

**Reduced-Dimensionality Semiclassical Transition State
Theory: Application to Hydrogen Atom Abstraction and
Exchange Reactions of Hydrocarbons**

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Abstract

Quantum mechanical methods for calculating rate constants are often intractable for reactions involving many atoms. Semiclassical Transition State Theory (SCTST) offers computational advantages over these methods but nonetheless scales exponentially with the number of degrees of freedom (DOFs) of the system. Here we present a method with more favorable scaling, Reduced-Dimensionality SCTST (RD SCTST), that treats only a subset of DOFs of the system explicitly. We apply it to three H abstraction and exchange reactions for which two-dimensional potential energy surfaces (PESs) have previously been constructed and evaluated using RD quantum scattering calculations. We differentiated these PESs to calculate harmonic frequencies and anharmonic constants, which were then used to calculate cumulative reaction probabilities and rate constants by RD SCTST. This method yielded rate constants in good agreement with quantum scattering results. Notably, it performed well for a heavy-light-heavy reaction, even though it does not explicitly account for corner-cutting effects. Recent extensions to SCTST that improve its treatment of deep tunneling were also evaluated within the reduced-dimensionality framework. The success of RD SCTST in this study suggests its potential applicability to larger systems.

1. Introduction

Quantum mechanical methods for calculating reaction rate constants normally involve constructing a potential energy surface (PES) from *ab initio* energy calculations and then performing either time-dependent or time-independent scattering calculations on this PES.¹⁻¹⁰ For reactions involving more than a few atoms, constructing a PES for all internal degrees of freedom (DOFs) of the system and performing scattering calculations are often prohibitively expensive in terms of computational effort.¹⁰ To our knowledge, the largest systems to which these methods have been applied, with full treatment of all DOFs, are the reactions $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ ¹¹ and $\text{H}_2 + \text{CH}_3 \rightarrow \text{H} + \text{CH}_4$ (and isotopologues).¹² Semiclassical Transition State Theory (SCTST), developed originally by Miller and colleagues,¹³⁻¹⁷ is a computationally more efficient method for calculating reaction rate constants that is more tractable for larger systems. In its original form, it is based on second-order vibrational perturbation theory (VPT2),¹⁸⁻¹⁹ which requires only a fourth-order expansion of the PES about the transition state, although SCTST can also accommodate higher-order perturbative approaches.¹⁷ As VPT2 treats anharmonic coupling among all internal degrees of freedom of the system, SCTST relies upon *ab initio* calculations of vibrational frequencies and anharmonic constants at the transition state.

SCTST simulates semiclassical tunneling through a potential barrier and recovers in an approximate manner quantum mechanical effects not included in conventional Transition State Theory (TST). SCTST offers computational advantages over quantum scattering methods because (1) it requires only derivatives of the PES near the transition state, rather than the entire PES, thereby reducing the number of *ab initio* energy

calculations required, and (2) rate constant calculations are considerably less computationally intensive in SCTST than in quantum scattering methods. Recently, Wagner²⁰ developed an extension to SCTST that more accurately treats tunneling through the potential barrier at low energies, which enables further improvements in the accuracy of SCTST, particularly at low temperature. SCTST has been applied previously to reactions such as $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$,¹⁶ $\text{HBr} + \text{Cl} \rightarrow \text{Br} + \text{HCl}$,²¹ $\text{HO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ and isotopologues,²² and $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ and isotopologues.²³ Calculating the anharmonic constants required by SCTST involves on the order of 3^F *ab initio* energy calculations, where F is the number of internal DOFs of the system. Applying SCTST to larger systems is computationally expensive, and a method with better scaling is desirable.

Improvements in the scaling of quantum scattering methods have been achieved with reduced-dimensionality (RD) approaches.^{8, 24-30} In these approaches, the potential is calculated by *ab initio* methods as a function of only a subset of the internal DOFs, and the remaining DOFs are treated via their zero-point energy (ZPE) contribution to the potential. Substantially fewer *ab initio* calculations are therefore required to construct an RD PES than a full dimensionality PES. Quantum scattering calculations have been performed previously on RD PESs for a number of reactions,³¹⁻⁵² and the results suggest that only a subset of DOFs need to be considered explicitly in order to calculate rate constants with reasonable accuracy.

In this study, we seek to determine whether treating only a subset of DOFs in SCTST can also yield rate constants with acceptable accuracy. We present a modified version of SCTST, Reduced-Dimensionality Semiclassical Transition State Theory (RD

SCTST), in which only a subset of DOFs are treated explicitly. We apply RD SCTST to the following H abstraction and exchange reactions of hydrocarbon molecules:



Rate constants for these reactions have been calculated previously by quantum scattering methods on 2-D PESs.^{44, 51} We use these 2-D PESs in our RD SCTST calculations to evaluate frequencies and anharmonic constants at the transition state and to calculate barrier heights. Rate constants from RD SCTST are compared to quantum scattering results, thereby enabling a systematic evaluation of the accuracy of RD SCTST with respect to RD quantum scattering methods.

R1 and R2, both light-light-heavy reactions, are the simplest H abstraction reactions involving an alkane and a cyclic alkane, respectively, and therefore serve as suitable prototypical reactions for our method. All three reactions involve cleavage of a strong C-H bond⁵³ and are important in hydrocarbon combustion reactions.⁵⁴ R3 is a heavy-light-heavy reaction with a small skew angle and large reaction path curvature. Corner-cutting effects have been shown to be important for such reactions, meaning that tunneling along paths in the concave region of the PES in between the reactant and product channels contributes significantly to the reaction rate.⁵⁵⁻⁵⁶ We apply the RD SCTST method to R3 in order to determine whether it can replicate the results of quantum scattering calculations, which implicitly include corner-cutting effects. All three reactions involve the transfer of a light H atom, suggesting that quantum mechanical tunneling effects are particularly important in determining rate constants at low

temperature. Consequently, we expect rate constants calculated using RD SCTST and quantum scattering methods to be considerably greater than those calculated using conventional TST at low temperature. Comparing our RD SCTST results to TST results will enable us to determine the extent to which RD SCTST recovers quantum mechanical effects.

In section 2 of this paper, we provide a brief overview of SCTST before discussing the modifications required to apply it within an RD framework. We then discuss briefly the methods used to construct the RD PESs we use in this study and discuss in detail how we calculate the parameters required by SCTST. In section 3, we compare results from our RD SCTST method to quantum scattering and experimental results. Section 4 summarizes the key findings of this study.

2. Theoretical Background

2.1 Semiclassical Transition State Theory

2.1.1 Theoretical Overview

In Semiclassical Transition State Theory (SCTST), the cumulative reaction probability (CRP) is calculated from harmonic frequencies and anharmonic constants of the vibrational modes of the transition state. Harmonic frequencies are calculated by diagonalizing the mass-weighted Hessian matrix, evaluated at the transition state. If rovibrational coupling is neglected, anharmonic constants are calculated as follows:¹⁵

$$x_{kk} = \frac{\hbar^2}{16\omega_k^2} \left(f_{kkkk} - \sum_{i=1}^F \frac{f_{kki}^2(8\omega_k^2 - 3\omega_i^2)}{\omega_i^2(4\omega_k^2 - \omega_i^2)} \right) \quad (1)$$

$$x_{kl} = \frac{\hbar^2}{4\omega_k\omega_l} \left(f_{kkll} - \sum_{m=1}^F \frac{f_{kkm}f_{llm}}{\omega_m^2} + \sum_{m=1}^F \frac{2f_{klm}^2(\omega_k^2 + \omega_l^2 - \omega_m^2)}{[(\omega_k + \omega_l)^2 - \omega_m^2][(\omega_k - \omega_l)^2 - \omega_m^2]} \right) \quad (2)$$

where ω_i denotes the harmonic frequency of the i^{th} mode, and f_{klm} and f_{klmn} denote third and fourth vector derivatives, respectively, of the potential with respect to normalized normal mode eigenvectors. As the vibrational frequency of the reaction mode is imaginary, off-diagonal anharmonic constants for the reaction mode are imaginary.

The rate constant $k(T)$ is calculated from a Boltzmann-weighted average of the CRP, here denoted $N(E_v)$:²³

$$k(T) = \frac{1}{h} \frac{Q_{\text{trans}}^{\ddagger}(T) Q_{\text{rot}}^{\ddagger}(T) Q_{\text{elec}}^{\ddagger}(T) \int_{E_{\text{thresh}}}^{\infty} N(E_v) \exp\left(-\frac{E_v}{k_B T}\right) dE_v}{Q_r(T)} \quad (3)$$

where $Q_r(T)$ is the partition function for the reactants, and $Q_{\text{trans}}^{\ddagger}(T)$, $Q_{\text{rot}}^{\ddagger}(T)$, and $Q_{\text{elec}}^{\ddagger}(T)$ are the translational, rotational, and electronic partition functions for the transition state. E_v denotes the total energy in all vibrational degrees of freedom (DOFs) of the transition state and is defined with respect to the reactant energy. E_{thresh} , the reaction's quantum mechanical threshold energy, is the vibrationally corrected classical energy of reaction if the reaction is endothermic and zero otherwise.⁵⁶

The CRP is calculated in SCTST as

$$N(E_v) = \sum_{\{n\}} P_{\{n\}}(E_v) \quad (4)$$

The set $\{n\}$ consists of the $F - 1$ vibrational quantum numbers of the non-reactive modes of the transition state, where F is the total number of vibrational DOFs. The sum is calculated over all configurations $\{n\}$ allowed at energy E_v , so $N(E_v)$ is 0 for E_v less than the total ZPE of all non-reactive modes. The state-dependent reaction probability,

$P_{\{n\}}(E_v)$, for each configuration is calculated as

$$P_{\{n\}}(E_v) = \left(1 + \exp\left(2\theta_{\{n\}}(E_v)\right)\right)^{-1} \quad (5)$$

$\theta_{\{n\}}(E_v)$ represents a barrier penetration integral. For a general one-dimensional potential barrier $V(x)$, the barrier penetration integral is defined in WKB Theory as⁵⁷

$$\theta(E) = \frac{1}{\hbar} \int [2m(V(x) - E)]^{\frac{1}{2}} dx \quad (6)$$

Miller *et al.*¹⁵ give the following analytical expression for the barrier penetration integral along the reaction coordinate for each configuration $\{n\}$:

$$\theta_{\{n\}}(E_v) = \pi \hbar \frac{-\Omega_{\{n\}} + [\Omega_{\{n\}}^2 + 4 x_{FF} (\Delta V - E_v + E_{\{n\}})]^{\frac{1}{2}}}{2x_{FF}} \quad (7)$$

where the subscript F denotes the reaction mode, and ΔV represents the reaction's forward barrier height. The quantity $E_{\{n\}}$ represents the total amount of energy in the non-reactive modes of the system:

$$E_{\{n\}} = \sum_{i=1}^{F-1} \hbar \omega_i \left(n_i + \frac{1}{2}\right) + \sum_{j=1}^{F-1} \sum_{k=j}^{F-1} x_{jk} \left(n_j + \frac{1}{2}\right) \left(n_k + \frac{1}{2}\right) \quad (8)$$

$\Omega_{\{n\}}$ represents an effective reaction mode frequency, through which SCTST accounts for the influence of vibrational coupling on the rate constant:

$$\Omega_{\{n\}} = \text{Im}(\hbar \omega_F) + \sum_{i=1}^{F-1} \text{Im}(x_{iF}) \left(n_i + \frac{1}{2}\right) \quad (9)$$

The above treatment is analogous to calculating the barrier penetration integral for a symmetric Eckart potential, $V_{\text{se}}(s)$:²⁰

$$\theta_{\{n\}}(E_v) = \frac{1}{\hbar} \int [2(V_{\text{se}}(s) - E_v + E_{\{n\}})]^{\frac{1}{2}} ds \quad (10)$$

where s is the mass-weighted reaction coordinate, with units of $(\text{mass}^{1/2} \text{ length})$. $V_{\text{se}}(s)$ is defined as follows:

$$V_{\text{se}}(s) = \Delta V - D + 4 D \frac{\exp(\alpha s)}{[1 + \exp(\alpha s)]^2} \quad (11)$$

with

$$D = -\frac{\Omega_{\{n\}}^2}{4x_{FF}} \quad (12)$$

and

$$\alpha = \frac{(-8 x_{FF})^{\frac{1}{2}}}{\hbar} \quad (13)$$

The limits of integration in eq 10 are given by the classical turning points of $V_{se}(s)$ with respect to the energy ($E_v - E_{\{n\}}$). Due to this definition of the reaction coordinate, the factor of $m^{1/2}$ in eq 6 is not explicitly included in eq 10, as it is implicitly included in the differential ds .

2.1.2 Deep Tunneling Corrections

The deep tunneling extension to SCTST proposed by Wagner²⁰ more accurately represents tunneling through the potential barrier at energies close to the quantum mechanical threshold energy. Instead of a symmetric Eckart potential, the barrier is modeled as a 3-part piecewise Eckart potential, constructed such that its second, third, and fourth derivatives at the transition state equal those implied by $\Omega_{\{n\}}$ and x_{FF} , and the potential at $s = \pm\infty$ is equal to the reactant and product energies, respectively. As demonstrated by Wagner,²⁰ the corresponding barrier penetration integral, $\theta_{\{n\}}(E_v)$, can be calculated analytically, in analogy to eq 10. $P_{\{n\}}(E_v)$ is then calculated as follows:⁵⁶

$$P_{\{n\}}(E_v) = \begin{cases} \{1 + \exp[2 \theta_{\{n\}}(E_v)]\}^{-1}, & E_v - E_{\{n\}} \leq \Delta V \\ 1 - P_{\{n\}}(2 \Delta V - E_v), & \Delta V \leq E_v - E_{\{n\}} \leq \Delta V + \min(\Delta V, \Delta V_r) \\ 1, & \Delta V + \min(\Delta V, \Delta V_r) < E_v - E_{\{n\}} \end{cases} \quad (14)$$

We applied this method within the RD framework in addition to the SCTST method described in section 2.1.1 in order to gain insight into the importance of deep tunneling for the reactions in this study.

2.2 Reduced-Dimensionality Semiclassical Transition State Theory

In this section, we present the theoretical basis for Reduced-Dimensionality SCTST (RD SCTST). DOFs treated explicitly in the calculation of the CRP are referred to as the *active coordinates*. Vibrational DOFs consisting only of linear combinations of the *active coordinates* are *active modes*, and the remaining vibrational DOFs are *spectator modes*. The *active mode* with an imaginary frequency is the reaction mode, and the other modes, which have real frequencies, are the *transition modes*. The CRP in eq 4 is calculated as a sum over the energetically allowed configurations of the *transition modes*, and the energy E_v denotes only the energy in all *active modes*. The state-dependent reaction probability and barrier penetration integral for each configuration is calculated as described in section 2.1.1, except that only *transition modes* are considered in the sums in eqs 8 and 9.

The *spectator modes* are treated via an additional partition function, $Q_{\text{spec}}^\ddagger(T)$, in the expression for $k(T)$, as in other previous RD studies:^{40, 44, 51}

$$k(T) = \frac{1}{h} \frac{Q_{\text{trans}}^\ddagger(T) Q_{\text{rot}}^\ddagger(T) Q_{\text{elec}}^\ddagger(T) Q_{\text{spec}}^\ddagger(T) \int_{E_{\text{thresh}}}^{\infty} N(E_v) \exp\left(-\frac{E_v}{k_B T}\right) dE_v}{Q_r(T)} \quad (15)$$

$Q_{\text{spec}}^\ddagger(T)$ is a product of harmonic oscillator partition functions, calculated from frequencies obtained by projecting motion along the *active coordinates* out of the Hessian at the transition state and diagonalizing it. The details of this projection method will be discussed further in section 2.3.

2.3 Reduced-Dimensionality Potential Energy Surface Construction

Figure 1 presents a schematic representation of a generic hydrogen abstraction reaction from a hydrocarbon molecule, $Y + H_a Z \rightarrow YH_a + Z$. H_a denotes the abstracted H

atom, C represents the carbon atom from which it is abstracted, and R1, R2, and R3 represent the remainder of the Z moiety. In the previous studies considered in this paper,^{44, 51} reduced-dimensionality potential energy surfaces (RD PESs) were constructed as functions of only two *active coordinates*, the Y-H_a and H_a-C bond distances (r_1 and r_2 , respectively, Figure 1). It is important to note that the RD approach does not necessitate the treatment of these particular internal coordinates and that others have approached RD scattering calculations differently.^{31-34, 38} In the construction of the RD PESs considered in this study, *ab initio* calculations were performed on a grid of fixed r_1 and r_2 . At each grid point, a partial geometry optimization of the remaining internal DOFs was performed, followed by a high-level single point energy calculation and a frequency calculation to determine the Hessian. Motion along the *active coordinates* was projected out of the Hessian,^{44-45, 58} and the harmonic vibrational frequencies of the remaining $F - 2$ *spectator modes* were calculated from the mass-weighted Hessian. The total zero-point energy (ZPE) of the *spectator modes* was calculated from these post-projection frequencies and added to the *ab initio* energy of the system in order to account for the effect of the *spectator modes* on the PES.

The Jacobi coordinates R and r at each grid point were calculated from the optimized geometry of the system. Typically, R is defined as the distance between the centers of mass of the moieties YH_a and Z, and r as the distance between the moieties Y and H_a (Figure 1). For R2, R was defined differently as the distance between the center of mass of the moiety YH_a and the C atom from which H_a is abstracted.⁵¹ For R3, r is defined as the distance between H_a and the C atom of the reactant CH₃ moiety.⁴⁴ Note that this treatment does not assume that the Y, H_a, and Z moieties are collinear, as all

coordinates except for the Y-H_a and H_a-Z bond distances (but including the Y-H_a-Z angle) are optimized.

Jacobi coordinates were transformed into hyperspherical coordinates ρ and δ , defined as follows:

$$\frac{m_1}{\mu} R^2 = [\rho \cos(\delta)]^2, \quad \frac{m_2}{\mu} r^2 = [\rho \sin(\delta)]^2 \quad (16)$$

where

$$m_1 = \frac{(m_Y + m_H)m_Z}{m_Y + m_H + m_Z}, \quad m_2 = \frac{m_Y m_H}{m_Y + m_H}, \quad m_3 = \frac{m_C(m_Z - m_C)}{m_Z}, \quad \mu = (m_1 m_2 m_3)^{\frac{1}{3}} \quad (17)$$

m_Y and m_Z are the masses of the Y and Z moieties, and m_H and m_C are the masses of H and C atoms. The ZPE-corrected *ab initio* energies were then fit to a double-Morse potential function, $V(\rho, \delta)$, in hyperspherical coordinates.

The calculations used to construct the RD PESs considered in this study were performed using the MOLPRO package⁵⁹ for R2 and the Gaussian 03 package⁶⁰ for R1 and R3. Geometry optimizations were performed using second-order Møller-Plesset perturbation theory (MP2) with a correlation consistent polarized valence triple- ζ Dunning basis set⁶¹ (cc-pVTZ). Single-point energy calculations were performed at the coupled cluster level including single, double, and perturbative triple excitations [CCSD(T)] with the cc-pVTZ basis set, except for R2, in which the CCSD(T)-F12a/cc-pVTZ-F12 level of theory was used.^{51, 62-64} Hessians were calculated at the MP2 level of theory using a cc-pVTZ basis set, and projections were performed using the rectilinear projection method of Lu and Truhlar⁵⁸ for R2 and the curvilinear projection method for R1 and R3.⁴⁴⁻⁴⁵

2.4 Reduced-Dimensionality Energetics Calculations

For RD SCTST calculations, the frequencies of the *active modes* were calculated from the mass-weighted Hessian matrix, evaluated at the transition state of the PES. At the transition states of R1 and R3, the Y, H_a, and Z moieties are collinear,⁴⁴ and, for R2, they are nearly collinear, with a bond angle of 176.0°.⁵¹ For simplicity, we assumed that the transition states of all three reactions are collinear, which allowed us to consider only one dimensional motion of each of the moieties along the Y-H_a-Z axis in constructing the Hessian matrices. Second derivatives of the potential V with respect to the positions x_Y , x_H , and x_Z of the moieties Y, H_a, and Z, respectively, are calculated analytically as follows:

$$\frac{\partial}{\partial x_Y} = -\frac{m_Y}{m_H+m_X} \frac{\partial}{\partial R} - \frac{\partial}{\partial r} \quad (18)$$

$$\frac{\partial}{\partial x_H} = -\frac{m_H}{m_H+m_X} \frac{\partial}{\partial R} + \frac{\partial}{\partial r} \quad (19)$$

$$\frac{\partial}{\partial x_Z} = \frac{\partial}{\partial R} \quad (20)$$

The chain rule is applied to calculate derivatives of $V(\rho, \delta)$, in hyperspherical coordinates, with respect to the Jacobi coordinates r and R :

$$\frac{\partial}{\partial r} = \sqrt{\frac{m_2}{\mu}} \left(\sin \delta \frac{\partial}{\partial \rho} + \frac{\cos \delta}{\rho} \frac{\partial}{\partial \delta} \right) \quad (21)$$

$$\frac{\partial}{\partial R} = \sqrt{\frac{m_1}{\mu}} \left(\cos \delta \frac{\partial}{\partial \rho} - \frac{\sin \delta}{\rho} \frac{\partial}{\partial \delta} \right) \quad (22)$$

The masses m_Y , m_H , and m_Z are used to weight the 3×3 Hessian matrix before diagonalizing it in order to calculate the frequencies of the reaction mode and *transition mode*. Anharmonic constants are calculated from derivatives of the potential at the transition state with respect to the normal mode eigenvectors, $\{\mathbf{v}_n\}$:

$$\frac{\partial}{\partial v_n} = \mathbf{v}_n \cdot \left(m_Y^{-\frac{1}{2}} \frac{\partial}{\partial x_Y}, m_H^{-\frac{1}{2}} \frac{\partial}{\partial x_H}, m_Z^{-\frac{1}{2}} \frac{\partial}{\partial x_Z} \right) \quad (23)$$

The forward barrier height used in our RD SCTST calculations, $\Delta V_{SC}^\ddagger$, is calculated as follows:

$$\Delta V_{SC}^\ddagger = V(\rho_{TS}, \delta_{TS}) - V(\rho_{\max}, \delta_r) - \frac{\hbar}{2} \left(\frac{m_H + m_Z}{m_H m_Z} \frac{\partial^2 V}{\partial R^2} \Big|_{\rho=\rho_{\max}, \delta=\delta_r} \right)^{\frac{1}{2}} \quad (24)$$

where ρ_{TS} and δ_{TS} represent the hyperspherical coordinates of the transition state. $\rho_{\max}$ denotes the maximum value of ρ considered in the quantum mechanical scattering calculation for each reaction, and δ_r denotes the value of δ at the bottom of the reactant well of the PES at $\rho_{\max}$, which was calculated numerically. The last term in eq 24 represents an effective zero-point energy associated with vibration of the reactant H_a-Z bond. This definition of $\Delta V_{SC}^\ddagger$ includes the ZPE of all reactant vibrational modes, both explicitly via the last term of eq 24 and implicitly via the ZPE of the *spectator modes* included in the PES. As a result, ZPEs were not included in the reactant vibrational partition functions in eq 15. Additionally, $\Delta V_{SC}^\ddagger$ does not include the ZPE of the *transition mode* at the transition state, as this energy is included in $E_{\{n\}}$ (eq 8). The reaction's reverse barrier height, $\Delta V_r^\ddagger$ was determined similarly:

$$\Delta V_r^\ddagger = V(\rho_{TS}, \delta_{TS}) - V(\rho_{\max}, \delta_p) - \frac{\hbar}{2} \left(\frac{m_H + m_Y}{m_H m_Y} \frac{\partial^2 V}{\partial r^2} \Big|_{\rho=\rho_{\max}, \delta=\delta_p} \right)^{\frac{1}{2}} \quad (25)$$

where δ_p denotes the value of δ at the bottom of the product well of the PES. E_{thresh} , the reaction's quantum mechanical threshold energy, can be calculated as follows:

$$E_{\text{thresh}} = \max(0, \Delta V_{SC}^\ddagger - \Delta V_r^\ddagger) \quad (26)$$

2.5 Quantum Scattering Calculations

In this study, the accuracy of the RD SCTST method is evaluated with respect to RD quantum scattering calculations, in particular the *R*-matrix propagation scheme,⁶⁵ performed on the same two-dimensional PESs. We provide a brief overview of these scattering methods here; more detailed descriptions can be found in previous studies.^{38-45,}

⁴⁷⁻⁵⁰ The Hamiltonian in hyperspherical coordinates is given as follows:⁶⁶

$$\hat{H} = -\frac{1}{2\mu} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \delta^2} - \frac{3}{4\rho^2} - \frac{j^2}{\rho^2} \right) + V(\rho, \delta) \quad (27)$$

The *R*-matrix propagation scheme is used to solve the time-independent Schrödinger equation and calculate the scattering matrix *S*. The CRP, $N(E_v)$, is calculated from *S* as follows:

$$N(E_v) = \sum_{i,f} |S_{i \rightarrow f}(E)|^2 \quad (28)$$

where the subscripts *i* and *f* denote the initial and final states of the reactants and products, respectively. The quantum scattering calculations performed for R1, R2, and R3 employed the *J*-shifting approximation to calculate the CRP.^{25, 30, 67} With this approximation, the thermal rate constant, $k(T)$, can be calculated using eq 15.

3. Results and Discussion

3.1 H + CH₄ → H₂ + CH₃ (R1)

3.1.1 Energetics

Table 1 presents the relevant harmonic frequencies for the vibrational modes of the transition state of R1. The reported pre-projection frequencies were calculated by Banks et al.⁴⁴ from the full-dimensionality mass-weighted Hessian, and the post-

projection frequencies were calculated after motion along the *active coordinates*, r_1 and r_2 , was projected out of this Hessian. A comparison of these two sets of frequencies indicates that the *active modes* correspond to the pre-projection modes with frequencies $1648.6i\text{ cm}^{-1}$ and 1352.9 cm^{-1} and that projection left the other *spectator mode* frequencies predominantly unchanged. The frequency of the reaction mode from the RD PES ($1782.3i\text{ cm}^{-1}$) is similar to that of the pre-projection reaction mode ($1648.6i\text{ cm}^{-1}$). However, the frequency of the *transition mode* from the RD PES (1352.9 cm^{-1}) differs considerably from that of the corresponding pre-projection mode (1941.4 cm^{-1}). This difference arises from the RD nature of the PES, in particular that it only treats the two *active coordinates* explicitly. Anharmonic constants for R1 are also presented in Table 1.

Table 1. Pre- and Post-projection Frequencies, and Frequencies and Anharmonic Constants Calculated from the RD PES for R1 at the Transition State^a

Pre-projection frequencies	1648.6i , 543.5 (2), 1076.5, 1131.5 (2), 1457.6 (2), 1941.4 , 3127.8, 3289.4 (2)
Post-projection frequencies	543.5 (2), 1047.5, 1131.5 (2), 1457.6 (2), 3125.5, 3289.4 (2)
RD PES frequencies (ω_F , ω_1)	1782.3i, 1352.9
RD PES anharmonic constants (x_{11} , x_{1F} , x_{FF})	0.33, $-159.43i$, -165.24

^aAll frequencies and anharmonic constants are reported in cm^{-1} . Multiplicities are indicated in parentheses. The reported pre- and post-projection frequencies are from Banks et al.⁴⁴ The two pre-projection frequencies in bold represent those of *active modes*. The RD PES frequencies and anharmonic constants were calculated from derivatives of the RD PES at the transition state, as described in section 2.4. The subscript 1 denotes the *transition mode*, and the subscript *F* denotes the reaction mode.

Forward barrier heights for R1 are presented in Table 2. $\Delta V^\ddagger$ denotes the barrier height without any ZPE contributions, and $\Delta V_a^\ddagger$ denotes the vibrationally adiabatic barrier height. Both of these quantities were calculated directly using *ab initio* methods.

$\Delta V_{\text{SC},a}^\ddagger$ represents the adiabatic barrier height from the RD SCTST method, i.e. $\Delta V_{\text{SC}}^\ddagger$ plus the ZPE of the *transition mode* at the transition state. There is only a small difference between $\Delta V_{\text{SC},a}^\ddagger$ and $\Delta V_a^\ddagger$, which arises mainly because of the frequency differences shown in Table 1. It should be noted that the transition state ZPE includes an anharmonic term but that its contribution to $\Delta V_{\text{SC},a}^\ddagger$ is negligible (0.00024 kcal mol⁻¹).

Table 2. Reaction Energetics for R1^a

$\Delta V^\ddagger$	15.149
$\Delta V_a^\ddagger$	13.785
$\Delta V_{\text{SC},a}^\ddagger$	13.626

^a $\Delta V^\ddagger$ and $\Delta V_a^\ddagger$ represent the forward barrier height and vibrationally adiabatic forward barrier height, respectively, as calculated by Banks *et al.*⁴⁴ using *ab initio* methods. $\Delta V_{\text{SC},a}^\ddagger$ represents the barrier height used in RD SCTST calculations, as defined in eq 24, plus the harmonic and anharmonic ZPEs of the transition state. All barrier heights are reported in kcal mol⁻¹.

Figure 2a presents the potential barrier along the minimum-energy path (MEP) of the PES for R1, calculated by methods described in Truhlar *et al.*,⁵⁶ and the semiclassical approximation to the barrier (eq 11). In order to allow comparison between these barriers, the semiclassical barrier was constructed for $\Omega_{(n)}$ equal to $|\hbar \omega_F|$. **Figure 1.** A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $\text{Y} + \text{H}_a\text{Z} \rightarrow \text{YH}_a + \text{Z}$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2b presents the WKB barrier penetration integrals for each of these barriers, calculated as a function of energy using eq 6. At low energies, the MEP barrier is wider than the semiclassical barrier, resulting in a greater integral for the MEP barrier. The widths of the barriers are more similar near the transition state, so the integrals converge as E increases. It is important to note that integrals presented in **Figure 1.** A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $\text{Y} + \text{H}_a\text{Z} \rightarrow \text{YH}_a + \text{Z}$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2b cannot be used directly to calculate reaction probabilities because they do not include coupling effects. Nevertheless, comparing them provides an idea of the relative amount of quantum mechanical tunneling associated with each barrier.

3.1.2 Rate Constants

Calculated rate constants for R1 are presented in **Figure 1**. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3a. The RD SCTST method yields rate constants in good agreement with the quantum scattering results from Banks et al.⁴⁴ between 250 K and 1000 K, differing at most by a factor of 2.13 at 250 K. These RD SCTST rate constants were calculated without the deep tunneling corrections proposed by Wagner²⁰ (section 2.1.2). The effect of these corrections will be discussed in section 3.4. The ratio of the RD SCTST rate constant to the scattering rate constant is presented in the inset in **Figure 1**. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3a. This ratio decreases as T increases from 250 K to 800 K but increases from 800 K to 1000 K. However, it remains between 1 and 2.13 over this T range. It is worth reiterating that the same PES was used to calculate the rate constants in both methods, so discrepancies between the RD SCTST and quantum scattering rate constants arise from differences in dynamics calculations rather than those in the underlying potential energy calculations. The RD SCTST and scattering rate constants at 250 K are 399 and 187 times greater than the rate constant calculated using conventional TST, respectively, reflecting the inclusion of quantum mechanical tunneling effects in the RD SCTST method. Additionally, RD SCTST results exhibit good agreement with experimentally determined rate constants⁶⁸ (**Figure 1**. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3b). Rate constants calculated by all methods discussed in this study and experimentally determined rate constants are presented in Table 3.

Table 3. Rate Constants for R1 in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Calculated by the Methods Described in this Study and Determined Experimentally^a

T (K)	TST	RD SCTST	scattering ^b	RD SCTST-DT	exptl ^c
200	8.42(−26)	2.26(−21)	5.67(−22)	1.60(−21)	
250	8.17(−23)	3.26(−20)	1.53(−20)	2.83(−20)	
300	8.16(−21)	3.64(−19)	2.33(−19)	3.45(−19)	
350	2.24(−19)	3.04(−18)	2.25(−18)	2.97(−18)	2.47(−18)
400	2.74(−18)	1.86(−17)	1.50(−17)	1.84(−17)	1.82(−17)
450	1.96(−17)	8.63(−17)	7.34(−17)	8.60(−17)	8.96(−17)
500	9.62(−17)	3.17(−16)	2.80(−16)	3.17(−16)	3.33(−16)
600	1.09(−15)	2.54(−15)	2.34(−15)	2.54(−15)	2.57(−15)
700	6.49(−15)	1.24(−14)	1.16(−14)	1.24(−14)	1.19(−14)
800	2.56(−14)	4.34(−14)	4.07(−14)	4.36(−14)	3.99(−14)
1000	1.88(−13)	2.81(−13)	2.57(−13)	2.82(−13)	
1300	1.32(−12)	1.84(−12)	1.57(−12)	1.85(−12)	
1600	4.87(−12)	6.59(−12)	5.24(−12)	6.63(−12)	
2000	1.63(−11)	2.19(−11)	1.57(−11)	2.20(−11)	

^aNumbers in parentheses denote powers of 10. “RD SCTST-DT” denotes the RD SCTST method applied with the deep tunneling corrections discussed in section 2.1.2.

^bFrom ref. 44.

^cFrom ref. 68.

The RD SCTST rate constant is marginally greater than the scattering rate constant over the range of temperatures shown in **Figure 1**. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $\text{Y} + \text{H}_a\text{Z} \rightarrow \text{YH}_a + \text{Z}$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3a, although they converge as T increases to 1000 K. This behavior arises from differences in the cumulative reaction probability (CRP) calculated in both methods. The CRP is multiplied by a Boltzmann factor and integrated with respect to energy in order to calculate the rate constant (eq 15). Consequently, the CRP at lower energies contributes more to this integral than the CRP at greater energies. At 250 K, the integral is determined primarily by the CRP at energies less than approximately 0.6 eV. Because the CRP from the RD SCTST method is greater than that from the quantum scattering method at these energies (**Figure 1**. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the

Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4a), the Boltzmann-weighted CRP is also greater, and the RD SCTST method yields a greater rate constant at 250 K. At energies near $\Delta V_{SC,a}^\ddagger$ (indicated by vertical dashed lines in Figure 1. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4), the CRPs of the two methods are closer in value. The Boltzmann factor emphasizes this energy range more as T increases from 250 K to 800 K. Consequently, the Boltzmann-weighted CRPs from the two methods, and therefore the rate constants, become closer, as indicated by a decrease in the ratio of the rate constants from 250 K to 800 K (Figure 1. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with

H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4b, Figure 1. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $\text{Y} + \text{H}_a\text{Z} \rightarrow \text{YH}_a + \text{Z}$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3a inset). At higher energies, the quantum scattering CRP is less than the RD SCTST CRP. This range of the CRP contributes more to the integral as T increases further, which explains the increase in the ratio of the RD SCTST and scattering rate constants from 800 K to 1000 K.

3.2 $\text{H} + \text{cyc-C}_3\text{H}_6 \rightarrow \text{H}_2 + \text{cyc-C}_3\text{H}_5$ (R2)

The frequencies and anharmonic constants used in RD SCTST calculations for R2 are presented in Table 4. As in R1, the reaction mode pre-projection frequency (1342.30i

cm^{-1}) differs somewhat from that obtained from the RD PES ($1527.64i \text{ cm}^{-1}$), and there is a greater difference between the *transition mode* frequencies (2255.22 cm^{-1} vs. 1537.51 cm^{-1}). This contributes to a difference between the vibrationally adiabatic barrier height obtained from *ab initio* calculations ($\Delta V_a^\ddagger$, $13.47 \text{ kcal mol}^{-1}$) and vibrationally adiabatic semiclassical barrier height ($\Delta V_{\text{SC},a}^\ddagger$, $12.09 \text{ kcal mol}^{-1}$). The anharmonic ZPE of the *transition mode* contributes more to $\Delta V_{\text{SC},a}^\ddagger$ ($0.08 \text{ kcal mol}^{-1}$) than in R1.

Table 4. Energetic Parameters, Frequencies, and Anharmonic Constants for R2^a

Pre-projection frequencies	1342.30i, 2255.22
RD PES frequencies	1527.64i, 1537.51
RD PES anharmonic constants (x_{11} , x_{1F} , x_{FF})	108.96, -614.38i, -252.74
$\Delta V^\ddagger$	14.56
$\Delta V_a^\ddagger$	13.47
$\Delta V_{SC,a}^\ddagger$	12.09

^aThe reported pre-projection frequencies correspond to those of the *active modes*. $\Delta V^\ddagger$, $\Delta V_a^\ddagger$, and $\Delta V_{SC,a}^\ddagger$ are defined as in Table 2. Frequencies and anharmonic constants are reported in cm^{-1} , and barrier heights are reported in kcal mol^{-1} .

Potential barriers for R2 are presented in Figure 1. A schematic showing the definition of the active internal coordinates $r1$ and $r2$ and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4. The product of the cumulative reaction probability, $N(Ev)$, for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta V_{SC,a}^\ddagger$.

Figure 5a. Although the semiclassical barrier has a width similar to the MEP barrier near the top, their shapes differ significantly. The reactant and product asymptotes of the semiclassical barrier are significantly greater than the quantum mechanical threshold energy. Nevertheless, the rate constants calculated by RD SCTST (without deep tunneling corrections) exhibit very close agreement with quantum scattering rate constants (Figure 1. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4. The product of the cumulative reaction probability, $N(E_v)$, for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta\text{VSC}_{\text{a}}^{\ddagger}$.

Figure 5b). At 250 K, the RD SCTST rate constant is 1.67 times greater than the scattering rate constant and 92 times greater than the TST rate constant. The RD SCTST and scattering rate constants converge at high T . Additionally, the RD SCTST rate

constant agrees well with experimental results^{53, 69} from 250 K to 1000 K (Figure 1. A schematic showing the definition of the active internal coordinates $r1$ and $r2$ and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4. The product of the cumulative reaction probability, $N(Ev)$, for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta \text{VSC}_{\text{a}}^{\ddagger}$.

Figure 5c). Calculated and experimentally determined rate constants for R2 are presented in Table 5.

Table 5. Rate Constants for R2 in cm³ molecule⁻¹ s⁻¹, Calculated by the Methods Described in this Study and Determined Experimentally^a

T (K)	TST	RD SCTST	scattering ^b	RD SCTST-DT	exptl
360	6.42(-19)	1.04(-17)	8.08(-18)	1.08(-17)	2.05(-17) ^c
390	2.87(-18)	3.54(-17)	2.83(-17)	3.66(-17)	7.25(-17) ^c
420	1.04(-17)	1.02(-16)	8.38(-17)	1.05(-16)	2.14(-16) ^c
450	3.21(-17)	2.60(-16)	2.17(-16)	2.66(-16)	5.45(-16) ^c
480	8.64(-17)	5.92(-16)	5.02(-16)	6.06(-16)	1.24(-15) ^c
510	2.08(-16)	1.24(-15)	1.06(-15)	1.26(-15)	2.55(-15) ^c
540	4.58(-16)	2.40(-15)	2.08(-15)	2.45(-15)	4.84(-15) ^c
630	3.18(-15)	1.27(-14)	1.09(-14)	1.29(-14)	6.23(-15) ^d
660	5.43(-15)	2.00(-14)	1.73(-14)	2.04(-14)	9.50(-15) ^d
690	8.89(-15)	3.06(-14)	2.64(-14)	3.11(-14)	1.40(-14) ^d
720	1.40(-14)	4.54(-14)	3.91(-14)	4.62(-14)	1.99(-14) ^d
750	2.14(-14)	6.56(-14)	5.63(-14)	6.67(-14)	2.75(-14) ^d

^aNumbers in parentheses denote powers of 10. Methods for calculating rate constants are denoted as in Table 3.

^bFrom ref. 51.

^cFrom ref. 53.

^dFrom ref. 69.

3.3 CH₃ + CH₄ → CH₄ + CH₃ (R3)

Frequencies and anharmonic constants for R3 are presented in Table 6. The frequencies of both *active modes* as calculated from the RD PES differ somewhat from the corresponding pre-projection frequencies (1683.55i cm⁻¹ vs. 1948.8i cm⁻¹ for the reaction mode, and 494.74 cm⁻¹ vs. 540.8 cm⁻¹ for the *transition mode*). Additionally, the vibrationally adiabatic barrier height from *ab initio* calculations ($\Delta V_a^\ddagger$) is 0.691 kcal mol⁻¹ greater than that calculated from the RD PES ($\Delta V_{SC,a}^\ddagger$).

Table 6. Energetic Parameters, Frequencies, and Anharmonic Constants for R3^a

Pre-projection frequencies	1949.8i, 540.8
RD PES frequencies	1683.55i, 494.74
RD PES anharmonic constants (x_{11} , x_{1F} , x_{FF})	-1.63, -32.54i, -109.16
$\Delta V^\ddagger$	18.142
$\Delta V_a^\ddagger$	17.705
$\Delta V_{SC,a}^\ddagger$	17.014

^aThe parameters reported here are defined as in Table 2. Frequencies and anharmonic constants are reported in cm^{-1} , and barrier heights are reported in kcal mol^{-1} .

Figure 1. A schematic showing the definition of the active internal coordinates $r1$ and $r2$ and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4. The product of the cumulative reaction probability, $N(Ev)$, for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta V_{SC,a}^\ddagger$.

Figure 5. (a) The potential barrier for the $\text{H} + \text{cyc-C}_3\text{H}_6 \rightarrow \text{H}_2 + \text{cyc-C}_3\text{H}_5$ reaction (R2) along the MEP of the RD PES (solid curve), and the semiclassical Eckart potential

approximation (eq 11, dashed curve). (b) Rate constants for R2 calculated using TST (dashed red line) and RD SCTST (solid black curve), as well as scattering rate constants from Shan and Clary⁵¹ (dashed blue curve). (c) RD SCTST and TST rate constants as compared to experimentally determined rate constants.^{53, 69}

Figure 6a shows the potential barrier along the MEP of the RD PES and the symmetric Eckart potential representing the potential barrier in the RD SCTST method. The two barriers have very similar shapes near the transition state, but the MEP barrier is significantly wider than the semiclassical barrier at low energies. Nevertheless, the RD SCTST method (without deep tunneling corrections) yielded rate constants in good agreement with scattering results from Banks et al.⁴⁴ (Figure 1. A schematic showing the definition of the active internal coordinates $r1$ and $r2$ and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

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Figure 6b). The RD SCTST rate constant at 250 K is 2.25 times greater than the scattering rate constant and 4380 times greater than the TST rate constant. The RD SCTST and scattering rate constants converge at high T , although the Arrhenius plot of the RD SCTST rate constant exhibits more curvature than that of the scattering rate constant. Figure 1. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $\text{Y} + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

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Figure 5. (a) The potential barrier for the $\text{H} + \text{cyc-C}_3\text{H}_6 \rightarrow \text{H}_2 + \text{cyc-C}_3\text{H}_5$ reaction (R2) along the MEP of the RD PES (solid curve), and the semiclassical Eckart potential approximation (eq 11, dashed curve). (b) Rate constants for R2 calculated using TST (dashed red line) and RD SCTST (solid black curve), as well as scattering rate constants from Shan and Clary⁵¹ (dashed blue curve). (c) RD SCTST and TST rate constants as compared to experimentally determined rate constants.^{53, 69}

Figure 6c presents our RD SCTST rate constants in comparison with experimental

results.⁷⁰⁻⁷¹ Rate constants for R3 are presented in Table 7.

Table 7. Rate Constants for R3 in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Calculated by the Methods Described in this Study and Determined Experimentally^a

T (K)	TST	RD SCTST	scattering	RD SCTST-DT	exptl
200	1.64(−31)	3.68(−25)	1.83(−26)	1.70(−25)	1.46(−28) ^b
250	1.09(−27)	4.77(−24)	2.12(−24)	3.58(−24)	2.17(−25) ^b
300	4.00(−25)	7.39(−23)	8.90(−23)	6.74(−23)	2.82(−23) ^b
350	2.81(−23)	1.03(−21)	1.74(−21)	1.00(−21)	
400	7.09(−22)	1.06(−20)	1.91(−20)	1.05(−20)	1.45(−20) ^c
450	9.00(−21)	7.76(−20)	1.36(−19)	7.74(−20)	1.03(−19) ^c
500	7.07(−20)	4.24(−19)	7.02(−19)	4.23(−19)	4.94(−19) ^c
600	1.67(−18)	6.39(−18)	9.30(−18)	6.40(−18)	5.19(−18) ^c
700	1.72(−17)	5.07(−17)	6.51(−17)	5.08(−17)	2.78(−17) ^c
800	1.05(−16)	2.62(−16)	2.99(−16)	2.63(−16)	9.80(−17) ^c
1000	1.49(−15)	3.06(−15)	2.83(−15)	3.07(−15)	
1300	2.10(−14)	3.74(−14)	2.65(−14)	3.75(−14)	
1600	1.28(−13)	2.11(−13)	1.21(−13)	2.12(−13)	
2000	7.07(−13)	1.11(−12)	5.11(−13)	1.11(−12)	

^aNumbers in parentheses denote powers of 10. Methods for calculating rate constants are denoted as in Table 3.

^bFrom ref. 70.

^cFrom ref. 71.

For reactions with small skew angles and large reaction path curvature such as R3, corner-cutting effects have been shown to be important.^{55-56, 72-76} Corner-cutting involves tunneling along paths between the reactant and product channels of the PES other than the MEP. The barrier along a chosen corner-cutting path is narrower than that along the MEP, such that the associated barrier penetration integral is less than that of the MEP, even though the barrier is higher. One possible corner-cutting path on the RD PES for R3 is presented in Figure 1. A schematic showing the definition of the active internal coordinates $r1$ and $r2$ and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z

moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4. The product of the cumulative reaction probability, $N(Ev)$, for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta V_{\text{SC},a}^{\ddagger}$.

Figure 5. (a) The potential barrier for the $\text{H} + \text{cyc-C}_3\text{H}_6 \rightarrow \text{H}_2 + \text{cyc-C}_3\text{H}_5$ reaction (R2) along the MEP of the RD PES (solid curve), and the semiclassical Eckart potential approximation (eq 11, dashed curve). (b) Rate constants for R2 calculated using TST (dashed red line) and RD SCTST (solid black curve), as well as scattering rate constants from Shan and Clary⁵¹ (dashed blue curve). (c) RD SCTST and TST rate constants as compared to experimentally determined rate constants.^{53, 69}

Figure 6. (a) The potential barrier for the $\text{CH}_3 + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3$ reaction (R3) along the MEP of the RD PES (solid curve), and the semiclassical Eckart potential approximation (eq 11, dashed curve). (b) Rate constants for R3 calculated using TST (dashed red line) and RD SCTST (solid black curve), as well as scattering rate constants from Banks et al.⁴⁴ (dashed blue curve). (c) RD SCTST and TST rate constants as compared to experimentally determined rate constants.⁷⁰⁻⁷¹

Figure 7a as the blue line (“CC path”). The potential barrier associated with this path is presented in Figure 1. A schematic showing the definition of the active internal coordinates $r1$ and $r2$ and the Jacobi coordinates R and r for the general H

abstraction/exchange reaction $\text{Y} + \text{HaZ} \rightarrow \text{YHa} + \text{Z}$. HaZ represents a hydrocarbon, with

Ha bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YHa and Z moieties, respectively.

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Figure 4. The product of the cumulative reaction probability, $N(E_v)$, for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta\text{VSC}_{\text{a}}^{\ddagger}$.

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Figure 7b (blue curve) in comparison to the MEP barrier (red curve). Although the corner-cutting barrier is higher than the MEP barrier, it is considerably narrower, and it is also similar in width to the semiclassical barrier at lower energies (black dashed curve).

We believe that, because of this interesting behavior of the semiclassical barrier, our RD SCTST method simulates enough tunneling at low T , thereby giving reasonable rate constants without considering the concave region of the PES in between the reactant and product channels. This finding warrants further investigation and the application of RD SCTST to other reactions with different reaction path curvatures.

3.4 Rate Constants with Deep Tunneling Corrections

In order to evaluate the importance of the deep tunneling corrections to the SCTST method proposed by Wagner²⁰ (section 2.1.2) within the RD framework, we compared RD SCTST rate constants calculated with and without these corrections. We refer to RD SCTST applied with these corrections as “RD SCTST-DT.” The ratios of the RD SCTST-DT rate constants to the RD SCTST rate constants are presented in **Figure 1**. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

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Figure 4. The product of the cumulative reaction probability, $N(E_v)$, for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta V_{SC,a}^\ddagger$.

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Figure 7. (a) Contour plot of the fitted RD PES in hyperspherical coordinates from Banks et al.⁴⁴ The red curve is the minimum-energy path (MEP), and the blue line represents a possible corner-cutting (CC) path. (b) The potentials as a function of the reaction coordinate along each of these paths, as well as the semiclassical (SC) approximation to the potential (eq 11).

Figure 8a for R1, R2, and R3. Numerical values of these rate constants are presented in Tables 3, 5, and 7. For R1 and R2, the RD SCTST-DT rate constant differed from the RD SCTST rate constant by no more than 15% from 250 K to 1000 K. Differences were greater for R3, but the RD SCTST-DT rate constant was nonetheless only 25% less than the RD SCTST rate constant at 250 K. The RD SCTST-DT potential barrier was wider than the RD SCTST barrier at low energies for R3 (**Figure 1**). A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $\text{Y} + \text{H}_a\text{Z} \rightarrow \text{YH}_a + \text{Z}$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

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Figure 8b). This difference contributed more to a difference in rate constants at low T for R3 because its potential barrier height is significantly less than those of R1 and R2. These results indicate that, for the temperature range and reactions considered in this study, applying deep tunneling corrections does not significantly improve the accuracy of RD SCTST rate constant calculations with respect to quantum scattering calculations.

4. Conclusions

We present a Reduced-Dimensionality Semiclassical Transition State Theory (RD SCTST) for calculating reaction rate constants. It offers computational advantages over RD quantum mechanical scattering methods and full-dimensionality SCTST. RD potential energy surfaces (PESs) developed previously for three H abstraction and exchange reactions of hydrocarbon molecules were used to calculate the harmonic frequencies and barrier heights required by RD SCTST. These parameters exhibited acceptable agreement with those obtained from *ab initio* calculations. Rate constants for

the three reactions calculated using RD SCTST were compared to those from quantum scattering calculations performed on the same PESs, thereby enabling a systematic evaluation of RD SCTST. We observed good agreement between these rate constants from 250 K to 1000 K. RD SCTST results also agreed with experimental results for all three reactions. RD SCTST performed well also for R3, even though it does not account explicitly for the corner-cutting effects shown previously to be important for heavy-light-heavy reactions. Additionally, we applied deep tunneling extensions to SCTST within the RD framework and found that they did not appreciably improve the accuracy of calculated rate constants over the temperature range considered in this study. The results suggest that the RD SCTST method has significant potential for calculating reaction rate constants with minimal computational expense.

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Figures

Figure 1. A schematic showing the definition of the active internal coordinates r_1 and r_2 and the Jacobi coordinates R and r for the general H abstraction/exchange reaction $Y + H_aZ \rightarrow YH_a + Z$. H_aZ represents a hydrocarbon, with H_a bonded to a C atom in the Z moiety. R1, R2, and R3 represent the remainder of the Z moiety. The white and black circles represent the centers of mass of the YH_a and Z moieties, respectively.

Figure 2. (a) The potential barrier for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) as a function of the reaction coordinate along the minimum-energy path (MEP) of the PES (solid curve), and the symmetric Eckart potential that represents the effective barrier for SCTST calculations (eq 11, dashed curve). In constructing the semiclassical barrier, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$ in order to enable comparison with the MEP barrier. (b) Barrier penetration integrals, calculated using eq 6, for the MEP (solid curve) and semiclassical (dashed curve) barriers.

Figure 3. (a) Rate constants for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1) calculated by conventional TST (dashed red line) and by RD SCTST without deep tunneling corrections (solid black curve), presented with scattering results from Banks et al.⁴⁴ (dashed blue curve). The ratio of the RD SCTST rate constant to the scattering rate constant is plotted in the inset. (b) Experimental results from Sutherland et al.⁶⁸ presented with TST and RD SCTST results from this study.

Figure 4. The product of the cumulative reaction probability, $N(E_v)$, for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction (R1), calculated by RD SCTST and quantum scattering methods, and the Boltzmann factor evaluated at (a) $T = 250$ K and (b) $T = 800$ K. The dashed vertical line denotes the vibrationally adiabatic barrier height from the RD SCTST method, $\Delta V_{SC,a}^\ddagger$.

Figure 5. (a) The potential barrier for the $H + \text{cyc-}C_3H_6 \rightarrow H_2 + \text{cyc-}C_3H_5$ reaction (R2) along the MEP of the RD PES (solid curve), and the semiclassical Eckart potential approximation (eq 11, dashed curve). (b) Rate constants for R2 calculated using TST (dashed red line) and RD SCTST (solid black curve), as well as scattering rate constants from Shan and Clary⁵¹ (dashed blue curve). (c) RD SCTST and TST rate constants as compared to experimentally determined rate constants.^{53, 69}

Figure 6. (a) The potential barrier for the $CH_3 + CH_4 \rightarrow CH_4 + CH_3$ reaction (R3) along the MEP of the RD PES (solid curve), and the semiclassical Eckart potential approximation (eq 11, dashed curve). (b) Rate constants for R3 calculated using TST (dashed red line) and RD SCTST (solid black curve), as well as scattering rate constants from Banks et al.⁴⁴ (dashed blue curve). (c) RD SCTST and TST rate constants as compared to experimentally determined rate constants.⁷⁰⁻⁷¹

Figure 7. (a) Contour plot of the fitted RD PES in hyperspherical coordinates from Banks et al.⁴⁴ The red curve is the minimum-energy path (MEP), and the blue line represents a possible corner-cutting (CC) path. (b) The potentials as a function of the reaction coordinate along each of these paths, as well as the semiclassical (SC) approximation to the potential (eq 11).

Figure 8. (a) The ratio of the RD SCTST rate constants calculated with the deep tunneling corrections described in section 2.1.2 to those calculated without corrections for R1 (red curve), R2 (green curve), and R3 (blue curve). (b) The potential barrier for R3 used in deep tunneling RD SCTST calculations (blue curve), and the symmetric Eckart potential representing the potential barrier for the RD SCTST method without deep tunneling corrections (eq 11, red curve). In constructing these barriers, $\Omega_{\{n\}}$ was set to $|\hbar \omega_F|$.

