the center-of-mass coordinate system, provides an opportunity for dramatically increases the size of the test system.

The present paper reports VTST/OMT calculations for comparison to their results. As explained in the first paragraph, the essence of such a comparison is to employ the same potential energy surface for the accurate and approximate dynamics calculations, and we therefore employ the same Gilbert-Jordan (GJ) surface¹³ as used in Ref. 12. We note that the GJ surface may be considered to be a modified version of an older surface by Joseph *et al.*¹⁴

The version of VTST/OMT that we will test is CVT/ μ OMT, which is the standard form that has emerged as a widely available tool¹⁵ for polyatomic reaction rate theory. CVT denotes canonical variational theory⁵ in which VTST is optimized for a canonical ensemble, and μ OMT denotes microcanonical OMT⁷ in which the tunneling mechanism is optimized for each total energy. The optimization consists of choosing either the small-curvature tunneling^{16,17} (SCT) approximation or the large-curvature tunneling^{18,19} (LCT) approximation, whichever yields more tunneling (which corresponds to a practically applicable version of the least-action²⁰ tunneling method). The SCT calculations are based on the centrifugal-dominant small-curvature semiclassical adiabatic ground-state model,¹⁷ and the LCT calculations are based on version 4¹⁹ of the “large-curvature ground-state” model which is based on microscopic reversibility and a calculation of tunneling from the ground state of $\text{CH}_3 + \text{H}_2$ into the ground and vibrationally excited states of CH_4 . In order to test the method in its most widely applicable form, all vibrations are treated as harmonic using curvilinear vibrational coordinates.²¹

Table I presents the results, including, for comparison, conventional transition state theory (TST) and CVT without tunneling. We note that, for the present reaction, improved canonical variational theory²² in the form of ICVT/ μ OMT agrees with CVT/ μ OMT within 1%. Furthermore CVT/ μ OMT agrees with CVT/SCT within 1% for the present case (the CVT/LCT rate constants are 7–26% lower).

Table I shows an average absolute deviation between the CVT/ μ OMT and accurate rate constants of only 17% over the five temperatures, with a maximum deviation of only 23%. This is extremely encouraging for two reasons. First, this is a difficult test because of the large amount of tunneling; the transmission coefficient increases from 1.55 at 500K to 18.7 at 200K, and the dynamical bottleneck is not located at the saddle point, as illustrated by the significant differences (factors of 1.28 to 2.17) between CVT and TST. Second, the CVT/ μ OMT theory applied here is quite practical even for large systems, having recently been applied to the hydride transfer between benzyl alcoholate anion and nicotine adenine dinucleotide catalyzed by liver alcohol dehydrogenase (the system treated has 5560 atoms, and quantum effects were included on the nuclear motion of up to 31 of them). The CVT/SCT theory has also been applied to hydrogen site hopping on Cu(100) with up to 57 atoms quantum mechanical.

The accuracy attained in this study, 17% is actually better than we would expect in general. A recent systematic comparison of harmonic VTST/ μ OMT to 231 benchmark rate constants for 53 collinear and three-dimensional atom-diatom reactions over the temperature range 200–600K showed an average absolute deviation of 25%. A summary of the situation then is that harmonic CVT/ μ OMT appears to be at least as accurate for H + CH₄ as for typical atom-diatom reactions.

Reference 1c concludes with a statement that the rate constant differs significantly from experiment. That is a separate issue related to the inaccuracy of the JG potential energy surface. The JG potential energy surface has a classical barrier height of 10.9 kcal/mol and an imaginary frequency at the saddle point of 1094i cm⁻¹. However, on the basis of published²³ and unpublished²⁴ work, we estimate that a more accurate surface would have a classical barrier height of about 14 kcal/mol and an imaginary frequency of about 1625i cm⁻¹.

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Table I. Comparison of approximate and benchmark rate constants ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) for $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$

T(K)	TST	CVT	CVT/ μ OMT	accurate
200	8.2(-22)	3.8(-22)	7.1(-21)	9.0(-21)
250	1.2(-19)	6.8(-20)	4.3(-19)	5.5(-19)
300	3.6(-18)	2.2(-18)	7.7(-18)	9.8(-18)
400	2.5(-16)	1.8(-16)	3.6(-16)	4.0(-16)
500	3.4(-15)	2.7(-15)	4.1(-15)	3.8(-15)