Assessing Parameters for Ring Polymer Molecular Dynamics Simulations at Low Temperatures: DH+H Chemical Reaction

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Abstract

Ring polymer molecular dynamics (RPMD) is an accurate method for calculating thermal chemical reaction rates. It has recently been discovered that low-temperature calculations are strongly affected by the simulation parameters. Here, for the thermally activated reaction DH + H → D + H\textsubscript{2}, we calculate the RPMD rate constants at $T = 50$, 100, and 300 K and demonstrate that for $T \geq 100$ K the standard input parameters yield accurate results, but at low temperatures (e.g., 50 K) one must increase the asymptotic distance and force constant, and decrease the umbrella integration step.

Keywords: ring polymer molecular dynamics; chemical reaction rate; quantum mechanical effects; astrochemical reaction

1. Introduction

Accurate determination of rate constants for gas-phase bimolecular reactions is of great importance in modeling chemical kinetics in various atmospheric, astrochemical, and combustion systems. One of the most challenging classes of reactions is the astrochemical reactions taking place at low temperatures, at which quantum mechanical effects such as zero-point energy

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(ZPE), tunneling, and resonance effects become critically important. Recently, ring polymer molecular dynamics (RPMD) has been proposed as an efficient tool for calculating thermal chemical reaction rates. The method is based on the classical isomorphism between the quantum statistical mechanics of the physical system and the classical statistical mechanics of a fictitious ring polymer including a number of classical copies (beads) of the original system connected by harmonic springs. \[12\] RPMD is the full-dimensional approximate quantum mechanical method for computing Kubo-transformed real-time correlation functions for many dynamical properties, in particular, this method computes flux-side correlation functions \[32\] which are used in the formalism for calculating chemical reaction rates. The path integral nature of the RPMD method allows capturing quantum effects, such as ZPE effects \[33, 20\] and tunneling \[34\] that play a key role while calculating thermal rate coefficients at low temperatures. It has been shown that the RPMD technique \[13, 14, 15, 21\] provides systematically accurate approach for calculating rate coefficients in a wide temperature range. The RPMD method has been implemented in the RPMDrate code \[38\] and tested for numerous prototype chemical reactions \[33, 34, 7, 20, 30, 36, 11, 17, 37, 35, 23, 24, 25, 4\] 

Despite the instantaneous success of the RPMD approach, the calculation of reaction rate constants is computationally demanding at low temperatures due to the specifics of the technique (e.g., a large number of beads is necessary to capture the quantum mechanical effects, long propagation times are needed for the convergence of the rate constants, etc.). The present paper is focused on finding the optimal set of parameters for using the RPMDrate code effectively to predict reaction rate constants at low temperatures. For this aim, we selected the three-atom chemical reaction \( \text{DH} + \text{H} \rightarrow \text{D} + \text{H}_2 \) which despite being simple exhibits a number of unexpected effects, such as geometric phase effects \[22, 41\] and a narrow Feshbach resonance at energies below the reaction barrier. \[42\] This reaction also plays an important role in astrochemistry. The cooling of HD molecule is linked to the gravitational collapse and the fragmentation of clouds. \[16, 29, 31\] In the paper Ref. \[39\] it was reported that almost all deuterium can be converted to HD molecule and subsequent cooling may lead to the formation of primordial low mass stars and brown dwarfs.

In this manuscript, we show how to optimally set up the RPMDrate code calculations in order to achieve the sufficient convergence of the thermal chemical rate constants for the title reaction.
2. Ring Polymer Molecular Dynamics

The ring polymer Hamiltonian for a system of \( N \) atoms is written in atomic cartesian coordinates as

\[
H(p, q) = \sum_{i=1}^{N} \sum_{j=1}^{n} \left( \frac{p_{i,j}^2}{2m_i} + \frac{1}{2}m_i\omega^2 \left| q_{i,j} - q_{i,j-1} \right|^2 \right) + \sum_{j=1}^{n} V(q_{1,j}, \ldots, q_{N,j}),
\]

where \( n \) is the number of ring polymer beads, \( m_i \) is the mass of the \( i \)-th atom, \( q_{i,j} \) and \( p_{i,j} \), \( j = 1, \ldots, n \) are the position and the momentum vectors of the \( i \)-th atom of the system, correspondingly, \( q_{i,0} \equiv q_{i,n} \), \( i = 1, \ldots, N \). The force constant of the harmonic springs is \( \omega = \beta \hbar / n \), where \( \beta = 1/k_B T \), and \( T \) is the temperature of the system.

Ring polymer molecular dynamics is a classical molecular dynamics in an extended (\( n \)-bead imaginary time path integral) phase space. The real-time correlation function formalism is used for the RPMD rate coefficient calculation. The expression for the ring polymer flux-side correlation function \([32]\) is given by the \( t \to \infty \) limit (\( t \to t_{\text{plateau}} \) in practice, where \( t_{\text{plateau}} \) is a “plateau” time \([11]\) when all relevant to the chemical event correlations decay)

\[
c_{fs}^{(n)}(t) = \frac{1}{(2\pi \hbar)^{fN}} \int d^{fN} p_0 \int d^{fN} q_0 e^{-(\beta/n)H(p_0, q_0)} \delta[s(q_0)] \nu_s(p_0, q_0) h[s(q_t)],
\]

where \( f = 3N \), \( s(q) \) is the reaction coordinate at \( q \), \( \nu_s(p_0, q_0) \) is the initial velocity along the reaction coordinate

\[
\nu_s(p, q) = \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\partial s(q)}{\partial q_{i,j}} \frac{p_{i,j}}{m_i},
\]

and \( h[s(q_t)] \) is a Heaviside step function, which counts ring polymer trajectories \((p_t, q_t)\) that are on the product side of the dividing surface at time \( t \). The RPMD rate coefficient is

\[
k^{(n)}(T) = \frac{c_{fs}^{(n)}(t \to \infty)}{Q_r^{(n)}(T)},
\]
where $Q^{(n)}(T)$ is the $n$-bead path integral approximation to the quantum mechanical reactant partition function.\textsuperscript{[14, 15]} The partition function can be quite difficult to compute accurately.\textsuperscript{[6]} To avoid the direct computation of the partition function we apply the technique implemented in the RPMDrate code\textsuperscript{[38]} and briefly described below.

The calculation of RPMD rate coefficient starts with introducing two dividing surfaces. The first dividing surface is located in the asymptotic reactant valley

$$s_0(\mathbf{q}) = R_\infty - |\mathbf{R}|,$$  \hfill (5)

where $\mathbf{q} = (q_1, \ldots, q_N)$, $q_i = \frac{1}{n} \sum_{j=1}^{n} q_{ij}^{(j)}$, $\mathbf{R}$ is the centroid of the vector that connects the centres of mass of the reactants, $R_\infty$ is an asymptotic distance large enough to make interaction between the reactants negligible.

The second dividing surface, $s_1(\mathbf{q})$, is situated near the transition state region and is defined in terms of the bond-breaking and bond-forming distances. In this paper, we consider the reaction with one channel and three atoms A, B, and C: $AB + C \rightarrow A + BC$, i.e., one bond breaks between the atoms A and B and one bond forms between the atoms B and C. Therefore, the second dividing surface is determined as

$$s_1(\mathbf{q}) = s_0(\mathbf{q}) - \left|\mathbf{q}_{AB} - q^\dagger_{AB}\right| - \left|\mathbf{q}_{BC} - q^\dagger_{BC}\right|,$$  \hfill (6)

where $\mathbf{q}_{ij}$ is the vector that connects the centroids of $i$-th and $j$-th atoms, $q^\dagger_{ij}$ is the interatomic distance at the transition state.

The next step is the introduction of the reaction coordinate $\xi$ that connects two dividing surfaces

$$\xi(\mathbf{q}) = \frac{s_0(\mathbf{q})}{s_0(\mathbf{q}) - s_1(\mathbf{q})}.$$  \hfill (7)

As it was mentioned above, the direct computation of the RPMD rate coefficient with (4) can be quite difficult. Therefore, the Bennett-Chandler factorization\textsuperscript{[3, 11]} is used for the calculation:

$$k_{RPMD}(T) = k_{QTST}(T; \xi^\dagger)\kappa(t \rightarrow t_{\text{plateau}}; \xi^\dagger).$$  \hfill (8)

The first term, $k_{QTST}(T; \xi^\dagger)$, is the quantum transition state theory rate coefficient (its centroid-density version\textsuperscript{[19, 18, 40]}, cd-QTST, when the dividing surfaces are defined using the centroid variables, as in the present case)
evaluated near the transition state $\xi^\dagger$. It is defined in terms of the potential mean force (PMF), or free energy, $W(\xi)$, along the reaction coordinate

$$ k_{\text{QTST}}(T; \xi^\dagger) = 4\pi R^2 \left( \frac{1}{2\pi \beta \mu_R} \right)^{1/2} e^{-\beta (W(\xi^\dagger) - W(0))}, \quad (9) $$

where $\mu_R$ is the reduced mass of the reactants. The PMF difference $W(\xi^\dagger) - W(0)$ is calculated using umbrella integration $[27, 28, 26]$

$$ W(\xi^\dagger) - W(0) = \int_0^{\xi^\dagger} \sum_{i=1}^{N_{\text{windows}}} \left[ \frac{n_i N(\xi_i, \sigma_i^2)}{\sum_{i=1}^{N_{\text{windows}}} n_j N(\xi_j, \sigma_j^2)} \left( \frac{1}{\beta} \frac{\xi - \tilde{\xi}_i}{\sigma_i^2} - k_i (\xi_i - \tilde{\xi}_i) \right) \right] d\xi, \quad (10) $$

where $N_{\text{windows}}$ is the number of biasing windows, $n_i$ is the total number of steps sampled for the $i$-th window, $N(\tilde{\xi}_i, \sigma_i^2)$ is the normal distribution of the reaction coordinate $\xi$ with the mean value (or, center of the biasing window) $\tilde{\xi}_i$ and the variance $\sigma_i^2$, and $k_i$ is the force constant which defines the strength of the bias.

The second term in [5], $\kappa(t \rightarrow t_{\text{plateau}}; \xi^\dagger)$, is the ring polymer recrossing factor. This factor plays a role of a dynamical correction to cd-QTST and ensures that the resulting RPMD rate coefficient $k_{\text{RPMD}}(T)$ will be independent of the choice of the dividing surface. [13] It is expressed as the ratio between two real-time flux-side correlation functions

$$ \kappa(t \rightarrow t_{\text{plateau}}; \xi^\dagger) = \frac{c_{\text{fs}}^{(n)}(t \rightarrow t_{\text{plateau}}; \xi^\dagger)}{c_{\text{fs}}^{(n)}(t \rightarrow 0^+; \xi^\dagger)}. \quad (11) $$

Thus, after calculating the cd-QTST rate coefficient and the recrossing factor, we can calculate the RPMD rate coefficient.

3. Steps of the RPMDrate code calculation and parameters to be optimized

The RPMDrate code works in five sequential steps:

1. Generating the initial configurations for umbrella integration;
2. Umbrella integration along the reaction coordinate;
3. Calculation of the cd-QTST rate coefficient;

4. Computation of the recrossing factor;

5. Calculation of the resulting RPMD thermal rate coefficient.

We describe all the RPMD rate stages below and the crucial code parameters that significantly affect the resulting RPMD rate constant and, thus, should be optimized.

We start from the introduction of the umbrella sampling interval with the left end $\xi_{\text{min}}$ and the right end $\xi_{\text{max}}$ and divide it into a series of windows $\xi_i, \ i = 1, \ldots, N_{\text{windows}}$. At the first RPMD rate step we generate classical configurations ($n = 1$) for each window at $T = 300$ K. These configurations are used in subsequent umbrella integration RPMD simulations.

At the second RPMD rate step, we equilibrate the system for each $i$-th window (during the $t_{\text{equilibration}}$ time) and accumulate $\xi_i$ and $\sigma_i$ along the RPMD thermostatted trajectory run for $t_{\text{sampling}}$. This process is repeated $N_{\text{trajectory}}$ times for accumulating enough steps of sampling and is the main part of umbrella integration [27, 28, 26]. For the reaction investigated here, the trajectory is thermostatted using one of the generalized Langevin equation (GLE) thermostats [8, 9, 10]. As the result of the second RPMD rate stage, we obtain the potential of mean force, or, free energy, $W(\xi)$, and its maximum, $W(\xi^\dagger)$, which depends on temperature $T$. The cd-QTST rate coefficient, calculated at the next RPMD rate stage, exponentially depends on the difference between the maximum $\xi = \xi^\dagger$ of free energy and its value at $\xi = 0$ (see (9), (10)) and, thus, the difference $W(\xi^\dagger) - W(0)$ is the crucial value for estimation of the cd-QTST rate coefficient. As it was demonstrated in the previous papers [38, 37, 23, 24, 25], the accuracy of the mentioned difference calculation depends on the number of beads $n$, especially at low temperatures. Moreover, the choice of the asymptotic distance $R_{\infty}$ and, therefore, the umbrella integration step $d\xi$ and the force constant $k_i$ also affects the resulting cd-QTST rate coefficient. [4] Thus, the parameters $n$, $R_{\infty}$, $d\xi$, and $k_i$ are the most important ones to be optimized during the first three RPMD rate steps.

Next, at the fourth RPMD rate step, we calculate the recrossing factor. For this calculation, we use a constrained RPMD simulation in the presence of a thermostat (parent trajectory) to generate a series of independent configurations at the initial time moment $q_0$ with centroids on the transition state dividing surfaces $s_{\xi_i}(\bar{q}) = \xi^\dagger s_1(\bar{q}) + (1 - \xi^\dagger)s_0(\bar{q}) = 0$. The RATTLE.
algorithm \cite{2} is introduced into the time integration to constrain the centroid \( \bar{q}_0 \) to the dividing surfaces \( s_{\xi}(\bar{q}) = 0 \). For each of these constrained configurations obtained from the parent trajectory, a number of momentum vectors \( p_0 \) is randomly sampled from the Maxwell distribution and the resulting recrossing (child) trajectories are evolved forward in the propagation (“plateau”) time \( t_{\text{plateau}} \) without the thermostat or the dividing surface constraint. One of the reasons of inaccurate determining the recrossing factor may be a short “plateau” time, because the decay of the recrossing factor can occur rather slowly, and it is important to guarantee that the recrossing factor is a constant during a long time interval. Thus, the time \( t_{\text{plateau}} \) is one of the most important parameters to be optimized at the fourth RP MD rate step.

Finally, at the fifth step we calculate the resulting RPMD thermal rate coefficient. Note that the strategy is also suitable for the classical dynamics (with \( n = 1 \) beads) and at the classical high-temperature limit \((T \to \infty)\).

The RPMD rate code was successfully applied to many chemical reactions. The parameters used for calculation of different chemical reaction rates are shown in Table \( \text{I} \) \cite{33, 34, 7, 20, 30, 36, 1, 17, 37, 35, 23, 24, 25, 4}. Thermally activated reactions were mainly considered at the temperatures \( T \geq 100 \text{ K} \). For most of these reactions the standard number of beads, umbrella integration step, and force constant were chosen: \( n = 128, d\xi = 0.01, k_i = 2.72 \) (\(T/\text{K}\) eV). Thus, the above umbrella integration step and the force constant could be chosen for calculations with any asymptotic distance \( R_\infty \) at the temperatures \( T = 100 \) and 300 K. As opposed to the thermally activated reactions, barrierless reactions were also considered at low temperatures. In the paper Ref. \cite{4} it was shown that while increasing the asymptotic distance one should also increase the force constant for low temperatures. Moreover, if the temperature of the reaction under investigation is decreased, one should increase the number of beads for obtaining the correct rate constants. Finally, the longer “plateau” time is needed for barrierless reactions as compared to thermally activated ones due to slower decay of the oscillations in the ring polymer recrossing factor.

In this paper we investigate how the parameters \( n, R_\infty, d\xi, k_i, \) and \( t_{\text{plateau}} \) affect the resulting RPMD rate coefficient at different temperatures for the thermally activated reaction \( \text{DH} + \text{H} \to \text{D} + \text{H}_2 \).
Table 1: Input RPMDrate code parameters for thermally activated and barrierless reactions. The force constant $k_i$ is reported in (T/K) eV, the “plateau” time $t_{\text{plateau}}$ is reported in ps, and the temperature $T$ is reported in K.

| Thermally activated reaction | $R_\infty$ | $d\xi$ | $k_i$ | $n(T)$ | $t_{\text{plateau}}$ |
|-----------------------------|-----------|--------|-------|---------|------------------|
| Mu+H$_2$ → MuH+H [33]      | 30$a_0$  | 0.01   | 2.72  | 512(200-300) | 0.06             |
| D+HMu → DMu+H [34]         | 30$a_0$  | 0.01   | 2.72  | 128(150-300) | 0.05             |
| OH+H$_2$ → H+H$_2$O [7]    | 11$a_0$  | 0.01   | 2.72  | 128(150-300) | 0.05             |
| O($^3$P)+CX$_4$ → OX+CX$_3$ (X=H,D) [20] | 15$a_0$ | 0.01   | 2.72  | 128(200-300) | 0.1              |
| Cl+CX$_4$ → XCl+CX$_3$ (X=H,D) [30] | 30$a_0$ | 0.01   | 2.72  | 64(300)     | 0.1              |
| H+CH$_4$ → H$_2$+CH$_3$ [36] | 30$a_0$ | 0.01   | 2.72  | 128(200-300) | 0.1              |
| OH+CX$_4$ → HXO+CX$_3$ (X=H,D) [11] | 15$a_0$ | 0.01   | 2.72  | 128(200-300) | 0.05             |
| X+C$_2$H$_6$ → HX + C$_2$H$_5$ (X=H,Cl,F) [17] | 15$a_0$ | 0.01   | 2.72  | 128(200-300) | 0.05 (H)         |
|                             |           |        |       |         | 0.1 (Cl)         |
|                             |           |        |       |         | 0.2 (F)          |

| Barrierless reaction        | $R_\infty$ | $d\xi$ | $k_i$ | $n(T)$ | $t_{\text{plateau}}$ |
|-----------------------------|-----------|--------|-------|---------|------------------|
| X($^1$D)+H$_2$ → XH+H (X=C,S) [37] | 20$a_0$  | 0.01   | 2.72  | 256(50); 128(300) | 2                |
| C+CH$^+$ → C$_2^+$+H [35]   | 15$a_0$  | 0.01   | 2.72  | 128(20-300)    | 16               |
| C($^1$D)+H$_2$ → CH+H [23]  | 20$a_0$  | 0.01   | 2.72  | 256(50); 128(300) | 2                |
| C($^1$D)+D$_2$ → CD+D [24]  | 15$a_0$  | 0.01   | 2.72  | 128(50); 48(300) | 2                |
| O($^1$D)+X$_2$ → OX+X (X=H,D) [25] | 15$a_0$ | 0.01   | 2.72  | 296(50); 128(300) | 2                |
| D$^+$+H$_2$ → HD+H$^+$ [4]  | 12-30 Å  | 0.01   | 2.72-20.4 | 160(20,50); 128(75,100) | 3-8              |

4. Results and discussion

We used the BKMP2 [3] potential energy surface for all the computations described here. First, we optimize the parameters $R_\infty$, $d\xi$, $k_i$ at the fixed temperatures ($T = 50, 100, 300$ K) and $n = 64$ (we consider this number of beads as it is typically enough for approximate estimation the cd-QTST rate coefficient). The optimized parameters at these temperatures are summarized in Table 2. As for the reactions in Table 1 at the temperatures $T \geq 100$ K the standard parameters $d\xi = 0.01$ and $k_i = 2.72$ (T/K) eV are suitable for computations with $10a_0 \leq R_\infty \leq 30a_0$, the resulting $k_{\text{QTST}}$ coefficients are similar for all temperatures of interest. However, at low temperature $T = 50$ K, the force constant increases and the umbrella integration step decreases while the asymptotic distance is increased. Thus, at low tem-
temperatures, more attention should be paid to the choice of \( R_\infty, d\xi, \) and \( k_i \). We demonstrate further results for the standard parameters used in the past \((R_\infty = 15a_0, \ d\xi = 0.01, \ k_i = 2.72 \ (T/K) \text{ eV})\) at \( T = 50, 100, \) and \( 300 \) K, and for the modified parameters \((R_\infty = 30a_0, \ d\xi = 0.005, \ k_i = 13.6 \ (T/K) \text{ eV})\) at \( T = 50 \) K.

Table 2: Asymptotic distance \( R_\infty \), umbrella integration step \( d\xi \), and force constant \( k_i \) optimized at \( T = 50, 100, \) and \( 300 \) K. The force constants are reported in \((T/K) \text{ eV}\), the cd-QTST rate coefficients are reported in \(\text{cm}^3 \text{s}^{-1}\). The standard umbrella integration step \( d\xi = 0.01 \) and the force constant \( k_i = 2.72 \ (T/K) \text{ eV} \) could be chosen for calculation with any asymptotic distance at the temperatures \( T \geq 100 \) K. At the low temperature, \( T = 50 \) K, the parameter \( k_i \) increases and the step \( d\xi \) decreases while increasing the distance \( R_\infty \) for obtaining the similar cd-QTST rate coefficients.

| \( T = 50 \) K, \( n = 64 \) | \( T = 100 \) K, \( n = 64 \) | \( T = 300 \) K, \( n = 64 \) |
|---|---|---|
| \( R_\infty \) | \( d\xi \) | \( k_i \) | \( k_{\text{QTST}} \) | \( R_\infty \) | \( d\xi \) | \( k_i \) | \( k_{\text{QTST}} \) | \( R_\infty \) | \( d\xi \) | \( k_i \) | \( k_{\text{QTST}} \) |
| \( 15a_0 \) | 0.01 | 2.72 | \( 1.34 \times 10^{-26} \) | \( 15a_0 \) | 0.01 | 2.72 | \( 1.19 \times 10^{-23} \) | \( 15a_0 \) | 0.01 | 2.72 | \( 5.06 \times 10^{-17} \) |
| \( 20a_0 \) | 0.01 | 10.88 | \( 1.44 \times 10^{-26} \) | \( 20a_0 \) | 0.01 | 2.72 | \( 1.24 \times 10^{-23} \) | \( 20a_0 \) | 0.01 | 2.72 | \( 5.05 \times 10^{-17} \) |
| \( 30a_0 \) | 0.005 | 13.60 | \( 1.46 \times 10^{-26} \) | \( 30a_0 \) | 0.01 | 2.72 | \( 1.22 \times 10^{-23} \) | \( 30a_0 \) | 0.01 | 2.72 | \( 5.09 \times 10^{-17} \) |

Next, we investigate the convergence of free energy profiles used to calculate the cd-QTST rate coefficient with respect to the number of beads. The convergence is illustrated in Fig. 1. From the plots we conclude: while decreasing the temperatures one should increase the number of beads for the proper estimation of the difference \( W(\xi^\dagger) - W(0) \), and, therefore, the cd-QTST rate coefficient. Here we choose \( n = 128 \) at \( T = 300 \) K, \( n = 256 \) at \( T = 100 \) K, and \( n = 512 \) at \( T = 50 \) K. We also observe a conventional trend: free energy barrier increases as the temperature increases.

Finally, we study the convergence of the ring polymer recrossing factors with respect to the “plateau” time at different temperatures. The recrossing factors in the investigated temperature range are shown in Fig. 2. The longer “plateau” time is needed for obtaining the correct ring polymer recrossing factor if the temperature is decreased: \( t_{\text{plateau}} \approx 0.15 \) ps at \( T = 300 \) K, \( t_{\text{plateau}} \approx 0.35 \) ps at \( T = 100 \) K, and \( t_{\text{plateau}} \approx 1 \) ps at \( T = 50 \) K.

The resulting sets of input parameters for all the RPMD rate steps, cd-QTST rate coefficients, recrossing factors, and RPMD rate coefficients at \( T = 50, 100, \) and \( 300 \) K are summarized in Table 3. As it was expected
Figure 1: Free energy profiles for different number of beads, standard parameters $R_\infty = 15a_0$, $d\xi = 0.01$, and $k_i = 2.72 (T/K) \text{ eV}$ ($T = 50, 100, \text{ and } 300 \text{ K}$), and modified parameters $R_\infty = 30a_0$, $d\xi = 0.005$, and $k_i = 13.6 (T/K) \text{ eV}$ ($T = 50 \text{ K}$). The energy barrier increases while increasing the temperature. The convergence of the energy profiles with respect to the number of beads is observed for $n = 128$ at $T = 300 \text{ K}$, $n = 256$ at $T = 100 \text{ K}$, and $n = 512$ at $T = 50 \text{ K}$. The converged cd-QTST rate coefficients are similar for two various sets of parameters at $T = 50 \text{ K}$: $k_{\text{QTST}} = 4.16 \times 10^{-27} \text{ cm}^3 \text{ s}^{-1}$ for $R_\infty = 15a_0$, $k_{\text{QTST}} = 4.52 \times 10^{-27} \text{ cm}^3 \text{ s}^{-1}$ for $R_\infty = 30a_0$ ($n = 512$).

for the thermally activated reaction, the RPMD rate coefficient increases as the temperature increases. We also note that the resulting $k_{\text{RPMD}}$ rates are similar at $T = 50 \text{ K}$ for both the standard parameters $R_\infty$, $d\xi$, $k_i$ and the modified ones. However, the relative deviation between them is $\approx 10\%$. Therefore, if a very high accuracy of calculating the RPMD rate coefficient
is required one should increase the asymptotic distance at low temperatures.

5. Conclusions

In this paper, on the example of the thermally activated reaction DH + H → D + H₂ of astrochemical importance, we investigated the convergence of the ring polymer molecular dynamics (RPMD) rate constants with respect
Table 3: Input RPMDrate parameters, resulting recrossing factors and rate coefficients at $T = 50, 100, \text{ and } 300 \text{ K}$.

| $T$, K | $n$ | $R_\infty$ | $d\xi$ | $k_i$, (T/K) eV | $t_{\text{plateau}}$, ps | $k_{\text{QTST}}$, cm$^3$ s$^{-1}$ | $\kappa$ | $k_{\text{RPMD}}$, cm$^3$ s$^{-1}$ |
|--------|-----|------------|--------|----------------|------------------|-----------------|------|------------------|
| 300    | 128 | 15$a_0$    | 0.01   | 2.72           | 0.15             | $5.18 \times 10^{-17}$ | 0.751 | $3.89 \times 10^{-17}$ |
| 300    | 128 | 20$a_0$    | 0.01   | 2.72           | 0.15             | $5.19 \times 10^{-17}$ | 0.751 | $3.90 \times 10^{-17}$ |
| 300    | 128 | 30$a_0$    | 0.01   | 2.72           | 0.15             | $5.35 \times 10^{-17}$ | 0.749 | $4.01 \times 10^{-17}$ |
| 100    | 256 | 15$a_0$    | 0.01   | 2.72           | 0.35             | $1.13 \times 10^{-23}$ | 0.495 | $5.59 \times 10^{-24}$ |
| 100    | 256 | 20$a_0$    | 0.01   | 2.72           | 0.35             | $1.12 \times 10^{-23}$ | 0.487 | $5.45 \times 10^{-24}$ |
| 100    | 256 | 30$a_0$    | 0.01   | 2.72           | 0.35             | $1.13 \times 10^{-23}$ | 0.493 | $5.57 \times 10^{-24}$ |
| 50     | 512 | 15$a_0$    | 0.01   | 2.72           | 1                | $4.16 \times 10^{-27}$ | 0.271 | $1.13 \times 10^{-27}$ |
| 50     | 512 | 20$a_0$    | 0.01   | 10.88          | 1                | $4.35 \times 10^{-27}$ | 0.265 | $1.15 \times 10^{-27}$ |
| 50     | 512 | 30$a_0$    | 0.005  | 13.60          | 1                | $4.52 \times 10^{-27}$ | 0.269 | $1.22 \times 10^{-27}$ |

To several RPMDrate code input parameters at different temperatures. We demonstrated that for the temperatures $T = 100$ and $300 \text{ K}$ the standard umbrella integration step $d\xi = 0.01$ and the standard force constant $k_i = 2.72$ (T/K) eV, typically used in the RPMDrate code, could be utilized in a wide asymptotic distance range $10a_0 \leq R_\infty \leq 30a_0$, the resulting RPMD rate constants are close to each other in all the range of asymptotic distances. As opposed to the temperatures $T = 100$ and $300 \text{ K}$, at the low temperature $T = 50 \text{ K}$, the umbrella integration step should be decreased and the force constant should be increased (e.g., the modified input RPMDrate code parameters for $R_\infty = 30a_0$ are $d\xi = 0.005$ and $k_i = 13.6$ (T/K) eV) for obtaining the correct RPMD rate constants if the asymptotic distance is increased. The relative deviation between the resulting RPMD rates obtained for $R_\infty = 15a_0$ and $R_\infty = 30a_0$ is $\approx 10\%$ at $T = 50 \text{ K}$ whereas the same deviation is close to zero for $T \geq 100 \text{ K}$. Thus, if the RPMD rate constant should be computed very accurately then it is necessary to carefully choose the RPMDrate code input parameters, e.g., to increase the asymptotic distance as it was reported for the title reaction.

CRediT authorship contribution statement

Ivan S. Novikov: Calculations, Visualization, Writing - Original draft.
Yury V. Suleimanov: Conceptualization, Methodology, Writing - Original
draft. Alexander V. Shapeev: Conceptualization, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

None.

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