

High pressure rate constants for unimolecular dissociation/free radical recombination: Determination of the quantum correction via quantum Monte Carlo path integration

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The determination of a quantum correction factor for the transitional modes of a unimolecular dissociation/free radical recombination reaction having a transition state of varying looseness is described. The quantum correction factor for the high pressure canonical rate constant is calculated via Monte Carlo path integral evaluation of partition function ratios, and is applied to the recombination reaction $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$.

I. INTRODUCTION

In RRKM theory the (microcanonical) unimolecular rate constant k_{EJ} is given by¹⁻³

$$k_{EJ} = \frac{N_{EJ}^\ddagger}{h\rho_{EJ}}, \quad (1.1)$$

where N_{EJ}^\ddagger is the number of states of the transition state with energy equal to or less than E , and with a given total angular momentum J ; ρ_{EJ} is the density of states for the reactants at the given E and J . In the case of a unimolecular dissociation of the parent molecule into two particles, the coordinates which contribute to N_{EJ}^\ddagger are largely of two types: (i) vibrational modes, usually of high frequency, whose characteristic motion does not change appreciably from the parent molecule to the transition state, and (ii) the remaining modes whose characteristic motion does change. The latter consist, typically, of coupled degrees of freedom which are fragment bending plus overall rotational motions, and which subsequently become hindered relative rotations plus overall rotational motion in the transition state. In the fragment molecules these modes are typically the free rotations and relative translation of the two fragments. The fragment-fragment stretching in the parent molecule typically becomes the reaction coordinate itself.

Wardlaw and Marcus⁴⁻⁷ separated the modes into these "conserved" and "transitional" modes, respectively. In this separation the conserved modes were treated quantum mechanically and the transitional modes were treated classically. Their result for the number of states of the transition state for a given energy and total angular momentum J was, thereby, given as the convolution

$$N_{EJ}^\ddagger = \int_0^E N_\nu(E - \epsilon) \Omega_J(\epsilon) d\epsilon, \quad (1.2)$$

where $N_\nu(E - \epsilon)$ is the number of states in the conserved modes with energy less than or equal to $E - \epsilon$, and $\Omega_J(\epsilon)$ is the number of states in the transitional modes with total angular momentum equal to J , and with energy in the range ϵ to $\epsilon + d\epsilon$. $N_\nu(E - \epsilon)$ was calculated via a direct quantum

count, while $\Omega_J(\epsilon)$ was obtained by transformation to action angle coordinates followed by "crude" Monte Carlo evaluation of the phase space integral. Purely classical Monte Carlo phase space volume calculations are described in, e.g., Refs. 8-17.

Many other approaches to the treatment of the transitional modes have been given previously. (See, e.g., Refs. 18-26.) However, the only treatment which has included all of the couplings within the transitional modes, while maintaining a quantum treatment for the conserved modes, appears to be that of Wardlaw and Marcus.⁴⁻⁷ In a recent article, Pacey²⁷ has discussed and applied many of the approaches to the two-dimensional hindered rotor motion on a model sinusoidal potential. Comparison of the results obtained for the partition function from the various approaches with that determined from the exact quantum partition function for the same model potential shows the differences between the various approaches can be significant. In another recent study on the bending/rotation problem, Hase *et al.*²⁸ have compared rate constants for the $\text{H} + \text{CH}_3 \rightarrow \text{CH}_4$ recombination reaction with the transitional modes treated as either classical hindered rotors or harmonic oscillators (quantum or classical). They find that the partition functions and rate constants can vary by about 10% depending on how these modes are treated.

As noted in the studies of Wardlaw and Marcus, the question arises, what are the quantum corrections for the contribution of the transitional modes to the overall rate. When the transition state is nearly "loose" such a correction is expected to be minor. One direct approach to calculating the correction would be to determine the number of quantum states for the transitional modes as a function of energy and total angular momentum, and convolute that result with the quantum result for the "conserved" modes. This approach is currently under study. In the present manuscript, however, rather than looking at individual k_{EJ} 's, we have chosen to consider first the cumulative effect of the transitional modes by determining their quantum mechanical contribution to the high pressure canonical rate constant $k_\infty(T)$ defined below. The position of the transition state is determined variationally,²⁹⁻³¹ namely, as that value (the "transition value") of the reaction coordinate for which the calculated $k_\infty(T)$ is a minimum.

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In the present study we note that $k_{\infty}(T)$ is given by a ratio of partition functions and so the quantum mechanical corrections, aside from quantum corrections due to tunneling along the reaction coordinate, may be determined by considering the Monte Carlo path integral evaluation of partition function ratios. The correction factor can thus be obtained for any potential energy surface and is for the *canonical* rate constant. In Sec. II, for comparison, the canonical rate constant is determined using quantum partition functions for the conserved modes and classical partition functions for the transitional modes. The determination of the quantum correction for the transitional modes is presented in Sec. III. In Sec. IV results for the methyl radical recombination reaction: $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ are presented and discussed. The correction proves to be relatively small for the temperatures investigated.

II. DETERMINATION OF $k_{\infty}(T)$ USING CLASSICAL CANONICAL TST FOR THE TRANSITIONAL MODES

The canonical rate constant $k_{\infty}(T)$ is given in terms of N_{EJ}^{\dagger} by³²

$$k_{\infty}(T) = \frac{g_e}{hQ^{\dagger}(T)} \int_0^{\infty} dE \sum_{J=0}^{\infty} (2J+1) N_{EJ}^{\dagger} \exp(-\beta E), \quad (2.1)$$

where $Q^{\dagger}(T)$ is the partition function for the reactants (in the center-of-mass system and excluding electronic degrees of freedom), g_e is the ratio of the electronic partition function for the transition state to that for the reactants, and $\beta = 1/k_B T$. In a comparative study Wardlaw and Marcus have evaluated $k_{\infty}(T)$ at several levels.⁶ In the first method they determined the location of the transition state variationally for each E and J and then evaluated the sum and integral in Eq. (2.1) numerically. In a second calculation, which represents an approximation to the first, they determined the transition state location for each E by minimizing a J -sampled integrand, and in a third calculation, which represents still a further approximation, they found the transition state location of an ensemble which sampled over E and J at a given T . They noted that the three $k_{\infty}(T)$'s are related by $k_{\infty}^{\text{I}}(T) \leq k_{\infty}^{\text{II}}(T) \leq k_{\infty}^{\text{III}}(T) \leq k_{\infty}^{\text{I}}(T)$ being the correct

one. This last calculation, $k_{\infty}^{\text{III}}(T)$, is equivalent^{1,33} to determining $k_{\infty}(T)$ variationally from the expression

$$k_{\infty}(T) = g_e \frac{k_B T}{h} \frac{Q^{\dagger}}{Q^{\dagger}}, \quad (2.2)$$

where Q^{\dagger} is the partition function for the transition state. The Q^{\dagger} and Q^{\dagger} in Eq. (2.2) are calculated relative to the same energy zero. Separating the modes into the conserved modes (c) and the transitional modes (t) implies that

$$k_{\infty}(T) = g_e \frac{k_B T}{h} \frac{Q_c^{\dagger}}{Q_c^{\dagger}} \frac{Q_t^{\dagger}}{Q_t^{\dagger}}, \quad (2.3)$$

where Q_c^{\dagger} and Q_c^{\dagger} are the partition functions for the conserved modes at the transition state and at the reactant configuration, respectively. They can be evaluated using quantum oscillator partition functions. Q_t^{\dagger} and Q_t^{\dagger} are the partition functions for the transitional modes at the transition state and at the reactant configuration, respectively.

For a free radical recombination reaction, the classical partition function for the transitional modes of the reactants Q_t^{\dagger} separates into the translational partition function for a particle of mass μ_{12} , where μ_{12} is the reduced mass of the two fragments, and the product of the classical free-rotor partition functions for the two reactant fragments, $\Pi_{i=1}^2 \sigma_i^{-1} [\pi(2k_B T/\hbar^2)^3 I_{A_i} I_{B_i} I_{C_i}]^{1/2}$, where I_{A_i} , I_{B_i} , and I_{C_i} are the moments of inertia of reactant fragment i , and σ_i is the symmetry number for reactant fragment i . The classical partition function for the transitional modes of the transition state is given by

$$Q_t^{\dagger} = \frac{1}{\sigma^{\dagger}} \int dp_{\theta_{12}} dp_{\phi_{12}} d\theta_{12} d\phi_{12} \times \left(\prod_{i=1}^2 dp_{\theta_i} dp_{\phi_i} dp_{\psi_i} d\theta_i d\phi_i d\psi_i \right) \exp(-\beta H_t), \quad (2.4)$$

where σ^{\dagger} is the symmetry factor for the transition state, θ_i , ϕ_i , and ψ_i are the Euler angles³⁴ for the absolute orientation in space of fragment i , and θ_{12} and ϕ_{12} describe the absolute orientation in space of the line of centers. H_t is the classical Hamiltonian for the transitional degrees of freedom and is given by

$$H_t = \frac{1}{2I_d^{\dagger}} \left(p_{\theta_{12}}^2 + \frac{p_{\phi_{12}}^2}{\sin^2 \theta_{12}} \right) + \sum_{i=1}^2 \left\{ \frac{1}{2I_{A_i}^{\dagger} \sin^2 \theta_i} [(p_{\phi_i} - p_{\psi_i} \cos \theta_i) \cos \psi_i - p_{\theta_i} \sin \theta_i \sin \psi_i]^2 + \frac{1}{2I_{B_i}^{\dagger} \sin^2 \theta_i} [(p_{\phi_i} - p_{\psi_i} \cos \theta_i) \sin \psi_i + p_{\theta_i} \sin \theta_i \cos \psi_i]^2 + \frac{1}{2I_{C_i}^{\dagger}} p_{\psi_i}^2 \right\} + V(R^{\dagger}, \theta_{12}, \phi_{12}, \Theta, \Phi, \Psi), \quad (2.5)$$

where $\Theta \equiv (\theta_1, \theta_2)$, $\Phi \equiv (\phi_1, \phi_2)$, $\Psi \equiv (\psi_1, \psi_2)$, and $V(R^{\dagger}, \theta_{12}, \phi_{12}, \Theta, \Phi, \Psi)$ is the potential energy for the given separation R^{\dagger} , and orientation of the rigid rotor fragments. I_d^{\dagger} is the "diatomic" moment of inertia for the centers of mass of the two fragments and equals $\mu_{12} R^{\dagger 2}$. $I_{A_i}^{\dagger}$, $I_{B_i}^{\dagger}$, and $I_{C_i}^{\dagger}$ are the principal moments of inertia of the rigid body fragments with their transition state structure.

Evaluation of the integral over the momenta yields

$$Q_t^{\dagger} = \frac{1}{\sigma^{\dagger}} \frac{2\pi I_d^{\dagger} k_B T}{h^2} \left\{ \prod_{i=1}^2 [8\pi^3 I_{A_i}^{\dagger} I_{B_i}^{\dagger} I_{C_i}^{\dagger} (k_B T/h^2)^3]^{1/2} \right\} \times \int d\theta_{12} d\phi_{12} \sin \theta_{12} \left(\prod_{i=1}^2 d\theta_i d\phi_i d\psi_i \sin \theta_i \right) \times \exp[-\beta V(R^{\dagger}, \theta_{12}, \phi_{12}, \Theta, \Phi, \Psi)]. \quad (2.6)$$

Upon integration over the θ_i , ϕ_i , and ψ_i for a fixed θ_{12} and ϕ_{12} , the result, by symmetry, is independent of the actual

orientation in space, θ_{12} and ϕ_{12} , of the two fragments, and so the integral over θ_{12} and ϕ_{12} may be immediately evaluated to give

$$Q_i^\ddagger = \frac{1}{\sigma^\ddagger} Q_{i,d}^\ddagger Q_{i,hr}^\ddagger, \quad (2.7)$$

where $Q_{i,d}^\ddagger$ is the usual classical diatomic partition function $2I_d^\ddagger k_B T / \hbar^2$, and

$$Q_{i,hr}^\ddagger = \left\{ \prod_{i=1}^2 \left[8\pi^3 I_{A_i}^\ddagger I_{B_i}^\ddagger I_{C_i}^\ddagger (k_B T / h^2)^3 \right]^{1/2} \right\} \\ \times \int \left(\prod_{i=1}^2 d\theta_i d\phi_i d\psi_i \sin \theta_i \right) \\ \times \exp \left[-\beta V(R^\ddagger, 0, 0, \Theta, \Phi, \Psi) \right], \quad (2.8)$$

with θ_{12} and ϕ_{12} having been set equal to zero.

For the case of a reasonably loose transition state $Q_{i,hr}^\ddagger$ can be evaluated via crude Monte Carlo integration.³⁵ For a tight transition state many of the configurations sampled will not contribute to the integral and one might revert to the calculation method of Wardlaw and Marcus⁴⁻⁷ or else use some form of stratified sampling such as that discussed by Farantos *et al.*¹¹ for microcanonical RRKM determinations. In the present application to the methyl radical recombination reaction crude Monte Carlo integration sufficed. The final Monte Carlo result for the rate constant for the case of free radical recombination is

$$k_\infty^{cl}(T) \\ = g_e \frac{\sigma_1 \sigma_2}{\sigma^\ddagger} R^\ddagger \left(\frac{8\pi k_B T}{\mu_{12}} \right)^{1/2} \left\{ \prod_{i=1}^{N_v} \frac{\sinh\left(\frac{h\nu_i}{2k_B T}\right)}{\sinh\left(\frac{h\nu_i^\ddagger}{2k_B T}\right)} \right\} \\ \times \left(\prod_{i=1}^2 \frac{I_{A_i}^\ddagger I_{B_i}^\ddagger I_{C_i}^\ddagger}{I_{A_i} I_{B_i} I_{C_i}} \right)^{1/2} \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} \exp \left[-\beta V_i \right], \quad (2.9)$$

where N_v is the number of conserved vibrational modes for the two fragments, and ν_i and ν_i^\ddagger are the vibration frequencies for the i th conserved mode of the reactants and of the transition state, respectively. V_i is the value of the potential for the i th randomly selected configuration, and N_{MC} is the number of random points.

III. DETERMINATION OF THE QUANTUM PARTITION FUNCTION FOR THE TRANSITIONAL MODES

The primitive P -point discretization of the path integral expression for the quantum transitional mode partition function is given by

$$Q_i^\ddagger = \int d\Lambda^1 \cdots d\Lambda^P d\Omega^1 \cdots d\Omega^P \\ \times \prod_{s=1}^P \rho_0(\Lambda^{s+1}, \Lambda^s; \beta/P) \rho_0(\Omega^{s+1}, \Omega^s; \beta/P) \\ \times \exp \left[-\frac{\beta}{P} V(\Lambda^s, \Omega^s) \right], \quad (3.1)$$

where Λ^s refers to the line of centers orientations

$$\Lambda^s = (\cos \theta_{12}^s, \phi_{12}^s), \quad (3.2)$$

and Ω^s refers to the Euler angles

$$\Omega^s = \prod_{i=1}^2 \Omega_i^s = \prod_{i=1}^2 (\cos \theta_i^s, \phi_i^s, \psi_i^s). \quad (3.3)$$

In Eq. (3.1), $\Lambda^{P+1} = \Lambda^1$ and $\Omega^{P+1} = \Omega^1$, while $\rho_0(\Lambda^{s+1}, \Lambda^s; \beta/P)$ and $\rho_0(\Omega^{s+1}, \Omega^s; \beta/P)$, the "free density matrices," are the density matrices for the free-rotor system at a temperature PT . [The latter has $V(\Lambda, \Omega) \equiv 0$.]

In the present treatment the quantity of interest is the combined partition function for the hindered rotation of the two separate fragments and for the rotation of the line of centers. If the integrals over Ω^s at fixed line of centers orientations Λ^s are performed first, the resulting expression is independent of Λ^s because there is no external field acting on the reacting pair. Thus, the integrals over the Λ^s may be evaluated separately to give the partition function for the rotation of a diatomic molecule with point masses equal to those of the two fragments. Expressions for the remaining partition function for the hindered rotations are now easily obtained from the analogous expressions derived by Kuharski and Rossy,³⁶ who utilized some results of Schulman³⁷ and introduced a short-time ("fixed-axis") method³⁸ to determine the quantum partition function for the hindered translational and hindered rotational degrees of freedom of liquid H₂O and D₂O. A brief review of their derivations, with application to the present two fragment case, is presented below for clarity.

The quantum partition function may be expressed as in Eq. (2.7) except that now $Q_{i,d}^\ddagger$ and $Q_{i,hr}^\ddagger$ are to be evaluated quantum mechanically. In particular,

$$Q_{i,hr}^\ddagger = \int d\Omega^1 \cdots d\Omega^P \prod_{s=1}^P \rho_0(\Omega^{s+1}, \Omega^s; \beta/P) \\ \times \exp \left[-\frac{\beta}{P} V(\Omega^s) \right], \quad (3.4)$$

and $Q_{i,d}^\ddagger$, the quantum diatomic partition function, is given (for $T > 2I_d^\ddagger k_B / \hbar^2 \equiv \Theta_r^{-1}$) by the expansion³⁹

$$Q_{i,d}^\ddagger = \frac{T}{\Theta_r} \left[1 + \frac{1}{3} \left(\frac{\Theta_r}{T} \right) + \frac{1}{15} \left(\frac{\Theta_r}{T} \right)^2 \right. \\ \left. + \frac{4}{315} \left(\frac{\Theta_r}{T} \right)^3 + \cdots \right]. \quad (3.5)$$

Using the least action approximation to the sum over all classical paths for the transition from the orientation Ω^s to the orientation Ω^{s+1} in the time period $\beta\hbar/P$ gives the free rotation matrix as³⁷

$$\rho_0(\Omega^{s+1}, \Omega^s; \beta/P) = C \prod_{i=1}^2 [D(\Omega_i^{s+1}, \Omega_i^s; \beta/P)]^{1/2} \\ \times \exp \left[-S_{Cl}(\Omega_i^{s+1}, \Omega_i^s; \beta/P) / \hbar \right], \quad (3.6)$$

where C is a constant, $D(\Omega_i^{s+1}, \Omega_i^s; \beta/P)$ is the Van Vleck determinant⁴⁰ associated with the transition from Ω_i^s to Ω_i^{s+1} in a time period of $\beta\hbar/P$, and $S_{Cl}(\Omega_i^{s+1}, \Omega_i^s; \beta/P)$ is the action along the least action classical path between the two orientations. In the exact free rotation matrix there are

contributions from multiple rotations. However, for sufficiently large P ("sufficiently small times β/P ") these contributions are negligible, and, in the limit of large enough P , Eq. (3.6) becomes exact.

A fixed-axis approximation is next introduced to determine the Van Vleck determinant and the classical action.³⁶ This fixed-axis approximation, which is valid for short times and is thus accurate at large P or high temperature, yields³⁶

$$D_{FA}(\Omega_i^{s+1}, \Omega_i^s; \beta\hbar/P) = \frac{I_{A_i}^\dagger I_{B_i}^\dagger I_{C_i}^\dagger}{(\beta\hbar/P)^3} \left[\frac{\Gamma_i^{s+1,s}/2}{\sin(\Gamma_i^{s+1,s}/2)} \right]^2, \quad (3.7)$$

where $\Gamma_i^{s+1,s}$, the arc length of the rotation from orientation s to orientation $s+1$ of fragment i , is given by³⁶

$$\Gamma_i^{s+1,s} = 2 \cos^{-1}(\chi_i^{s+1,s}), \quad (3.8)$$

and $\chi_i^{s+1,s}$ is a quaternion parameter for the rotation from orientation Ω_i^s to orientation Ω_i^{s+1} , the four of which, in general, are given in terms of Euler angles as^{41,42}

$$\chi = \cos \frac{\theta}{2} \cos \frac{(\psi + \phi)}{2}, \quad \eta = \sin \frac{\theta}{2} \cos \frac{(\psi - \phi)}{2}, \quad (3.9)$$

$$\xi = \sin \frac{\theta}{2} \sin \frac{(\psi - \phi)}{2}, \quad \zeta = \cos \frac{\theta}{2} \sin \frac{(\psi + \phi)}{2}.$$

The use of these quaternion parameters provides a convenient set of parameters to describe the orientation after a rotation has been performed on some initial orientation, and they also provide a convenient method for determining the relative orientation of two orientations. (See, e.g., Refs. 41 and 42.)

The least classical action for the rotation from orientation s to orientation $s+1$ of fragment i , in the fixed-axis approximation, is given by

$$S_{FA}(\Omega_i^{s+1}, \Omega_i^s; \beta/P) = \frac{(\Gamma_i^{s+1,s})^2 P}{2\beta\hbar} (\hat{n}_i^{s+1,s} \cdot \mathbf{I} \hat{n}_i^{s+1,s}), \quad (3.10)$$

where, using the quaternions, the rotation axis $\hat{n}_i^{s+1,s}$ is given in the principal axis frame by³⁶

$$\hat{n}_i^{s+1,s} = \frac{1}{\sin(\Gamma_i^{s+1,s}/2)} (\eta_i^{s+1,s} \hat{i} - \xi_i^{s+1,s} \hat{j} + \zeta_i^{s+1,s} \hat{k}), \quad (3.11)$$

and the last term in parenthesis in Eq. (3.10) is a tensor product, \mathbf{I} being the moment of inertia tensor in the principal axis frame. Equation (3.10) has the form which parallels the usual one for a free translational coordinate: a distance squared (here an arc length squared), multiplied by a mass (here a moment of inertia), and divided by twice a time, $\beta\hbar/P$.

The final expression for the quantum partition function for the hindered rotation of two rigid rotor molecules is thus

$$Q_{i,hrQ}^\dagger = C \left[\prod_{i=1}^2 \frac{I_{A_i}^\dagger I_{B_i}^\dagger I_{C_i}^\dagger}{(\beta\hbar/P)^3} \right]^{1/2} \times \int d\Omega^1 \cdots d\Omega^P \prod_{s=1}^P \left\{ \prod_{i=1}^2 \frac{\Gamma_i^{s+1,s}/2}{\sin(\Gamma_i^{s+1,s}/2)} \right. \\ \times \exp \left[-\frac{1}{\hbar} S_{FA} \left(\Omega_i^{s+1}, \Omega_i^s; \frac{\beta\hbar}{P} \right) \right] \left. \right\} \\ \times \exp \left[-\frac{\beta}{P} V(\Omega^s) \right]. \quad (3.12)$$

As discussed by Doll and Myers,⁴³ quantum partition functions may be obtained from Monte Carlo evaluation of an appropriate partition function ratio. In the present article two alternative partition function ratios were used to determine the quantum partition function. One alternative involves the determination of the ratio of the quantum partition function relative to that for two free rotors:

$$\frac{Q_{i,hrQ}^\dagger}{Q_{i,frQ}^\dagger} = \frac{\int d\Gamma A \exp[-(\beta/P) \sum_{s=1}^P V(\Omega^s)]}{\int d\Gamma A}, \quad (3.13)$$

where

$$Q_{i,frQ}^\dagger = \int d\Gamma A, \quad (3.14a)$$

$$d\Gamma = d\Omega^1 \cdots d\Omega^P, \quad (3.14b)$$

and

$$A = \prod_{s=1}^P \rho_0(\Omega^{s+1}, \Omega^s; \beta/P). \quad (3.14c)$$

The quantum partition function for the free rotation of the two fragments in their transition state configuration, $Q_{i,frQ}^\dagger$, is given by the high temperature expansion⁴⁴

$$Q_{i,frQ}^\dagger = Q_{i,frCl}^\dagger \prod_{i=1}^2 \left[1 + \frac{\hbar^2}{24k_B T} \sum_{\text{cyclic}} \left(\frac{2}{I_{A_i}^\dagger} - \frac{I_{A_i}^\dagger}{I_{B_i}^\dagger I_{C_i}^\dagger} \right) \right], \quad (3.15)$$

where

$$Q_{i,frCl}^\dagger = \prod_{i=1}^2 8\pi^2 [8\pi^3 I_{A_i}^\dagger I_{B_i}^\dagger I_{C_i}^\dagger]^{1/2} (k_B T/h^2)^{3/2}. \quad (3.16)$$

Thus, $Q_{i,hrQ}^\dagger$ may be obtained from Eqs. (3.13)–(3.16) with Monte Carlo evaluation of the ratio given in Eq. (3.13). This alternative is once again restricted to reasonably loose transition states.

The other alternative is to calculate the ratio of the quantum to the classical partition function. The classical partition function for the hindered rotor degrees of freedom may be written as

$$Q_{i,hrCl}^\dagger = Q_{i,frCl}^\dagger \frac{\int d\Omega^1 \exp[-\beta V(\Omega^1)]}{\int d\Omega^1}. \quad (3.17)$$

Multiplying both sides of Eq. (3.17) by $Q_{i,frQ}^\dagger/Q_{i,frCl}^\dagger$, and using Eq. (3.14a), yields

$$Q_{i,hrCl}^\dagger \frac{Q_{i,frQ}^\dagger}{Q_{i,frCl}^\dagger} = \frac{\int d\Gamma A \int d\Omega^1 \exp[-\beta V(\Omega^1)]}{\int d\Omega^1}, \quad (3.18)$$

where $d\Gamma$ and A are given by Eqs. (3.14b) and (3.14c), respectively. Since $\int A d\Omega^2 \cdots d\Omega^P$ is independent of Ω^1 , $\int d\Gamma A$ can be written as $(\int d\Omega^1)(\int A d\Omega^2 \cdots d\Omega^P)$, and hence Eq. (3.18) may be written as

$$Q_{i,hrCl}^\dagger \frac{Q_{i,frQ}^\dagger}{Q_{i,frCl}^\dagger} = \int d\Gamma A \exp[-\beta V(\Omega^1)]. \quad (3.19)$$

Thus, using Eqs. (3.13), (3.14a), and (3.19), the ratio of the quantum to classical partition functions for the transitional modes may be written as

$$\frac{Q_{i,hrQ}^\dagger}{Q_{i,hrCl}^\dagger} = \frac{Q_{i,frQ}^\dagger \int d\Gamma A \exp[-(\beta/P)\sum_{s=1}^P V(\Omega^s)]}{Q_{i,frCl}^\dagger \int d\Gamma A \exp[-\beta V(\Omega^1)]}. \quad (3.20)$$

The Monte Carlo calculation of this ratio is feasible regardless of how tight or loose the transition state is. On the other hand, the determination of $k_\infty^Q(T)$ (the quantum free radical recombination rate constant) from the $Q_{i,hrQ}^\dagger$ in Eq. (3.13) requires only a single Monte Carlo integration, rather than, as in Eq. (3.20), the Monte Carlo evaluation of both the ratio $Q_{i,hrQ}^\dagger/Q_{i,hrCl}^\dagger$ and the quantity $Q_{i,hrQ}^\dagger$.

Importance sampling techniques^{45,46} may now be used together with the fixed-axis approximation for A discussed above, in the Monte Carlo evaluation of the path integral ratios given in Eqs. (3.13) and (3.20). In particular, in the evaluation of Eq. (3.20) a weighting factor

$$W_j = A \exp\left[-\frac{\beta}{P} V(\Omega^1)\right], \quad (3.21)$$

with A given by Eq. (3.14c), is used to determine whether to accept or reject each random step generated in accordance with the parameters described in the next section.

The integrand in Eq. (3.20) which is summed up is then

$$Y_j = \exp\left\{-\frac{\beta}{P} \left[\sum_{s=1}^P V(\Omega^s) - V(\Omega^1)P\right]\right\}, \quad (3.22)$$

with the quantum to classical ratio being given by

$$\frac{Q_{i,hrQ}^\dagger}{Q_{i,hrCl}^\dagger} = \frac{Q_{i,frQ}^\dagger}{Q_{i,frCl}^\dagger} \sum_{j=1}^{N_{MC}} Y_j. \quad (3.23)$$

Multiplying the result of this Monte Carlo evaluation of Eq. (3.13) by the quantum correction factor for the diatomic term $Q_{i,d}^\dagger$ [given by the quantity in brackets in Eq. (3.5)] and then dividing by the quantum correction factor for Q_i^\dagger [given by the term multiplying $Q_{i,frCl}^\dagger$ in Eq. (3.15), with the transition state moments of inertia replaced by those for the reactant configuration] yields the ratio $k_\infty^Q(T)/k_\infty^{Cl}(T)$.

For the quantum to free-rotor ratio given in Eq. (3.13) the weighting factor is, instead,

$$W_j = A, \quad (3.24)$$

and the integrand in Eq. (3.13) is now given by

$$Y_j = \exp\left[-\frac{\beta}{P} \sum_{s=1}^P V(\Omega^s)\right]. \quad (3.25)$$

The result of this Monte Carlo evaluation of Eq. (3.13) is next multiplied by the quantum expression for $Q_{i,d}^\dagger$, given by Eq. (3.5), to give the quantum result for Q_i^\dagger . Substituting

this result into Eq. (2.3) and inserting the quantum correction factor for Q_i^\dagger yields the quantum free radical recombination rate constant $k_\infty^Q(T)$.

IV. RESULTS AND DISCUSSION

The two formalisms described above were implemented for the methyl radical recombination reaction using the potential energy function employed by Wardlaw and Marcus.^{5,6} The structure of the rigid body fragments for a given R^\dagger were also taken to be as in Refs. 5, and 6. g_e, σ_{CH_3} , and σ^\dagger were taken to be 1/4, 6, and 72, respectively.

For the evaluation of the quantum to free-rotor ratio the following procedure was followed: (1) One of the two fragments i was chosen randomly and an absolute orientation in space, which we will denote by $s = 0$, was chosen randomly.⁴⁷ The subsequent points [the path integral points in Eq. (3.1)] correspond to $s = 1, \dots, P$. The molecule corresponding to fragment i , and path integral discretization point s will be denoted as (i,s) , and the molecule corresponding to the $s = 0$ point is denoted by $(i,0)$. For this method, this orientation has no effect on the weighting factor and so was always accepted. (2) Next, one of the discretization points s was chosen randomly, and then a rotation about a randomly chosen axis⁴⁸ of the old orientation of molecule (i,s) relative to molecule $(i,0)$ was performed. The magnitude of the rotation was chosen as $R \delta_1^r$, where R is a random number between 0 and 1, and δ_1^r , the maximum magnitude of the rotation, was chosen to give a roughly 50% acceptance ratio⁴⁹ of the rotations. (3) The new orientation of molecule (i,s) relative to the zeroth order orientation $(i,0)$ was then calculated using the formula for the composition of quaternions given in Eq. (33) of Ref. 41. (4) The new orientation of molecule (i,s) relative to that of $(i,s+1)$, and that of $(i,s-1)$ was next calculated from the known orientations of (i,s) , $(i,s+1)$, and $(i,s-1)$ relative to that of $(i,0)$, using the formula for relative quaternions given by Eq. (38) of Ref. 41. (5) The ratio of the weighting factor W_j , given in Eq. (3.24), for this new orientation relative to W_j for the old orientation was calculated. If this number was greater than a random number between 0 and 1 then the rotation was accepted. Otherwise the rotation in step (2) was rejected and the old relative orientations of (i,s) to $(i,0)$, (i,s) to $(i,s+1)$, and (i,s) to $(i,s-1)$ were restored to their old values. (6) The absolute orientation in space of molecule (i,s) was then calculated, from Eq. (33) of Ref. 41 for the composition of quaternions, using the orientation of molecule (i,s) relative to that of molecule $(i,0)$ and the absolute orientation in space of molecule $(i,0)$. The new value of the integrand was then calculated from Eq. (3.25) using the new absolute orientation in space of molecule (i,s) . This process was then repeated until the desired number of Monte Carlo points was reached.

The evaluation of the quantum to classical ratio was calculated in a similar manner except that now the weighting factor W_j given in Eq. (3.21) is used. In this case W_j does depend on the "zeroth" order orientation so that step (1) now involves a rotation of random magnitude, within a maximum magnitude δ_0^{Cl} , of the zeroth order orientation about a randomly chosen axis.⁴⁸ The maximum magnitude of the

rotation here was much larger than that of step (2) (labeled δ_1^{Cl}) in order to allow for an efficient sampling over configuration space, as discussed by Kuharski and Rossky.³⁶ The other steps were identical to those in the quantum to free-rotor case, except in the present case the old ($i,0$) absolute orientation also had to be restored in step (5) whenever a move was rejected. The overall acceptance ratio was once again kept at about 50%⁴⁹ by varying the parameters δ_0^{Cl} and δ_1^{Cl} .

All of the calculations discussed here were easily programmed and large computation times were not required.⁵⁰ The results for $k_{\infty}^{\text{Cl}}(T)$, $k_{\infty}^{\text{Q}}(T)$, and the ratio $k_{\infty}^{\text{Q}}(T)/k_{\infty}^{\text{Cl}}(T)$ obtained from these calculations are given in Table I for the four temperatures 300, 500, 1000, and 2000 K. All of the quantum results reported in Table I were calculated using $P = 6$ discretization points, since it was found that the results had converged by this value of P .⁵¹ In the classical calculations the estimated error, σ^{MC} , was evaluated from

$$\sigma^{\text{MC}} = \left[\left| f^2 - \frac{\sum_{i=1}^{N_{\text{MC}}} f_i^2 / N_{\text{MC}}}{N_{\text{MC}}} \right| \right]^{1/2}, \quad (4.1)$$

where f is the Monte Carlo result for the quantity being evaluated [in the present case $k_{\infty}^{\text{Cl}}(T)$] and f_i is a particular value of the integrand. In the quantum calculations, due to the strong correlation between successive states, σ^{MC} was instead calculated from the variance of sequences of estimates to f [f being either $k_{\infty}^{\text{Q}}(T)$ or the ratio $k_{\infty}^{\text{Q}}(T)/k_{\infty}^{\text{Cl}}(T)$] over blocks of 100 to 1000 Monte Carlo steps. (See, e.g., Ref. 46.)

Comparison of the results for $k_{\infty}^{\text{Cl}}(T)$ given in Table I, with those given in Table VII of Ref. 6, shows that within the Monte Carlo error bars the two calculations give the same result. One also sees from Table I that, within the Monte Carlo error bars, the quantum correction for recombination in the present case is negligible, and is at most about 1% to 2%, and its temperature dependence is, within the statistical error, also negligible. At low temperatures one might expect that there would be a larger quantum correction for these modes. However, when the temperature is reduced the loca-

TABLE I. Quantum corrections from path integration.

Temp (K)	$R^{\ddagger a}$ (Å)	$k_{\infty}^{\text{Cl}}(T)^b \pm \sigma_{\text{MC}}^c$ ($10^{13} \text{ cm}^3 \text{ mol}^{-1}$)	$k_{\infty}^{\text{Q}}(T)^d \pm \sigma_{\text{MC}}^c$ ($10^{13} \text{ cm}^3 \text{ mol}^{-1}$)	Ratio ^e $\pm \sigma_{\text{MC}}^c$
300	4.2	5.06 ± 0.02	4.99 ± 0.02	1.002 ± 0.004
500	3.8	4.32 ± 0.03	4.31 ± 0.04	0.999 ± 0.006
1000	3.4	2.83 ± 0.03	2.75 ± 0.04	0.997 ± 0.007
2000	3.0	1.38 ± 0.02	1.34 ± 0.03	1.024 ± 0.008

^a As determined in Ref. 6.

^b As determined by the present classical Monte Carlo calculation.

^c σ_{MC} refers to the Monte Carlo uncertainties determined as discussed in the text.

^d As determined by the quantum to free-rotor ratio path integral ratio calculation. [See Eq. (3.13).]

^e $k_{\infty}^{\text{Q}}/k_{\infty}^{\text{Cl}}$ as determined by the quantum to classical ratio path integral calculation. [See Eq. (3.20).]

tion of the transition state moves to larger separation distances and so the partition function for the transitional modes becomes more and more like the product of free-rotor partition functions for which the quantum correction is relatively minor (except at quite low temperatures in which case one expects the quantum corrections for the transitional modes of the transition state and for the transitional modes of the reactants to cancel). Conversely, at high temperatures one might expect a quantum correction due to the decrease in R^{\ddagger} , causing an increase in the steepness of the potential energy function. That this is not the case here must be because the increase in temperature causing more classical behavior balances out the increase in steepness causing quantum effects. In other systems which are "tighter" in the transition state region (have stronger fragment-fragment bending forces there) there may be larger quantum effects and the present method may be used to determine the quantum correction.

It is interesting to compare these results with those which can be obtained from a generalized Wigner-Kirkwood expansion of the partition function.^{52,53} For the present system of two symmetric tops plus a linear rigid rotor this expansion of the partition function is given by^{52,53}

$$\frac{Q_{i,hrQ}^{\ddagger}}{Q_{i,hrCl}^{\ddagger}} = \frac{Q_{i,frQ}^{\ddagger}}{Q_{i,frCl}^{\ddagger}} \frac{\int d\theta_{12} d\phi_{12} \prod_{i=1}^2 d\theta_i d\phi_i d\psi_i \exp(-\beta V) [1 - \beta^3 \hbar^2 \sum_k (\nabla_k V)^2 / 24m_k]}{\int d\theta_{12} d\phi_{12} \prod_{i=1}^2 d\theta_i d\phi_i d\psi_i \exp(-\beta V)}, \quad (4.2)$$

where

$$\frac{1}{m_k} (\nabla_k V)^2 = \frac{1}{I_d^{\ddagger}} \left[\left(\frac{\partial}{\partial \theta_{12}} V \right)^2 + \frac{1}{\sin^2 \theta_{12}} \left(\frac{\partial}{\partial \phi} V \right)^2 \right] + \sum_{i=1}^2 \left[\frac{1}{I_{A_i}^{\ddagger}} \left(\frac{\partial}{\partial \theta_i} V \right)^2 + \frac{1}{I_{A_i}^{\ddagger} \sin^2 \theta_i} \left(\frac{\partial}{\partial \phi_i} V - \frac{\partial}{\partial \psi_i} V \right)^2 + \frac{1}{I_{C_i}^{\ddagger}} \left(\frac{\partial}{\partial \psi_i} V \right)^2 \right]. \quad (4.3)$$

The derivation of the Wigner-Kirkwood expansion for symmetric tops and for diatomic rotors has been given previously (see, e.g., Refs. 54 and 55).

Results based on Eqs. (4.2) and (4.3) are presented in Table II. The Monte Carlo evaluations in the calculation of $k_{\infty}^{\text{Q}}(T)$ have been performed in exact analogy to the classical calculations of Table I. The ratio calculations have been

performed along the lines of the quantum calculations in Table I. In both cases the derivatives given in Eq. (4.3) were calculated numerically, and, as a result of the extra potential calls thus required, the evaluation of Eq. (4.2) required more CPU time than the exact calculations. However, this would not be the case if the potential was given in a form which was easily differentiated analytically. Comparison of

TABLE II. Quantum corrections from generalized Wigner–Kirkwood expansion.

Temp (K)	R^{a} (Å)	$k_{\infty}^{\text{Q}}(T)^{\text{b}} \pm \sigma_{\text{MC}}^{\text{c}}$ ($10^{13} \text{ cm}^3 \text{ mol}^{-1}$)	Ratio ^d $\pm \sigma_{\text{MC}}^{\text{c}}$
300	4.2	5.00 ± 0.03	0.990 ± 0.001
500	3.8	4.22 ± 0.05	0.980 ± 0.001
1000	3.4	2.70 ± 0.06	0.980 ± 0.001
2000	3.0	1.29 ± 0.05	0.982 ± 0.001

^a As determined in Ref. 6.

^b Determined by the direct evaluation of $k_{\infty}^{\text{Q}}(T)$ from the generalized Wigner–Kirkwood expansion.

^c σ_{MC} refers to the Monte Carlo uncertainties determined as discussed in the text.

^d Determined by the direct evaluation of $k_{\infty}^{\text{Q}}/k_{\infty}^{\text{Cl}}$ from the generalized Wigner–Kirkwood expansion calculation. The Monte Carlo error bars in this calculation are negligible.

the results given for $k_{\infty}^{\text{Q}}(T)$ in Tables I and II shows that the Wigner–Kirkwood result is approximately within the error bars of the nonperturbative result. The smallness of σ_{MC} in the last column of Table II is presumably because in that calculation of a ratio $k_{\infty}^{\text{Q}}(T)/k_{\infty}^{\text{Cl}}(T)$ only a small correction term had to be averaged.

Although the results given in Table I indicate a very small correction for the transitional modes of a relatively loose transition state at reasonable temperatures, there may still be a large correction to some of the $k_{E,J}$'s at lower energies. For some experimental situations quantities of particular interest are these $k_{E,J}$'s, and, for this reason, we are presently studying the possibility of obtaining accurate microcanonical correction factors. When only microcanonical rate constants k_E are needed, they can be obtained by inverse Laplace transformation of results at fixed R , provided one evaluates $k_{\infty, \text{Q}}(T)$ over a wide enough range of temperatures. However, the determination of the constant E and J rate constants requires a different approach.

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⁴⁷For example, $\theta_i = \pi R_1$, $\phi_i = 2\pi R_2$, and $\psi_i = 2\pi R_3$, where R_1 , R_2 , and R_3 are random numbers between 0 and 1.

⁴⁸First, χ is set equal to $\cos(\Gamma/2)$, where Γ is the magnitude of the rotation. An axis of rotation is then chosen randomly by choosing a random point on a sphere of radius $\sqrt{1-\chi^2}$ and taking η , ξ , and ζ as the three Cartesian coordinates of this point.

⁴⁹The acceptance ratio is defined as the number of moves accepted divided by the number of moves attempted. It has been empirically determined that acceptance ratios of about 50% lead to the most rapid convergence. See, for example, J. A. Barker, *Lattice Theories of the Liquid State* (MacMillan, New York, 1963).

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