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Well converged quantum rate constants for the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction via transition state wave packet

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Transition state wave packet calculations have been carried out to compute cumulative reaction probabilities for the $\text{H}_2 + \text{OH}$ reaction on the NN1 potential energy surface, as given in the work of Chen *et al.*, from which well converged thermal rate constants for the reaction up to a temperature of 1000 K were obtained. It was found that both the centrifugal sudden approximation and the “ J - K -shifting” approximation slightly underestimated the thermal rate constants, while the ring-polymer molecular dynamics overestimated the rates in the low temperature region. After considering the correction of the barrier height by spin-orbit coupling effect and the more accurate level of theory, the calculated rate constants were in good consistency with experimental measurements in the entire temperature region for this benchmark reaction. Published by AIP Publishing. <https://doi.org/10.1063/1.5046890>

I. INTRODUCTION

In the past decades, significant progress has been made on accurate quantum reactive scattering studies of four-atom chemical reactions. It is possible now to calculate fully converged integral cross sections (ICSSs)^{1–5} and state-to-state differential cross sections (DCSSs)^{6–12} without any dynamical approximation for some four-atom reactions, mainly through the development of the initial state selected wave packet (ISSWP) method. Excellent agreements were achieved for the first time for a four-atom reaction between the theory and high-resolution crossed-molecular beam experiment on DCSSs for the $\text{HD} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{D}$ reaction.⁶ Meanwhile, it is necessary to carry out accurate quantum calculations of the rate constants for a four-atom reaction, which can be used to compare with experimental results unambiguously, and to assess various approximate methods for polyatomic reactions.

The $\text{H}_2 + \text{OH}$ reaction represents the prototype for four-atom reactions, in much the same way that the $\text{H} + \text{H}_2$ reaction served as the prototype for triatomics. Because of its important role in combustion and atmospheric chemistry,^{13,14} the thermal rate constants of the reaction have been measured over a wide temperature range. Both the rate constants measured by Orkin *et al.*¹⁷ between 200 K and 480 K and by Ravishankara *et al.*^{15,16} between 250 K and 1050 K revealed a noticeable curvature on the Arrhenius plots. Theoretically, because three of the four atoms are hydrogen atoms, the system is an ideal candidate to carry out high quality *ab initio* electronic structure calculations and accurate quantum dynamical studies. Since Schatz and Elgersma fitted an analytic potential energy surface (PES), known as the Walch-Dunning-Schatz-Elgersma

(WDSE) PES,¹⁸ in past decades, a number of new PESs have been constructed for the reaction system, including the recently developed highly accurate and computationally efficient global PES using neural networks method (NN1). The earliest cumulative reaction probabilities (CRP) for the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction were calculated only for total angular momentum $J = 0$,^{23–26} from which the thermal rate constants were estimated by using the “ J - K -shifting” approximation.^{27–29} In 1998, Zhang and co-workers reported the transition state wave packet (TSWP) calculation of CRP summed over all J under the centrifugal sudden (CS) approximation on the WDSE PES.³⁰ In 2000, Manthe and co-workers provided a full-dimensional quantum description of the rate constants employing a statistical sampling scheme for the overall rotational motion and the multi-configurational time-dependent Hartree (MCTDH) approach for the wavefunction propagation.³¹ However, comparisons showed significant differences between the above theoretical rate constants and the experimental results, indicating that the previous PES is not sufficiently accurate. Recently, Welsch reported the thermal rate constants between 300 K and 1000 K using the same method as Manthe on the NN1 PES and found very good agreement with the experimental work of $\text{H}_2 + \text{OH}$.³² Additionally, good agreement with the experimental rate constants was also achieved by using instanton theory and canonical variational theory with microcanonical optimized multidimensional tunneling (CVT/mOMT) or the ring polymer molecular dynamics (RPMD) method on the NN1 PES.^{33,34}

In this letter, we present time-dependent TSWP calculations for the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction to provide coupled-channel (CC) CRP on the NN1 PES. From which, well converged thermal rate constants for the reaction are obtained. The calculated rates cannot only be used to compare with experimental measurements unambiguously

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but also provide benchmarks to assess the accuracy of various approximate methods for polyatomic reaction rate calculations.

Since Yamamoto and Miller *et al.* introduced a flux correlation function based expression,^{35–37} the CRP $N(E)$ and thermal rate constants can be calculated directly without solving the complete scattering problem. The TSWP approach was derived by Zhang and Light in 1996 from this famous expression.³⁸ It can efficiently calculate the CRP $N(E)$ at all energies desired from a single propagation of each transition state wave packet forward and backward in time. From these $N(E)$'s, one can obtain the thermal rate constants via the Boltzmann average. The high efficiency of the method has been demonstrated on some reactive systems consisting of more than only three atoms, such as $\text{H}_2 + \text{OH}$, $\text{H}_2(\text{D}_2) + \text{CN}$, and $\text{H} + \text{CH}_4$ reactions.^{25,30,39–42} Shortly after that, Manthe and co-workers introduced a similar approach, using the MCTDH scheme to calculate the eigenstates of the thermal flux operator and to propagate the eigenfunctions in time, and applied it to the $\text{H}_2 + \text{OH}$, $\text{H} + \text{CH}_4$, and $\text{O} + \text{CH}_4$ reactions.^{26,43–45}

The paper is organized as follows: In Sec. II, we outline the theoretical methodology of the TSWP approach to $N(E)$ for the $\text{H}_2 + \text{OH}$ reaction. Section III presents the results of our calculation, including $N(E)$ and rate constants for the title reaction as well as comparisons with the CS and “ J - and K -shifting” approximations. We conclude in Sec. IV.

II. THEORY

The time-dependent TSWP approach to the CRP $N(E)$ was derived by Zhang and Light³⁸ from the famous formulation given by Miller and co-workers,³⁷

$$N(E) = \frac{(2\pi)^2}{2} \text{tr}[\delta(E - H)F_2\delta(E - H)F_1], \quad (1)$$

where the F_i 's are quantum flux operators at dividing surfaces (which may or may not be the same).

In the TSWP approach, we first choose a dividing surface S_1 separating the products from reactants preferably located to minimize the density of internal (transition) states for the energy region considered. Then initial wave packets $|\phi_i^+\rangle$ ($i = 1, N$) are constructed as the direct products of the Hamiltonian eigenstates on S_1 , $|\phi_i\rangle$, and flux operator eigenstate $|+\rangle$ with positive eigenvalue λ for the coordinate perpendicular to S_1 , i.e.,

$$\begin{aligned} H_{S_1}|\phi_i\rangle &= \varepsilon_i|\phi_i\rangle, \\ F|+\rangle &= \lambda|+\rangle, \\ |\phi_i^+\rangle &= |\phi_i\rangle|+\rangle, \end{aligned} \quad (2)$$

where the flux operator F is defined as

$$F = \frac{1}{2\mu}[\delta(q - q_0)\hat{p}_q + \hat{p}_q\delta(q - q_0)]. \quad (3)$$

Here μ is the reduced mass of the system, q is the coordinate perpendicular to the dividing surface located at $q = q_0$ which separates products from reactants, and \hat{p}_q is the momentum operator conjugate to the coordinate q . It is well known that

in one dimension the flux operator only has a \pm pair of non-vanishing eigenvalues, and the corresponding eigenstates are also complex conjugates.^{46–48}

After constructing the initial wave packets, we propagated them in time as in the ISSWP approach. The CRP $N(E)$ can be computed as

$$N(E) = \sum_{i=1}^n N_i(E) = \sum_{i=1}^n \langle \psi_i(E) | F | \psi_i(E) \rangle. \quad (4)$$

The energy-dependent wavefunctions $|\psi_i(E)\rangle$ are calculated on the second dividing surface as

$$\psi_i(E) = \sqrt{\lambda} \int_{-\infty}^{+\infty} dt e^{i(E-H)t} |\phi_i^+\rangle. \quad (5)$$

Applying to the $\text{H}_2 + \text{OH}$ reaction, the Hamiltonian in mass-scaled Jacobi coordinates can be written as^{25,49}

$$H = \frac{1}{2\mu} \sum_{i=1}^3 \left(-\frac{\partial^2}{\partial s_i^2} + \frac{j_i^2}{s_i^2} \right) + V(s_1, s_2, s_3, \theta_1, \theta_2, \phi), \quad (6)$$

where j_1 and j_2 are the rotational angular momenta of H_2 and OH , which are coupled to form j_{12} . In the body-fixed frame, the orbital angular momentum j_3 is represented as $(J - j_{12})^2$, and J is the total angular momentum. In Eq. (6), μ is the mass of the system,

$$\mu = (\mu_1 \mu_2 \mu_3)^{1/3}, \quad (7)$$

with μ_i being the reduced mass for H_2 , OH , and the system,

$$\begin{aligned} \mu_1 &= \frac{m_H m_H}{m_H + m_H}, \\ \mu_2 &= \frac{m_H m_O}{m_H + m_O}, \\ \mu_3 &= \frac{(m_H + m_H)(m_H + m_O)}{m_H + m_H + m_H + m_O}. \end{aligned} \quad (8)$$

The mass-scaled coordinates s_i are defined as

$$s_i^2 = \frac{\mu_i}{\mu} R_i^2, \quad (9)$$

where R_i ($i = 1-3$) are the bond lengths for H_2 , OH , and the intermolecular distance between the centers of mass of H_2 and OH , respectively.

The coupled angular momentum basis sets used to expand the TD wavefunction under the body-fixed frame are defined as

$$\begin{aligned} y_{jK}^{JM\epsilon} &= (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \left[D_{KM}^J Y_{j_1 j_2}^{j_{12} K} \right. \\ &\quad \left. + \epsilon (-1)^{j_1 + j_2 + j_{12} + J} D_{-KM}^J Y_{j_1 j_2}^{j_{12} -K} \right], \end{aligned} \quad (10)$$

where D_{KM}^J is the Wigner rotation matrix,⁵⁰ ϵ is the parity of the system, K is the projection of the total angular momentum on the body-fixed axis, and $Y_{j_1 j_2}^{j_{12} K}$ is the angular momentum eigenfunction of j_{12} ,

$$Y_{j_1 j_2}^{j_{12} K} = \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle y_{j_1 m_1}(\theta_1, 0) y_{j_2 K - m_1}(\theta_2, \phi), \quad (11)$$

where y_{jm} are spherical harmonics. Note that in Eq. (10), the restriction $\epsilon(-1)^{j_1 + j_2 + j_{12} + J} = 1$ for $K = 0$ partitions the whole rotational basis set into even and odd parities. Thus a $K = 0$ initial state can only appear in one of these two parity blocks.

For the convenience of choosing the dividing surface S_1 , we define two new “reaction coordinate” variables q_1 and q_3 by translating and rotating the s_1 and s_3 axes,

$$\begin{pmatrix} q_1 \\ q_3 \end{pmatrix} = \begin{pmatrix} \cos \chi & \sin \chi \\ -\sin \chi & \cos \chi \end{pmatrix} \begin{pmatrix} s_1 - s_1^0 \\ s_3 - s_3^0 \end{pmatrix}. \quad (12)$$

The Hamiltonian in Eq. (6) can be rewritten as

$$H = \frac{1}{2\mu} \left(-\frac{\partial^2}{\partial q_1^2} - \frac{\partial^2}{\partial s_2^2} - \frac{\partial^2}{\partial q_3^2} + \frac{j_1^2}{s_1(q_1, q_3, s_1^0, s_3^0)^2} + \frac{j_2^2}{s_2^2} + \frac{j_3^2}{s_3(q_1, q_3, s_1^0, s_3^0)^2} \right) + V. \quad (13)$$

Generally, we can choose the dividing surface S_1 at $q_1 = 0$ by changing s_1^0 , s_3^0 and χ , construct the initial wave packets in $(q_1, s_2, q_3, \theta_1, \theta_2, \phi)$ coordinates, then transfer them to the $(s_1, s_2, s_3, \theta_1, \theta_2, \phi)$ coordinates, and propagate them to generate $\psi_i(E)$ and $N(E)$.

III. RESULTS

The numerical parameters used in the current study are as follows: We used a total number of 60 sine functions (among them 20 for the interaction region) for the translational coordinate s_3 in a range of $[3.0, 11.5] a_0$. A total of 33 vibrational functions are employed for s_1 in the range of $[0.36, 3.64] a_0$ for the reagents H_2 . For full-dimensional (6D) calculation, the number of vibrational basis functions used for the reagent OH is 3. For the rotational basis, we used $j_{1max} = 20$ for H_2 and $j_{2max} = 16$ for OH. The values of s_1^0 , s_3^0 and χ which define the transition state surface were carefully chosen to be $1.2 a_0$, $4.6 a_0$, and 30° to minimize the density of states on the dividing surface. The vibrational eigenfunctions on the first dividing surface were solved using the same basis sets as described above. A total number of 30 transition states were used in order to obtain a well converged CRP. We propagated the wave packets for 6000 a.u. of time with a time step of 15 to converge the low energy CRP at the second dividing surface located at $s_1 = 1.9 a_0$. In the present study, we calculated the $N(E)$ only for the even rotation of H_2 . Because the rotation barrier for H_2 in the transition state region on the PES is quite high, the H_2 is constrained, requiring a number of rotational basis functions of either symmetry. Thus the $N(E)$ for the even and odd rotational states are almost the same. We can simply obtain the total $N(E)$ by multiplying the $N(E)$ for even rotational states of H_2 by a factor of 2.

Figure 1 shows the 6D CRP $N(E)$, for $(J = 0, K = 0, \epsilon = 1)$ as a function of total energy corresponding to the ground initial transition state, in comparison with the potential-averaged five-dimensional (PA5D) results. The PA5D probabilities are identical as the 6D ones. The relative error of PA5D contributions to thermal rate constants (obtained by Boltzmann average) with respect to the 6D ones is less than 0.5% in the entire temperature range considered here, indicating the OH bond is a good spectator for the reaction. Thus PA5D is an effective approximation for the reaction without losing any accuracy of calculations. The following results are based on the PA5D calculation.

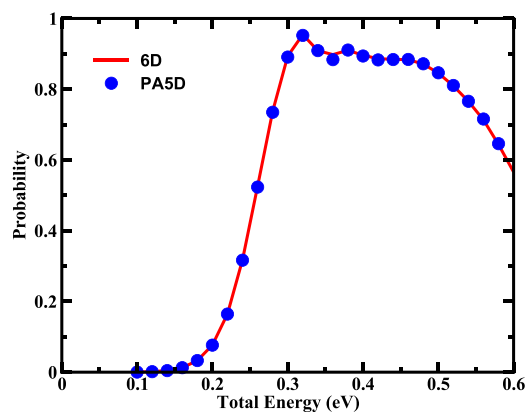


FIG. 1. The 6D and PA5D probabilities under $(J = 0, K = 0, \epsilon = 1)$ as a function of total energy corresponding to the ground initial transition state.

By testing the convergence of probabilities with the number of K -blocks in the CC calculation, we found that only the coupling between $K = (\max(0, K_0 - 1), K_0, K_0 + 1)$ needs to be considered in propagation. Figure 2 shows the CC CRP $N(\epsilon, J, K_0, E)$ at total angular momentum $J = K_0, 10, 20$ for $K_0 = 0, 1, 2$. As can be seen, the J -dependent curves as a function of total energy shifted toward a higher energy roughly as a quadratic function of J , implying the J -shifting approach should work well here. For $K_0 = 0$, the different basis sets for even and odd parities result in different values of $N(\epsilon, J, K_0 = 0, E)$. For $K_0 = 1$, the coupling between $K = 0$ and $K = 1$ cannot be neglect in the CC calculations for propagation. Thus $N(\epsilon = +1, J, K_0 = 1, E)$ and $N(\epsilon = -1, J, K_0 = 1, E)$ show some small differences. On the other hand, $\epsilon = \pm 1$ yield the same value of $N(\epsilon, J, K_0, E)$ for $K_0 \geq 2$. Thus we calculated $N(\epsilon, J, K_0 \geq 2, E)$ for only one parity, which should be multiplied by a factor of 2 to obtain the CRP with parities summed.

The contributions of individual K_0 to thermal rate constants within a temperature range between 200 K and 1000 K

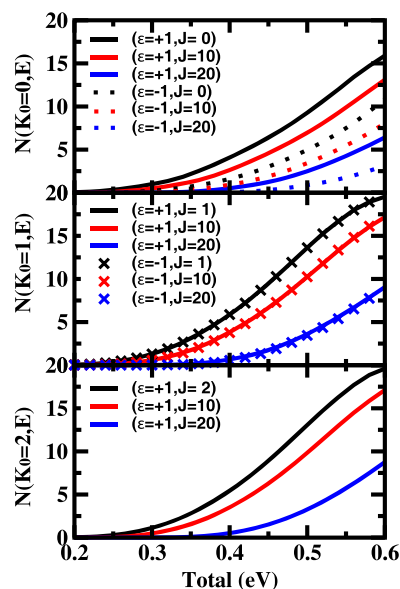


FIG. 2. The CC CRP $N(\epsilon, J, K_0, E)$ at $J = K_0, 10, 20$ for $K_0 = 0, 1, 2$.

are obtained from the CRP via the Boltzmann average

$$k(K_0, T) = \frac{1}{2\pi Q_r(T)} \sum_J (2J+1) \int_0^\infty dE e^{-E/k_B T} N(J, K_0, E), \quad (14)$$

where k_B is the Boltzmann constant, T is the temperature, and $Q_r(T)$ is the reactant partition function. The electronic partition function $Q_{elec}(T)$ can be calculated as

$$Q_{elec}(T) = (1 + e^{-\Delta E/k_B T}), \quad (15)$$

where $\Delta E = 140 \text{ cm}^{-1}$ is the spin-orbit splitting energy of OH. By using the uniform J -shifting approach with a temperature-dependent shifting constant,⁵¹ all we have to do is to calculate CRP at only a few total angular momentum values of J . In Fig. 3(a), we compared the $K_0 = 0, 6, 9$ rate constants calculated by utilizing the CRP at three J values ($J = K_0, 10, 20$) with those calculated at four J values ($J = K_0, 10, 20, 25$), indicating that three J values are sufficient to get the fully converged rate. As shown in Fig. 3(a), the $K_0 = 1, 2$ rate constants are larger than the $K_0 = 0$ ones for all the temperatures considered here. For high temperatures, the $K_0 = 0$ results are even smaller than the $K_0 = 3, 4$ ones. Thus it is clear that for this reaction we cannot fit $k(K_0 > 0, T)$ curves in terms of $k(K_0 = 0, T)$ curves by a simple energy shift, indicating that the K -shifting approximation is not good here. Figure 3(b) shows the fraction of rate constant for each K_0 . As can be seen, $K_0 > 6$ mainly contributes to rate constants for temperatures higher than 300 K. In the entire temperature range considered here, the fraction of $K_0 = 10$ is less than 2%, which can be neglect. Therefore, the thermal rate constants up to 1000 K are dominated by contributions from $0 \leq K_0 \leq 9$.

Figure 4(a) shows the converged total rate constants for the title reaction on the NN1 PES summed over $K_0 = 0-9$. Results calculated using the CS approximation and “ J - K -shifting” approximation on the same PES are also displayed

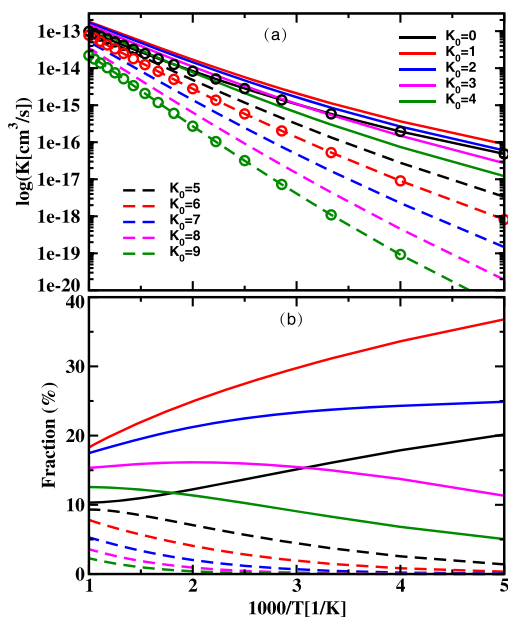


FIG. 3. (a) The contributions of individual K_0 to thermal rate constants within a temperature range between 200 K and 1000 K calculated from CRP at $J = K_0, 10, 20$ with those of $K_0 = 0, 6, 9$ calculated from CRP at $J = K_0, 10, 20, 25$ (circles). (b) The fraction of rate constant for each K_0 .

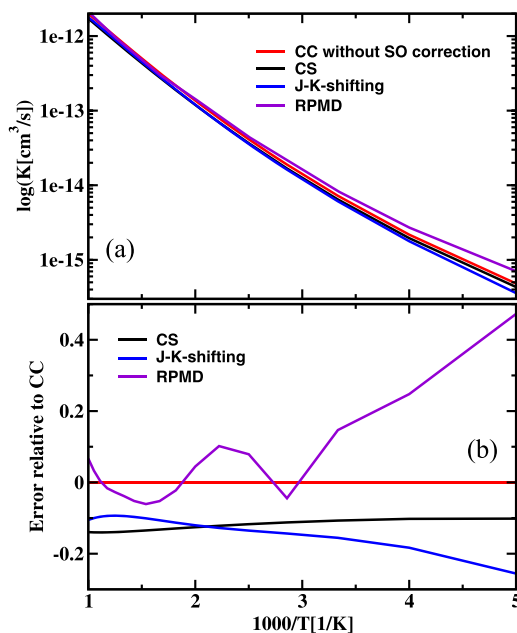


FIG. 4. (a) CC rate constants of the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction, in comparison with theoretical results by using the CS or “ J - K -shifting” approximation, and the RPMD method on the same PES. (b) The relative errors of the CS, “ J - K -shifting,” and RPMD rate constants with respect to the accurate CC result.

for comparison, together with the rate constants from theoretical calculations by the RPMD method.³⁴ Figure 4(b) shows the relative errors of the CS, “ J - K -shifting,” and RPMD rate constants with respect to the accurate CC results. In the entire temperature range we considered, the CS rate constant has the same trend as the CC result, except that the CS value is underestimated. Moreover, the “ J - K -shifting” approximation in which we calculate the rate constant solely from $N(J = K = 0, E)$ considerably underestimates the rate constants for low temperatures, again demonstrating that the K -shifting approximation is not good for this reaction. The RPMD rate curve gives the correct rate near 1000 K but deviates from the CC rate by 45% at the lowest temperature of 200 K.

In fact, the spin-orbit free state used in our calculation is an equal average of the true ground state and the spin-orbit excited state. We should take the spin-orbit coupling effect into account by raising the barrier height by $\Delta E/2$ (which is not included in the NN1 PES). As can be seen in Fig. 5, after considering the spin-orbit correction, the CC rate constants agree well with those calculated by the MCTDH method on the same PES,³² both of which underestimated the experimental values.¹⁵⁻¹⁷ The slightly overestimated barrier height of NN1 PES calculated at the UCCSD(T)/AVTZ level of theory is the main reason for this discrepancy. So we recalculated the barrier height for the title reaction with more accurate methods or larger basis sets. Compared with the UCCSD(T) method, the unrestricted coupled cluster theory with singles, doubles, triples and perturbative quadruples, together with the augmented correlation consistent triple zeta basis set (UCCSDT(Q)/AVTZ) level of calculations decrease the barrier height by 52 cm^{-1} . The barrier-correction TSWP rate constants can pass through the experimental data points perfectly and reveal an appropriate curvature on the

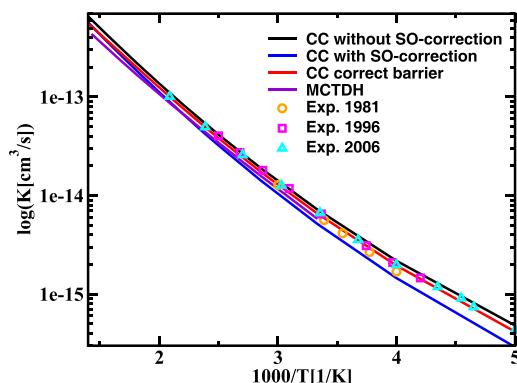


FIG. 5. CC rate constants after considering the correction by the spin-orbit coupling effect and the UCCSDT(Q)/AVTZ level of theory, in comparison with theoretical results by using the MCTDH method on the same PES and various experimental values.

Arrhenius plot. Therefore, in order to achieve a complete agreement with the experiments, we need to improve the PES to the UCCSDT(Q)/AVTZ level in the future.

IV. CONCLUSIONS

The TSWP simulations have been carried out to study the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction on the NN1 PES. We computed the CC CRP $N(J, K_0, E)$ at some total angular momentum J for each K_0 , from which the contributions of individual K_0 to rate constants were obtained via the Boltzmann average. The thermal rate constants up to 1000 K are dominated by contributions from $0 \leq K_0 \leq 9$. It is found the CS and “ J - K -shifting” approximations underestimate the rate constants in the entire temperature range we considered, while RPMD considerably overestimates the rates in the low temperature region. After considering the spin-orbit correction, the CC rate constants agree well with those calculated by the MCTDH method on the same PES, both of which underestimated the experiments because of the slightly overestimated barrier height of NN1 PES. By correcting the barrier height according to the UCCSDT(Q)/AVTZ level of calculations, the present TSWP results were in good consistency with the values of experiments.

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