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TESTING THE ACCURACY OF PRACTICAL SEMICLASSICAL METHODS: VARIATIONAL TRANSITION STATE THEORY WITH OPTIMIZED MULTIDIMENSIONAL TUNNELING

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Variational transition state theory (VTST) with multidimensional tunneling (MT) contributions provides a practical way to include zero-point energies and semiclassical estimates of barrier penetration in reaction rate computations for polyatomic reactions. In this chapter we compare rate coefficients calculated by variational transition state theory (VTST) with optimized multidimensional tunneling (OMT) transmission coefficients to accurate quantal calculations for 74 three-body systems for which accurate quantal rate coefficients are available. These comparisons include both one-dimensional and three-dimensional treatments and both thermal and state-selected reactions. Rate coefficient data are given at a standard set of temperatures in the range 200–2400 K. Rate coefficients are calculated by conventional transition state theory (TST) and improved canonical variational transition state theory (ICVT). Transmission coefficients to account for tunneling are calculated using the small-curvature-tunneling (SCT) approximation, the large-curvature-tunneling (LCT) approximation, the microcanonical optimized multidimensional tunneling (μOMT) approximation, and the least-action-tunneling (LAT) approximation. It is shown that ICVT/μOMT and ICVT/LAT rate coefficients are generally in excellent agreement with the accurate quantal data.

1 Introduction

Many methods are available for the theoretical calculation of gas-phase bimolecular reaction rates. One of the most widely applicable approaches is transition state theory. Although the physical basis of transition state theory is ultimately related to the flow of classical trajectories through phase space,[1–5] the theory may be improved by treating vibrations quantum mechanically[6–8] and including multidimensional tunneling contributions in a transmission coefficient.[8,9] In order to do this consistently it is required to use variational transition state theory.[10] Furthermore, variational transition state theory (VTST) is expected to give much more accurate results than conventional transition state theory (TST) when tunneling is unimportant because it optimizes the location of the transition state.

In order to obtain reliable results from variational transition state theory with multidimensional tunneling (MT) contributions, it is necessary to take account of the fact the reaction paths are curved, and the optimal tunneling paths involve corner cutting.[11–14] Practical and general semiclassical methods for doing this in multidimensional systems have been developed and shown to be quite accurate. In particular, we note the centrifugal-dominant, small-curvature semiclassical adiabatic (CD–SCSA) approximation[15,16] (also called small-curvature tunneling or SCT) and the large-curvature tunneling approximation, version 3[15,17–19] (originally called large-curvature ground-state version-3 or LCG3, now called LCT) appear to be quite accurate in their respective domains, and the least-action tunneling approximation[20] (originally called least-action ground-state or LAG, more systematically called LAT) and the microcanonical optimized multidimensional tunneling[19] (μOMT) methods appear to be accurate under quite general conditions. All these methods have been tested against accurate quantal results, both for full three-dimensional (3D) collisions and also for the case where all three atoms are restricted to lie on a straight line in both the VTST/MT calculations and in the fully quantal calculations. The reduced-dimensionality calculations where all three atoms are constrained to lie on a line are called collinear or one-dimensional (1D), to denote one physical dimension although they involve two mathematical dimensions after the center-of-mass motion of the three-body system is separated. These comparisons are exceedingly encouraging;[21-23] however they are less useful than they might otherwise be because they are spread over a large number of papers, and furthermore they were reported with a variety of treatments of anharmonicity and nonclassical reflection. Moreover, sometimes the tunneling was treated by approximate quantal calculations and in other cases by semiclassical methods, and in most cases the published tests do not include all four methods. In the present paper we rectify this situation. In particular we present a series of consistent tests of all four VTST/MT calculations, in all cases employing our most accurate methods for anharmonicity and a consistent set of approximations for nonclassical reflection and treating tunneling semiclassically. We will also test the less accurate zero-curvature tunneling approximation[10,17,24] (ZCT, also called vibrationally adiabatic zero-curvature or VAZC, minimum-energy-path vibrationally adiabatic ground-state or MEPVAG, and minimum-energy-path semiclassical adiabatic ground-state or MEPSAG), which includes multidimensional zero point effects but neglects corner cutting.

Accurate quantal rate coefficients are generally computed from the results of numerically converged scattering calculations. In such calculations, the results are computed for a given potential energy surface (PES) which describes the interaction of the particles present in the reaction. We use the word "accurate" in reference to these calculations to indicate that these calculations, when fully converged, are the exact solution to the Schrödinger equation for the potential energy surface used in the calculation. For this reason, these calculations are very useful for assessing the reliability of the more approximate VTST/MT calculations. The price that is paid for this accuracy is computational expense. For this reason, almost all accurate quantum mechanical rate coefficient calculations are for systems with only three atoms (the only exception being $OH + H_2 \rightarrow H_2O + H$, which is just starting to yield this kind of accurate treatment[25,26]), and in the present chapter we limit ourselves to the three-body case.

The VTST/MT calculations presented in this chapter have the advantage of being relatively inexpensive to compute, but the disadvantage of being less accurate. This loss of accuracy may be quite tolerable for systems with five or more atoms where VTST/MT is probably the most reliable method that is affordable.

For high temperatures and/or heavier masses, the tunneling contributions are less significant, and VTST without a transmission coefficient (or with a transmission coefficient that tends to unity) becomes of utmost interest. In principle a variety of VTST algorithms could be employed, but we will center attention on a single version of VTST called improved canonical variational transition state theory or, in shortened form, improved canonical variational theory[10,17] (ICVT). We note that for most systems studied to date, ICVT and canonical variational theory[8,10,17] (CVT) provide very similar results. But ICVT requires only a little more effort than CVT, and it should be more accurate when the two theories do differ appreciably.

The goal of this chapter is to provide a consistent check of the results of TST, ICVT, ICVT/SCT, ICVT/LAT, ICVT/LCT, and ICVT/μOMT methods against accurate quantum mechanical scattering data for bimolecular gas-phase rate coefficients. In doing so, we will report rate coefficients at the following set of standard temperatures for every reaction studied: 200, 250, 300, 400, 600, 1000, 1500, and 2400 K. (These temperatures are approximately evenly distributed in 1/T.) We will demonstrate that VTST/MT calculations are excellent predictors of both thermal and state-selected reaction rate coefficients for both one- and three-dimensional reactions. Specifically we will present data from 74 unique combinations of 35 different reactions on 22 different potential energy surfaces. We include references to the potential energy surfaces, accurate quantal calculations, and previous comparisons to accurate quantal data.

The remainder of this chapter is organized as follows. Section 2 gives an overview of the relevant variational transition state theory and multidimensional tunneling methods employed in this paper. Section 3 presents details of the VTST calculations. An explanation of the statistical methods used to measure the accuracy of the VTST calculations is given in section 4. The results are presented and discussed in Section 5. Comprehensive statistical data, averaged over the various reactions studied, are presented in Section 6. Concluding remarks are given in Section 7.

2 Theory

In this section we will introduce the elements of variational transition state theory and of semiclassical multidimensional tunneling calculations that are necessary to specify the computations made for this study. This is not intended to be an exhaustive review of the theory or a complete explanation of the methods. The interested reader is directed to the references given for more detailed accounts of the theoretical framework presented below.

2.1 Variational Transition State Theory

First we consider the 1D case. We note here the curious fact that all atom-diatom reactions for which accurate quantal rate coefficients have been calculated either have collinear minimum-energy paths[4,24] (MEPs) or nearly collinear ones. In the latter case we base the VTST calculation on a collinear reference path, which – for convenience – we still label MEP (since it is the true MEP in a 1D world).

In the 1D case the TST rate coefficient at a temperature T is[8]

$$k^{\mathrm{TST}}(T)=\frac{kT}{h}\frac{Q^{\ddagger}(T)}{\Phi^{\mathrm{R}}(T)}e^{-V^{\ddagger}/RT}, \tag{1}$$

where k is Boltzmann's constant, T is the temperature, h is Planck's constant, $Q^{\ddagger}$ is the one-degree-of-freedom vibrational partition function for the bound vibration at the saddle point (in general a superscript ‡ is used to denote a quantity evaluated at the saddle point or a rate coefficient evaluated using conventional TST), Φ^{R} is the partition function per unit length of reactants (including relative translation but not overall translation of the center of mass of the three-body system), $V^{\ddagger}$ is the classical barrier height in molar energy units, and R is the gas constant.

Define $V_{\mathrm{MEP}}(s)$ as the Born-Oppenheimer potential energy along the MEP as a function of the reaction coordinate s, with the zero of energy at reactants:

$$V_{\mathrm{MEP}}(s=-\infty)=0. \tag{2}$$

Then

$$V^{\ddagger}=\max_{s}\ V_{\mathrm{MEP}}(s)=V_{\mathrm{MEP}}(s=0)=V^{\ddagger}. \tag{3}$$

With these conventions, we note that the zero of energy for the computation of $Q^{\ddagger}(T)$ is $V^{\ddagger}$, and the zero of energy for the computation of Φ^{R} is $V_{\mathrm{MEP}}(s=-\infty)$. An alternative way to write Eq. (1) is

$$k^{\mathrm{TST}}(T)=\frac{kT}{h}\frac{\tilde{Q}^{\ddagger}(T)}{\tilde{\Phi}^{\mathrm{R}}(T)}e^{-\Delta V_{\mathrm{a}}^{\mathrm{G}\ddagger}/RT}, \tag{4}$$

where

$$V_a^G(s) = V_{MEP}(s) + \varepsilon_{ZPE}(s), \tag{5}$$

$$\Delta V_a^G(s) = V_a^G(s) - V_a^G(s=-\infty), \tag{6}$$

$$\Delta V_a^{G\ddagger} = \Delta V_a^G(s=0) = V_a^{G\ddagger} - V_a^G(s=-\infty), \tag{7}$$

$\varepsilon_{ZPE}(s)$ is the molar zero point energy of the bound vibrational motion transverse to the MEP at s, and the tildes on the partition functions means that they are computed with zero of energy equal to $V_a^{G\ddagger}$ for $\tilde{Q}^\ddagger$ and $V_a^G(s=-\infty)$ for $\tilde{\Phi}^R$.

The ICVT rate constant in 1D is

$$k^{ICVT}(T) = \frac{kT}{h} K^{\ddagger,0} \min_s e^{-\Delta G^{IGT,0}(T,s)/RT}, \tag{8}$$

where $K^{\ddagger,0}$ is the reciprocal of the concentration in the standard state, and $\Delta G^{IGT,0}(T,s)$ is the standard-state improved generalized free energy of activation[10] at temperature T for a generalized transition state at s.

In 3D, we replace (1) and (8) by[10]

$$k^{TST}(T) = \sigma \frac{kT}{h} \frac{Q^\ddagger(T,s=0)}{\Phi^R(T)} e^{-V_{MEP}(s=0)/RT} \tag{9}$$

and

$$k^{ICVT}(T) = \sigma \frac{kT}{h} K^{\ddagger,0} \min_s e^{-\Delta G^{ICVT}(T,s)/RT}, \tag{10}$$

where σ is the number of equivalent reaction paths (σ=2 for A + $B_2 \rightarrow$ AB + B and σ=1 for A + BC $\rightarrow$ AB + C where B$\neq$C),

$$Q^\ddagger(T,s) = Q_{el}(T) Q_{vib}(T,s) Q_{rot}(T,s), \tag{11}$$

$Q_{el}(T)$ is the electronic partition function of the transition state at temperature T, $Q_{vib}(T,s)$ is the vibrational partition function of the three bound vibrational modes (one stretch and a doubly-degenerate bend since we assume the MEP is linear) transverse to the MEP at s and T, and $Q_{rot}(T,s)$ is the rotational partition function of the generalized transition state at location s along the MEP at temperature T. Of course, $\Phi^R(T)$ and $\Delta G^{IGT,0}(T,s)$ now also include electronic and rotational degrees of freedom and three vibrations.

2.2 *Multidimensional Tunneling*

To add tunneling we multiply $k^{ICVT}(T)$ by a ground-state transmission coefficient[10,27] $\kappa^{MT}(T)$:

$$k^{ICVT/MT}(T) = \kappa^{MT}(T) k^{ICVT}(T), \tag{12}$$

where MT = ZCT, SCT, LCT, LAT, or μOMT. Note that the ZCT, SCT, LCT, and LAT methods were earlier called MEPSAG, SCSAG, LCG3, and LAG, respectively, where G denotes ground-state transmission coefficient, but we have now introduced the simpler, more systematic notation. We also note that for reactions with four or more atoms or for atom-atom reactions with nonlinear reaction paths, the original SCSAG method[17,28] should be replaced by the CD–SCSAG method.[15,16] Technically SCT denotes CD–SCSAG, but since CD–SCSAG and the original SCSAG method are identical for atom-diatom reactions with collinear MEPs, the distinction is not important in the present paper.

In general, $\kappa(T)$ is the ratio of the Boltzmann-averaged transmission probability $P(E)$ at energy E as computed by the multidimensional semiclassical method to the same quantity as computed without tunneling or nonclassical reflection. The latter is a unit step function at $E = V_{\mathrm{a}}^{\mathrm{AG}}$ where

$$V_{\mathrm{a}}^{\mathrm{AG}} = \max_{s} V_{\mathrm{a}}^{\mathrm{G}}(s) = V_{\mathrm{a}}^{\mathrm{G}}\left(s_*^{\mathrm{AG}}\right) = V_{\mathrm{a}}^{\mathrm{G,max}} = V_{\mathrm{a}}^{\mathrm{AG}}. \tag{13}$$

Thus

$$\kappa(T) = \frac{\int_{V_{\mathrm{a}}^{\mathrm{G}}(s=-\infty)}^{\infty} P(E) e^{-E/RT} \mathrm{d}E}{\int_{V_{\mathrm{a}}^{\mathrm{G}}(s=-\infty)}^{\infty} e^{-E/RT} \mathrm{d}E}. \tag{14}$$

In all cases, $P(E)$ is approximated for $E > V_{\mathrm{a}}^{\mathrm{AG}}$ by the parabolic uniform approximation[17,29] from the corresponding $P(E)$ for $E < V_{\mathrm{a}}^{\mathrm{AG}}$.

In the ZCT approximation,[10,11] $P(E)$ is computed as a one-dimensional transmission coefficient through $V_{\mathrm{a}}^{\mathrm{G}}(s)$; this is still a multidimensional approximation because of the multidimensional zero point energy in Eq. 5. The SCT approximation is similar to ZCT except that the effective reduced mass is a function of the s, depending on the reaction-path curvature components and the bound-mode vibrational turning points;[15,16] to account for corner cutting, the effective reduced mass is smaller than the constant physical reduced mass. The LCT approximation[15,18,19] involves an average for each E over a sequence of straight-line paths from the entrance valley to the exit valley and requires more information about the potential than just $V_{\mathrm{a}}^{\mathrm{G}}(s)$, the reaction-path curvature components, and the bound-mode vibrational turning points. The LAT approximation[20] is similar to LCT except the tunneling path is optimized from among a sequence of basis sets varying between the LCT paths, which are straight lines and hence show the most possible corner cutting, and the ZCT paths, which follow the MEP and hence show no corner cutting. Thus the LAT is an optimized multidimensional tunneling approximation and is designed to be valid for any reaction-path curvature. The μOMT method[16] is a simpler OMT method. At each energy it simply accepts the larger of the $P(E)$ calculated by the LCT method and that calculated by the SCT method.

Note that it is necessary to specify how distance along the MEP is scaled in order to give meaning to quantities like s_*^{AG} in Eq. 13. Throughout this paper we establish this scale by specifying the reduced mass to which all the coordinates are scaled, and in particular we take this mass to be the reduced mass of relative translation of A with respect to BC.[4,8]

3 Calculations

All reactions are considered to occur on a single Born-Oppenheimer potential energy surface.

The accurate quantum mechanical rates coefficient data presented in this chapter are calculated by a variety of methods, and it is beyond the scope of this chapter to review the methods employed. However, for each reaction studied, references to the original quantum mechanical calculations are given.

Conventional and variational transition state theory calculations including semiclassical transmission coefficients were carried out using the computer program ABCRATE.[30] This program is restricted to three-atom systems with collinear reaction paths, and is thus quite well suited for the work presented here. Rate coefficients are calculated for this chapter using conventional transition state theory (TST) and improved canonical variational transition state theory (ICVT).[10] Transmission coefficients to account for tunneling effects are computed using the zero-curvature tunneling[10,11,17] (ZCT), small-curvature tunneling[15,16] (SCT), large-curvature tunneling[15,17,18] (LCT), least-action tunneling[20] (LAT), and microcanonical optimized multidimensional tunneling (μOMT) methods.[19] Stretching vibrational motion is treated by a WKB formalism[31] for the ground state and for excited states. Bending vibrations are treated using harmonic and quartic force constants[10,32] with energy levels computed by a centrifugal oscillator method.[33] All rate coefficients are converged numerically to better than 1%.

The contribution of low-lying excited states to the electronic partition function is also included in 3D calculations, making the assumption that only the ground potential energy surface is reactive.[34] For atoms in P states, all low-lying spin-orbit states ($^3P_2$, $^3P_1$, and $^3P_0$ for O and $^3P_{3/2}$, and $^3P_{1/2}$ for halogen atoms) were included with appropriate degeneracies and excitation energies. Closed-shell species were treated as ground states with a degeneracy of one, and transition states and atoms with high-lying excited states (Mu, H, D, and T) were treated as ground states with a degeneracy of two, except for $O + H_2$, where the transition state is treated as having a degeneracy of three ($^3\Pi$). It should be noted that one obtains a consistent comparison only if these electronic degeneracies are treated the same way in both sets of calculations. In 1D calculations we omit electronic degeneracies and electronic excited states in both VTST/MT and in the accurate quantal calculations.

In the 3D calculations, we included a symmetry factor σ of two for $A + B_2 \rightarrow AB + B$, but in the 1D calculations all symmetry numbers are set equal to one.

4 Error Measures

In order to assess the accuracy of the TST, VTST, and VTST/MT calculations relative to the accurate quantum mechanical rate coefficient data, we compute two statistical measures of the average deviation.

The first statistical measure is the mean unsigned percentage error (MUPE) which is defined as

$$\mathrm{MUPE} = \left(\frac{1}{N} \sum_{i=1}^{N} \left| \frac{k_i^{\mathrm{calc}} - k_i^{\mathrm{acc}}}{k_i^{\mathrm{acc}}} \right| \right) \times 100\%, \tag{15}$$

where i is an index which labels the rate coefficient for a given system at a given temperature, N is the number of accurate rate coefficients k_i^{acc} that are involved in the mean error computation, and k_i^{calc} is the approximate rate coefficient calculated by TST, VTST, and VTST/MT methods.

In order to treat overestimates and underestimates of the accurate rate coefficient equivalently also estimated the error on the basis of unsigned logarithms. In order to make the results easily appreciated, we convert the resulting statistical quantity to a percentage. In particular we define the logarithmically averaged percentage error (LAPE) as

$$\mathrm{LAPE} = \left(10^{\mathrm{AUPD}} - 1\right) \times 100\%, \tag{16}$$

where

$$\mathrm{AUPD} = \frac{1}{N} \sum_{i=1}^{N} \left| \log_{10} \frac{k_i^{\mathrm{calc}}}{k_i^{\mathrm{acc}}} \right|. \tag{17}$$

All rate coefficients used in Eqs. 15 and 17 correspond to one of the eight standard temperatures specified in Section 1. Furthermore, k_i^{acc} is always the value obtained from quantum scattering calculations. When the accurate quantal rate coefficient is not available at one of the standard temperatures, we proceed in one of two ways. If the temperature for which we desire the accurate data lies between the end points of the temperature range for which the accurate data is available we obtain the accurate rate coefficient by interpolation. Specifically we choose three accurate rate coefficients whose temperatures are closest to and bracket the desired temperature and use a three-parameter rate coefficient formula, *i.e.*,

$$k = a(T/1\ \mathrm{K})^n e^{-b/T}, \tag{18}$$

where k is the desired rate coefficient, T is the temperature, and a, b, and n are adjustable parameters. Three accurate rate coefficients at three temperatures yield a unique solution to Eq. 20 which is used to interpolate the accurate data.

5 Results and Discussion

In order to facilitate the presentation of the large amount of rate coefficient data in this chapter, the data have been organized into sections as follows. The results are first divided into four sections: thermal one-dimensional (1D) reactions, state-selected 1D reactions, thermal three-dimensional (3D) reactions, and state-selected 3D reactions. Within each of these sections, the results are further divided by the molecular species under investigation, with all isotopic analogs grouped together and various species arranged in the order of decreasing number of hydrogen atoms and increasing mass. Thus the presentation of the results in these subsections will consider H_2X systems first, followed by HX_2 and HXY systems, where X, Y = H, O, or a halogen atom. Within these three system types, results are given in order of increasing X mass.

Throughout this section, we will refer to the transition state and variational transition state properties of the various molecular species being studied. This data is presented in order of decreasing skew angle β in Tables 1 and 2 respectively. The skew angle β is the angle between the entrance and exit valleys of the potential energy surface in mass-scaled, isoinertial coordinates.[35,36] (Isoinertial coordinates are coordinates scaled to correspond to the same reduced mass for every direction of motion.) For a bimolecular reaction with atoms A, B, and C, the skew angle is given by

$$\beta = \cos^{-1}\sqrt{\frac{m_A m_C}{m_{AB} m_{BC}}}. \tag{19}$$

The angle β is in the range 0–90 degrees. Large values of the skew angle (i.e., close to 90 degrees) imply small reaction-path curvature, and small values of the skew angle (i.e., close to zero degrees) imply large reaction-path curvature. The data in Table 1 also includes nearest-neighbor bond distances at the saddle point, the classical barrier height, and the normal mode frequencies. Table 2 gives properties of the zero-temperature variational transition states which are located at the maximum of the vibrationally adiabatic ground-state potential curve as in Eq. 13. The superscript AG denotes a quantity evaluated at this location. Table 2 also compares the value of the vibrationally adiabatic ground-state potential curve at the AG maximum to its value at the saddle point, in particular by tabulating

$$\Delta\Delta V_a^G \equiv V_a^{AG} - V_a^{G\ddagger}. \tag{20}$$

When the results of the present study are compared to the accurate quantum mechanical rate coefficients (Tables 3–78), we will always give the accurate result on an absolute basis followed by the ratios of the various approximate results to the accurate result. If the temperature for which we desire accurate data lies outside of the temperature range for which the accurate data is given, we compare the TST, ICVT, and ICVT/MT results at this temperature to the ICVT/LAT result. These results are presented in a distinct (bottom) section of the Table, and the data at the temperatures in these lower sections are never used to calculate the MUPE or LAPE. In all cases the ratio shown in Tables 3–76 is that of the VTST/MT calculations to the accurate quantum mechanical or the ICVT/LAT rate coefficients. Thus a ratio greater than one means that the VTST/MT result exceeds the most accurate available rate coefficient, and a ratio less than one means that the VTST/MT result is smaller than the most accurate available one.

5.1 Thermal One-Dimensional (Collinear) Reactions

In this section we will compare the results of VTST calculations to accurate quantum mechanical calculations for thermal A + BC → AB + C reactions where the molecular species is constrained to a collinear configuration (*i.e.*, the ABC bond angle is fixed at 180 degrees). In the case of the VTST calculations, this means that only the stretching vibrational degree of freedom is treated – bending vibrations are ignored. The bulk of the results presented in this chapter will be found in this section. This is due to the fact that these reduced-dimensionality calculations are considerably less computationally demanding for accurate quantum mechanical methods. The accurate one-dimensional results are quite useful for validation of more approximate methods such as the VTST/MT methods presented here. However, the one-dimensional results, whether accurate quantum mechanics or VTST, have very limited utility as predictors of the full-dimensional rate coefficient.[37,38]

Table 1: Conventional transition state properties for various ABC systems.

ABC	Surface	β (deg)	$R^{\ddagger}_{\mathrm{AB}}$ (Å)	$R^{\ddagger}_{\mathrm{BC}}$ (Å)	$V^{\ddagger}$ (kcal)	$\nu^{\ddagger}_{\mathrm{imag}}$ (cm^{-1})	$\nu^{\ddagger}_{\mathrm{str}}$ (cm^{-1})	$\nu^{\ddagger}_{\mathrm{bend}}$ (cm^{-1})
HBrH	DIM–3C	89.3	1.581	1.581	5.49	1281*i*	1794	781
HBrD	DIM–3C	89.0	1.581	1.581	5.49	1073*i*	1525	679
HFH	SK	87.1	1.326	0.943	1.75	454*i*	3642	291
DFD	SK	84.5	1.326	0.943	1.75	330*i*	2625	215
HClCl	KNPRY	83.2	2.251	2.017	2.42	488*i*	524	37
HFF	JOT–II	80.9	1.897	1.437	2.35	605*i*	787	58
MuDD	LSTH	80.6	0.930	0.930	9.80	1302*i*	4158	1253
MuDD	PK2	80.6	0.900	0.900	9.13	2006*i*	4159	1350
DFF	JOT–II	77.4	1.897	1.437	2.35	447*i*	771	46
MuHH	LSTH	77.0	0.930	0.930	9.80	1784*i*	4346	1384
TFF	JOT–II	74.8	1.897	1.437	2.35	370*i*	763	41
HDH	PK2	70.5	0.900	0.900	9.13	1787*i*	2183	800
HDD	TK	65.9	0.934	0.934	9.79	1097*i*	1742	533
DDD	TK	60.0	0.934	0.934	9.79	1034*i*	1432	494
HHH	LSTH	60.0	0.930	0.930	9.80	1506*i*	2059	910
HHH	PK2	60.0	0.900	0.900	9.13	2189*i*	2183	980
HHH	TK	60.0	0.934	0.934	9.79	1461*i*	2025	698
ODH	JWS	57.0	1.118	0.955	12.55	1492*i*	1470	574
ClDH	SPK/GSW	55.8	1.397	0.993	7.67	1160*i*	1252	563
HHD	PK2	54.7	0.900	0.900	9.13	2081*i*	1875	938
DHH	PK2	54.7	0.900	0.900	9.13	2081*i*	1875	938
DHH	TK	54.7	0.934	0.934	9.79	1386*i*	1743	668
ODD	JWS	48.2	1.118	0.955	12.55	1405*i*	1133	520
FDD	M5	47.8	1.541	0.762	1.06	266*i*	273	320
ClTT	SPK/GSW	47.3	1.397	0.993	7.67	865*i*	824	412
OHH	JW	46.7	1.118	0.953	12.49	1963*i*	1532	725
OHH	ModPolCI	46.7	1.213	0.921	12.58	1805*i*	1622	836
OHH	PolCI	46.7	1.216	0.920	12.58	1782*i*	1628	513
OHH	DIM-RMOS	46.7	1.064	1.095	13.35	1813*i*	1727	478
OHH	SL	46.7	1.199	0.946	13.79	1808*i*	1532	703
OHH	JWS	46.7	1.118	0.955	12.55	1970*i*	1531	731
ClDD	SPK/GSW	46.6	1.397	0.993	7.67	1057*i*	985	503
FHH	M5	46.4	1.541	0.762	1.06	360*i*	385	452
ClHH	G3	45.8	1.401	0.990	7.88	1520*i*	1358	581
ClHH	SPK/GSW	45.8	1.397	0.993	7.67	1491*i*	1358	710
IHH	RSPTS	45.2	1.678	1.280	35.87	1396*i*	1320	483

IHH	RMC	45.2	1.678	1.280	35.88	333*i*	1291	368
THD	LSTH	45.0	0.930	0.930	9.80	1349*i*	1328	817
OHD	JWS	37.6	1.118	0.955	12.55	1877*i*	1168	689
ClHD	SPK/GSW	36.4	1.397	0.993	7.67	1369*i*	1061	664
ClDCl	BCMR	19.0	1.467	1.467	8.55	996*i*	344	362
ClDCl	PK3	19.0	1.487	1.487	8.54	1046*i*	347	493
ClHCl	BCMR	13.6	1.467	1.467	8.55	1398*i*	344	508
ClHCl	PK3	13.6	1.487	1.487	8.54	1468*i*	347	692
ClHBr	BLM	11.6	1.660	1.548	11.00	1563*i*	306	452
IHI	KK–A	7.2	1.781	1.781	1.35	526*i*	149	394
ClMuCl	BCMR	4.6	1.467	1.467	8.55	4140*i*	344	1505

[a] Bending frequencies were not computed for this transition state because the harmonic force constant is negative.

5.1.1 Collinear H_3 Reactions

Three potential energy surfaces will be considered for H_3 reactions, potential energy surface number 2 of Porter and Karplus[39] which will be referred to as the PK2 surface, the TK surface of one of the authors and Kuppermann,[11,40] and the LSTH surface of one of the authors and Horowitz.[41] The LSTH surface is the result of a fit to the *ab initio* data of Liu and Siegbahn.[42,43] Of the three potential energy surfaces considered in this section, the LSTH surface is the most accurate, and it remains one of the most accurate surfaces available for the study of H_3 reactions. The TK surface is similar to the LSTH surface, as may be partially verified by the transition state data given in Table 1. The PK2 surface is the least accurate of the surfaces considered here, and it is known to suffer from a barrier which is too thin.[41,44]

The first reaction we consider is one of the most studied reactions in chemical dynamics, namely

$$\mathrm{H} + \mathrm{HH'} \rightarrow \mathrm{HH} + \mathrm{H'} \tag{R1}$$

Accurate quantum mechanical collinear rate coefficients were calculated for the PK2 surface by Schatz and Kuppermann,[45] for the TK surface by one of the authors and various coworkers,[11,46–48] and for the LSTH surface by one of the authors and coworkers.[49] Previous comparison of VTST results to accurate quantum mechanical results have been made for the PK2 surface as described in Ref 31, for the TK surface as described in Refs 8, 10, 27, 28, and 50–53, and for the LSTH surface as described in Refs 20, 31, and 49. Rate coefficients data for selected VTST/MT methods for reaction (R1) are presented in Tables 3–5 for the PK2, TK, and LSTH surfaces, respectively.

Table 2: Variational transition state properties for various ABC systems.[a]

ABC	Surface	s^{AG} (a_0)	V_a^{AG} (kcal)	$V_a^{\mathrm{G\ddagger}}$ (kcal)	$\Delta\Delta V_a^{\mathrm{G}}$ (kcal)	$\nu_{\mathrm{str}}^{\mathrm{AG}}$ (cm^{-1})	$\nu_{\mathrm{bend}}^{\mathrm{AG}}$ (cm^{-1})
1D Thermal Reactions							
HHH	PK2	0.000	12.23	12.23	0.00	2183	980
HHH	TK	0.000	12.66	12.66	0.00	2025	698
HHH	LSTH	0.000	12.72	12.72	0.00	2059	910
MuHH	LSTH	1.128	18.10	15.45	2.65	8096	1232
MuDD	PK2	1.060	17.40	15.00	2.40	8764	1333
MuDD	LSTH	1.488	17.95	14.78	3.17	7826	1162
DHH	TK	–0.216	12.39	12.26	0.13	2576	660
HDD	TK	0.133	12.32	12.26	0.07	1939	537
DDD	TK	0.000	11.82	11.82	0.00	1432	494
THD	LSTH	–0.171	11.70	11.69	0.01	2009	774
OHH	JW	–0.005	14.67	14.67	0.00	1535	727
OHH	ModPolCI	–0.086	14.99	14.83	0.16	2106	851
OHH	DIM–RMOS	0.113	15.95	15.74	0.21	2410	435
OHH	PolCI	–0.082	15.00	14.84	0.16	2073	522
OHH	SL	–0.038	16.01	15.95	0.06	1657	720
FHH	M5	–0.410	6.76	6.34	0.42	4231	286
FDD	M5	–0.295	5.07	4.85	0.22	2949	230
HFH	SK	–0.277	7.08	6.87	0.21	3879	225
DFD	SK	–0.219	5.58	5.45	0.13	2777	176
ClHH	SPK/GSW	0.023	9.62	9.61	0.01	1386	691
ClHD	SPK/GSW	0.260	9.44	9.18	0.26	2380	457
ClDH	SPK/GSW	–0.017	9.46	9.46	0.01	1267	575
ClDD	SPK/GSW	0.014	9.08	9.08	0.01	996	496
ClTT	SPK/GSW	0.012	8.85	8.85	0.00	832	407
HBrH	DIM–3C–B	0.000	8.03	8.03	0.00	1794	358
DBrH	DIM–3C–B	–0.024	7.66	7.65	0.02	1546	312
IHH	RSPTS	–[b]	39.14	37.69	1.44	–[b]	–[b]
IHH	RMC	1.919	39.15	37.54	1.60	4469	253
HFF	JOT–II	–0.031	3.47	3.47	0.00	793	56
DFF	JOT–II	–0.049	3.45	3.44	0.01	784	44
TFF	JOT–II	–0.057	3.44	3.43	0.02	782	39
HClCl	KNPRY	–0.011	3.17	3.17	0.00	524	37
ClMuCl	BCMR	–0.732	14.30	9.04	5.26	8372	694
ClHCl	BCMR	–0.211	9.16	9.04	0.12	2303	409
ClDCl	BCMR	0.000	10.12	10.12	0.00	344	362

IHI	KK–A	–0.990	3.48	1.57	1.91	2221	156
ClHBr	BLM	–0.213	11.79	11.43	0.36	2242	355
1D State-selected Reactions							
HHH	PK2	–0.915	20.57	18.27	2.31	4370	576
HHH	TK	–0.822	20.85	18.28	2.57	4455	500
HHH	LSTH	0.844	20.82	18.45	2.37	4074	564
OHH	JW	–0.663	21.39	18.95	2.44	4129	450
OHH	ModPolCI	–0.584	21.98	18.89	3.09	4053	615
OHH	DIM–RMOS	–0.907	18.18	20.08	1.90	4216	437
HHO	JW	–0.867	17.94	16.15	1.79	3576	289
HHO	ModPolCI	–1.538	15.41	15.99	0.58	3636	215
HHO	DIM–RMOS	–0.717	18.99	16.23	2.76	3485	298
ClHH	SPK/GSW	–1.346	18.33	13.41	4.93	4294	268
ClDD	SPK/GSW	–0.809	13.73	11.85	1.89	2864	319
ClTT	SPK/GSW	–0.601	11.91	11.17	0.73	2206	318
HFF	JOT–II	–0.105	5.66	5.63	0.03	806	51
DFF	JOT–II	–0.163	5.61	5.52	0.09	812	39
TFF	JOT–II	–0.187	5.59	5.46	0.13	817	34
ClHBr	BLM	–0.607	16.07	12.25	3.82	2608	249
3D Thermal Reactions							
HHH	PK2	0.000	15.17	15.17	0.00	2183	980
HHH	LSTH	0.000	15.43	15.43	0.00	2059	910
HHD	PK2	0.024	14.70	14.60	0.10	1901	940
HDH	PK2	0.000	14.61	14.61	0.00	2183	800
DHH	PK2	–0.021	14.62	14.60	0.02	1901	940
DHH	LSTH	–0.102	14.98	14.90	0.08	2042	863
DHH	DMBE	–0.146	14.91	14.77	0.14	2279	854
DHH	BKMP	–0.111	14.84	14.75	0.08	2077	858
OHH	JWS	–0.015	16.98	16.96	0.01	1540	737
OHD	JWS	0.000	16.31	16.31	0.00	1168	689
ODH	JWS	–0.032	16.42	16.37	0.05	1527	587
ODD	JWS	–0.008	15.73	15.72	0.00	1134	522
ClHH	G3	–0.013	11.82	11.81	0.01	1353	584
HBrH	DIM–3C–B	0.000	9.09	9.09	0.00	1794	358
DBrH	DIM–3C–B	–0.027	8.58	8.57	0.02	1525	312
ClHCl	BCMR	0.000	10.58	10.58	0.00	344	508
ClHCl	PK3	0.000	11.10	11.10	0.00	347	692
ClDCl	BCMR	0.000	10.12	10.12	0.00	344	362
ClDCl	PK3	0.000	10.49	10.49	0.00	347	493

3D State-selected Reactions							
HHH	PK2	–0.808	22.39	21.21	1.18	4316	617
DHH	LSTH	–0.772	22.49	19.84	2.65	4032	570

[a] These are the properties of a system at the maximum of the vibrationally adiabatic ground-state potential curve, which is the variational transition state at 0 K.

[b] No maximum was found along the reaction path for this reaction. Stretching and bending frequencies were not computed. The value of V_a^{AG} given is that of the reactants.

[c] Bending frequencies were not computed for this transition state because the harmonic force constant is negative.

Results obtained using the PK2 potential energy surface for reaction (R1) are in good agreement with the accurate quantal rate coefficient data at all of the temperatures studied for most of the VTST methods employed. The TST and ICVT results are identical up to 1000 K, and deviate somewhat at the higher temperatures. The TST, ICVT, and ICVT/ZCT results all show somewhat poorer agreement with the accurate data than the other ICVT/MT calculations which we now consider. At temperatures above 300 K, the ICVT/LAT results show the best agreement with that accurate data. The ICVT/LCT and ICVT/μOMT results show similar although slightly poorer agreement over the same temperature range. At 300 K and below, the ICVT/μOMT results show the best agreement with the accurate data. The ICVT/LAT results show larger deviations from the accurate data at 300 K and below, with a factor of 1.47 at 200 K. Overall, the ICVT/μOMT results show the best agreement with the accurate data, with an MUPE of 9% and an LAPE of 10%.

The results for reaction (R1) on the TK surface show slightly poorer agreement than was seen for the PK2 surface. Once again the TST, ICVT, and ICVT/ZCT results seriously underestimate the accurate data at all but the highest temperatures. The ICVT/LCT results show somewhat better agreement with the accurate data, with factors rising from 0.44 at 200 K to 1.03 at 1000 K. The ICVT/SCT results show better agreement with the accurate data but reverse the trend seen in the LCT results, with factors dropping from 1.29 at 200 K to 0.94 at 600 K and back up to 0.98 at 1000 K. The ICVT/LAT and ICVT/μOMT results are identical above the 300 K, and the ICVT/μOMT results are more accurate at temperatures of 300 K and below. All VTST results are in good agreement with the ICVT/LAT results at the two highest temperatures with the TST, ICVT, ICVT/ZCT, and ICVT/SCT calculations showing the greatest discrepancies. Overall, the ICVT/SCT yield the best results with an MUPE of 13% and LAPE of 12%.

We conclude the study of reaction (R1) in this section with results from the LSTH potential energy surface. As seen previously, the TST, ICVT, and ICVT/ZCT results yield poor agreement with the accurate data at lower temperatures but are in good agreement good agreement at the highest temperatures.

Table 3: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R1), H + HH′ → HH + H′, on the PK2 potential energy surface.[a]

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	9.38(−1)[b]	0.02	0.02	0.16	0.91	0.82	1.06	1.47
250	7.26	0.06	0.06	0.22	0.82	0.86	0.98	1.25
300	3.15(1)	0.12	0.12	0.28	0.77	0.85	0.93	1.11
400	2.22(2)	0.23	0.23	0.38	0.72	0.83	0.86	0.97
600	1.83(3)	0.41	0.41	0.51	0.71	0.81	0.82	0.88
1000	1.15(4)	0.64	0.62	0.67	0.76	0.85	0.85	0.88
1500	3.19(4)	0.83	0.75	0.78	0.83	0.90	0.90	0.91
2400	7.30(4)	1.10	0.91	0.92	0.94	0.99	1.00	1.01

[a] All TST, ICVT, and ICVT/MT results in Tables 3–77 include WKB anharmonicity for stretching vibrations and centrifugal oscillator anharmonicity for bending vibrations.

[b] Values in parentheses denote multiplicative powers of ten.

Table 4: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R1), H + HH → HH + H, on the TK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.07(−1)	0.03	0.03	0.09	1.29	0.44	1.30	1.60
250	1.19	0.16	0.16	0.28	1.26	0.78	1.28	1.39
300	5.87	0.30	0.30	0.43	1.14	0.91	1.19	1.22
400	5.93(1)	0.50	0.50	0.60	1.00	0.96	1.07	1.07
600	7.53(2)	0.70	0.70	0.76	0.94	0.98	1.01	1.01
1000	6.84(3)	0.88	0.88	0.90	0.98	1.03	1.04	1.04
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	2.27(4)	1.04	0.91	0.92	0.95	0.99	1.00	1.00
2400	6.26(4)	1.22	0.95	0.95	0.97	1.00	1.00	1.00

The ICVT/LCT results underestimate the accurate rate coefficient at all but the highest temperature considered. The ICVT/SCT results exceed the accurate data at the lowest two temperatures and at the highest temperature, and are generally more accurate the LCT results. The ICVT/LAT and ICVT/μOMT results have similar

Table 5: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R1), H + HH′ → HH + H′, on the LSTH potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	6.20(−2)	0.08	0.08	0.21	1.25	0.75	1.29	1.50
250	7.72(−1)	0.19	0.19	0.33	1.05	0.85	1.10	1.22
300	4.81	0.29	0.29	0.42	0.96	0.88	1.02	1.08
400	5.46(1)	0.45	0.45	0.55	0.88	0.89	0.95	0.98
600	7.26(2)	0.64	0.64	0.70	0.86	0.91	0.93	0.95
1000	6.68(3)	0.84	0.84	0.87	0.93	0.99	1.00	1.00
1500	2.22(4)	1.00	0.89	0.91	0.94	0.98	0.99	0.99
2400	5.84(4)	1.25	1.01	1.02	1.03	1.07	1.07	1.07

accuracy except at the lowest temperatures where the μOMT results are more accurate. Overall, the ICVT/μOMT results are the most accurate with an MUPE of 8% and LAPE of 7%.

A very interesting reaction to study is an isotopic analog of reaction (R1) involving the substitution of muonium for one of the hydrogens,

$$\mathrm{Mu} + \mathrm{HH'} \rightarrow \mathrm{MuH} + \mathrm{H'} \qquad \text{(R2)}$$

Muonium is composed of a muon and an electron and has a mass nearly 1/9 that of hydrogen, in particular 207.81 amu. Due to the extremely small mass of muonium, the treatment of tunneling is expected to play a critical role in the accuracy of the VTST results. Accurate quantal results for reaction (R2) have only been computed for the LSTH surface,[49] and previous comparisons to these results are given in Refs 31, 49, and 52. The results of the present chapter are given in Table 6.

The results for reaction (R2) on the LSTH surface show good agreement with the accurate data for many of the VTST methods used. The TST results are in very poor agreement with the accurate data, even at the highest temperature where the results are only reliable to slightly better than a factor of two. The ICVT results show a remarkable improvement over the TST results, with perfect agreement with the accurate rate coefficient at the highest temperature, and results within a factor of two down to 400 K. The ICVT/ZCT results are in excellent agreement with the accurate data. At 300 K and above, the results are accurate within 2%, and at the lowest temperature, 200 K, the ZCT results compare to the accurate results with a factor of 0.86. The remaining results show very good agreement, although not quite as good as the ZCT results. The SCT and μOMT results agree well with one another, and are in very good agreement with the accurate data at all but the lowest temperatures. The LCT and LAT results give results which are nearly as good as the ZCT results, and are in excellent agreement with the accurate data at all but the lowest temperature. The ZCT results have both MUPE and LAPE equal to 3%.

Another interesting reaction involving muonium is the isotopic analog of reaction (R2),

$$\mathrm{Mu} + \mathrm{DD}' \rightarrow \mathrm{MuD} + \mathrm{D}' \qquad \text{(R3)}$$

Deuterium has a mass which is 17.7 times that of muonium, and again we expect the isotope to be large with commensurate importance placed on the accuracy of the tunneling calculations in the approximate results. Reaction (R3) has been studied via accurate quantum mechanical methods on the PK2 and LSTH potential energy surfaces.[49] Comparisons of the accurate results to the more approximate VTST calculations are reported in Refs 31 and 49 for the PK2 surface and in Refs 31, 49, and 52 for the LSTH surface. The results of the present study are given in Tables 7 and 8 for the PK2 and LSTH surfaces respectively.

The results of calculations of reaction (R3) on the PK2 surface show that the VTST/MT results are in very good agreement with the accurate data. The TST results are quite poor for this reaction, and only agree with the accurate rate coefficient within a factor of two at the highest temperature. The ICVT results are much better when compared to the accurate data, with perfect agreement at the highest temperature, but with discrepancies increasing with decreasing temperature. The inclusion of tunneling corrections brings the ICVT/MT results into very good agreement with the accurate data. The ICVT/ZCT results tend to underestimate the accurate data at all but the endpoints of the temperature range. The SCT and μOMT results are nearly identical, and give comparable or better agreement with the accurate data than the ZCT at all but the lowest temperature. The LCT and LAT results are indistinguishable, and give results comparable in accuracy to the other ICVT/MT methods at temperatures above 300 K. Agreement below 300 K for these methods is somewhat poorer, although still reasonable. Overall, the ZCT method yields the lowest MUPE, 8%. However, the ZCT, SCT, and μOMT methods all yield an LAPE of 9%.

The results for reaction (R3) on the LSTH potential energy surface are similar in agreement to those of the PK2 surface. The TST results are again in very poor agreement and overestimate the accurate rate coefficient by more than a factor of two at the highest temperature. The ICVT results are in much better agreement with the accurate rate coefficient, with nearly perfect agreement at the highest temperature. Inclusion of corrections due to tunneling again bring the ICVT/MT results into very good agreement with the accurate data. The ZCT results agree with the accurate data within 2% at all but the lowest temperature. The SCT, LCT, LAT, and μOMT methods also show agreement with the accurate data within about 2% above 300 K with somewhat larger discrepancies at the lower temperatures. Overall, the ZCT method yields the lowest MUPE, 3%, and the lowest LAPE, also 3%.

Table 6: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R2), Mu + HH → MuH + H, on the LSTH potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.97(−7)	41.75	0.05	0.86	1.40	0.77	1.40	0.77
250	3.96(−5)	36.68	0.18	0.95	1.27	0.94	1.27	0.94
300	1.29(−3)	27.42	0.32	1.00	1.19	1.01	1.20	1.01
400	1.28(−1)	15.40	0.55	1.02	1.11	1.03	1.12	1.03
600	1.62(1)	7.19	0.78	1.02	1.06	1.03	1.06	1.03
1000	9.55(2)	3.50	0.92	1.01	1.02	1.02	1.03	1.02
1500	8.06(3)	2.39	0.97	1.01	1.01	1.01	1.02	1.01
2400	4.15(4)	1.87	1.00	1.01	1.02	1.01	1.02	1.01

Table 7: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R3), Mu + DD → MuD + D, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	8.54(−9)	411.80	0.21	1.00	1.17	0.72	1.17	0.72
250	3.54(−6)	149.34	0.34	0.86	0.92	0.77	0.92	0.77
300	2.11(−4)	72.03	0.45	0.84	0.87	0.80	0.88	0.80
400	3.80(−2)	27.43	0.61	0.86	0.87	0.85	0.88	0.85
600	7.80	9.72	0.77	0.89	0.90	0.89	0.90	0.89
1000	6.20(2)	4.10	0.90	0.94	0.95	0.94	0.95	0.94
1500	5.90(3)	2.63	0.94	0.96	0.96	0.96	0.96	0.96
2400	3.10(4)	2.04	1.00	1.01	1.01	1.01	1.01	1.01

Other isotopic analogs of reaction (R1) which have been studied with accurate quantum mechanical methods are the reactions

$$\mathrm{D} + \mathrm{HH}' \rightarrow \mathrm{DH} + \mathrm{H}' \tag{R4}$$

$$\mathrm{H} + \mathrm{DD}' \rightarrow \mathrm{HD} + \mathrm{D}' \tag{R5}$$

$$\mathrm{D} + \mathrm{DD}' \rightarrow \mathrm{DD} + \mathrm{D}' \tag{R6}$$

$$\mathrm{T} + \mathrm{HD} \rightarrow \mathrm{TH} + \mathrm{D} \tag{R7}$$

It should be noted that in reaction (R1) – (R6) which contain identical atoms, one must consider quantum mechanical particle permutation symmetry when computing rate coefficients.[53,54] (This is also true for the remainder of the reactions in this

Table 8: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R3), Mu + DD $\rightarrow$ MuD + D, on the LSTH potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.30(–9)	559.01	0.19	1.19	1.56	0.84	1.56	0.84
250	6.90(–7)	217.01	0.37	1.01	1.13	0.93	1.13	0.93
300	5.10(–5)	104.16	0.51	0.99	1.05	0.96	1.05	0.96
400	1.27(–2)	37.31	0.69	0.99	1.01	0.98	1.02	0.98
600	3.70	12.11	0.85	0.99	1.00	0.99	1.00	0.99
1000	4.00(2)	4.63	0.94	0.99	0.99	0.99	1.00	0.99
1500	4.40(3)	2.85	0.97	0.99	0.99	0.99	0.99	0.99
2400	2.60(4)	2.12	1.01	1.02	1.02	1.02	1.02	1.02

paper which contain identical atoms.) However, it has been found by Schatz and Kuppermann[45] for reaction (R1) that the differences in treating identical atoms as distinguishable or indistinguishable had a very small effect on the rate coefficients. Thus most accurate quantum mechanical calculations of rate coefficients will assume distinguishable identical atoms without a significant effect on the computed rate coefficients.

Reactions (R4) – (R6) have been studied on the TK potential energy surface via accurate quantal methods, and these results may be found in Ref 47 for all reactions. Previous comparisons of these results to more approximate methods have been made and are given in Refs 8, 10, 28 and 50 for reaction (R4), in Refs 8 and 10 for reaction (R5), and in Refs 8, 10, 20, 28, and 50–52 for reaction (R6). Results of this study are given in Table 9 for reaction (R4), in Table 10 for reaction (R5), and in Table 11 for reaction (R6). Finally we consider reaction (R7), which is the only reaction of the isotopic analogs of reaction (R1) which does not involve particle permutation symmetry. Accurate quantum mechanical results for this reaction are reported in Ref. 55, and comparison is made to more approximate methods in Refs. 27, 31, and 55. The results of the present study are given in Table 12.

First we will consider the results of calculations of reaction (R4) on the TK surface. The TST, ICVT, and ICVT/ZCT results are poor at the lower temperatures compared to the accurate rate coefficients, and yield reasonable results at the highest temperatures. The ICVT/LCT results are accurate within a factor of two at the lowest temperature, and their accuracy improves with increasing temperature. The SCT results are in somewhat better agreement with the accurate data, especially at the lower temperatures. The LAT method gives excellent agreement with the accurate quantal rate coefficient at all temperatures except the lowest where the accurate rate coefficient is overestimated by about 40%. The μOMT results give excellent accuracy at all temperatures with a maximum discrepancy of about 11%. The μOMT results are the best overall with an MUPE and LAPE of 4%. All ICVT and ICVT/MT results are in good agreement with the ICVT/LAT result at 2400 K, while the TST results is somewhat higher.

The ICVT/LAT results for reaction (R5) on the TK surface show excellent agreement with the accurate quantal data at all but the lowest temperature. The TST and ICVT results are again poor at the lower temperatures and in good agreement with the accurate data at the higher temperatures. The ZCT results give somewhat better agreement with the accurate data than the TST or ICVT results, particularly at the lowest temperatures. The SCT and μOMT results are surprisingly poor for this reaction, with discrepancies over a factor of two at the lowest temperature, but with very good agreement with the accurate data at the highest temperatures. The LAT results show excellent agreement at all but the lowest temperature. The LCT results show slightly poorer agreement with the accurate rate coefficients, but the agreement is improved at the lowest temperature. All ICVT and ICVT/MT results are in excellent agreement with the LAT results at 2400 K where the TST result is somewhat too large. Overall, the LCT method yields the best results with an MUPE of 9% and an LAPE of 10%.

The results for reaction (R6) on the TK surface show trends similar to those in the previous paragraph. The TST, ICVT, and ICVT/ZCT results are poor compared to the accurate data at the lower temperatures, but give good agreement at the higher temperatures. The SCT and μOMT yield very similar results and show discrepancies of a little less than a factor of two at the lowest temperature although the results are in good agreement with the accurate rate coefficients at 300 K and above. The LAT results show excellent agreement at all but the lowest temperature where the factor is 1.51. The LCT results show accuracy comparable to the LAT results with improved accuracy at the lowest temperature. Again, the ICVT results agree well with the LAT result at 2400 K and the TST result is somewhat too large. The LCT results are again the most accurate with an MUPE of 5% and an LAPE of 6%.

Finally, we consider the results of calculations of reaction (R7) using the LSTH potential energy surface. The TST and ICVT results are similar at the lowest temperatures, but the TST results give much poorer agreement with the accurate data at the highest temperatures. The ICVT/ZCT results improve the agreement with the accurate rate coefficients only slightly over that of the ICVT results. Of the methods remaining to be considered, all overestimate the accurate rate coefficients at the highest two temperatures. The LAT results are the most accurate at all but the lowest temperatures. The LCT and μOMT results are only slightly worse, but give an better estimate of the rate coefficient at the lowest temperatures. In most cases the ICVT/μOMT results are superior to the LCT results. The SCT results give

Table 9: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R4), D + HH → DH + H, on the TK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.14(–1)	0.07	0.05	0.13	1.10	0.53	1.11	1.41
250	1.58	0.22	0.17	0.29	0.99	0.73	1.02	1.13
300	7.24	0.39	0.32	0.45	1.00	0.88	1.05	1.10
400	6.82(1)	0.59	0.50	0.60	0.93	0.92	0.99	1.00
600	7.61(2)	0.80	0.70	0.76	0.92	0.96	0.99	0.99
1000	6.31(3)	0.99	0.85	0.87	0.93	0.98	0.99	0.99
1500	1.89(4)	1.23	0.97	0.99	1.01	1.06	1.06	1.06

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	5.35(4)	1.38	0.95	0.96	0.97	1.00	1.00	1.00

Table 10: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R5), H + DD → HD + D, on the TK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.27(–3)	0.14	0.12	0.34	2.11	0.84	2.11	1.58
250	3.23(–2)	0.31	0.27	0.50	1.41	0.86	1.43	1.06
300	3.17(–1)	0.47	0.42	0.63	1.25	0.91	1.28	0.99
400	6.93	0.65	0.60	0.75	1.07	0.91	1.11	0.93
600	1.75(2)	0.84	0.78	0.86	1.01	0.95	1.05	0.95
1000	2.73(3)	1.01	0.90	0.94	0.99	0.98	1.03	0.98
1500	1.11(4)	1.22	1.02	1.04	1.06	1.06	1.10	1.06

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	3.93(4)	1.30	0.98	0.99	0.99	1.00	1.02	1.00

good agreement over the entire temperature range, but are not as good as some of the other ICVT/MT results except at the highest temperatures. Overall the μOMT

Table 11: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R6), D + DD → DD + D, on the TK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.68(−3)	0.15	0.15	0.35	1.82	0.94	1.83	1.51
250	6.19(−2)	0.30	0.30	0.49	1.33	0.92	1.36	1.10
300	5.54(−1)	0.43	0.43	0.61	1.19	0.94	1.22	1.02
400	1.02(1)	0.60	0.60	0.72	1.04	0.92	1.08	0.95
600	2.14(2)	0.78	0.78	0.85	1.00	0.96	1.05	0.97
1000	2.86(3)	0.98	0.98	1.01	1.07	1.07	1.12	1.07
1500	1.16(4)	1.14	0.95	0.96	0.99	1.00	1.02	1.00

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	3.77(4)	1.30	0.97	0.98	0.99	1.00	1.01	1.00

Table 12: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R7), T + HD → TH + D, on the LSTH potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.38(−2)	0.16	0.16	0.25	0.79	0.88	0.95	1.24
250	5.11(−1)	0.29	0.28	0.37	0.77	0.92	0.95	1.11
300	3.41	0.39	0.38	0.46	0.77	0.93	0.95	1.05
400	4.00(1)	0.54	0.53	0.58	0.78	0.94	0.95	1.00
600	5.22(2)	0.74	0.70	0.73	0.83	0.97	0.97	1.00
1000	4.51(3)	1.03	0.88	0.89	0.93	1.03	1.04	1.05
1500	1.38(4)	1.37	1.03	1.04	1.06	1.14	1.14	1.15
2400	3.21(4)	1.99	1.29	1.29	1.30	1.37	1.37	1.37

results are in the best agreement with the accurate data, yielding an MUPE of 10% and an LAPE of 9%.

5.1.2 Collinear H_2O Reactions

In this subsection we consider only one reaction, namely,

$$\mathrm{O} + \mathrm{HH'} \rightarrow \mathrm{OH} + \mathrm{H'} \qquad \text{(R8)}$$

on five different potential energy surfaces for which accurate one-dimensional quantum mechanical data is available. Specifically the JW potential energy surface of Johnson and Winter,[56] the ModPolCI surface,[57] the DIM–RMOS surface,[58–60] the PolCI surface,[61] and the surface due to Schinke and Lester[62] hereafter called the SL surface. The JW surface is a LEPS-type surface.[63,64] The PolCI and ModPolCI surfaces are rotated-Morse-oscillator-spline-type (RMOS) surfaces[60] based on *ab initio* data.[61,65–68] The DIM–RMOS surface is also of the RMOS type, but was fit to the diatomics-in-molecules[69] (DIM) surface of Whitlock *et al.*[58,59] The SL surface is fit to the *ab initio* calculations of Howard, McLean, and Lester.[70] Accurate quantum mechanical calculations for these five surfaces are given in a four-article series by Bowman, Wagner, and coworkers.[57,61,65,71] Comparisons of the accurate quantum mechanical rate coefficients to VTST calculations have been given previously for the JW surface in Refs 20, 72, and 73, for the ModPolCI surface in Refs 31, 72, and 73, for the DIM–RMOS surface in Refs 72 and 73, for the PolCI surface in Ref 72, and for the SL surface in Ref 72. The one-dimensional results of the present study for reaction (R8) are given in Table 13 for the JW surface, in Table 14 for the ModPolCI surface, in Table 15 for the DIM–RMOS surface, in Table 16 for the PolCI surface, and Table 17 for the SL surface.

We first consider the results for reaction (R8) on the JW potential energy surface. The TST, ICVT, and ICVT/ZCT methods all yield results in poor agreement with the accurate data at all but the highest temperatures. The SCT results are in good agreement with the accurate data at all temperatures, but tend to underestimate the accurate rate coefficient. The LCT results also underestimate the accurate rate coefficient, but are closer to the accurate data in all cases. The LAT results yield agreement with the accurate data similar or superior to the LCT results at all but the lowest temperature. The μOMT results are comparable to the LCT results but yield the best results at the lowest temperatures. The μOMT results are the best overall with an MUPE of 10% and an LAPE of 12%. All ICVT and ICVT/MT results are in good agreement with the ICVT/LAT result at 2400 K and the TST result is too large.

The results for reaction (R8) on the ModPolCI surface are in reasonable agreement with the accurate data, although the agreement is poorer than that seen for the previous surface. The TST, ICVT, and ICVT/ZCT methods all severely underestimate the accurate rate coefficient at the lower temperatures and overestimate the accurate rate coefficient at higher temperatures. The best agreement with the accurate data is seen around 600 K for these methods. All of the remaining ICVT/MT methods, SCT, LCT, LAT, and μOMT overestimate the accurate rate coefficient at the highest temperature by 55–70%. At the lowest temperatures, the LCT results are accurate within a factor of two, but the agreement of the SCT, LAT, and μOMT with the accurate data is much better. At 2400 K, the ICVT and

Table 13: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH → OH + H, on the JW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.25(−3)	0.02	0.02	0.10	0.75	0.87	0.94	1.30
250	3.13(−2)	0.05	0.05	0.17	0.72	0.88	0.91	1.10
300	2.95(−1)	0.11	0.11	0.24	0.71	0.88	0.90	1.01
400	5.75	0.22	0.22	0.35	0.70	0.85	0.85	0.90
600	1.33(2)	0.42	0.41	0.50	0.71	0.83	0.83	0.85
1000	1.92(3)	0.71	0.64	0.68	0.78	0.87	0.87	0.88
1500	7.84(3)	1.01	0.81	0.84	0.89	0.97	0.97	0.97

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	2.69(4)	1.31	0.91	0.92	0.94	1.00	1.00	1.00

ICVT/MT results are in good agreement with the ICVT/LAT result and the TST result is larger. The LAT results are the best overall with an MUPE of 25% and an LAPE of 26%.

The agreement of VTST/MT calculations for reaction (R8) on the DIM–RMOS surface show rather poor agreement with the accurate rate coefficients. The TST and all ICVT methods exceed the accurate data by a factor of three or more at 1500 K. The TST, ICVT, and ICVT/ZCT methods underestimate the accurate rate coefficient at the lowest temperatures. The SCT and μOMT results are too large compared to the accurate data at the lowest temperature by about a factor of two. The LCT and LAT results show good agreement with the accurate rate coefficient at 300 K and below, but become too large at higher temperatures. As expected, the agreement of the ICVT and ICVT/MT results with the ICVT/LAT result at 2400 K is good with the TST results being somewhat too large. The best results overall are the LAT results with an MUPE of 75% and an LAPE of 63%.

The results for reaction (R8) on the PolCI surface are better than for the previous surface. The TST and ICVT results seriously underestimate the accurate rate coefficient at the lower temperatures, but eventually yield reasonable agreement at the highest temperatures. The ZCT results improve the low-temperature agreement of the ICVT results with the accurate data but are slightly larger for the higher temperatures. The SCT and μOMT results overestimate the accurate rate coefficient at all temperatures. The LCT results underestimate the accurate data by about a factor of two at the lowest temperature but overestimate the accurate data

Table 14: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH → OH + H, on the ModPolCI potential energy surface.

				ICVT	ICVT	ICVT	ICVT	ICVT
T (K)	Accurate	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT
200	1.09(−3)	0.01	0.01	0.08	0.94	0.54	0.95	1.02
250	1.57(−2)	0.05	0.04	0.18	1.05	0.56	1.06	0.80
300	1.11(−1)	0.16	0.12	0.33	1.19	0.63	1.21	0.77
400	1.75	0.47	0.38	0.64	1.37	0.84	1.41	0.89
600	4.10(1)	1.01	0.87	1.08	1.52	1.17	1.60	1.19
1000	7.32(2)	1.54	1.29	1.39	1.58	1.43	1.66	1.43
1500	3.60(3)	1.90	1.48	1.53	1.62	1.55	1.70	1.56
2400	2.22(4)	1.41	0.98	0.99	1.01	1.00	1.05	1.00

Table 15: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH → OH + H, on the DIM–RMOS potential energy surface.

				ICVT	ICVT	ICVT	ICVT	ICVT
T (K)	Accurate	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT
200	2.53(−5)	0.06	0.03	0.39	2.09	0.83	2.09	0.85
250	7.96(−4)	0.24	0.16	0.67	2.26	1.01	2.27	1.01
300	9.59(−3)	0.55	0.38	0.98	2.41	1.24	2.44	1.24
400	3.02(−1)	1.10	0.84	1.38	2.37	1.53	2.44	1.53
600	1.39(1)	1.62	1.34	1.65	2.13	1.72	2.22	1.72
1000	2.78(2)	2.77	2.31	2.49	2.73	2.52	2.86	2.52
1500	1.40(3)	3.74	2.98	3.08	3.21	3.10	3.34	3.10

	ICVT			ICVT	ICVT	ICVT	ICVT	ICVT
T (K)	/LAT	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT
2400	1.95(4)	1.33	0.98	1.00	1.01	1.00	1.04	1.00

with a factor of 1.27 at the highest temperature. The LAT results are very similar to the LCT results above 300 K, but dramatically improve the agreement with the accurate data at low temperature. At 2400 K, the ICVT and ICVT/MT results agree

Table 16: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH → OH + H, on the PolCI potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.36(–3)	0.01	0.005	0.08	1.20	0.49	1.22	0.94
250	1.61(–2)	0.06	0.04	0.20	1.30	0.58	1.32	0.77
300	1.07(–1)	0.17	0.13	0.38	1.43	0.69	1.45	0.78
400	1.79	0.48	0.39	0.67	1.46	0.86	1.50	0.88
600	4.07(1)	1.05	0.90	1.13	1.61	1.23	1.69	1.23
1000	8.94(2)	1.28	1.08	1.17	1.33	1.20	1.40	1.20
1500	4.47(3)	1.55	1.21	1.26	1.33	1.27	1.39	1.27

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	2.25(4)	1.41	0.98	0.99	1.02	1.00	1.05	1.00

Table 17: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH → OH + H, on the SL potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.88(–4)	0.004	0.004	0.09	2.05	1.38	2.05	2.56
250	4.82(–3)	0.03	0.02	0.15	1.47	1.06	1.47	1.48
300	4.91(–2)	0.07	0.06	0.24	1.28	0.92	1.29	1.11
400	1.18	0.21	0.19	0.40	1.09	0.80	1.11	0.86
600	3.87(1)	0.48	0.45	0.61	0.99	0.81	1.03	0.82
1000	8.22(2)	0.86	0.75	0.84	1.00	0.92	1.05	0.92
1500	4.24(3)	1.21	0.96	1.01	1.09	1.06	1.15	1.06

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	1.96(4)	1.37	0.96	0.98	1.01	1.00	1.05	1.00

well with the ICVT/LAT results and the TST results are too large. Overall the LAT results are the most reliable with an MUPE of 19% and an LAPE of 21%.

The final case of reaction (R8) uses the SL potential energy surface. The TST, ICVT, and ICVT/ZCT results for this reaction are in poor agreement with the accurate quantal rate coefficient data at the lower temperatures where they underestimate the accurate rate coefficient, sometimes severely, but agreement improves at the higher temperatures. The SCT and μOMT results are similar and overestimate the accurate data by about a factor of two at the lowest temperature and come into good agreement above 300 K. The LAT results agree well with the accurate data at higher temperatures, but overestimate the accurate rate coefficient at lower temperatures with a maximum factor of 2.6 at 200 K. The LCT results give accuracy comparable to the LAT results at higher temperatures, but give improved agreement with the accurate data at low temperature. As might be expected, the ICVT and ICVT/MT data agree well with the ICVT/LAT data at 2400 K where the TST result is somewhat larger. The LCT results are the best overall with an MUPE value of 15% and an LAPE value of 16%.

5.1.3 Collinear H_2F Reactions

In this subsection we study two different reaction types, each involving two isotopic variants. The first of these is the abstraction reaction

$$\mathrm{F} + \mathrm{HH'} \rightarrow \mathrm{FH} + \mathrm{H'} \qquad \text{(R9)}$$

and its isotopic analog

$$\mathrm{F} + \mathrm{DD'} \rightarrow \mathrm{FD} + \mathrm{D'} \qquad \text{(R10)}$$

These reactions were studied using potential energy surface number 5 of Muckerman.[74] Accurate quantum mechanical rate coefficients were calculated by Schatz *et al.* for both reactions (R9)[75] and (R10).[76] Accurate quantum mechanical rate coefficients for reaction (R9) were also computed by one of the authors and coworkers.[77] The two sets of results for reaction (R9) were found to be in good agreement.[77] Previous comparisons of the accurate quantum mechanical rate coefficients to the results of VTST calculations are given in Refs 27, 50, and 77 for reaction (R9) and in Refs 50 and 77 for reaction (R10). Rate coefficients calculated in the present study are given in Table 18 for reaction (R9) and in Table 19 for reaction (R10).

VTST results for reaction (R9) on the M5 surface exceed the accurate rate coefficient data at all temperatures. The TST results show the poorest agreement, overestimating the accurate rate coefficients by factors ranging from 3.2 to 4.4. All ICVT results yield similar results, overestimating the accurate rate coefficients by factors ranging from 1.4 to 2.6. At the two highest temperatures, all of the ICVT and ICVT/MT data is in nearly perfect agreement with the ICVT/LAT data and the TST data is in good agreement as well although it is a little too large. The best

Table 18: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R9), F + HH → FH + H, on the M5 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.99(3)	4.37	1.53	1.66	1.66	1.66	1.66	1.66
250	7.48(3)	4.22	1.82	1.92	1.92	1.92	1.92	1.92
300	8.86(3)	4.10	2.04	2.11	2.11	2.11	2.11	2.11
400	1.15(4)	3.88	2.30	2.35	2.35	2.35	2.35	2.35
600	1.66(4)	3.51	2.47	2.50	2.50	2.50	2.50	2.50
1000	2.51(4)	3.16	2.55	2.56	2.56	2.56	2.56	2.56

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	8.66(4)	1.16	1.00	1.00	1.00	1.00	1.00	1.00
2400	1.18(5)	1.12	1.00	1.00	1.00	1.00	1.00	1.00

overall method is ICVT with an MUPE value of 112% and an LAPE value of 109%. The values for ICVT/MT methods are slightly larger.

The agreement for reaction (R10) on the M5 surface is much better than for the previous reaction. Again tunneling effects seem unimportant, and the ICVT results are slightly better than the ICVT/MT results. The TST data exceed the accurate results at all temperatures and their ratio to the accurate data decreases as temperature increases (unlike the ICVT and ICVT/MT results whose ratio to the accurate data increases with temperature). Nevertheless, the TST data are accurate within less than a factor of two. The ICVT and ICVT/MT results all overestimate the accurate rate coefficient by 2–51%. Agreement with the ICVT/LAT data at the two highest temperatures is very good for all methods. The best overall method is again the ICVT method with an MUPE value of 24% and an LAPE value of 23%. The ICVT/MT methods have slightly larger values.

The exchange reactions

$$\text{H} + \text{FH}' \rightarrow \text{HF} + \text{H}' \tag{R11}$$

and

$$\text{D} + \text{FD}' \rightarrow \text{DF} + \text{D}' \tag{R12}$$

were studied on the potential energy surface of Schatz and Kuppermann,[78] hereafter referred to as the SK surface, which is very similar to surface number 5 of Muckerman. Accurate quantum mechanical calculations of the rate coefficient for both reactions (R11) and (R12) are given in Ref 79. Refs 31 and 79 compare the

Table 19: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R10), F + DD → FD + D, on the M5 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.13(3)	1.77	1.02	1.09	1.09	1.09	1.09	1.09
250	7.36(3)	1.73	1.12	1.16	1.16	1.16	1.16	1.16
300	9.53(3)	1.70	1.18	1.21	1.21	1.22	1.22	1.22
400	1.36(4)	1.66	1.27	1.29	1.29	1.29	1.29	1.29
600	2.07(4)	1.62	1.35	1.36	1.36	1.36	1.36	1.36
1000	3.00(4)	1.69	1.51	1.51	1.51	1.51	1.51	1.51

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	6.22(4)	1.09	1.00	1.00	1.00	1.00	1.00	1.00
2400	8.59(4)	1.08	1.00	1.00	1.00	1.00	1.00	1.00

accurate rate coefficients to VTST results. The VTST results of this chapter are given in Table 20 for reaction (R11) and in Table 21 for reaction (R12).

The VTST results for reaction (R11) on the SK potential energy surface exceed the accurate quantum mechanical rate coefficients over the entire temperature range considered. The TST results show the poorest agreement with ratios to the accurate data ranging from 2.5 at 200 K to 1.2 at 2400 K. The ICVT results show the best agreement with the accurate data, being too large by factors ranging from 1.5 at 200 K to 1.1 at 2400 K. The ICVT/MT results show slightly worse agreement at lower temperatures and nearly identical agreement to that of the ICVT results at higher temperatures. Overall the ICVT results are the most reliable, with an MUPE of 36% and an LAPE value of 35%. The ICVT/MT methods give results which are slightly larger.

The results for reaction (R12) on the SK surface are in slightly better agreement with the accurate data than in the previous reaction. The TST results give the poorest agreement with the accurate data, but are within a factor of two at all temperatures with much better agreement at the higher temperatures. The ICVT results again show the best agreement with the accurate data, particularly at lower temperatures. At higher temperatures the ICVT results and the ICVT/MT results are nearly indistinguishable. The ICVT results are the best overall with an MUPE of 21% and an LAPE of 20%. The ICVT/MT methods yield slightly larger MUPE and LAPE values.

Table 20: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R11), H + FH → HF + H, on the SK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.51(3)	2.53	1.51	1.64	1.65	1.64	1.65	1.81
250	3.02(3)	2.39	1.58	1.66	1.67	1.67	1.67	1.80
300	5.20(3)	2.15	1.53	1.58	1.59	1.59	1.59	1.69
400	1.08(4)	1.85	1.43	1.46	1.46	1.46	1.47	1.53
600	2.43(4)	1.56	1.32	1.33	1.33	1.33	1.33	1.37
1000	5.22(4)	1.34	1.20	1.21	1.21	1.21	1.21	1.23
1500	8.24(4)	1.25	1.15	1.15	1.15	1.15	1.16	1.17
2400	1.25(5)	1.21	1.13	1.13	1.13	1.13	1.13	1.14

Table 21: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R12), D + FD → DF + D, on the SK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	9.33(2)	1.91	1.39	1.45	1.46	1.46	1.46	1.51
250	2.12(3)	1.73	1.34	1.38	1.39	1.38	1.39	1.43
300	3.77(3)	1.61	1.30	1.32	1.33	1.33	1.33	1.36
400	8.07(3)	1.44	1.23	1.24	1.24	1.24	1.25	1.27
600	1.84(4)	1.29	1.16	1.16	1.17	1.17	1.17	1.18
1000	3.90(4)	1.19	1.11	1.11	1.11	1.11	1.11	1.12
1500	6.05(4)	1.17	1.10	1.11	1.11	1.11	1.11	1.11
2400	9.90(4)	1.08	1.02	1.02	1.02	1.02	1.02	1.02

5.1.4 Collinear H_2Cl Reactions

Another important reaction in the study of chemical dynamics is

$$\mathrm{Cl + HH' \rightarrow ClH + H'} \qquad \text{(R13)}$$

Details of the rich history of this important reaction are given in Ref 80. In this subsection we examine reaction (R13) and four of its isotopic analogs

$$\mathrm{Cl + HD \rightarrow ClH + D} \qquad \text{(R14)}$$

$$\mathrm{Cl + DH \rightarrow ClD + H} \qquad \text{(R15)}$$

$$\mathrm{Cl + DD' \rightarrow ClD + D'} \qquad \text{(R16)}$$

$$\mathrm{Cl + TT' \rightarrow ClT + T'} \qquad \text{(R17)}$$

All of these reactions, (R13) – (R17), are studied using the GSW potential energy surface of Stern, Persky, and Klein,[57] hereafter denoted SPK/GSW. (It should be noted that some older publications refer to the SPK/GSW surface as the Baer surface,[72] and others refer to it as the SPK surface). Of the five reactions in this section, reaction (R17) is perhaps the most interesting in terms of its mass combination. Of all the H_2X (X = H, D, T, O, F, Cl, Br, I) systems reviewed in this chapter, reaction (R17) has the largest mass of hydrogen isotopes. Since tritium has a mass three times that of hydrogen, we expect that the importance of tunneling contributions to on overall VTST/MT rate coefficient will be small. Therefore the calculations of the rate coefficients of reaction (R17) will provide a more sensitive test of the VTST methods used. Of course, the same will be true of reactions (R14) – (R16) and other previous reactions, but to a lesser extent. Accurate quantum mechanical rate coefficients for all five reactions, (R14) – (R17), have been given by Baer and coworkers.[84] Rate coefficient data at higher temperatures for reactions (R13) and (R17) based on the work of Persky and Baer[85] are presented in Ref 14. Comparison of these accurate results to VTST/MT calculations have been made previously in a number of papers; reaction (R13) is studied in Refs 8, 10, 20, 31, 50, and 51, reaction (R14) in Refs 8, 10, 20, 27,31, 50, 52, and 83, reaction (R15) in Refs 8, 10, 20, 27, 50, 52, and 83, reaction (R16) in Refs 8, 10, 50 and 83, and reaction (R17) in Refs 8, 10, 27, 31, 50–52, and 83. Rate coefficient calculations for the present study are given in Table 22 for reaction (R13), in Table 23 for reaction (R14), in Table 24 for reaction (R15), in Table 25 for reaction (R16), and in Table 26 for reaction (R17).

The results for reaction (R13) on the SPK/GSW surface show good agreement with the accurate quantal data. The TST and ICVT results yield results similar to one another which are too small compared to the accurate data by about a factor of five at the lowest temperature but which are in good agreement at higher temperatures. In this case, the TST calculation is too large at the highest temperature compared to the accurate rate coefficient, but the ICVT results is in nearly perfect agreement. The ICVT/ZCT results give somewhat better agreement with the accurate data than the ICVT results, particularly at lower temperatures. The SCT results are within a factor of two of the accurate results at the lowest temperature and are in good agreement with the accurate rate coefficients at the higher temperatures. The LCT and μOMT results are similar to one another and are in good agreement with the accurate results over the entire temperature range. The LAT results are in the best agreement with the accurate data over the entire temperature range considered. At 2400 K, the ICVT and ICVT/MT results are all in good agreement with the ICVT/LAT result and the TST result is too large. The best results overall are given by the LAT method which has an MUPE of 10% and an LAPE of 11%.

Table 22: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R13), Cl + HH → ClH + H, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.35(1)	0.21	0.20	0.31	0.54	0.72	0.75	0.93
250	1.45(2)	0.30	0.29	0.38	0.56	0.74	0.75	0.88
300	3.97(2)	0.38	0.37	0.44	0.58	0.75	0.76	0.86
400	1.45(3)	0.50	0.49	0.54	0.64	0.79	0.79	0.86
600	5.57(3)	0.69	0.66	0.69	0.74	0.86	0.87	0.91
1000	1.78(4)	0.98	0.84	0.86	0.88	0.97	0.97	0.99
1500	3.30(4)	1.34	1.00	1.01	1.02	1.09	1.10	1.11

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	7.09(4)	1.50	0.94	0.95	0.95	0.99	0.99	1.00

Table 23: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R14), Cl + HD → ClH + D, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.16	0.68	0.35	0.55	0.69	0.71	0.74	0.92
250	1.95(1)	0.84	0.50	0.66	0.76	0.78	0.81	0.93
300	6.76(1)	0.95	0.61	0.74	0.82	0.85	0.87	0.96
400	3.32(2)	1.12	0.79	0.88	0.94	0.96	0.98	1.03

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
600	2.03(3)	1.18	0.87	0.92	0.94	0.96	0.97	1.00
1000	9.68(3)	1.34	0.94	0.96	0.97	0.98	0.99	1.00
1500	2.38(4)	1.53	0.97	0.97	0.98	0.99	0.99	1.00
2400	5.14(4)	1.80	0.98	0.98	0.99	0.99	1.00	1.00

The results of reaction (R14) on the SPK/GSW surface show agreement to accurate data comparable to that of the previous reaction. The TST results actually show somewhat better agreement with the accurate data than do the ICVT and

Table 24: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R15), Cl + DH → ClD + H, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.19	0.21	0.20	0.38	0.88	0.85	0.95	1.03
250	2.96(1)	0.31	0.31	0.47	0.82	0.83	0.88	0.93
300	9.89(1)	0.41	0.40	0.53	0.80	0.83	0.86	0.90
400	4.77(2)	0.54	0.53	0.62	0.79	0.84	0.86	0.87

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
600	2.24(3)	0.82	0.77	0.83	0.93	0.98	0.99	1.00
1000	1.01(4)	1.05	0.89	0.91	0.95	0.99	1.00	1.00
1500	2.41(4)	1.25	0.93	0.94	0.96	1.00	1.00	1.00
2400	5.18(4)	1.50	0.96	0.97	0.97	1.00	1.00	1.00

ICVT/ZCT results, although we expect that this is largely fortuitous. The SCT, LCT, and μOMT results are comparable, and tend to underestimate the accurate data somewhat. The most accurate results are the LAT data which agree with the accurate quantal data within about 10%. At temperatures of 600 K and above, the data is compared to the ICVT/LAT data where all ICVT and ICVT/MT methods show very good agreement, and the TST results are too large. The best overall method is the ICVT/LAT method which has MUPE and LAPE values of 6%.

VTST results for reaction (R15) on the SPK/GSW surface are also in good agreement with the accurate data. The TST and ICVT results are too small at low temperatures compared to the accurate data, and the ICVT/ZCT results improve this agreement only slightly. The SCT and LCT results are comparable in the temperature range 200–400 K and give good agreement with the accurate quantal results. The μOMT results are even more accurate compared to the accurate data over the same temperature range, but the best agreement is given by the LAT results. At temperatures above 400 K, the data are compared to the ICVT/LAT data. All of the ICVT and ICVT/MT results agree well with the LAT data. The TST data is smaller than the ICVT/LAT data at 600 K, is in very good agreement at 1000 K, but is too large at the highest two temperatures. The LAT results are the most reliable for this reaction with an MUPE value of 8% and an LAPE value of 9%.

Calculations for reaction (R16) on the SPK/GSW surface are in good agreement with accurate quantum mechanical rate coefficient data, as in the previous reactions using this surface. The TST and ICVT results are quite similar to one another at

Table 25: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R16), Cl + DD → ClD + D, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	9.39(−1)	0.22	0.22	0.39	0.82	0.86	0.91	1.00
250	7.53	0.33	0.32	0.47	0.78	0.83	0.86	0.91
300	3.15(1)	0.42	0.41	0.53	0.76	0.82	0.84	0.87
400	1.98(2)	0.55	0.54	0.62	0.77	0.83	0.84	0.86
600	1.36(3)	0.75	0.69	0.74	0.82	0.87	0.88	0.89
1000	6.94(3)	1.09	0.87	0.89	0.92	0.97	0.97	0.97
1500	1.64(4)	1.47	1.04	1.05	1.07	1.11	1.11	1.11

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	4.28(4)	1.57	0.96	0.97	0.97	1.00	1.00	1.00

low temperatures, but the TST results are too large at high temperatures compared to the accurate results. The ICVT/ZCT results show improved accuracy with the accurate rate coefficients compared to the ICVT results, especially at low temperatures. The SCT results show even better agreement with the accurate data than the previously mentioned methods. The LCT and μOMT results are of comparable accuracy compared to the accurate data, with the μOMT results being more reliable at the lower temperatures. Both the LCT and μOMT methods show very good agreement with the accurate data. The best results compared to the accurate data are given by the LAT method over the entire temperature range. The ICVT and ICVT/MT results at 2400 K are in good agreement with the ICVT/LAT value, but the TST value is too large. The best method overall in the LAT method with an MUPE and an LAPE of 9%.

The final reaction considered in this series is reaction (R17) on the SPK/GSW surface. The TST and ICVT results are again similar to one another at lower temperatures, and the ICVT results yield better agreement with the accurate data at higher temperatures. The ICVT/ZCT results give improved agreement with the accurate data compared to the ICVT results, especially at lower temperatures. The LCT results are in good agreement with the accurate data, but are too small at lower temperatures. The LAT results are slightly better than the LCT results, but suffer the same discrepancies at lower temperatures. The SCT and μOMT results are of comparable accuracy, but the μOMT results are slightly more accurate at all but the highest temperature. At 2400 K, all ICVT and ICVT/MT results agree well with

Table 26: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R17), Cl + TT → ClT + T, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.54(–1)	0.27	0.27	0.46	0.94	0.79	0.96	0.87
250	1.68	0.39	0.39	0.55	0.88	0.79	0.91	0.83
300	8.66	0.49	0.48	0.61	0.86	0.79	0.89	0.82
400	7.10(1)	0.65	0.62	0.71	0.86	0.83	0.90	0.84
600	6.56(2)	0.85	0.77	0.82	0.90	0.89	0.94	0.90
1000	4.38(3)	1.17	0.92	0.94	0.97	0.98	1.01	0.98
1500	1.19(4)	1.51	1.07	1.08	1.10	1.11	1.13	1.11

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	3.37(4)	1.56	0.98	0.98	0.99	1.00	1.01	1.00

the ICVT/LAT result, and the TST results is too large. The μOMT results are the best overall with MUPE and LAPE values both equal to 8%.

5.1.5 Collinear H_2Br Reactions

In this section two exchange reactions, namely,

$$\mathrm{H + BrH' \rightarrow HBr + H'} \qquad \text{(R18)}$$

and its isotopic analog

$$\mathrm{D + BrH' \rightarrow DBr + H'} \qquad \text{(R19)}$$

Rate coefficient data for both reactions (R18) and (R19) were calculated using an optimized surface due to Clary[86] based on the DIM–3C potential energy surface of Last and Baer.[87,88] We denote this surface DIM–3C–B. Accurate quantum mechanical rate coefficient data is given in Ref 89, and comparison to previous VTST calculations is made in Refs 20, 89, and 90. The rate coefficient data of the present study is given in Table 27 for reaction (R18) and in Table 28 for reaction (R19).

We now consider the results for reaction (R18) on the DIM–3C–B surface. The TST and ICVT results are of comparable accuracy, underestimating the accurate rate coefficient at all temperatures for which the accurate data is available and most severely at the lower temperatures. The ICVT/ZCT data is more accurate compared to the accurate data than the TST and ICVT data, particularly at the lower

Table 27: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R18), H + BrH → HBr + H, on the DIM–3C–B potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.80(1)	0.03	0.03	0.45	1.83	0.86	1.83	0.89
250	1.10(2)	0.09	0.09	0.52	1.39	0.73	1.39	0.74
300	2.50(2)	0.19	0.19	0.61	1.22	0.73	1.23	0.74
400	8.90(2)	0.37	0.37	0.71	1.05	0.76	1.06	0.76
600	4.00(3)	0.62	0.62	0.82	0.97	0.84	0.99	0.84

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1000	1.57(4)	0.90	0.90	0.99	1.05	1.00	1.08	1.00
1500	3.96(4)	0.95	0.95	1.00	1.02	1.00	1.04	1.00
2400	8.98(4)	0.98	0.98	1.00	1.01	1.00	1.02	1.00

temperatures. The SCT and μOMT data are of comparable accuracy and overestimate the accurate rate coefficient at 200 K significantly, but are in good agreement at 300 K and above. The LCT and LAT results are similar to one another and underestimate the accurate rate coefficient in the temperature range 200 to 600 K, but are nevertheless in good agreement with the accurate data. The data at 1000 K and above is compared to the ICVT/LAT rate coefficients and all methods show good agreement. The best method overall is the LAT method which has an MUPE of 21% and an LAPE of 27%. The mean errors for the LCT method are slightly larger.

Agreement of the VTST data with the accurate data for reaction (R19) on the DIM–3C–B surface is similar to that seen for the previous reaction. The TST and ICVT methods yield similar results which underestimate the accurate rate coefficient, especially at lower temperatures. The ICVT/ZCT results give improved agreement with the accurate data compared to the ICVT results, particularly at lower temperatures. The LCT and LAT results are mutually indistinguishable, are of comparable accuracy, and give good agreement with the accurate data, underestimating the accurate rate coefficient in the temperature range 200 to 600 K by 7–21%. The SCT and μOMT results are similar to one another and both overestimate the accurate rate coefficient at all temperatures in the range 200–600 K. The SCT and μOMT results are the most accurate at 300 K and above, but the LCT and LAT results are more accurate temperatures below 300 K. All results at 1000 K and above show good agreement with the ICVT/LAT results. The best methods

Table 28: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R19), D + BrH $\rightarrow$ DBr + H, on the DIM–3C–B potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.30(1)	0.09	0.08	0.58	1.58	0.79	1.59	0.79
250	7.30(1)	0.22	0.21	0.69	1.33	0.79	1.34	0.79
300	1.90(2)	0.34	0.33	0.73	1.16	0.79	1.17	0.79
400	7.00(2)	0.55	0.54	0.83	1.07	0.86	1.09	0.86
600	3.20(3)	0.77	0.76	0.92	1.02	0.93	1.05	0.93

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1000	1.33(4)	0.96	0.93	1.00	1.04	1.00	1.06	1.00
1500	3.20(4)	1.02	0.97	1.00	1.02	1.00	1.03	1.00
2400	6.87(4)	1.09	0.99	1.00	1.01	1.00	1.02	1.00

overall are the LCT and LAT methods which have an MUPE of 17% and an LAPE of 20%.

5.1.6 Collinear H_2I Reaction

In this subsection, w consider results for the reaction

$$\mathrm{I + HH' \rightarrow IH + H'} \qquad \text{(R20)}$$

on two potential energy surfaces. The first surface is due to Raff *et al.*,[91] and we refer to it as the RSPTS surface. The second surface is the rotated Morse curve (RMC) type surface of Duff and one of the authors,[92] hereafter denoted the RMC surface. The RMC surface is, by design, very similar to the RSPTS surface at the conventional transition state dividing surface, as may be readily seen in Table 1, and in the reactant and product regions. The largest difference is seen in the imaginary frequency of the saddle point where the RMC surface is more realistic. However, the two surfaces differ, sometimes considerably, in other regions. Accurate quantum mechanical rate coefficients for reaction (R20) on both potential surfaces have been calculated by one of the authors and coworkers.[93] Previous comparisons to VTST results may be found in Refs 8, 10, and 50 for the RSPTS surface and in Refs 8, 10, 27, 50, and 52 for the RMC surface. The VTST calculations of the present study are given in Table 29 for the RSPTS surface and in Table 30 for the RMC surface.

Table 29: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R20), I + HH → IH + H, on the RSPTS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	4.92(–20)	12.13	0.97	0.97	0.97	0.97	0.97	0.97
400	5.51(–14)	6.59	0.99	0.99	0.99	0.99	0.99	0.99
600	6.51(–8)	3.71	1.01	1.01	1.01	1.01	1.01	1.01
1000	5.14(–3)	2.58	1.06	1.06	1.06	1.06	1.06	1.06
1500	1.54	2.40	1.16	1.16	1.16	1.16	1.16	1.16
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	4.72(–32)	37.62	1.00	1.00	1.00	1.00	1.00	1.00
250	7.94(–25)	18.22	1.00	1.00	1.00	1.00	1.00	1.00
2400	1.60(2)	1.89	1.00	1.00	1.00	1.00	1.00	1.00

The results for reaction (R20) on the RSPTS surface are now compared to the accurate data. The TST results severely overestimate the accurate data, particularly at low temperatures. All of the ICVT and ICVT/MT results are indistinguishable from one another, a sign that the tunneling contribution is negligible at all the temperatures considered. The ICVT and ICVT/MT results are in excellent agreement with the accurate data. At 200, 250, and 2400 K the TST and VTST data are compared to the ICVT/LAT data. All ICVT and ICVT/MT data agree perfectly with the LAT data, but the TST data is too large, particularly at the lower temperatures. The ICVT and ICVT/MT methods have an MUPE of 6% and an LAPE of 5%.

The results for reaction (R20) on the RMC surface show slightly better agreement than for the RSPTS surface. Again the TST results severely overestimate the accurate data. Tunneling corrections turn out to be unimportant, and all ICVT and ICVT/MT methods are indistinguishable from one another at all temperatures studied. The ICVT and ICVT/MT data are in excellent agreement with the accurate data. At the temperatures 200, 250, and 2400 K, the data are compared to the ICVT/LAT data. The TST data is found to be too large, particularly at low temperatures, and all ICVT and ICVT/MT data is in perfect agreement with the ICVT/LAT data. All ICVT and ICVT/MT methods have MUPE and LAPE values of 5%.

Table 30: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R20), I + HH → IH + H, on the RMC potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	4.79(–20)	16.07	1.09	1.09	1.09	1.09	1.09	1.09
400	5.43(–14)	8.10	1.07	1.07	1.07	1.07	1.07	1.07
600	6.55(–8)	4.18	1.05	1.05	1.05	1.05	1.05	1.05
1000	5.43(–3)	2.63	1.03	1.03	1.03	1.03	1.03	1.03
1500	1.76	2.21	1.03	1.03	1.03	1.03	1.03	1.03
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	4.59(–32)	56.71	1.00	1.00	1.00	1.00	1.00	1.00
250	7.76(–25)	25.30	1.00	1.00	1.00	1.00	1.00	1.00
2400	1.61(2)	1.94	1.00	1.00	1.00	1.00	1.00	1.00

5.1.7 Collinear HF_2 Reactions

The isotopically substituted series of reactions

$$H + FF' \rightarrow HF + F' \qquad (R21)$$

$$D + FF' \rightarrow DF + F' \qquad (R22)$$

$$T + FF' \rightarrow TF + F' \qquad (R23)$$

are now considered. For all three reactions, the potential energy surface number 2 of Jonathon *et al.*,[94] which is denoted JOT–II, is used. These three reactions (and all of the reactions considered in the remainder of this section) are exhibit somewhat different dynamics from those introduced in the previous subsections in that the reactions (R21) – (R23) contain two heavy atoms. Again we will expect the importance of the tunneling contribution to the overall VTST rate coefficient to be diminished somewhat, especially in the case of the tritium substituted reaction (R23). Accurate quantum mechanical rate coefficients for reactions (R21) – (R23) are reported in Refs 95–101. Previous comparison of these accurate data to the results of VTST calculations is given in Refs 27 and 77 for all three reactions (R21) – (R23). Rate coefficient data for the present work is given in Table 31 for reaction (R21), in Table 32 for reaction (R22), and in Table 33 for reaction (R23).

The results for reaction (R21) on the JOT–II potential energy surface are in excellent agreement with the accurate quantal rate coefficient data. TST and ICVT data in the temperature range 250 to 1000 K show reasonable agreement with the

Table 31: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R21), H + FF $\rightarrow$ HF + F, on the JOT–II potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	1.15(3)	0.61	0.60	0.86	0.95	0.86	0.96	0.86
300	2.28(3)	0.70	0.70	0.89	0.96	0.89	0.97	0.89
400	5.76(3)	0.82	0.81	0.93	0.97	0.93	0.98	0.93
600	1.61(4)	0.92	0.91	0.97	0.98	0.97	1.00	0.97
1000	4.13(4)	0.99	0.98	1.00	1.01	1.00	1.02	1.00

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.59(2)	0.57	0.56	0.99	1.16	1.00	1.17	1.00
1500	7.34(4)	1.01	0.99	1.00	1.00	1.00	1.01	1.00
2400	1.23(5)	1.02	1.00	1.00	1.00	1.00	1.01	1.00

Table 32: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R22), D + FF $\rightarrow$ DF + F, on the JOT–II potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	6.76(2)	0.78	0.76	0.93	0.98	0.93	1.00	0.93
300	1.42(3)	0.85	0.83	0.95	0.99	0.95	1.00	0.95
400	3.83(3)	0.91	0.90	0.97	0.99	0.97	1.00	0.97
600	1.12(4)	0.97	0.95	0.99	1.00	0.99	1.01	0.99
1000	2.94(4)	1.02	1.00	1.01	1.01	1.01	1.02	1.01

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.10(2)	0.75	0.73	1.00	1.09	1.00	1.10	1.00
1500	5.27(4)	1.03	0.99	1.00	1.00	1.00	1.01	1.00
2400	8.81(4)	1.05	1.00	1.00	1.00	1.00	1.00	1.00

accurate data at the lower temperatures and very good agreement at the higher temperatures. The ZCT, LCT, and LAT results are in very good agreement with one another and with the accurate data. The SCT and μOMT data show slightly

Table 33: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R23), T + FF → TF + F, on the JOT–II potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	5.25(2)	0.85	0.83	0.95	0.99	0.95	1.00	0.95
300	1.13(3)	0.90	0.88	0.97	0.99	0.97	1.00	0.97
400	3.11(3)	0.95	0.92	0.97	0.99	0.98	1.00	0.98
600	9.23(3)	0.99	0.96	0.99	0.99	0.99	1.00	0.99
1000	2.42(4)	1.04	1.01	1.01	1.02	1.01	1.02	1.01

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.62(2)	0.83	0.80	1.00	1.05	1.00	1.07	1.00
1500	4.36(4)	1.04	1.00	1.00	1.00	1.00	1.00	1.00
2400	7.28(4)	1.06	1.00	1.00	1.00	1.00	1.00	1.00

better agreement with the accurate data than the other methods and are in excellent overall agreement with the accurate data. At the temperatures 200, 1500, and 2400 K, the ICVT/MT results are in good agreement with the ICVT/LAT results. At higher temperatures, the TST and ICVT results are also in good agreement with the ICVT/LAT results, but at 200 K, the TST and ICVT results are about a factor of two too small. The best results overall are the μOMT results which have MUPE and LAPE values of 2%.

The results of reaction (R22) in the JOT–II surface show slightly better agreement that the results of the previous reaction. The TST and ICVT results again agree well with one another and with the accurate data. The ZCT, LCT, and LAT results agree well with one another and with the accurate data as well. The best results are the SCT and μOMT results which are within 2% of the accurate data. The data are compared to the ICVT/LAT data at temperatures of 200, 1500, and 2400 K. The 200 K, the TST and ICVT results show reasonable agreement with the LAT data, but are too small, while the ICVT/MT data are in good agreement with the ICVT/LAT data. All of the results agree well with the ICVT/LAT data at the highest two temperatures. The best overall methods for this reaction are the SCT and μOMT methods which both have MUPE and LAPE values equal to 1%.

Finally we consider the results for reaction (R23) on the JOT–II surface. The results are in excellent agreement with the accurate quantal rate coefficient. The TST and ICVT results are in very good agreement with the accurate data, and the

ZCT, LCT, and LAT results are in excellent agreement with the accurate data. The SCT and μOMT results are slightly more accurate still compared to the accurate data. The data are compared to ICVT/LAT data at temperatures of 200, 1500, and 2400 K. The TST and ICVT results show good agreement with the ICVT/LAT results at 200 K. The ICVT/MT methods are in very good agreement with the ICVT/LAT result at 200 K, and all methods show very good agreement with the LAT results at the two highest temperatures. The best overall methods for this reaction are the SCT and μOMT which both have MUPE and LAPE values equal to 1%.

5.1.8 Collinear HCl_2 Reactions

In this subsection we again consider two types of reactions. The first is the abstraction reaction

$$\mathrm{H + ClCl' \rightarrow HCl + Cl'} \quad \text{(R24)}$$

This is an interesting reaction in that, like the HF_2 reaction of the previous subsection, it involves abstraction from a heavy-heavy diatom by a light atom. The potential energy surface used for the study of reaction (R24) is the KNPRY[63]

The results for reaction (R24) on the KNPRY surface are now compared to the accurate quantal data. The TST and ICVT results show reasonable agreement with the accurate data. The ICVT/ZCT results yield even better agreement with the accurate rate coefficients, with larger deviations at small temperatures. The LCT and LAT results are indistinguishable from the ZCT results. The SCT and μOMT results are the most accurate compared to the accurate data and show very good overall agreement. The data are compared to ICVT/LAT data at 200, 250, 1500, and 2400 K and are found to agree very well except for the TST and ICVT results at the lower temperatures. The best results overall are the SCT and μOMT results which both have an MUPE of 11% and an LAPE of 12%.

The remainder of the reactions in this subsection are the isotopic series of exchange reactions

$$\mathrm{Cl + MuCl' \rightarrow ClMu + Cl'} \quad \text{(R25)}$$
$$\mathrm{Cl + HCl' \rightarrow ClH + Cl'} \quad \text{(R26)}$$
$$\mathrm{Cl + DCl' \rightarrow ClD + Cl'} \quad \text{(R27)}$$

These reactions are interesting to study because the motion along the minimum energy path from reactants to products (or from products to reactants) involves the tunneling of the hydrogen atom (or an isotope) between the two heavy atoms. The series of reactions (R25) – (R27) is the only one-dimensional sequence of isotopically substituted reaction of the heavy-light-heavy type for which accurate quantum mechanical rate coefficient data is available. The reactions (R25) – (R27) are all studied using the BCMR potential energy surface of Bondi *et al.*[107,108] Rate

Table 34: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R24), H + ClCl $\rightarrow$ HCl + Cl, on the KNPRY potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	1.80(3)	0.67	0.67	0.81	0.84	0.81	0.85	0.81
400	4.80(3)	0.79	0.79	0.88	0.90	0.88	0.90	0.88
600	1.40(4)	0.91	0.91	0.95	0.96	0.95	0.96	0.95
1000	3.30(4)	1.11	1.11	1.13	1.13	1.13	1.14	1.13

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.08(2)	0.65	0.65	1.00	1.07	1.00	1.08	1.00
250	6.54(2)	0.76	0.76	1.00	1.05	1.00	1.05	1.00
1500	6.784)	1.00	0.99	1.00	1.00	1.00	1.00	1.00
2400	1.16(5)	1.00	1.00	1.00	1.00	1.00	1.00	1.00

coefficient data from accurate quantum mechanical calculations for all three reactions is given in Ref 107. The calculations of the present study are given in Table 35 for reaction (R25), in Table 36 for reaction (R26), and in Table 37 for reaction (R27).

The results for reaction (R25) on the BCMR surface are in fair agreement with the accurate rate coefficients. The TST results show the worst agreement with the accurate data and are orders of magnitude too large at the lowest temperatures. The ICVT, ICVT/ZCT, and ICVT/SCT results are mutually indistinguishable and improve agreement with the accurate results dramatically. However, all of the ICVT methods underestimate the accurate rate coefficient at low temperatures are overestimate it at high temperatures. Further improvements in accuracy compared to the accurate data are given by the LCT, LAT, and μOMT results. Of these, the LAT results are slightly less accurate, but all three results agree well within a factor of two with the accurate data at all temperatures. Overall the LCT and μOMT results are the most reliable with an MUPE of 34% and an LAPE of 32%.

The results for reaction (R26) on the BCMR surface show trends similar to those for the previous reaction, except for the TST results which are dramatically improved compared to the accurate rate coefficient data. Nevertheless, the TST results are too small at low temperatures and too large at high temperatures. The ICVT, ICVT/ZCT, and ICVT/SCT results are of similar accuracy compared to the accurate data at all temperatures, and are in poor agreement at low temperatures. The LCT, LAT, and μOMT results are more accurate at lower temperatures compared to the accurate data, but are somewhat larger than the SCT results at higher

Table 35: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R25), Cl + MuCl → ClMu + Cl, on the BCMR potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.97(2)	92300	0.15	0.15	0.15	0.80	0.80	0.67
250	7.68(2)	11700	0.25	0.25	0.25	0.91	0.91	0.81
300	1.21(3)	3010	0.36	0.36	0.36	1.00	1.00	0.93
400	2.21(3)	580.95	0.55	0.55	0.55	1.13	1.14	1.10
600	4.27(3)	124.79	0.84	0.84	0.84	1.33	1.33	1.33
1000	7.95(3)	43.55	1.19	1.19	1.19	1.54	1.54	1.55
1500	1.17(4)	29.86	1.41	1.41	1.41	1.67	1.67	1.68
2400	1.71(4)	26.27	1.60	1.60	1.60	1.77	1.77	1.78

Table 36: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R26), Cl + HCl → ClH + Cl, on the BCMR potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.85(–1)	0.19	0.13	0.15	0.15	0.62	0.62	0.56
250	2.95	0.34	0.23	0.25	0.25	0.72	0.72	0.67
300	1.16(1)	0.50	0.33	0.35	0.35	0.83	0.83	0.77
400	6.66(1)	0.87	0.53	0.54	0.54	0.99	0.99	0.94
600	4.14(2)	1.62	0.82	0.83	0.83	1.21	1.21	1.17
1000	2.04(3)	3.04	1.14	1.15	1.15	1.41	1.41	1.38
1500	4.93(3)	4.58	1.35	1.36	1.36	1.55	1.55	1.53
2400	1.04(4)	6.69	1.56	1.56	1.56	1.70	1.70	1.68

temperatures. Even so, the results lie within a factor of two of the accurate data. The best results overall are the LCT and μOMT results which have MUPE values of 34% and LAPE values of 37%.

We conclude this subsection with a comparison of the results of calculations for reaction (R27) on the BCMR surface to the accurate quantal data. The TST results again show the largest discrepancies, seriously underestimating the accurate rate coefficient at the lowest temperatures and seriously overestimating the accurate rate coefficient at the highest temperatures. The ICVT, ICVT/ZCT, and ICVT/SCT results are of similar accuracy to the TST results at low temperatures, but are in

Table 37: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R27), Cl + DCl → ClD + Cl, on the BCMR potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.68(−2)	0.14	0.13	0.17	0.20	0.63	0.63	0.61
250	3.69(−1)	0.25	0.21	0.25	0.28	0.66	0.66	0.65
300	2.16	0.37	0.30	0.34	0.36	0.70	0.71	0.69
400	2.01(1)	0.64	0.45	0.49	0.51	0.80	0.81	0.79
600	1.91(2)	1.28	0.74	0.76	0.78	1.02	1.02	1.01
1000	1.30(3)	2.51	1.10	1.11	1.12	1.29	1.29	1.29
1500	3.84(3)	3.61	1.31	1.32	1.32	1.45	1.45	1.44
2400	9.06(3)	5.15	1.56	1.57	1.57	1.66	1.66	1.66

much better agreement at higher temperatures. The LCT, LAT, and μOMT results are in reasonable agreement with the accurate data as was seen for the previous two reactions, generally well within a factor of two. The best overall results are the LCT and μOMT results which have MUPE values of 33% and LAPE values of 38%. The LAT results also have an MUPE of 33%, but the LAPE value is 40%.

5.1.9 Collinear HI_2 Reaction

In this subsection we consider the reaction

$$\mathrm{I} + \mathrm{HI}' \rightarrow \mathrm{IH} + \mathrm{I}' \qquad \text{(R28)}$$

using surface A of Kaye and Kuppermann.[109] The reaction probability as a function of energy is given in Ref 109, and thermal rate coefficients were calculated from this data and are compared to VTST results in Ref 110. The results of the calculations made for the present study are given in Table 38.

Reaction (R28) is another example of a reaction where tunneling effects are unimportant. The TST results are in poor agreement with the accurate data, even at the highest temperatures. All ICVT and ICVT/MT results are mutually indistinguishable at all of the standard temperatures. These results all overestimate the accurate rate coefficient by factors ranging from 1.1 to 1.5 and are thus in good agreement with the accurate results. At 1500 and 2400 K, the results are compared to the ICVT/LAT values. The TST results are found to agree poorly with the ICVT/LAT results, but all of the ICVT results are in perfect agreement. The ICVT and ICVT/MT methods all yield results which have MUPE values of 24% and LAPE values of 23%.

Table 38: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R28), I + HI → IH + I, on the KK–A potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.89(3)	214.33	1.14	1.14	1.14	1.14	1.14	1.14
250	4.61(3)	95.16	1.16	1.16	1.16	1.16	1.16	1.16
300	5.26(3)	57.02	1.17	1.17	1.17	1.17	1.17	1.17
400	6.31(3)	32.27	1.20	1.20	1.20	1.20	1.20	1.20
600	7.69(3)	21.34	1.28	1.28	1.28	1.28	1.28	1.28
1000	9.17(3)	19.31	1.46	1.46	1.46	1.46	1.46	1.46

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	1.69(4)	12.81	1.00	1.00	1.00	1.00	1.00	1.00
2400	2.18(4)	13.20	1.00	1.00	1.00	1.00	1.00	1.00

5.1.10 Collinear ClHBr Reaction

For the final reaction of this subsection, the reaction

$$\mathrm{Cl + HBr \rightarrow ClH + Br} \qquad \text{(R29)}$$

is examined. The potential energy surface used for the study of this reaction is due to Babamov, Lopez, and Marcus,[111–113] and is of the extended LEPS[63,64] type. This is an interesting reaction to study because it has an asymmetric saddle point, involves hydrogen tunneling between two heavy atoms, and has large reaction-path curvature. Accurate quantum mechanical reaction probabilities are reported for this surface in Refs 114 and 115. These results were used to produce thermally averaged rate coefficients which are compared to the results of VTST calculations in Ref 116. Table 39 presents the results of the current study.

The section on one-dimensional thermal reactions is concluded with a comparison of the results for reaction (R29) on the BLM surface to the accurate quantal rate coefficient data. The TST results give poor agreement, underestimating the accurate data at low temperatures and seriously overestimating the accurate data at high temperatures. All of the ICVT results are in reasonable agreement with the accurate data, an indication that the role of tunneling is diminished in this reaction. The ICVT/MT results do show some slight differences at low temperatures, but are otherwise indistinguishable from one another. The μOMT results yield the best agreement overall with an MUPE of 54% and an LAPE of 113%.

Table 39: One-dimensional rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R29), Cl + HBr → ClH + Br, on the BLM potential energy surface.

				ICVT	ICVT	ICVT	ICVT	ICVT
T (K)	Accurate	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT
200	2.16(–4)	0.27	0.10	0.14	0.14	0.14	0.15	0.14
250	6.38(–3)	0.50	0.20	0.26	0.26	0.25	0.26	0.25
300	6.38(–2)	0.76	0.32	0.38	0.38	0.37	0.38	0.37
400	1.20	1.30	0.55	0.61	0.61	0.60	0.61	0.60
600	2.52(1)	2.36	0.90	0.95	0.95	0.94	0.95	0.94
1000	3.32(2)	4.25	1.30	1.32	1.32	1.31	1.32	1.31
1500	1.34(3)	6.10	1.52	1.54	1.54	1.53	1.54	1.53
2400	4.06(3)	8.73	1.79	1.79	1.79	1.79	1.79	1.79

5.2 State-Selected One-Dimensional (Collinear) Reactions

In this section we will consider the state-selected rate coefficients of several of the reactions of the previous section. Specifically we focus our attention on reactions where the reactant diatom has one quantum of vibrational excitation, rather than the thermal distribution of states considered in the previous section. The general equation for this type of reaction is

$$A + BC\,(n = 1) \rightarrow AB + C$$

where n is the diatomic vibrational quantum number. The rate coefficients of such state-selected reactions are particularly interesting because they provide a stringent test of the approximate methods. Without additional assumptions, TST, VTST, and VTST/MT only predict thermal rate coefficients. However, for high-frequency modes of the reactants one can extend TST and VTST to predict state-selected rate coefficients by making the assumption that the mode is vibrationally adiabatic all the way from reactants to the transition state.[31] To include tunneling one must make the further assumption that the mode is adiabatic over the entire extent of the reaction path that is important for tunneling,[51] although not necessarily in the regions "far" from the reaction path that contribute to the LCT and LAT tunneling probabilities but not to the ZCT and SCT ones.[116]

We will examine state-selected one-dimensional rate coefficients for six reactions (not including isotopic variants), five of which were considered in the previous section.

5.2.1 State-selected Collinear H_3 Reactions

We return our attention to reaction (R1) of the previous section, but now consider the excited-state rate coefficients. Accurate quantum mechanical rate coefficients for reaction (R1) in the excited state (n = 1) are reported in Ref 49 for the PK2 and LSTH surfaces, and in Refs 11 and 117 for the TK surface. Comparisons to VTST results are made for all three surfaces in Refs 31 and 118. Rate coefficient calculations of the present study for reaction (R1) in the excited state (n = 1) are given in Table 40 for the PK2 surface, in Table 41 for the TK surface, and in Table 42 for the LSTH surface.

We first consider the results for reaction (R1) on the PK2 surface. The TST results yield poor agreement with the accurate data, especially at low temperatures. The ICVT results show a great improvement over the TST results, but tend to underestimate the accurate rate coefficient at low temperatures and overestimate the accurate rate coefficient at high temperatures. This trend is seen in all of the ICVT/MT results. The ZCT, SCT, LCT, and μOMT results of comparable accuracy compared to the accurate data and give improved accuracy of the low-temperature results as compared to the ICVT results. The LAT results are the most accurate at low temperatures compared to the accurate data, and they are the most reliable overall, with the MUPE and LAPE both equal to 24%.

The agreement of calculated results with the accurate quantal data is better for reaction (R1) on the TK surface than for the previous surface. The TST results still show a large discrepancy from the accurate data, particularly at low temperatures. The ICVT results yield considerably better agreement with the accurate data compared to the TST results, but the agreement of the low-temperature results compared to the accurate quantal data is poor. The ZCT, SCT, LCT, and μOMT results are of similar accuracy, and give reasonable agreement with the accurate data except at the lowest temperatures. The LAT results give better agreement with the accurate data at low temperatures, but tend to overestimate the rate coefficient at higher temperatures more than the other ICVT/MT results. At 200, 1500, and 2400 K, the data are compared to the ICVT/LAT results. All ICVT and ICVT/MT results are found to be in good agreement except the ICVT result at 200 K. The TST results are in poor agreement with the ICVT/LAT results. The best overall results are given by the LAT method which has an MUPE and an LAPE both equal to 12%.

The final case of reaction (R1) is for the LSTH surface. As was seen in the previous results, the conventional TST results are generally in poor agreement with the accurate data. Again the ICVT method yields a dramatic improvement in accuracy compared to the accurate data over the TST results, but it predicts a rate coefficient that is a factor of 3.6 too low at 200 K. The ZCT, SCT, LCT, and

Table 40: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R1), H + HH(n = 1) → HH + H, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.11(2)	139.59	0.42	0.53	0.54	0.54	0.54	0.77
250	1.30(3)	59.80	0.58	0.67	0.67	0.68	0.68	0.89
300	2.47(3)	33.89	0.71	0.78	0.79	0.79	0.80	0.99
400	5.82(3)	16.26	0.89	0.95	0.95	0.95	0.96	1.12
600	1.50(4)	7.56	1.09	1.12	1.12	1.13	1.13	1.25
1000	3.61(4)	3.99	1.25	1.26	1.26	1.27	1.27	1.34
1500	6.10(4)	2.87	1.32	1.33	1.33	1.33	1.33	1.38
2400	9.50(4)	2.31	1.43	1.43	1.43	1.43	1.43	1.46

Table 41: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R1), H + HH(n = 1) → HH + H, on the TK potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	1.50(3)	50.69	0.29	0.57	0.58	0.55	0.60	0.91
300	2.60(3)	31.61	0.42	0.68	0.68	0.66	0.70	0.94
400	5.60(3)	16.66	0.65	0.85	0.85	0.84	0.87	1.03
600	1.37(4)	8.22	0.95	1.06	1.06	1.07	1.08	1.17
1000	3.40(4)	4.21	1.15	1.20	1.20	1.21	1.21	1.26
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	6.87(2)	101.03	0.16	0.48	0.50	0.44	0.52	1.00
1500	7.70(4)	2.26	0.95	0.97	0.97	0.97	0.98	1.00
2400	1.31(5)	1.68	0.98	0.98	0.98	0.99	0.99	1.00

μOMT results are similar to each other and all yield rate coefficients reliable within a factor of 1.5 from 300 to 2400 K compared to the accurate data. These errors increase to a factor of 1.7–1.8 at 250 K and a factor of 2.2–2.4 at 200 K. The LAT results yield the best results compared to the accurate data at the lower temperatures, and yield rate coefficients which are slightly larger than the other ICVT methods at higher temperatures but are still in good agreement with the accurate data. The LAT

Table 42: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R1), H + HH(n = 1) $\rightarrow$ HH + H, on the LSTH potential energy surface.

T(K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.47(2)	107.88	0.28	0.42	0.44	0.43	0.46	0.73
250	7.06(2)	50.08	0.43	0.55	0.57	0.57	0.59	0.84
300	1.48(3)	29.34	0.55	0.66	0.67	0.68	0.70	0.92
400	3.95(3)	14.64	0.75	0.82	0.83	0.84	0.86	1.03
600	1.15(4)	7.10	0.98	1.02	1.02	1.03	1.05	1.17
1000	3.07(4)	3.85	1.17	1.19	1.19	1.20	1.21	1.29
1500	5.40(4)	2.84	1.28	1.29	1.29	1.30	1.31	1.36
2400	9.00(4)	2.25	1.37	1.37	1.37	1.38	1.38	1.42

method is the best overall with an MUPE value of 22% and an LAPE value of 23%. Perhaps even more impressive is that the LAT results agree with the accurate ones within a factor of 1.4 over the whole factor-of-12 range of temperature.

5.2.2 State-selected Collinear H_2O Reactions

In this subsection we consider the excited state (n = 1) rate coefficients of the reaction (R8) and its reverse reaction

$$\mathrm{H} + \mathrm{H'O}\,(n = 1) \rightarrow \mathrm{HH'} + \mathrm{O} \qquad \text{(R30)}$$

Accurate quantum mechanical results are available in Ref 71 for three of the five potential energy surfaces reviewed in section 5.1.2, namely the JW surface, the ModPolCI surface, and the DIM–RMOS surface. There is one previous set of comparisons of accurate rate coefficients to VTST results, and this is given in Ref 73. Rate coefficient data of the current study for the stretch-excited reaction (R8) is presented in Table 43 for the JW surface, in Table 44 for the ModPolCI surface, and in Table 45 for the DIM–RMOS surface. The same data for the reverse reaction (R30) is given in Table 46 for the JW surface, in Table 47 for the ModPolCI surface, and in Table 48 for the DIM–RMOS surface.

One additional note is in order before we discuss the results in this subsection. The calculations in this subsection were performed using the partial reaction path (PRP) method in which it is assumed that the excited degree of freedom is adiabatic from the reactants up to the first occurrence of an appreciable local maximum in the reaction path curvature. In calculations of all of the other reactions presented in this subsection it is assumed that the excited degree of freedom is adiabatic from the

Table 43: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH(n = 1) → OH + H, on the JW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.79(1)	215.61	0.46	1.24	1.26	1.23	1.26	1.23
250	7.56(1)	90.42	0.66	1.23	1.24	1.23	1.24	1.23
300	2.05(2)	49.61	0.83	1.26	1.27	1.26	1.27	1.26
400	7.63(2)	22.58	1.05	1.32	1.33	1.32	1.33	1.32
600	3.11(3)	9.95	1.29	1.42	1.43	1.42	1.43	1.42

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1000	1.65(4)	3.29	0.96	1.00	1.00	1.00	1.00	1.00
1500	3.47(4)	2.23	0.98	1.00	1.00	1.00	1.00	1.00
2400	6.63(4)	1.66	0.99	1.00	1.00	1.00	1.00	1.00

reactants all the way to the dynamical bottleneck. Our treatment is consistent with previous work[77] in which the PRP method was introduced.

We now compare the results for reaction (R8) on the JW surface to the accurate quantal data. The TST results are very inaccurate compared to the accurate data, consistently overestimating the rate coefficient by an order of magnitude or more. The ICVT data is in much better agreement, but is of factor of 2 too small at 200 K. All of the ICVT/MT data is of similar accuracy to and is in reasonable agreement with the accurate data, but is too large at all temperatures by 23–43%. At 1000, 1500, and 2400 K, the data are compared to the ICVT/LAT results. The ICVT and ICVT/MT data is found to be in good agreement, but the conventional TST results are too large. The best methods overall for this reaction are the ZCT, LCT, and LAT methods with MUPE and LAPE values of 29%.

We now consider reaction (R8) on the ModPolCI potential energy surface. As we have seen for all of the state-selected reactions thus far, the TST results are consistently much larger than the accurate data, particularly at low temperatures. The ICVT results are too small at low temperatures and too large at high temperatures compared to the accurate data. When tunneling is included, the ICVT/MT methods are in good agreement with the ICVT/LAT results, and the TST results are too large as might by now be expected. The best overall method is the ICVT method with an MUPE of 61% and an LAPE of 120%. The ZCT and LCT methods give a larger MUPE, 94%, but give a smaller LAPE value, 85%.

Table 44: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH(n = 1) → OH + H, on the ModPolCI potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.96	320.32	0.14	0.97	1.04	0.97	1.04	0.97
250	9.13	243.43	0.49	1.61	1.69	1.61	1.69	1.61
300	2.37(1)	168.34	0.95	2.12	2.19	2.12	2.19	2.12
400	1.12(2)	76.24	1.57	2.43	2.47	2.43	2.48	2.43
600	7.04(2)	27.54	2.07	2.50	2.52	2.50	2.52	2.50
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1000	9.28(3)	4.40	0.93	1.00	1.00	1.00	1.00	1.00
1500	2.35(4)	2.73	0.97	1.00	1.00	1.00	1.00	1.00
2400	5.18(4)	1.89	0.99	1.00	1.00	1.00	1.00	1.00

The results for reaction (R8) on the DIM–RMOS potential energy surface are in reasonable agreement with the accurate quantal rate coefficient data. The TST results underestimate the accurate results at all temperatures with larger discrepancies seen at lower temperatures. The ICVT and ICVT/MT methods all yield results of comparable accuracy compared to the accurate quantal results. All ICVT and ICVT/MT methods predict rate coefficients which exceed the accurate value by 43–55% in the temperatures range 200–600 K. At temperatures above 600 K, the data are compared to the ICVT/LAT data. All of the ICVT and ICVT/MT data is found to be indistinguishable from the ICVT/LAT data at these temperatures. The TST results are smaller than the ICVT/LAT results at the three highest temperatures with a mean discrepancy of about a factor of two. The best overall methods for this reaction are the ICVT, ICVT/LCT, and ICVT/LAT methods which have MUPE and LAPE values of 47%.

The results for reaction (R30) on the JW surface are now considered. The TST results systematically overestimate the accurate rate coefficient, especially at low temperature. The ZCT, SCT, and μOMT methods yield results of similar accuracy compared to the accurate data which are 40–73% too large. The LCT and LAT methods yield results similar to one another which overestimate the accurate results by 40–57%. The LCT and LAT methods yield smaller discrepancies at lower temperatures compared to the ZCT, SCT, and μOMT results. The ICVT method gives results which are in the best agreement with the accurate data for this reaction. At 200 K, the ICVT result is 28% smaller than the accurate value, but at 1000 K

Table 45: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R8), O + HH($n = 1$) $\rightarrow$ OH + H, on the DIM–RMOS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.80(4)	0.01	1.52	1.55	1.55	1.52	1.55	1.52
250	2.20(4)	0.03	1.49	1.51	1.51	1.49	1.51	1.49
300	2.55(4)	0.06	1.47	1.48	1.48	1.47	1.48	1.47
400	3.16(4)	0.13	1.45	1.46	1.46	1.45	1.46	1.45
600	4.14(4)	0.29	1.43	1.44	1.44	1.43	1.44	1.43
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1000	8.01(4)	0.38	1.00	1.00	1.00	1.00	1.00	1.00
1500	1.00(5)	0.53	1.00	1.00	1.00	1.00	1.00	1.00
2400	1.29(5)	0.67	1.00	1.00	1.00	1.00	1.00	1.00

Table 46: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R30), H + HO($n = 1$) $\rightarrow$ HH + O, on the JW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.27(2)	66.33	0.72	1.71	1.73	1.57	1.73	1.57
250	4.14(2)	32.82	0.88	1.51	1.52	1.45	1.52	1.45
300	9.34(2)	20.36	1.00	1.44	1.45	1.41	1.45	1.41
400	2.70(3)	11.04	1.15	1.41	1.41	1.40	1.42	1.40
600	8.45(3)	5.87	1.30	1.42	1.42	1.42	1.42	1.42
1000	2.30(4)	3.55	1.44	1.49	1.49	1.48	1.49	1.48
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	6.27(4)	1.80	0.99	1.00	1.00	1.00	1.00	1.00
2400	1.08(5)	1.45	0.99	1.00	1.00	1.00	1.00	1.00

the ICVT result is 44% larger than the accurate value. The results above 1000 K are compared to the ICVT/LAT results. All of the ICVT and ICVT/MT data are found to be in good agreement with the ICVT/LAT data, and the TST data are larger than

Table 47: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R30), H + HO(n = 1) → HH + O, on the ModPolCI potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.57(4)	0.29	1.22	1.43	1.44	1.31	1.45	1.31
250	2.04(4)	0.40	1.28	1.42	1.43	1.33	1.44	1.33
300	2.48(4)	0.50	1.32	1.42	1.43	1.35	1.43	1.35
400	3.27(4)	0.67	1.37	1.43	1.43	1.38	1.44	1.38
600	4.58(4)	0.88	1.42	1.45	1.45	1.42	1.45	1.42
1000	6.55(4)	1.10	1.47	1.48	1.48	1.46	1.48	1.46

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	1.26(5)	0.83	1.00	1.01	1.01	1.00	1.01	1.00
2400	1.67(5)	0.89	1.00	1.00	1.00	1.00	1.01	1.00

Table 48: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R30), H + HO(n = 1) → HH + O, on the DIM–RMOS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	6.00	1130.00	1.09	4.02	4.25	3.74	4.25	3.74
250	2.88(1)	396.28	1.53	3.42	3.53	3.34	3.53	3.34
300	8.77(1)	187.63	1.83	3.17	3.23	3.13	3.24	3.13
400	3.96(2)	67.54	2.10	2.84	2.87	2.83	2.87	2.83
600	1.98(3)	23.29	2.30	2.63	2.64	2.63	2.64	2.63
1000	7.54(3)	10.38	2.59	2.71	2.72	2.71	2.72	2.71

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	4.45(4)	2.47	0.98	1.00	1.00	1.00	1.00	1.00
2400	8.70(4)	1.77	0.99	1.00	1.00	1.00	1.00	1.00

the ICVT/LAT data. The best method overall for this reaction is the ICVT method which has an MUPE of 21% and an LAPE of 23%.

The results of calculations of reaction (R30) on the ModPolCI surface are now presented. The TST results show reasonable agreement at 300 K and above, but are too small compared to the accurate data at the lower temperatures. The ICVT results overestimate the accurate rate coefficient in the temperature range 200–600 K by 22–47%. The ZCT, SCT, and μOMT methods yield results similar to one another which overestimate the accurate rate coefficient by 42–48%. The LCT and LAT results yield slightly smaller errors than the other ICVT/MT methods although they still overestimate the accurate rate coefficient by 31–46%. The data above 1000 K are compared to the ICVT/LAT results and all methods are found to be in good agreement although the TST results are slightly smaller than the others. The best method overall for this reaction is the ICVT method which has MUPE and LAPE values of 35%.

We conclude our study of state-selected OH_2 reactions by considering the results of calculations on the DIM–RMOS potential energy surface for reaction (R30). The TST results overestimate the accurate rate coefficient by 1 to 3 orders of magnitude in the temperature range 200–1000 K. The ICVT/MT methods also overestimate the accurate data, but by factors of 2.7 to 4.0, with the larger discrepancies at the lower temperatures. The ICVT data show the best agreement with the accurate data. At 200 K, the ICVT results overestimate the accurate data by 9%, but at 1000 K the ICVT results are a factor of 2.6 too large. The results above 1000 K are compared to the ICVT/LAT data. The ICVT and ICVT/MT results are found to be in good agreement with the ICVT/LAT data. The TST data overestimate the LAT data by factors in the range 1.8 to 2.5. The best overall method for this reaction in the ICVT method which has an MUPE of 91% and an LAPE of 84%.

Although the present tests of VTST and VTST/MT methods for O + H_2 ($n = 1$) are for collinear reactions, there is also important evidence in 3D studies about the validity of the assumptions involved. In particular, Chatfield *et al.*[119] carried out accurate quantal scattering calculations for zero-total-angular-momentum 3D collisions and found essentially no reaction for O + H_2 ($n = 1$) at total energies below the state-selected variational transition state. This confirms that the high-frequency vibration is essentially adiabatic from reactants to the variational transition state, which is the essential assumption of state-selected VTST.

5.2.3 H_2Cl Reactions

We return to the study of reactions (R13), (R16), and (R17), again on the SPK/GSW potential energy surface, but now for the excited ($n = 1$) state. Accurate rate coefficient calculations are reported in Refs 84 and 85. Previous comparison to VTST results is given in Ref 31. Rate coefficient calculations for the present study

Table 49: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R13), Cl + HH(n = 1) → ClH + H, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	8.81(3)	481000	1.99	2.06	2.06	2.06	2.06	2.06
250	1.19(4)	38900	1.92	1.97	1.97	1.97	1.97	1.97
300	1.46(4)	7340	1.89	1.92	1.92	1.92	1.92	1.92
400	1.92(4)	925.47	1.88	1.90	1.90	1.90	1.90	1.90
600	2.60(4)	120.26	1.93	1.94	1.94	1.94	1.94	1.94
1000	3.40(4)	25.14	2.11	2.11	2.11	2.11	2.11	2.11
1500	3.94(4)	12.23	2.34	2.34	2.34	2.34	2.34	2.34

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	1.21(5)	2.81	1.00	1.00	1.00	1.00	1.00	1.00

Table 50: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R16), Cl + DD(n = 1) → ClD + D, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.08(3)	375.81	3.26	3.57	3.58	3.57	3.58	3.57
250	2.11(3)	125.20	2.81	2.98	2.98	2.98	2.98	2.98
300	3.34(3)	60.36	2.55	2.65	2.66	2.65	2.66	2.66
400	6.08(3)	24.38	2.27	2.32	2.32	2.32	2.33	2.32
600	1.16(4)	9.97	2.05	2.07	2.07	2.07	2.07	2.07
1000	2.07(4)	5.03	1.95	1.95	1.95	1.95	1.95	1.95
1500	2.91(4)	3.65	1.94	1.94	1.94	1.94	1.94	1.94

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	7.92(4)	1.48	1.00	1.00	1.00	1.00	1.00	1.00

may be found for the stretch-excited reaction (R13) in Table 49, reaction (R16) in Table 50, and reaction (R17) in Table 51.

Table 51: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R17), $\mathrm{Cl} + \mathrm{TT}(n = 1) \rightarrow \mathrm{ClT} + \mathrm{T}$, on the SPK/GSW potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	7.86(2)	7.23	1.14	1.22	1.22	1.22	1.23	1.37
250	1.57(3)	5.34	1.22	1.27	1.27	1.27	1.28	1.39
300	2.54(3)	4.35	1.27	1.31	1.31	1.31	1.31	1.40
400	4.79(3)	3.35	1.33	1.35	1.36	1.35	1.36	1.42
600	9.55(3)	2.59	1.40	1.41	1.41	1.41	1.41	1.46
1000	1.78(4)	2.16	1.49	1.50	1.50	1.50	1.50	1.52
1500	2.54(4)	2.03	1.59	1.59	1.59	1.59	1.59	1.61

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	6.05(4)	1.16	0.99	0.99	0.99	0.99	0.99	1.00

The results of reaction (R13) on the SPK/GSW surface are now considered. The previous state-selected examples have shown that the TST results are generally unreliable predictors of the state-selected rate coefficient, and the present results are consistent with this assessment. The ICVT and ICVT/MT results give about the same prediction for the rate coefficient. On the average, this prediction is about a factor of two larger than the accurate data at temperatures up to 1500 K. At 2400 K, the ICVT and ICVT/MT data is in good agreement with the ICVT/LAT data, but the TST data is too large. The best overall method for this reaction is the ICVT method with an MUPE and an LAPE of 101%. The ICVT/MT methods give slightly larger values for these quantities.

The results for reaction (R16), on the SPK/GSW surface show somewhat worse agreement with the accurate data. The TST results do not give good agreement with the accurate data. The ICVT results again predict the most accurate rate coefficients, but the discrepancies are large with factors ranging from 3.3 at 200 K to 1.9 at 1500 K. The ICVT/MT results are slightly larger at the lower temperatures. As might be expected, all ICVT and ICVT/MT results are in good agreement with the ICVT/LAT result at 2400 K, and the TST result is too large. The best overall method is the ICVT method with an MUPE of 140% and an LAPE of 136%. The ICVT/MT methods give slightly larger values for these quantities.

Surprisingly, the results for reaction (R17) on the SPK/GSW surface show reasonable agreement with the accurate quantal rate coefficient data. The TST data still overestimate the accurate data, but the factors are much smaller than in the previous reactions on this surface. The ICVT results overestimate the accurate data by 14–59%. When tunneling corrections are included, the low-temperature results increase somewhat, and this leads to slightly larger errors. Nevertheless, the overall agreement with the accurate data is good. All methods show good agreement with the ICVT/LAT result at 2400 K. The best method overall is the ICVT method with an MUPE of 35% and an LAPE of 34%.

5.2.4 State-selected Collinear HF_2 Reactions

The reactions (R21) – (R23) are studied for the excited state ($n = 1$), again using the JOT–II surface. Accurate quantum mechanical rate coefficients for these reactions were reported by Garrett *et al.*,[77] and a previous comparison to VTST calculations was made by Steckler, one of the authors, and Garrett.[120] The results of the present study for the stretch-excited state one-dimensional reaction (R21) is given in Table 52, in Table 53 for reaction (R22), and in Table 54 for reaction (R23).

All of the methods give results in good agreement with the accurate quantal rate coefficient data for reaction (R21) in the JOT–II surface. Interestingly, the TST results are quite good for this reaction, underestimating the accurate rate coefficient by only a factor of 0.72 at 250 K, and overestimating the accurate rate coefficient by a factor of 1.1 at 600 K. The ICVT and ICVT/MT results yield similar agreement to one another but are slightly smaller than the accurate data at the lower temperatures. The ZCT, LCT, and LAT methods yield indistinguishable results and are in very good agreement with the accurate data. The SCT and μOMT results overestimate the accurate data at all temperatures, but yield results which are in very good agreement with the accurate data. At 200, 1500, and 2400 K, the data are compared to the ICVT/LAT results. The conventional TST, ICVT, and ICVT/MT data are in good agreement with the ICVT/LAT results at the higher temperatures. At the lower temperatures, the TST and ICVT results are within a factor of two of the ICVT/LAT value and the other results are in good agreement, although the SCT and μOMT results are somewhat too large. The overall best method for this reaction are the SCT, LCT, and LAT methods which have an MUPE and LAPE values of 9%.

For reaction (R22) on the JOT–II surface, all results are in excellent agreement with the accurate quantal rate coefficient data. The TST results overestimate the accurate rate coefficient by a maximum of 3%. The largest discrepancy seen for the ICVT results is at 250 K where the factor is 0.85. The ZCT, LCT, and LAT methods all underestimate the accurate rate coefficient slightly with maximum discrepancies of about 4%. The SCT and μOMT results tend to overestimate the accurate rate coefficient slightly with maximum deviations of 6 and 8%, respectively, at 250 K. At 200, 1500, and 2400 K, the TST, ICVT, and ICVT/MT data are all in good agreement with the ICVT/LAT result. The best methods overall

Table 52: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R21), H + FF(n = 1) → HF + F, on the JOT–II potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	1.78(3)	0.72	0.67	0.88	1.03	0.88	1.06	0.88
300	3.22(3)	0.82	0.78	0.94	1.05	0.94	1.08	0.94
400	6.47(3)	1.05	1.00	1.11	1.19	1.11	1.22	1.11
600	1.61(4)	1.14	1.11	1.16	1.19	1.16	1.22	1.16
1000	4.45(4)	1.00	0.99	1.00	1.01	1.00	1.03	1.00

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	6.23(2)	0.71	0.65	1.00	1.27	1.00	1.30	1.00
1500	7.50(4)	1.00	0.99	1.00	1.00	1.00	1.02	1.00
2400	1.20(5)	1.00	1.00	1.00	1.00	1.00	1.01	1.00

Table 53: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R22), D + FF(n = 1) → DF + F, on the JOT–II potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	1.12(3)	1.01	0.85	0.98	1.06	0.98	1.08	0.98
300	2.25(3)	1.01	0.87	0.96	1.01	0.96	1.03	0.96
400	5.38(3)	1.03	0.92	0.97	1.00	0.98	1.02	0.98
600	1.39(4)	1.03	0.96	0.98	1.00	0.98	1.01	0.98
1000	3.29(4)	1.03	0.97	0.98	0.98	0.98	1.00	0.98

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	4.18(2)	0.99	0.79	1.00	1.12	1.00	1.14	1.00
1500	5.45(4)	1.03	1.00	1.00	1.00	1.00	1.01	1.00
2400	8.71(4)	1.02	1.00	1.00	1.00	1.00	1.01	1.00

for this reaction are the ZCT, SCT, LCT, and LAT methods which have MUPE and LAPE values of 2%.

Table 54: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R23), T + FF(n = 1) → TF + F, on the JOT–II potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
250	9.37(2)	1.13	0.87	0.97	1.01	0.97	1.03	0.97
300	1.84(3)	1.12	0.91	0.98	1.01	0.98	1.02	0.98
400	4.44(3)	1.11	0.95	0.99	1.00	0.99	1.02	0.99
600	1.15(4)	1.09	0.98	0.99	1.00	0.99	1.01	0.99
1000	2.73(4)	1.06	0.99	1.00	1.00	1.00	1.01	1.00

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.40(2)	1.16	0.84	1.00	1.07	1.00	1.08	1.00
1500	4.53(4)	1.04	1.00	1.00	1.00	1.00	1.01	1.00
2400	7.23(4)	1.03	1.00	1.00	1.00	1.00	1.00	1.00

The results of reaction (R23) on the JOT–II surface show excellent agreement with the accurate data. The TST results are in very good agreement with the accurate data, but the maximum discrepancy is 13% at 250 K. The ICVT results underestimate the accurate data with a maximum discrepancy at 250 K, where the deviation is 13%. The ZCT, LCT, and LAT results are indistinguishable from each other and tend to underestimate the accurate data by a few percent at most. The SCT and μOMT results are also in excellent agreement with the accurate data and tend to overestimate the accurate data slightly at lower temperatures. The TST, ICVT, and ICVT/MT data at 200, 1500, and 2400 K are in good agreement with the ICVT/LAT values. The best overall method for this reaction is the SCT method which has MUPE and LAPE values less than 1%.

5.2.5 State-selected Collinear ClHBr Reaction

To conclude this section, we return to the study of reaction (R29) for the stretch-excited state (n = 1) case. Accurate state-selected quantum mechanical rate coefficients were computed as detailed in Ref 91 from the accurate results of Refs 114 and 115. Comparison to VTST calculations was also made in Ref 116. The results of the present study for the stretch-excited (n = 1) case for reaction (R29) are given in Table 55.

Table 55: One-dimensional state–selected rate coefficient data (cm molecule^{-1} s^{-1}) for reaction (R29), Cl + HBr(n = 1) → ClH + Br, on the BLM potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.52	231.24	0.02	0.02	0.02	0.02	0.02	0.02
250	3.97	381.79	0.18	0.20	0.20	0.20	0.20	0.20
300	5.55	420.32	0.70	0.75	0.75	0.75	0.75	0.75
400	1.83(1)	225.17	1.85	1.93	1.93	1.93	1.93	1.93
600	1.30(2)	59.39	2.42	2.47	2.47	2.47	2.47	2.47
1000	8.92(2)	15.70	2.30	2.32	2.32	2.32	2.32	2.32
1500	2.59(3)	7.85	2.18	2.19	2.19	2.19	2.19	2.19
2400	5.81(3)	5.03	2.26	2.26	2.26	2.26	2.26	2.26

Although the ICVT and ICVT/MT results for reaction (R29) on the BLM surface are a great improvement over conventional TST, their absolute accuracy is poor. The tunneling contribution is small. All of the rate coefficients are about 50 times too small at 200 K, but overestimate the accurate rate coefficient by a factor of 2.3 at 2400 K. The best methods overall are the ICVT/MT methods which have an MUPE of 102% and an LAPE of 245%.

5.3 Three-Dimensional Reactions

In this section we review the systems for which three-dimensional rate coefficients have been calculated via accurate quantum methods. Due to the difficulty in performing these full-dimensional calculations, there are considerably fewer data available compared to the one-dimensional reactions reviewed in section 5.1. This makes the comparison to VTST results all the more interesting, since the VTST calculations are comparatively easy and inexpensive to perform. We seek to establish the accuracy of the VTST calculations relative to the accurate quantum mechanical rate coefficients and thus validate the more approximate method as reliable for rate calculations. Another compelling reason for the study of the three-dimensional rate coefficients is that they may be directly compared to the experimental data. As pointed out earlier in this chapter, however, differences between the experimental data and accurate quantum mechanical calculations may be due to inaccuracies in the potential energy surface. Therefore we do not compare our results to experimental values, although this is done in many of the references given in this section.

Table 56: Three-dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R1), H + HH → HH + H, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	8.02(−18)	0.004	0.004	0.09	1.22	1.02	1.37	2.05
250	1.16(−16)	0.02	0.02	0.15	1.13	1.13	1.31	1.70
300	7.99(−16)	0.05	0.05	0.22	1.06	1.12	1.23	1.45
400	1.05(−14)	0.16	0.16	0.34	0.97	1.04	1.10	1.19
600	1.76(−13)	0.36	0.36	0.51	0.88	0.94	0.97	0.99

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1000	2.10(−12)	0.66	0.66	0.75	0.93	0.98	1.00	1.00
1500	9.83(−12)	0.80	0.80	0.85	0.94	0.99	1.01	1.00
2400	4.21(−11)	0.90	0.90	0.92	0.95	1.00	1.00	1.00

5.3.1 H_3 Reactions

We return once again to the study of reaction (R1) for the three-dimensional case. Accurate quantum mechanical results were calculated by Schatz and Kuppermann[121,122] for the PK2 potential energy surface, and by Park and Light[123] for the LSTH surface. A number of comparisons between the accurate results and the results of VTST calculations have been made for the PK2 surface; these are given in Refs 10, 20, 31, 50, 52, 124, and 125. Results of VTST calculations are compared to experimental results[126,127] in Ref 18. Results from the present study are given in Table 56 for the PK2 surface, and in Table 57 for the LSTH surface.

The results of reaction (R1) on the PK2 potential energy surface are now compared to the accurate data. The TST and ICVT data are very similar to one another for this reaction, and both methods underestimate the accurate rate coefficient, most severely at the lower temperatures. The ICVT/ZCT results give some improvement, particularly at low temperatures, but agreement with the accurate data is still poor. The SCT, LCT, LAT, and μOMT results all tend to overestimate the accurate rate coefficient at low temperatures but come into excellent agreement at the higher temperatures. The LAT method predicts a larger tunneling correction at the lower temperatures making it less accurate compared to the accurate rate coefficients than the other methods. The μOMT also tends to overestimate the accurate data but the results are in better agreement with the accurate data than the

Table 57: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R1), H + HH → HH + H, on the LSTH potential energy surface.

				ICVT	ICVT	ICVT	ICVT	ICVT
T (K)	Accurate	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT
300	2.76(−16)	0.10	0.10	0.20	0.78	0.64	0.80	0.82
400	5.67(−15)	0.20	0.20	0.30	0.68	0.62	0.71	0.68
600	1.36(−13)	0.39	0.39	0.46	0.67	0.66	0.71	0.68
1000	1.98(−12)	0.68	0.68	0.72	0.83	0.84	0.88	0.85
1500	8.27(−12)	1.02	1.02	1.04	1.11	1.14	1.17	1.15

	ICVT			ICVT	ICVT	ICVT	ICVT	ICVT
T (K)	/LAT	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT
200	1.83(−18)	0.007	0.007	0.05	0.79	0.42	0.79	1.00
250	2.88(−17)	0.04	0.04	0.13	0.89	0.65	0.91	1.00
2400	4.61(−11)	0.94	0.94	0.95	0.97	1.00	1.01	1.00

LAT results. The SCT results begin to underestimate the accurate data at higher temperatures, and thus the LCT method yields the best rate coefficients. The data above 600 K are compared to the ICVT/LAT result. The SCT, LCT, and μOMT are found to be in good agreement with the LAT results. The TST, ICVT, and ICVT/ZCT results are too small compared to the ICVT/LAT data, but are within a factor of two. The LCT method is the best overall with an MUPE and an LAPE of 8%.

The results of reaction (R1) on the LSTH potential energy surface are now considered. The TST and ICVT methods yield similar rate coefficients which are smaller than the accurate values up to 1000 K. The ICVT/ZCT results give improved agreement with the accurate data, particularly at lower temperatures. The LCT results underestimate the accurate rate coefficient up to 1000 K but are in reasonable agreement. The SCT results are similar to the LCT results, but give better agreement with the accurate data below 600 K. The LAT and μOMT results yield similar results are in good agreement with the accurate results. At 200, 250, and 2400 K, the TST, ICVT, and ICVT/MT data are compared to the ICVT/LAT results. The TST and ICVT results are much too small at the two lower temperatures. At 2400 K, the TST and ICVT results are in good agreement with the ICVT/LAT result. The LCT result agrees well with the LAT result at 2400 K, but is too small at the lower temperatures. The SCT and μOMT results are in good agreement with the LAT data at all three temperatures. The best overall method for this reaction is the μOMT method which yields an MUPE of 21% and an LAPE of 27%.

Two reactions which were not studied for the one-dimensional case (by accurate quantum mechanical methods) have been studied for the three-dimensional case on the PK2 potential energy surface by Schatz and Kuppermann.[128] These are

$$\mathrm{H} + \mathrm{H'D} \rightarrow \mathrm{HH'} + \mathrm{D} \tag{R31}$$

$$\mathrm{H} + \mathrm{DH'} \rightarrow \mathrm{HD} + \mathrm{H'} \tag{R32}$$

The results of VTST calculations are compared to the accurate quantum mechanical rate coefficients in Ref 125. Results from the present study are given in Table 58 for reaction (R31) and in Table 59 for reaction (R32).

The results for reaction (R31) on the PK2 potential energy surface are now considered. The TST and ICVT results seriously underestimate the accurate rate coefficient in the temperature range 200 to 300 K. The ZCT results yield only a slight improvement in accuracy over the TST and ICVT results. The SCT, LCT, and μOMT results show better agreement with the accurate data. The LAT results, however, show the best agreement with the accurate data.. The data above 300 K are compared to the ICVT/LAT results. The TST and ICVT rate coefficients agree poorly with the largest discrepancies coming at lower temperatures. The ZCT results also show larger discrepancies at lower temperatures but give slightly better agreement with the LAT data. The remainder of the ICVT/MT methods show good agreement with the ICVT/LAT results. The best method overall is the LAT method with an MUPE value of 11% and an LAPE value of 13%.

The same comparison is now made for reaction (R32) on the PK2 surface. As before, the TST and ICVT results are much too small compared to the accurate quantal data in the temperature range 200 to 300 K. The ZCT results improve the agreement with the accurate data somewhat. The SCT and μOMT results tend to overestimate the accurate data, but by a maximum of about 50%. The LAT results further overestimate the accurate rate coefficient and agreement is only within a factor of two. The best results are the LCT results which are in good agreement with the accurate data. The results above 300 K are compared to the ICVT/LAT data. The TST, ICVT, and ICVT/ZCT results are in poorer agreement with the ICVT/LAT data at the lower temperatures, and all other ICVT/MT data is in good agreement. The best overall method for this reaction is the LCT method which has an MUPE of 15% and an LAPE of 17%.

Reaction (R4) was studied in three dimensions on the PK2 surface by Schatz and Kuppermann,[128] and comparison was made between the accurate quantum mechanical and VTST rate coefficients in Ref 125. Table 60 presents the three-dimensional results of the current study for the PK2 surface. Reaction (R4) was also studied in three dimensions on the LSTH surface,[41] the DMBE surface,[129] and the BKMP[130] surface by Mielke *et al.*[131] over a wide range of temperatures. The results of the present study may be found in Table 61 for the LSTH surface, Table

Table 58: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R31), $\mathrm{H + HD \rightarrow HH + D}$, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.00(−18)	0.003	0.003	0.04	0.43	0.44	0.52	0.78
250	3.00(−17)	0.02	0.02	0.10	0.57	0.63	0.69	0.89
300	2.00(−16)	0.06	0.05	0.19	0.69	0.79	0.83	0.99
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	2.82(−15)	0.18	0.16	0.34	0.79	0.89	0.92	1.00
600	5.18(−14)	0.44	0.40	0.56	0.87	0.95	0.97	1.00
1000	7.78(−13)	0.72	0.68	0.77	0.91	0.98	1.00	1.00
1500	3.99(−12)	0.86	0.82	0.86	0.94	0.99	1.00	1.00
2400	1.85(−11)	0.93	0.90	0.92	0.95	0.99	1.00	1.00

Table 59: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R32), $\mathrm{H + DH \rightarrow HD + H}$, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.20(−18)	0.004	0.004	0.11	1.23	0.77	1.27	1.62
250	1.50(−17)	0.03	0.03	0.24	1.45	1.10	1.51	1.91
300	1.10(−16)	0.08	0.08	0.35	1.38	1.13	1.45	1.81
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	2.65(−15)	0.15	0.15	0.33	0.79	0.69	0.84	1.00
600	4.63(−14)	0.39	0.39	0.55	0.85	0.79	0.90	1.00
1000	6.82(−13)	0.67	0.67	0.77	0.91	0.89	0.96	1.00
1500	3.53(−12)	0.82	0.82	0.86	0.93	0.94	0.98	1.00
2400	1.62(−11)	0.91	0.91	0.93	0.95	0.96	0.99	1.00

Table 60: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R4), D + HH → DH + H, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	2.60(−17)	0.004	0.004	0.04	0.46	0.44	0.54	0.80
250	2.60(−16)	0.02	0.02	0.10	0.60	0.63	0.70	0.89
300	1.40(−15)	0.06	0.06	0.18	0.69	0.74	0.80	0.92

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	1.30(−14)	0.19	0.19	0.35	0.84	0.90	0.95	1.00
600	1.73(−13)	0.45	0.45	0.59	0.91	0.96	1.00	1.00
1000	2.02(−12)	0.72	0.72	0.79	0.94	0.99	1.01	1.00
1500	9.28(−12)	0.85	0.84	0.88	0.95	0.99	1.01	1.00
2400	3.87(−11)	0.95	0.92	0.93	0.96	1.00	1.01	1.00

62 for the DMBE surface, and in Table 63 for the BKMP surface. No previous comparisons of VTST results to accurate quantal rate coefficients have been given for the LSTH, DMBE, or BKMP surfaces.

We first consider the results for reaction (R4) on the PK2 surface. Comparison to the accurate data is made at 200, 250, and 300 K. The TST and ICVT results are much smaller than the accurate data at the temperatures studied, and the ICVT/ZCT results are in better agreement but still much too small. The SCT and LCT results are similar and underestimate the accurate data as well, but are in reasonable agreement at the higher temperatures. The μOMT data is within a factor of two of the accurate data at the lowest temperature, and is in good agreement at the highest temperature. The LAT results are the most reliable for this reaction, however, and are in very good agreement with the accurate data. The data above 300 K are compared to the ICVT/LAT data. Agreement with the ICVT/LAT data is poorer for the TST, ICVT, and ICVT/ZCT methods at the lower temperatures, otherwise all of the ICVT/MT data is in good agreement. The best method overall in the LAT method which has an MUPE value of 13% and an LAPE value of 15%.

We next consider reaction (R4) on the LSTH surface. The TST, ICVT, and ICVT/ZCT results all underestimate the accurate data at lower temperatures but come into good agreement at higher temperatures. The LCT results tend to underestimate the accurate rate coefficient, but are in reasonable agreement. The LAT rate coefficients are larger than the accurate data at low temperatures, but are in

Table 61: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R4), D + HH → DH + H, on the LSTH potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.76(−18)	0.02	0.02	0.08	0.96	0.62	0.97	1.23
250	3.19(−17)	0.09	0.07	0.19	0.97	0.77	0.99	1.07
300	2.76(−16)	0.17	0.15	0.28	0.92	0.79	0.95	0.95
400	5.03(−15)	0.34	0.31	0.43	0.86	0.79	0.90	0.85
600	1.14(−13)	0.55	0.53	0.61	0.83	0.82	0.88	0.84
1000	1.80(−12)	0.78	0.75	0.78	0.88	0.90	0.94	0.90
1500	8.99(−12)	0.93	0.88	0.90	0.95	0.97	1.00	0.97

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	4.02(−11)	1.04	0.95	0.96	0.98	1.00	1.01	1.00

Table 62: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R4), D + HH → DH + H, on the DMBE potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.64(−18)	0.03	0.02	0.09	0.95	0.62	0.96	1.19
250	3.14(−17)	0.10	0.08	0.19	0.93	0.75	0.95	1.02
300	2.78(−16)	0.20	0.16	0.29	0.89	0.77	0.91	0.91
400	5.13(−15)	0.37	0.32	0.43	0.83	0.78	0.87	0.83
600	1.16(−13)	0.58	0.53	0.61	0.82	0.81	0.87	0.82
1000	1.83(−12)	0.79	0.73	0.77	0.85	0.87	0.91	0.88
1500	9.12(−12)	0.92	0.84	0.86	0.90	0.92	0.95	0.93

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	3.80(−11)	1.08	0.95	0.96	0.98	1.00	1.01	1.00

Table 63: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R4), D + HH → DH + H, on the BKMP potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.21(–18)	0.02	0.01	0.07	0.75	0.49	0.76	0.97
250	5.24(–17)	0.07	0.06	0.15	0.78	0.62	0.79	0.86
300	4.21(–16)	0.14	0.13	0.23	0.76	0.66	0.78	0.78
400	6.93(–15)	0.29	0.26	0.37	0.73	0.68	0.76	0.72
600	1.42(–13)	0.48	0.45	0.52	0.72	0.71	0.76	0.72
1000	2.07(–12)	0.67	0.64	0.67	0.75	0.77	0.80	0.77
1500	9.97(–12)	0.78	0.73	0.75	0.79	0.81	0.83	0.81

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	3.47(–11)	1.06	0.95	0.96	0.98	1.00	1.02	1.00

good agreement overall. The SCT results also underestimate the accurate rate coefficient, give slightly better agreement than the LAT results. The μOMT results are in the best agreement with the accurate data but still underestimate the accurate rate coefficient at all temperatures. The data at 2400 K are compared to the ICVT/LAT result and are found to be in good agreement. The μOMT results are the best overall with an MUPE of 5% and an LAPE of 6%.

The comparison of the results for reaction (R4) on the DMBE surface shows similar trends to those seen for the previous surface. The TST, ICVT, and ICVT/ZCT results again underestimate the accurate rate coefficient, particularly at than in the previous case. The data at 2400 K are compared to the ICVT/LAT result and found to be in good agreement. The best overall method for this reaction is the μOMT method which has MUPE and LAPE values of 9%.

The final case of reaction (R4) using the BKMP potential energy surface is now considered. The TST and ICVT results are similar and seriously underestimate the accurate rate coefficient at lower temperatures. At the highest temperatures these methods begin to give good agreement with the accurate data. The ICVT/ZCT results improve slightly over the previous results at low temperatures but the agreement with accurate data is still not good. The LCT results for this reaction are in slightly better agreement, particularly at low temperatures, but the accurate rate coefficient is still underestimated at all temperatures. The SCT and μOMT results are in good agreement with the accurate values. The LAT method gives improved agreement for low-temperature rate coefficients but show larger discrepancies at higher temperatures than the SCT or μOMT methods. The data at 2400 K are compared to the ICVT/LAT result and found to be in good agreement. The best method overall for this reaction in the LAT method which has an MUPE value of 19% and an LAPE value of 25%.

5.3.2 H_2O Reactions

We now consider the reaction (R8) in three-dimensions and its isotopic analogs

$$O + HD \rightarrow OH + D \quad \text{(R33)}$$

$$O + DH \rightarrow OD + H \quad \text{(R34)}$$

$$O + DD' \rightarrow OD + D' \quad \text{(R35)}$$

The reactions, (R8) and (R33) – (R35), were studied on a modified version of the JW potential energy surface which included a correction term due to Schatz.[132] The accurate quantum mechanical rate constant data was also calculated by Schatz.[132] Previous comparison to VTST data is given in reference 125. Rate coefficients calculated in the present study are given for the three-dimensional case in Table 64 for reaction (R8), in Table 65 for reaction (R33), in Table 66 for reaction (R34), and in Table 67 for reaction (R35).

Agreement between the VTST results and the accurate quantal data for reaction (R8) on the JWS surface is reasonably good when the ICVT/MT results are examined. The accurate data at temperatures of 300 and 400 K is considered. The TST and ICVT results are similar to each other and underestimate the accurate rate coefficient. The ZCT results show better agreement with the accurate data but are still too small. The SCT method yields results which are slightly too small but are in very good agreement with the accurate data. The LCT method yields results which are in excellent agreement with the accurate data with a maximum discrepancy of 12%. The μOMT results, like the LCT results, overestimate the accurate rate coefficient and yield slightly larger discrepancies than those seen for the LCT results. The LAT results also overestimate the accurate rate coefficient and these results yield errors which are slightly larger than those for the μOMT results. The data below 300 K and above 400 K are compared to the ICVT/LAT data. It is found that all of the methods yield rate coefficients smaller than the LAT results at temperatures less than 300 K. At temperatures above 400 K, the TST, ICVT, and ICVT/ZCT methods yield results which are usually smaller than the ICVT/LAT results with the discrepancy decreasing with increasing temperature. The remainder of the ICVT/MT results above 400 K are in good agreement with the ICVT/LAT results. The best method overall for this reaction is the LCT method which has an MUPE and an LAPE of 9%.

Table 64: Three-dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R8), O + HH → OH + H, on the JWS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	1.10(−17)	0.05	0.05	0.16	0.86	1.12	1.16	1.30
400	2.90(−16)	0.16	0.16	0.30	0.88	1.05	1.10	1.11

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.26(−20)	0.002	0.002	0.02	0.44	0.62	0.63	1.00
250	1.39(−18)	0.01	0.01	0.06	0.56	0.78	0.80	1.00
600	1.03(−14)	0.40	0.39	0.53	0.90	0.99	1.03	1.00
1000	2.63(−13)	0.70	0.68	0.76	0.94	1.00	1.03	1.00
1500	1.85(−12)	0.84	0.82	0.86	0.95	1.00	1.02	1.00
2400	9.91(−12)	1.03	0.91	0.92	0.96	1.00	1.01	1.00

Table 65: Three-dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R33), O + HD → OH + D, on the JWS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	2.00(−18)	0.08	0.08	0.20	0.63	1.16	1.16	1.24
400	7.30(−17)	0.20	0.20	0.33	0.69	1.07	1.07	1.10

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.96(−21)	0.005	0.005	0.04	0.31	0.78	0.78	1.00
250	1.76(−19)	0.03	0.03	0.09	0.42	0.88	0.88	1.00
600	3.43(−15)	0.42	0.42	0.53	0.76	1.00	1.00	1.00
1000	1.07(−15)	0.69	0.68	0.74	0.85	1.00	1.00	1.00
1500	8.29(−13)	0.81	0.81	0.84	0.90	1.00	1.00	1.00
2400	4.62(−12)	1.01	0.90	0.91	0.93	1.00	1.00	1.00

The results for reaction (R33) on the JWS surface show similar agreement to those of the previous reaction. The accurate data is available at 300 and 400 K.

Table 66: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R34), O + DH → OD + H, on the JWS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	7.30(−19)	0.15	0.14	0.38	1.46	0.83	1.47	0.91
400	2.70(−17)	0.38	0.36	0.62	1.37	0.89	1.39	0.91

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.61(−21)	0.008	0.007	0.09	1.25	0.63	1.25	1.00
250	5.08(−20)	0.06	0.05	0.24	1.51	0.82	1.51	1.00
600	1.48(−15)	0.73	0.69	0.87	1.25	1.00	1.30	1.00
1000	6.10(−14)	0.93	0.88	0.95	1.09	1.00	1.14	1.00
1500	5.17(−13)	1.02	0.94	0.98	1.04	1.00	1.08	1.00
2400	3.20(−12)	1.15	0.97	0.99	1.01	1.00	1.04	1.00

Table 67: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R35), O + DD → OD + D, on the JWS potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
300	6.90(−19)	0.14	0.14	0.36	1.27	0.94	1.29	1.01
400	3.70(−17)	0.29	0.29	0.49	1.06	0.81	1.08	0.83

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	8.79(−22)	0.01	0.01	0.08	0.94	0.74	0.95	1.00
250	4.28(−20)	0.06	0.05	0.21	1.16	0.87	1.17	1.00
600	2.11(−15)	0.65	0.64	0.81	1.17	1.00	1.21	1.00
1000	1.01(−13)	0.86	0.85	0.93	1.06	1.00	1.10	1.00
1500	9.53(−13)	0.94	0.93	0.96	1.02	1.00	1.06	1.00
2400	6.54(−12)	1.02	0.97	0.98	1.00	1.00	1.03	1.00

The TST and ICVT methods yield results indistinguishable from one another which underestimate the accurate rate coefficient. The ZCT method yields rate coefficients which are in slightly better agreement with the accurate data but which are still too small. The SCT results show reasonable agreement with the accurate data but are 33% too small on the average. The LCT, μOMT, and LAT results all exceed the accurate data and the LCT and μOMT results are slightly more accurate than the LAT data. The data below 300 K and above 400 K are compared to the ICVT/LAT data. The TST, ICVT, and ICVT/MT methods all underestimate the ICVT/LAT results below 300 K although the ICVT/MT results are generally in much better agreement. At temperatures above 400 K, the TST, ICVT, ICVT/ZCT, and ICVT/SCT methods yield rate coefficients which are usually smaller than the ICVT/LAT results but are in reasonable agreement. The LCT and μOMT data are in excellent agreement with the LAT data above 300 K. The best method overall for this reaction is the LCT method which has an MUPE of 12% and an LAPE of 11%. The μOMT method has an MUPE and LAPE of 12%.

The results for reaction (R34) on the JWS surface show reasonable agreement with the accurate quantal data. The TST and ICVT results are too small compared to the accurate quantal data. The ICVT/ZCT results are also too small compared to the accurate data, but are in better agreement than the TST and ICVT results. The SCT and μOMT methods yield results which are similar to one another and overestimate the accurate data by 37–47%. The LCT results are in good agreement with the accurate quantal data although they are 11–17% too small. The LAT results agree with the accurate data within 9%. The data below 300 K and above 400 K are compared to the ICVT/LAT data. At the lowest two temperatures the TST, ICVT, and ICVT/ZCT methods underestimate the ICVT/LAT results significantly. The SCT and μOMT results exceed the LAT results while the LCT results are smaller than the LAT results. Above 400 K, all of the results are in good agreement with the ICVT/LAT results with a maximum discrepancy of 31%. The best method overall for this reaction is the ICVT/LAT method which has an MUPE and LAPE of 9%.

We conclude the study of OH_2 reactions by considering the results of reaction (R35) on the JWS surface. The TST and ICVT results are mutually indistinguishable and both underestimate the accurate rate coefficient. The ZCT results yield slightly better agreement with the accurate data than the TST or ICVT results, but still underestimate the accurate rate coefficient. The SCT and μOMT methods yield results of similar accuracy compared to the accurate data and which overestimate the accurate rate coefficient somewhat. The LCT results are in good agreement with the accurate values underestimating the accurate data by 6–19%. The LAT results are somewhat more accurate than the LCT results compared to the accurate values, especially at 300 K where the LAT method yields a discrepancy of only 1%. The data below 300 K and above 400 K are compared to the ICVT/LAT results. The TST, ICVT, and ICVT/ZCT methods tend to underestimate the ICVT/LAT rate coefficients, especially at lower temperatures. The remainder of the

Table 68: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R15), Cl + HH → ClH + H, on the G3 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	8.77(−16)	0.06	0.06	0.14	0.50	0.79	0.80	1.01
250	6.34(−15)	0.12	0.12	0.21	0.54	0.82	0.83	0.95
300	2.52(−14)	0.19	0.19	0.28	0.56	0.82	0.82	0.91
400	1.51(−13)	0.32	0.32	0.39	0.60	0.82	0.82	0.86
600	1.01(−12)	0.50	0.49	0.55	0.67	0.83	0.83	0.85
1000	5.46(−12)	0.74	0.69	0.71	0.77	0.89	0.89	0.90
1500	1.54(−11)	0.92	0.72	0.73	0.75	0.83	0.83	0.84

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
2400	3.25(−11)	1.43	0.92	0.92	0.94	1.00	1.00	1.00

results are in good agreement with the ICVT/LAT data. The best method overall for this reaction is the ICVT/LAT method which has an MUPE of 9% and an LAPE of 10%.

5.3.3 H_2Cl Reactions

We return to the study of reaction (R13), but on a newer potential energy surface due to the authors and coworkers,[133] which is called G3. This surface is believed to be the most accurate surface currently available for reaction (R13) and its isotopic analogs. Accurate quantum mechanical rate coefficients were computed by Mielke *et al.*[134] using the separable rotation approximation (SRA).[135,136] Comparison to VTST/LAT rate coefficient calculations was made in Ref 134. Results from the present study for the three-dimensional treatment of reaction (R13) are given in Table 68.

The results of VTST calculation of reaction (R15) on the G3 potential energy surface are now considered. The TST, ICVT, and ICVT/ZCT results are too small compared to the accurate quantal rate coefficient data at lower temperatures but come into reasonable agreement at higher temperatures. The SCT results systematically underestimate the accurate rate coefficients but yield better accuracy than the previous methods, particularly at lower temperatures. The LCT and μOMT results are similar to each other and are in good agreement with the accurate rate coefficients. It is the LAT results which give the best agreement with the accurate data for this reaction, however. The low-temperature agreement is the most improved but the LAT calculations still underestimate the accurate data. Nevertheless, the agreement is excellent which a maximum discrepancy of 16% at 1500 K. The data at 2400 K are compared to the ICVT/LAT result and are found to be in good agreement except for the TST rate coefficient which is too large. The best method overall is the LAT method which has an MUPE value of 10% and an LAPE value of 11%.

5.3.4 H_2Br Reactions

Reactions (R18) and (R19) are again studied on the DIM–3C–B potential energy surface, but in three dimensions. Accurate quantum mechanical rate coefficient calculations are reported in Refs 89 and 137. Comparison to VTST/MT calculations is made in Refs 20, 89, and 90 for reaction (R18) and in Refs 20, 31, and 89 for reaction (R19). Rate coefficient data from the present study for the three-dimensional case are given in Table 69 for reaction (R18) and in Table 70 for reaction (R19).

One note is in order before we discuss the results. The VTST calculations presented for reactions (R18) and (R19) were made using bending vibrational energies computed from a fit to the potential at bending angles of 10 and 20 degrees. In all other cases in this chapter, except where noted, the bending vibrational energies are computed from a fit to the potential made using the second derivative along the MEP. A fit made at two bending angles was necessary to avoid errors due to the approximate numerical derivatives employed in the DIM–3C–B surface.

The results for reaction (R18) on the DIM–3C–B surface are now considered. The TST and ICVT results are too small at low temperatures but are within a factor of three of the accurate data at 400 K. The ZCT results yield improved agreement with the accurate data compared to the TST and ICVT results although the low-temperature results are still too small. The LCT results show reasonable agreement with the accurate data but are too small at lower temperatures. The LAT method gives results in good agreement with the accurate data and improves the low-temperature agreement compared to the LCT results. The SCT and μOMT results overestimate the accurate rate coefficient at the lower temperatures but are in very good agreement overall. The data above 400 K are compared to the ICVT/LAT data. All of the ICVT/MT data are in good agreement with the ICVT/LAT data. The TST and ICVT data are a little too small at lower temperatures, and the TST data is much too large at 2400 K. The best method overall in the SCT method which has an MUPE and an LAPE of 11%. The μOMT method also has an LAPE of 11% but has an MUPE of 12%.

Table 69: Three-dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R18), H + BrH → HBr + H, on the DIM–3C–B potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.50(−15)	0.02	0.02	0.30	1.24	0.58	1.24	0.74
250	5.60(−15)	0.08	0.08	0.43	1.12	0.60	1.12	0.66
300	1.60(−14)	0.18	0.18	0.54	1.07	0.65	1.07	0.68
400	7.80(−14)	0.38	0.38	0.70	1.01	0.75	1.03	0.76
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
600	4.69(−13)	0.75	0.75	0.97	1.15	1.00	1.17	1.00
1000	3.66(−12)	0.90	0.90	0.99	1.05	1.00	1.07	1.00
1500	1.03(−11)	1.23	0.96	1.00	1.02	1.00	1.04	1.00
2400	1.18(−11)	3.70	0.98	1.00	1.01	1.00	1.02	1.00

Table 70: Three-dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R19), D + BrH → DBr + H, on the DIM–3C–B potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.00(−16)	0.07	0.07	0.41	1.10	0.57	1.10	0.59
250	4.20(−15)	0.19	0.18	0.55	1.05	0.64	1.06	0.65
300	1.30(−14)	0.32	0.31	0.66	1.03	0.72	1.04	0.72
400	6.60(−14)	0.54	0.53	0.80	1.02	0.82	1.03	0.83
T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
600	4.24(−13)	0.84	0.83	0.99	1.10	1.00	1.12	1.00
1000	3.15(−12)	0.95	0.93	1.00	1.03	1.00	1.06	1.00
1500	7.43(−12)	1.48	0.97	1.00	1.01	1.00	1.03	1.00
2400	7.93(−12)	4.68	0.99	1.00	1.01	1.00	1.02	1.00

The results for reaction (R19) on the DIM–3C–B surface are similar to those of the previous reaction. The TST and ICVT results underestimate the accurate rate

Table 71: Three-dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R26), Cl + HCl $\rightarrow$ ClH + Cl, on the PK3 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	9.13(−15)	0.11	0.11	0.13	0.13	0.41	0.42	0.40

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.35(−18)	0.03	0.03	0.06	0.06	1.07	1.08	1.00
250	6.59(−17)	0.08	0.08	0.12	0.12	1.06	1.06	1.00
300	3.74(−16)	0.14	0.14	0.18	0.19	1.04	1.05	1.00
600	3.58(−14)	0.61	0.48	0.52	0.52	1.02	1.03	1.00
1000	2.77(−13)	1.25	0.70	0.71	0.72	1.01	1.02	1.00
1500	9.06(−13)	1.95	0.81	0.82	0.82	1.01	1.01	1.00
2400	2.70(−12)	2.87	0.89	0.89	0.89	1.00	1.01	1.00

coefficient especially at low temperatures. The ZCT results yield better agreement with the accurate data, particularly at higher temperatures. The LCT and LAT results yield reasonable agreement with the accurate rate coefficients but are somewhat too small at lower temperatures. The SCT and μOMT results are similar to one another and are in excellent agreement with the accurate data. The data above 400 K are compared to the ICVT/LAT data and are found to be in good agreement with the exception of the TST data which severely overestimate the rate coefficient at 2400 K. The best overall method for this reaction is the SCT method which has an MUPE and LAPE of 5%.

5.3.5 HCl$_2$ Reactions

We conclude this section with the study of the three-dimensional reactions (R26) and (R27). Two potential energy surfaces will be considered for these reactions, in particular the BCMR surface[107,108] and the PK3 surface of Persky and Kornweitz.[138] Accurate quantum mechanical rate coefficients were made for both reactions on both surfaces, as well as on the sf-PolCI surface[139] by Schatz *et al.;*[140] however, we will not consider the sf-PolCI surface here because of its unusual anharmonicity, which makes it an inconclusive test of the dynamical methods.[33] For all the cases studied here, accurate quantal data are available at three temperatures, 312.5, 368.2, and 423.2 K. Thus the accurate data is only presented at 400 K where it may be accurately interpolated. The remainder of the data is compared to the ICVT/LAT

Table 72: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R26), Cl + HCl → ClH + Cl, on the BCMR potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	1.07(−14)	0.20	0.20	0.21	0.21	0.51	0.51	0.49

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	7.09(−18)	0.09	0.09	0.12	0.12	1.08	1.09	1.00
250	8.96(−17)	0.17	0.17	0.21	0.21	1.06	1.07	1.00
300	5.20(−16)	0.26	0.26	0.29	0.30	1.05	1.06	1.00
600	5.21(−14)	0.78	0.59	0.61	0.62	1.02	1.03	1.00
1000	4.39(−13)	1.35	0.76	0.77	0.77	1.01	1.02	1.00
1500	1.43(−12)	2.04	0.85	0.85	0.85	1.01	1.01	1.00
2400	4.22(−12)	2.93	0.91	0.91	0.91	1.00	1.01	1.00

Table 73: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R27), Cl + DCl → ClD + Cl, on the PK3 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	8.01(−16)	0.37	0.37	0.44	0.50	1.00	1.00	1.00

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	3.56(−19)	0.06	0.06	0.12	0.18	1.02	1.02	1.00
250	6.80(−18)	0.13	0.13	0.21	0.27	1.02	1.02	1.00
300	5.30(−17)	0.21	0.21	0.29	0.36	1.01	1.01	1.00
600	1.45(−14)	0.63	0.57	0.62	0.66	1.00	1.00	1.00
1000	1.56(−13)	1.23	0.76	0.78	0.80	1.00	1.00	1.00
1500	6.35(−13)	1.76	0.85	0.86	0.87	1.00	1.00	1.00
2400	2.28(−12)	2.31	0.91	0.92	0.93	1.00	1.00	1.00

results. Comparison to previous VTST results for both reactions may be found in Ref 33. Rate coefficients calculated for the present study may be found for the three-

Table 74: Three–dimensional rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R27), Cl + DCl → ClD + Cl, on the BCMR potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
400	1.51(−15)	0.37	0.37	0.42	0.45	0.83	0.83	0.82

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	5.00(−19)	0.11	0.11	0.17	0.22	1.03	1.03	1.00
250	9.93(−18)	0.21	0.21	0.27	0.33	1.02	1.02	1.00
300	7.93(−17)	0.30	0.30	0.37	0.41	1.02	1.02	1.00
600	2.05(−14)	0.79	0.64	0.68	0.70	1.01	1.01	1.00
1000	2.42(−13)	1.34	0.80	0.81	0.82	1.00	1.00	1.00
1500	1.00(−12)	1.82	0.87	0.88	0.89	1.00	1.00	1.00
2400	3.54(−12)	2.36	0.93	0.93	0.93	1.00	1.00	1.00

dimensional case of reaction (R26) in Table 71 for the PK3 surface and in Table 72 for the BMCR surface, and for reaction (R27) in Table 73 for the PK3 surface and in Table 74 for the BCMR surface.

The results for reaction (R26) on the PK3 surface are now considered. The only comparison to the accurate data is made at 400 K where all of the methods underestimate the accurate rate coefficient. The best agreement is given by the LCT, LAT, and μOMT methods which underestimate the accurate rate coefficient by a factor of about 2.5. The remainder of the data are compared to the ICVT/LAT data. The LCT and μOMT data show good agreement while the other methods systematically underestimate the LAT value. The LCT method is the best overall method for this reaction and has an MUPE of 58% and an LAPE of 141%.

The results for reaction (R26) on the BCMR surface show slightly better agreement. The LCT, LAT, and μOMT results are within a factor of two of the accurate results at 400 K, and the remainder of the results are accurate within a factor of five. The remainder of the data is compared to the ICVT/LAT data, and the LCT and μOMT data are found to be in good agreement. The ICVT, ICVT/ZCT, and ICVT/SCT results are too small at lower temperatures but are in good agreement at higher temperatures. The TST results are too small compared to the accurate data at lower temperatures and too large at higher temperatures. The best overall method for this reaction is the μOMT method which has an MUPE of 49% and an LAPE of 96%.

The results of reaction (R27) on the PK3 surface are now considered. The LCT, LAT, and μOMT data is found to be in nearly perfect agreement with the accurate data at 400 K. The remaining methods yield rate coefficients which are factors of two to three times too small compared to the accurate data at 400 K. The remaining data are compared to the ICVT/LAT results and the LCT and μOMT methods are in good agreement. The ICVT, ICVT/ZCT, and ICVT/SCT results are too small at lower temperatures compared to the ICVT/LAT data but give good agreement at higher temperatures. The TST results are too small at lower temperatures and too large at higher temperatures compared to the ICVT/LAT data. The best methods overall are the LCT, μOMT, and LAT methods which have MUPE and LAPE values less than 1%.

We now consider the results of reaction (R27) on the BCMR surface. The LCT, LAT, and μOMT results slightly underestimate the accurate rate coefficient at 400 K but are in good agreement. The remaining methods seriously underestimate the accurate rate coefficient at 400 K. The data at the other temperatures is compared to the ICVT/LAT results. The LCT and μOMT methods are in good agreement with the LAT data while the ICVT, ICVT/ZCT, and ICVT/SCT methods underestimate the rate coefficient, particularly at low temperatures. The TST results are too small at low temperatures and too large at high temperatures compared to the ICVT/LAT data. The best methods overall are the LCT and μOMT method which have MUPE values of 17% and LAPE values of 21%.

5.4 State-Selected Three-Dimensional Reactions

In this section, we consider two accurate calculations of state-selected three-dimensional rate coefficients. The first is the calculation of Schatz[141] for the state-selected three-dimensional case of reaction (R1) on the PK2 surface. The results of the present study are given in Table 75.

All ICVT results that include tunneling, with the exception of the LAT results, yield comparable results for this reaction, and in particular they overestimate the accurate rate coefficient by 13–85%. The ICVT/LAT method overestimates the accurate rate coefficient by a factor of about two in the temperature range 200–400 K. The ICVT rate coefficients for this reaction are also in reasonably good agreement compared to the accurate results. The TST results overestimate the accurate rate coefficient by factors ranging from 4.6 to 10.3. Rate coefficient data at temperatures of 600 K and above agree well with the ICVT/LAT data. The ICVT results yield the best overall agreement for this reaction with MUPE and LAPE values of 28%.

Table 75: Three–dimensional state–selected rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R1), H + HH(n = 1) → HH + H, on the PK2 potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.01(–14)	10.29	0.74	1.13	1.15	1.16	1.20	1.90
250	5.39(–14)	7.58	1.00	1.31	1.33	1.35	1.38	1.96
300	1.65(–13)	6.10	1.23	1.48	1.49	1.52	1.54	2.05
400	6.66(–13)	4.61	1.62	1.80	1.80	1.84	1.85	2.27

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
600	7.44(–12)	1.29	0.82	0.86	0.86	0.88	0.88	1.00
1000	2.96(–11)	0.91	0.90	0.92	0.92	0.93	0.93	1.00
1500	5.52(–11)	0.94	0.94	0.95	0.95	0.95	0.96	1.00
2400	1.06(–10)	0.97	0.96	0.97	0.97	0.97	0.97	1.00

Table 76: Three–dimensional state–selected rate coefficient data (cm^3 molecule^{-1} s^{-1}) for reaction (R4), D + HH(n = 1) → DH + H, on the LSTH potential energy surface.

T (K)	Accurate	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
200	1.12(–14)	137.15	0.25	1.15	1.23	1.15	1.23	1.62
250	5.26(–14)	64.29	0.45	1.17	1.22	1.17	1.23	1.39
300	1.63(–13)	34.80	0.61	1.17	1.21	1.17	1.21	1.29
400	7.87(–13)	13.74	0.78	1.12	1.13	1.12	1.14	1.16
600	4.70(–12)	4.57	0.87	1.02	1.02	1.02	1.03	1.03
1000	2.09(–11)	2.06	1.05	1.11	1.11	1.11	1.11	1.11

T (K)	ICVT /LAT	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT
1500	6.03(–11)	1.18	0.97	1.00	1.00	1.00	1.00	1.00
2400	1.19(–10)	1.06	0.99	1.00	1.00	1.00	1.00	1.00

The other reaction for which accurate state-selected three-dimensional rate coefficients are available is reaction (R4). Zhang and Miller[142] calculated accurate

rate coefficients for this reaction using the LSTH surface. Their results are presented along with the results of the present study in Table 76. No previous comparison of this data to VTST/MT calculations has been made.

As in the previous reaction, the ICVT/ZCT, ICVT/SCT, ICVT/LCT, and ICVT/μOMT results are in good agreement with the accurate rate coefficients. These methods overestimate the accurate rate coefficient by 2–23%. The ICVT/LAT results are somewhat worse, overestimating the accurate data by three to 62%. The ICVT results underestimate the accurate rate coefficient at temperatures up to 600 K by as much as a factor of four. The TST results show the largest errors which decrease from a factor of 137 at 200 K to a factor of two at 1000 K. Both the TST and all ICVT and ICVT/MT results agree well with the ICVT/LAT data at the highest two temperatures. The ZCT and LCT results yield the best overall agreement with the accurate data for this reaction with MUPE and LAPE values of 12%.

6 Statistics for Thermal Reactions

In order to summarize the individual results given in Section 5 and to obtain an overall estimate of the reliability of the VTST and VTST/MT calculations versus accurate quantal rate coefficient data, we calculated average values of the two statistical measures, MUPE and LAPE. In computing these averages both 1D and 3D rate coefficient data are used, but the state-selected results are not included. Thus the averaged values presented in this section are a measure of the reliability of the thermally averaged VTST rate coefficients. In Table 77, statistics are presented for TST, VTST, and VTST/MT data calculated by treating the stretching and bending vibrations anharmonically. Table 78 presents the same statistical measures but with the stretching and bending vibrations treated harmonically. In both tables the averages are given at each of the standard temperatures. The column labeled *N* gives the number of data which were used to compute the averages.

From the data presented in Tables 77 and 78 it is easy to see that the ICVT/MT methods are considerably more accurate than the conventional TST method. At low temperatures, the LAT and μOMT methods are the most accurate on the average. As the temperature is increased several of the VTST/MT methods give results that are comparable to or slightly more accurate than the LAT or μOMT results. However, over the entire temperature range the LAT and μOMT methods appear to be the most systematically accurate.

Tables 77 and 78 contain an extra column corresponding to CVT/μOMT, where CVT[8,27] is canonical variational theory. CVT results were not tabulated for every reaction because they are usually very similar to ICVT results. This is confirmed by comparing the CVT/μOMT and ICVT/μOMT columns in Tables 77 and 78. We

Table 77: Average errors as a function of temperature as compared to accurate quantal rate coefficients for 1D and 3D VTST thermal results including anharmonicity.[a]

				ICVT	ICVT	ICVT	ICVT	ICVT	CVT
T (K)	*N*	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT	/μOMT
200	41	2750	1576	332	63	49	41	40	41
		22800	84	68	42	32	36	35	36
250	44	826	488	167	43	32	28	28	27
		27700	74	56	32	24	26	24	25
300	52	481	273	116	34	24	23	21	22
		6400	65	49	28	21	23	20	22
400	53	225	124	75	36	22	21	20	21
		1370	52	40	27	19	20	18	20
600	41	121	45	33	21	18	17	16	17
		465	32	27	22	18	19	17	19
1000	38	85	25	23	20	19	20	19	21
		234	24	24	22	22	24	22	24
1500	30	83	20	19	20	20	21	20	25
		185	22	22	23	23	26	24	29
2400	12	180	23	23	23	26	26	26	27
		396	26	26	26	30	30	30	30

[a]The upper entry gives the logarithmically averaged percentage error (LAPE) as defined in Eq. 15. The lower entry gives the mean unsigned percentage error (MUPE) as defined in Eq. 16. See also footnote of Table 3.

note that ICVT is not much harder to calculate than CVT, but in applications papers we often report CVT results without mentioning ICVT simply because CVT is easier for readers to understand. Table 79 is like Table 78 except that we exclude all data involving Mu. Muonium reactions provide a difficult challenge for theory, and perhaps some readers will be interested in the statistics absent such a tough test.

In Table 80 the statistical measures are further averaged to present an overall measure of the reliability of the VTST methods versus accurate quantal calculations. Again harmonic and anharmonic treatments of the vibrations are considered. The averages now include contributions from a range of temperatures. The value given in the table is the geometric mean of the average MUPE value and the average LAPE value which we will call the mean error. For this table, *N* is the number of

Table 78: Average errors as a function of temperature as compared to accurate quantal rate coefficients for 1D and 3D harmonic VTST thermal results.[a]

				ICVT	ICVT	ICVT	ICVT	ICVT	CVT
T (K)	*N*	TST	ICVT	/ZCT	/SCT	/LCT	/μOMT	/LAT	/μOMT
200	41	2010	2258	525	139	72	58	71	58
		571000	85	75	45	36	34	43	34
250	44	638	656	254	98	50	43	50	43
		56100	77	63	40	30	28	32	28
300	52	380	333	161	71	37	35	38	35
		11100	69	55	35	26	26	28	26
400	53	180	164	107	70	33	32	32	32
		1920	56	46	35	25	25	24	25
600	41	100	60	47	38	24	24	23	23
		536	37	32	28	21	22	21	22
1000	38	76	28	26	24	22	23	22	23
		244	26	25	24	24	25	24	25
1500	30	85	19	20	20	25	26	25	28
		195	21	22	23	28	30	28	32
2400	12	171	20	20	20	28	28	27	30
		402	20	20	20	30	30	29	32

[a]The upper entry gives the logarithmically averaged percentage error (LAPE) as defined in Eq. 15. The lower entry gives the mean unsigned percentage error (MUPE) as defined in Eq. 16.

pairs of reactions and temperatures for which an accurate quantum rate coefficient is available; these *N* values are tabulated in Table 81. By using the geometric mean we give a single statistic which includes information from both of the statistical measures used in this chapter. For each VTST method, mean errors are given for all 1D cases, all 3D cases, cases with $\beta \leq 50°$, cases with $\beta > 50°$, all 1D and 3D cases excluding muonium cases, and finally *all* 1D and 3D cases. Again we note that the state-selected results are not included in these statistics.

Several trends may be noticed in the data presented in Table 80. The most reliable results are again given by the LAT and μOMT methods while the least reliable results are the conventional TST results. At the VTST/MT level the 1D and 3D results are generally of comparable accuracy. VTST and VTST/MT calculations on systems with large skew angles ($\beta > 50°$) are usually more accurate

Table 79: Average errors as a function of temperature as compared to accurate quantal rate coefficients for 1D and 3D harmonic VTST thermal results, excluding reactions involving muonium (Mu).[a]

T (K)	*N*	TST	ICVT	ICVT /ZCT	ICVT /SCT	ICVT /LCT	ICVT /μOMT	ICVT /LAT	CVT /μOMT
200	37	1480	1952	473	102	54	48	52	48
		720	84	73	41	32	31	40	31
250	40	452	569	223	72	38	34	37	34
		329	75	61	36	26	25	29	25
300	48	283	296	142	54	30	28	30	28
		240	67	53	32	24	24	25	24
400	49	131	148	96	59	27	27	27	26
		140	54	44	32	22	23	22	23
600	37	65	51	39	30	18	19	18	18
		107	34	29	25	18	19	18	19
1000	34	53	24	23	21	19	20	19	20
		107	24	24	23	22	23	22	24
1500	26	63	18	18	20	23	24	23	26
		88	21	22	23	27	29	27	31
2400	8	139	21	22	22	27	27	27	30
		240	23	23	23	30	30	30	33

[a] The upper entry gives the logarithmically averaged percentage error (LAPE) as defined in the text. The lower entry gives the mean unsigned percentage error (MUPE) as defined in the text.

than those on systems with small skew angles. The overall result is that the LAT and μOMT calculations including anharmonicity are, on the average, accurate within 20 – 24% over a large range of temperatures.

7 Conclusion

We have demonstrated that VTST calculations including multidimensional-tunneling (MT) transmission coefficients are reasonably accurate for a variety of reactions in both the one-dimensional and three-dimensional cases. By comparing the results of VTST/MT calculations to accurate quantum mechanical rate coefficient calculations

Table 80: Average errors over various temperature ranges and in various groupings for 1D and 3D thermal reactions. The error term is the geometric mean of the MUPE and LAPE averages.[a]

		Harmonic		Anharmonic	
Method	Case	200–2400 K	300–1500 K	200–2400 K	300–1500 K
TST	all 1D	5392	809	3735	674
	all 3D	171	102	211	127
	$\beta \leq 50^\circ$	8180	1223	5416	958
	$\beta > 50^\circ$	232	117	605	222
	without Mu	238	131	279	194
	all cases	5046	731	3579	625
ICVT	all 1D	97	61	76	46
	all 3D	190	115	221	133
	$\beta \leq 50^\circ$	115	78	94	65
	$\beta > 50^\circ$	114	65	105	60
	without Mu	108	67	105	65
	all cases	114	71	100	62
ICVT/ZCT	all 1D	68	47	48	33
	all 3D	105	75	118	85
	$\beta \leq 50^\circ$	87	65	69	52
	$\beta > 50^\circ$	66	43	55	36
	without Mu	71	50	67	47
	all cases	75	53	61	44
ICVT/SCT	all 1D	48	38	31	25
	all 3D	36	36	30	30
	$\beta \leq 50^\circ$	64	53	47	41
	$\beta > 50^\circ$	30	24	18	13
	without Mu	39	33	31	27
	all cases	45	38	31	26

		Harmonic		*Anharmonic*	
		200–2400 K	*300–1500 K*	*200–2400 K*	*300–1500 K*
ICVT/LCT	all 1D	32	27	23	20
	all 3D	30	27	28	22
	$\beta \leq 50°$	38	34	31	28
	$\beta > 50°$	26	20	19	14
	without Mu	27	23	26	22
	all cases	32	27	24	21
ICVT/μOMT	all 1D	31	26	25	22
	all 3D	29	29	20	19
	$\beta \leq 50°$	40	36	34	32
	$\beta > 50°$	23	18	16	12
	without Mu	27	24	25	22
	all cases	30	27	24	21
ICVT/LAT	all 1D	31	25	23	19
	all 3D	36	31	24	21
	$\beta \leq 50°$	39	34	29	27
	$\beta > 50°$	26	20	18	13
	without Mu	28	23	24	20
	all cases	32	27	23	20
CVT/μOMT	all 1D	31	27	26	22
	all 3D	29	29	21	20
	$\beta \leq 50°$	40	37	35	33
	$\beta > 50°$	23	18	16	12
	without Mu	27	24	26	23
	all cases	31	27	25	22

[a] From the top down the error terms refer to all 1D cases, all 3D cases, all cases with $\beta \leq 50°$, all cases with $\beta > 50°$, all cases except reaction involving muonium (Mu), and all cases. State-selected results are not included. The error term reported in this table is the geometric mean of the MUPE and the LAPE.

for the same potential energy surfaces, we have confined the source of error to the dynamical approximations made in the VTST/MT calculations. This provides more definitive conclusions about the validity of the dynamical approximations than are provided by comparing theoretical predictions to experimental results where deficiencies in the potential energy surface also contribute to the overall error.

A critical issue for the value of the present study is that the TST, CVT, ICVT, ICVT/ZCT, ICVT/SCT, ICVT/LCT, CVT/μOMT, and ICVT/μOMT methods are

Table 81: Number of cases used to calculate the error statistics in Table 80.

Case	200–2400 K	300–1500 K
all 1D	244	167
all 3D	67	47
$\beta \leq 50°$	145	104
$\beta > 50°$	166	110
all cases except Mu	279	194
all cases	311	214

applicable to polyatomic reactions with many degrees of freedom[5,15–19,22,23] If fact they are the best available methods for calculating polyatomic rate coefficients. Thus, what we learn here is very relevant to polyatomic reaction dynamics as well as to the specific systems for which the tests were made. In a number of the cases examined here, the VTST/MT results are reliable within a few percent, and in almost all cases, they are accurate within a factor of two. This is remarkable agreement, especially in the cases where the tunneling calculations are known to be very sensitive to approximations (e.g., low temperatures and large-curvature systems). The comparisons in this chapter show that the least-action tunneling (LAT) calculations are generally the most reliable, although microcanonical optimized multidimensional tunneling (μOMT) calculations are usually of nearly the same accuracy and sometimes even more reliable. It has also been demonstrated that in cases where tunneling corrections are negligible, improved canonical variational theory (ICVT) is generally very reliable.

In the cases where the VTST results are less reliable, we can usually attribute the disagreement to inaccuracies in the tunneling methods. In a few cases the underlying VTST results are also inaccurate, but seldom by a large amount.

The computer program which was used for the VTST calculations presented in this chapter, ABCRATE, is limited to triatomic systems with collinear or collinear-dominated minimum energy paths. For VTST calculations of polyatomic systems the authors recommend the use of the computer program POLYRATE[143] which implements a large subset of the methods available in ABCRATE.

This chapter has focused on a very limited, but extremely important aspect of TST, VTST, and VTST/MT methods, namely, how accurate are they? Other aspects of conventional and generalized transition state theory have been reviewed elsewhere.[22,23]

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Glossary

This glossary provides an explanation of all acronyms used in this paper:

PES	potential energy surface (sometimes called potential energy hypersurface or potential energy function)
TST	transition state theory in general, or—in tables and quantitative discussions—conventional transition state theory
VTST	variational TST
CVT	canonical VTST (also called canonical variational theory)
ICVT	improved canonical VTST (also called improved canonical variational theory)
MT	multidimensional tunneling
ZCT	zero-curvature tunneling approximation, which is the simplest MT approximation
SCT	small-curvature tunneling approximation, which is an MT approximation that is valid when the curvature of the reaction path in isoinertial coordinates is small in the region of the barrier
LCT	large-curvature tunneling approximation, which is an MT approximation that is valid when the curvature of the reaction path in isoinertial coordinates is large in the region of the barrier
μOMT	microcanonical optimized MT approximation
LAT	least-action tunneling, an MT approximation based on tunneling paths with least imaginary action
LAPE	logarithmically averaged percentage error, defined by Eq. 16
MUPE	mean unsigned percentage error, defined by Eq. 15
AUPD	intermediate quantity in the calculation of the LAPE
MEP	minimum energy path (in fact this usually denotes the MEP in isoinertial coordinates)
1D	one-dimensional
3D	three-dimensional
ZPE	zero-point energy
G	ground state
A	adiabatic theory of reactions (also called adiabatic TST)

AG	A + G
IGT	improved generalized transition state theory
WKB	Wentzel-Kramers-Brillouin semiclassical approximation

We note that VAZC, MEPVAG, MEPSAG, SCSAG, CD–SCSA, CD–SCSAG, LCG3, and LAG are alternative names used for the ZCT, SCT, LCT, and LAT methods or methods similar to these methods (as explained in Sections 1 and 2.2) or for transmission coefficients based on these methods.

Finally, we note that all abbreviations used for potential energy surfaces are listed in Table 1, and in every case one or more references is given for each surface in the subsection of Section 5 where the corresponding reaction is discussed.

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