Nonadiabatic unimolecular reaction kinetic theory based on *l*th-order semi-Markov model

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We present a microcanonical kinetic theory, which we refer to as the *l*th-order semi-Markov phase space theory (SM*l*-PST), for nonadiabatic unimolecular dissociations dominated by standard surface hopping dynamics. In this theory, reaction dynamics is considered as a stochastic transport, which is described as an *l*th-order Markov chain, among cells produced from partition of the available phase space. Kinetic equations are derived by importing residence time of stay cells as a random variable into the Markov chain. An efficient method to determine the parameters of the kinetic equations is developed, which is made up of Monte Carlo phase space integration and short-time trajectory calculations. As a test calculation, the SM*l*-PST has been applied to a model system for the predissociation of collinear N_2O. We show that the SM*l*-PST works well, giving rate coefficients of much better accuracy than conventional statistical theory and of comparable accuracy to standard trajectory calculations with a lower computational effort. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1451246]

I. INTRODUCTION

The conventional statistical reaction theories such as the transition state theory[1] and Rice–Ramsperger–Kassel–Marcus (RRKM) theory[2–5] are widely utilized to predict the rates of elementary chemical reactions. In this theory the estimation of reaction rates is performed without dynamical scrutiny by adopting a statistical approximation called ''transition state'' assumption.[6–8] ''*A priori* equal probability'' is the central component of this. In *a priori* equal probability assumption, the following conditions are supposed for a reaction system: phase space distribution in a molecular region is supposed to be maintained in the equilibrium distribution throughout the reaction, and all states in the phase space arrive at a transition state in equal probability. In other words, the intramolecular energy redistribution is rapid in comparison with the reaction rate and a phase point wanders the available phase space ergodically until it locates the transition state. The progress of experimental and computational works has revealed that there exist reaction systems for which the theories fail to estimate the rates because of the breakdown of the assumption. Especially, such unusual reactions have been investigated vigorously for unimolecular reactions, and are called ''non-RRKM'' behavior.

Some advanced statistical theories which predict or account for the nonstatistical behavior have been proposed.[9–18] Almost all such theories deal with reactions on adiabatic potentials. In this paper we propose an advanced microcanonical statistical theory, called the *l*th-order semi-Markov phase space theory (SM*l*-PST), for nonadiabatic unimolecular reactions. Our theory is closely related to theories which decompose reaction dynamics into a hierarchy of recrossing motion.[14–18] In our theory, reaction dynamics is decomposed according to recrossing motion of a crossing seam.

The present theory can be divided into three parts. (i) Phase space partition into cells. Transport of phase points among cells is treated as an *l*th-order Markov chain. A manner of symbolic dynamics provides a refined description for the process. (ii) Conversion of discrete time into real time for the transport process, i.e., replacing the Markov chain into the corresponding semi-Markov process. This is achieved by introducing a sort of local equilibrium assumption that distribution in each $n-1$ dimensional small hypersurface (where n is the dimensionality of the available phase space), called ''isoage hypersurface,'' is regarded as microcanonical, but one dimension that runs along trajectories is in nonequilibrium. Kinetic equations describing the population decay are obtained in this part. (iii) Computational method to determine the parameters contained in the kinetic equations and to solve the kinetic equations. An efficient computational procedure for the special condition when only two primitive cells (defined below) are available is also proposed. This is made up of Monte Carlo phase space integration and short-time trajectory calculations.

As a test calculation, we apply the SM*l*-PST with two primitive cells to a model system of spin-forbidden predissociation of collinear N_2O

$$N_2O(^1\Sigma^+) \rightarrow N_2(^1\Sigma_g^+) + O(^3P). \tag{1}$$

This reaction involves two diabatic potential energy surfaces, an attractive singlet state potential V_A that traps the reactant molecule, and a repulsive triplet state potential V_B that leads the reactant into the product. The model of dynamics for our test case is identical with that in Ref. 19. At time $t=0$, only an initial ensemble distributed on the state V_A is prepared. A

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phase point in the ensemble moves on V_A followed by a classical equation of motion. The standard ''surface hopping'' assumption is supposed; that is, transition between two states must occur only locally on the crossing seam ξ, defined as

$$\xi := \{\mathbf{q} | \Delta V(\mathbf{q}) = 0\}, \tag{2}$$

where $\mathbf{q}$ is a coordinate in the configuration space, and $\Delta V(\mathbf{q})$ is the energy difference between the two potential surfaces. When a trajectory passes across ξ, a transition $V_A \rightarrow V_B$ may occur with a probability depending on the phase space coordinate of the crossing point. The flux from V_R to V_A is supposed to be negligible. Phase points passing through the seam ξ from the inner side of the potential well without a transition $V_A \rightarrow V_R$ will soon return to ξ from the outer side. Marks and Thompson developed the nonadiabatic Monte Carlo transition state theory (NMC-TST) based on the conventional statistical reaction theory by treating a ''return flux'' statistically.[19]

In Sec. II we present the SM*l*-PST. In Sec. III the theory is applied to the reaction of collinear N_2O. The results are compared with the results of trajectory calculations and the NMC-TST.

II. THEORY

A. Symbolic dynamics

In this subsection we describe a phase space partition and prepare a notation.

For completeness, we shall review set-theoretic terms, a ''partition'' and a ''cell.'' A family of sets $\mathcal{A}$, whose cardinality is not necessarily countable, is called a partition of a set X, and each element of $\mathcal{A}$ is a ''cell'' when the following conditions hold:

$$\mathcal{A} \ni \emptyset, \tag{3}$$

$$\bigcup_{A \in \mathcal{A}} A = X, \tag{4}$$

$$A \cap B = \emptyset \quad \text{if } A \neq B \quad \text{for all } A \in \mathcal{A}, B \in \mathcal{A}. \tag{5}$$

For example, $\{\{1,5\},\{2,4\},\{3\},\{6\}\}$ is a partition of $\{1,2,\ldots,6\}$, and the subsets $\{1,5\}$, $\{2,4\}$, $\{3\}$, and $\{6\}$ are the cells of the partition.

A partition of a partition of a set X provides a partition of the set X as follows. Let $\mathcal{A} := \{A_s | s \in S\}$ be a partition of X, and $\mathcal{A}' := \{A'_s | s \in S'\}$ be a partition of $\mathcal{A}$ (each A'_s is a subset of $\mathcal{A}$). It is clear that the family of sets $\{\cup_{A \in A'_s} A | s \in S'\}$ is a partition of X. For example, $\{\{1,5\},\{3\}\}$, $\{\{2,4\},\{6\}\}\}$ is a partition of $\{\{1,5\},\{2,4\},\{3\},\{6\}\})$, and $\{\{1,3,5\}, \{2,4,6\}\}$ is a partition of $\{1,2,\ldots,6\}$.

We define a combination of two partitions: if $\mathcal{A}_1 := \{A^1_s | s \in S_1\}$ and $\mathcal{A}_2 := \{A^2_s | s \in S_2\}$ are partitions of an identical set X, then

$$\mathcal{A}_1 \vee \mathcal{A}_2 := \{A^1_{s_1} \cap A^2_{s_2} \neq \emptyset | s_1 \in S_1, s_2 \in S_2\} \tag{6}$$

provides a finer partition of X. For example,

$$\{\{1,2,3,4\},\{5,6,7,8\}\} \vee \{\{1,3,5\},\{2,4,6,8\},\{7\}\}$$
$$= \{\{1,3\},\{2,4\},\{5\},\{6,8\},\{7\}\}\}.$$

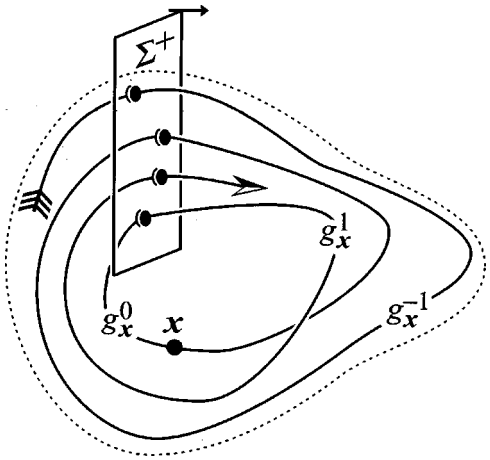

FIG. 1. Schematic drawing of segments in available phase space Γ. A trajectory $\{\mathbf{x}_t\}$ is divided by an oriented surface of section Σ^+ into segments $\{g^n_{\mathbf{x}}\}$. A point in Σ^+ is included not in the end point of the earlier segment in time but the beginning point of the later segment. Integer n corresponds to the discrete time and $g^0_{\mathbf{x}}$ denotes the segment containing $\mathbf{x}$.

Since the associative law $(\mathcal{A}_1 \vee \mathcal{A}_2) \vee \mathcal{A}_3 = \mathcal{A}_1 \vee (\mathcal{A}_2 \vee \mathcal{A}_3)$ holds, we can denote $(\mathcal{A}_1 \vee \mathcal{A}_2) \vee \mathcal{A}_3$ as $\mathcal{A}_1 \vee \mathcal{A}_2 \vee \mathcal{A}_3$ without ambiguity. Further, $\vee_{i=1}^n \mathcal{A}_1 := \mathcal{A}_1 \vee \mathcal{A}_2 \vee, \cdots, \vee \mathcal{A}_n$ is also well-defined.

In this paper we deal with dynamics on an indecomposable subset of phase space of the state V_A, denoted by Γ; that is, Γ is an ergodic subset of an energy hypersurface.[20] If one is interested in dynamics of a decomposable manifold, the dynamics can be constructed from the set of elementary indecomposable dynamics.

Suppose a Poincaré surface of section traversed by trajectories in Γ

$$\Sigma^+ := \{\mathbf{x} \in \Gamma | q_\diamond(\mathbf{x}) = q^0_\diamond, \dot{q}_\diamond(\mathbf{x}) > 0\}, \tag{7}$$

where $\mathbf{x}$ denotes a phase point, $q_\diamond(\mathbf{x})$ is a particular element of the configuration coordinate of $\mathbf{x}$, and $q^0_\diamond$ is some fixed value of the coordinate element. The section Σ^+ divides each trajectory $\{\mathbf{x}_t | t \in \mathbf{R}\}$ in Γ into Σ^+-to-Σ^+ segments $\{x_t | t^{\Sigma^+}_n(\mathbf{x}) \leqslant t < t^{\Sigma^+}_{n+1}(\mathbf{x})\}_{n \in \mathbf{Z}}$, where $\mathbf{x}_t$ is the classical time evolution of $\mathbf{x}$ after time t, $\{t^{\Sigma^+}_n(\mathbf{x})\}(\cdots < t^{\Sigma^+}_{-1}(\mathbf{x}) < t^{\Sigma^+}_0(\mathbf{x}) \leqslant 0 < t^{\Sigma^+}_1(\mathbf{x}) < t^{\Sigma^+}_2(\mathbf{x}) < \cdots)$ is a set of times at which the trajectory passes across Σ^+ (see Fig. 1), and $\mathbf{R}$ and $\mathbf{Z}$ is the set of all real numbers and all integers, respectively. Hereafter, Σ^+-to-Σ^+ segments are called ''segments'' for short. The temporal length of each segment is supposed to be significantly short in comparison with the reaction time scale. It is important to note that the set of all segments in the system, denoted by G, is a partition of Γ,[21] and that a partition $\{A_s\}$ of G provides a partition $\{A'_s\}$ of Γ; i.e., A'_s is a phase space region occupied by all segments contained in A_s. In this sense, we shall regard a partition of G also as a partition of Γ.

Let $g^n_{\mathbf{x}}$ be a segment defined to be

$$g^n_{\mathbf{x}} := \{\mathbf{x}_t | t^{\Sigma^+}_n(\mathbf{x}) \leqslant t < t^{\Sigma^+}_{n+1}(\mathbf{x})\}. \tag{8}$$

A segment $g^0_{\mathbf{x}}$ is a set of phase points containing $\mathbf{x} \in \Gamma$. Generally

$$\mathbf{x}_t \in g_{\mathbf{x}}^{\nu(\mathbf{x},t)}, \tag{9}$$

where $\nu(\mathbf{x},t)$ is a function giving an integer ν such that

$$t_{\nu}^{\Sigma^+}(\mathbf{x}) \leqslant t < t_{\nu+1}^{\Sigma^+}(\mathbf{x}). \tag{10}$$

Let u be a mapping operator that maps a segment to the consecutive one

$$u g_{\mathbf{x}}^{n} := g_{\mathbf{x}}^{n+1}, \tag{11}$$

that is

$$u^m g_{\mathbf{x}}^{n} = g_{\mathbf{x}}^{n+m}. \tag{12}$$

Suppose a partition of G into n_{state} cells, $\mathcal{P}_0 := \{R_s^0 | s \in \sigma\}$, where $\sigma := \{0,1,\ldots,n_{\text{state}}-1\}$. We refer to these cells as "primitive cells." Let R_s^m be a set of segments defined to be

$$R_s^m := u^m R_s^0. \tag{13}$$

Since the mapping $u: G \to G$ is bijective, a family of sets $\mathcal{P}_m := \{R_s^m | s \in \sigma\}$ is also a partition of G for an arbitrary integer m.

Consider a partition $\vee_{m=-\infty}^{\infty} \mathcal{P}_m$. We represent a cell $\cdots \cap R_{s_2}^2 \cap R_{s_1}^1 \cap R_{s_0}^0 \cap R_{s_{-1}}^{-1} \cap R_{s_{-2}}^{-2} \cap \cdots$ as a bi-infinite symbol sequence $(\cdots s_2 s_1 . s_0 s_{-1} s_{-2} \cdots)$, where a "." is placed between two symbols corresponding to $\mathcal{P}_1$ and $\mathcal{P}_0$ (we omit a "." when it is not needed). This sequence denotes not only a cell of a partition Γ and G but also an itinerary of a phase point; if a phase point $\mathbf{x}$ is contained in $(\cdots s_2 s_1 . s_0 s_{-1} s_{-2} \cdots)$, a point $\mathbf{x}_t$ must be contained in a primitive cell $R_{s_{\nu(\mathbf{x},t)}}^0$ at time t.

From the definition

$$u^m R_s^n = R_s^{n+m}. \tag{14}$$

Thus, we have

$$\begin{aligned} u^m(\cdots \cap R_{s_1}^1 \cap R_{s_0}^0 \cap R_{s_{-1}}^{-1} \cap \cdots \\ \cap R_{s_{-m+1}}^{-m+1} \cap R_{s_{-m}}^{-m} \cap R_{s_{-m-1}}^{-m-1} \cap \cdots) \\ = (\cdots \cap R_{s_1}^{m+1} \cap R_{s_0}^{m} \cap R_{s_{-1}}^{m-1} \cap \cdots \\ \cap R_{s_{-m+1}}^{1} \cap R_{s_{-m}}^{0} \cap R_{s_{-m-1}}^{-1} \cap \cdots). \end{aligned} \tag{15}$$

This equation shows that u acts for bi-infinite sequences as the "shift map"

$$u^m(\cdots s_1 . s_0 s_{-1} \cdots) = (\cdots s_{-m+1} . s_{-m} s_{-m-1} \cdots). \tag{16}$$

The shift map dynamics of bi-infinite sequences reproduces a feature of the original dynamics on Γ if the partition $\{R_s^0\}$ is defined properly. Since we are interested in the process where phase points pass across the seam ξ, it is an acceptable choice that $R_0^0 \cup \cdots \cup R_a^0$ is the set of all segments passing across ξ, and the complement $R_{a+1}^0 \cup \cdots \cup R_{n_{\text{state}}-1}^0$ is the set of all segments do not.

From a practical point of view, we approximately truncate bi-infinite sequences into "coarse-grained" counterparts $(s_{m_\triangleleft} \cdots s_1 . s_0 \cdots s_{m_\triangleright})$, where $m_\triangleleft$ and $m_\triangleright$ are integers such that $m_\triangleleft \geqslant 0 \geqslant m_\triangleright$. A positive integer

$$l := m_\triangleleft - m_\triangleright + 1, \tag{17}$$

signifies a length of the finite sequence. Let $\mathcal{C}$ be the set of all finite sequences with a fixed $m_\triangleleft$ and $m_\triangleright$. The number of elements in $\mathcal{C}$ is equal to n_{state} to the lth power. However, not all sequences in $\mathcal{C}$ exist as cells in the system. We denote a subset of $\mathcal{C}$ containing only actual cells by $\mathcal{C}_{\text{exist}}$.

Although a dynamical system of finite sequences asymptotically approaches a system of bi-infinite sequences with increasing l, there are intrinsic differences between the two systems. First, whereas bi-infinite sequences divide the available phase space into the infinite number of cells, finite sequences divide the space into finite cells. Second, more remarkably, whereas the dynamics of a bi-infinite sequence is deterministic, finite sequence dynamics is indeterministic or stochastic. A finite sequence generally evolves into one out of n_{state} different sequences by indeterministic or stochastic dynamics, provided $m_\triangleleft$ and $m_\triangleright$ are fixed. For instance, when $n_{\text{state}}=4$, then (012.302) may be evolved into (123.020), (123.021), (123.022), or (123.023). We approximately regard the transport dynamics among $\mathcal{C}_{\text{exist}}$ as a Markov chain, i.e., the dynamics among $\mathcal{P}_0$ as an lth order Markov chain.

We introduce a notation and terminology as follows: for a cell $C \in \mathcal{C}_{\text{exist}}$

$$\begin{aligned} &\text{par}(s_{m_\triangleleft} \cdots s_1 . s_0 \cdots s_{m_\triangleright}) \\ &\quad := \mathcal{C}_{\text{exist}} \cap \{(s s_{m_\triangleleft} \cdots s_2 . s_1 \cdots s_{m_\triangleright+1}) | s \in \sigma\}, \end{aligned} \tag{18}$$

$$\begin{aligned} &\text{chi}(s_{m_\triangleleft} \cdots s_1 . s_0 \cdots s_{m_\triangleright}) \\ &\quad := \mathcal{C}_{\text{exist}} \cap \{(s_{m_\triangleleft - 1} \cdots s_0 . s_{-1} \cdots s_{m_\triangleright} s) | s \in \sigma\}. \end{aligned} \tag{19}$$

We call par C the "parents," chi C the "children" for C. If $g_{\mathbf{x}}^n$ is contained in a cell C, $g_{\mathbf{x}}^{n-1}$ and $g_{\mathbf{x}}^{n+1}$ must be contained in cells which are one of the parents and one of the children of the cell C, respectively.

B. Kinetic formulation

We start on kinetic formulation based on the usual dynamics. From Liouville's theorem, the time evolution of reactant phase space distribution $\rho(\mathbf{x},t)$ is given by

$$\rho(\mathbf{x}_{\Delta t}, t+\Delta t) = \rho(\mathbf{x},t) Q(\mathbf{x},\Delta t), \tag{20}$$

for an interval $\Delta t \geqslant 0$, where $Q(\mathbf{x},\Delta t)$ is the probability that the phase point $\mathbf{x}$ will not lead to a transition $V_A \to V_R$ within Δt

$$Q(\mathbf{x},\Delta t) := \prod_{\substack{t \in \{t_n^\xi(\mathbf{x})\}, \\ 0 \leqslant t < \Delta t}} [1 - P_{\text{hop}}(\mathbf{x}_t)], \tag{21}$$

where $\{t_n^\xi(\mathbf{x})\}(\cdots < t_{-1}^\xi(\mathbf{x}) < t_0^\xi(\mathbf{x}) \leqslant 0 < t_1^\xi(\mathbf{x}) < t_2^\xi(\mathbf{x}) < \cdots)$ is a set of timers at which the trajectory $\{\mathbf{x}_t | t \in \mathbf{R}\}$ passes across the crossing seam ξ, and $P_{\text{hop}}(\mathbf{x})$ is the probability of a transition $V_A \to V_R$ at $\mathbf{x} \in \xi$. The reactant population $N(t)$ is obtained from the distribution by

$$N(t) := \langle \rho(\mathbf{x},t) \rangle, \tag{22}$$

where $\langle \cdots \rangle$ denotes a phase space average

$$\langle F(\mathbf{x})\rangle := \frac{\int_\Gamma d\mathbf{x} F(\mathbf{x})}{\int_\Gamma d\mathbf{x}}, \tag{23}$$

where $F(\mathbf{x})$ is an arbitrary function.

Next, we derive kinetic equations for the SM*l*-PST on the basis of the above consideration. From Eq. (9), $\mathbf{x}_t \in g^0_{\mathbf{x}_t}$ and $\mathbf{x}_t \in g^{\nu(\mathbf{x},t)}_{\mathbf{x}}$. This implies that $g^0_{\mathbf{x}_t} = g^{\nu(\mathbf{x},t)}_{\mathbf{x}}$; hence, $u^m g^0_{\mathbf{x}_t} = u^m g^{\nu(\mathbf{x},t)}_{\mathbf{x}}$ with an arbitrary integer m. Therefore, we obtain

$$g^m_{\mathbf{x}_t} = g^{m+\nu(\mathbf{x},t)}_{\mathbf{x}}. \tag{24}$$

Consider two phase points $\mathbf{x}$ and $\mathbf{x}' := \mathbf{x}_t$. The point $\mathbf{x}'$ is contained in $g^{\nu(\mathbf{x},t)}_{\mathbf{x}}$. In addition, consider another phase point $\mathbf{x}''$ which is the beginning point of a segment $g^{m+\nu(\mathbf{x},t)}_{\mathbf{x}} = g^m_{\mathbf{x}_t}$, where m is an arbitrary integer. From the standpoints of $\mathbf{x}$ and $\mathbf{x}'$, we have $\mathbf{x}'' = \mathbf{x}_{t^{\Sigma^+}_{m+\nu(\mathbf{x},t)}(\mathbf{x})}$ and $\mathbf{x}'_{t^{\Sigma^+}_m(\mathbf{x}')} = \mathbf{x}_{t+t^{\Sigma^+}_m(\mathbf{x}_t)}$, respectively. Therefore, the following relation holds:

$$t^{\Sigma^+}_{m+\nu(\mathbf{x},t)}(\mathbf{x}) = t + t^{\Sigma^+}_m(\mathbf{x}_t). \tag{25}$$

We introduce τ and τ_{seg} as

$$\tau(\mathbf{x}) := -t^{\Sigma^+}_0(\mathbf{x}), \tag{26}$$

$$\tau_{\mathrm{seg}}(g) := t^{\Sigma^+}_1(\mathbf{x}) - t^{\Sigma^+}_0(\mathbf{x}) = t^{\Sigma^+}_1(\mathbf{x}) + \tau(\mathbf{x}), \tag{27}$$

where $\mathbf{x}$ in Eq. (27) is an arbitrary phase point contained in g. $\tau(\mathbf{x})$ is referred to as the "age," which signifies the elapsed time for the point $\mathbf{x}$ from the last entrance into the current segment, and $\tau_{\mathrm{seg}}(g)$ represents the temporal length of the segment g. Since $t^{\Sigma^+}_1(\mathbf{x}) > 0$ and $t^{\Sigma^+}_0(\mathbf{x}) \leqslant 0$, the relation $0 \leqslant \tau(\mathbf{x}) < \tau_{\mathrm{seg}}(g^0_{\mathbf{x}})$ holds for an arbitrary point $\mathbf{x} \in \Gamma$. From Eqs. (25) and (26), we obtain

$$\tau(\mathbf{x}_t) = t - t^{\Sigma^+}_{\nu(\mathbf{x},t)}(\mathbf{x}). \tag{28}$$

Let $\chi(a|A)$ be a characteristic function defined to equal unity if $a \in A$ (or $a \subset A$) and zero otherwise (in this paper, a is a phase point or a segment, and A is a phase space regions). Note that

$$\chi(\mathbf{x}|C) = \chi(g^0_{\mathbf{x}}|C), \tag{29}$$

with $C \in \mathcal{C}_{\mathrm{exist}}$, since $\mathbf{x}$ is contained in $g^0_{\mathbf{x}}$ (where we use the idea that C is not only a set of segments but also a set of phase points). We shall usually employ $\chi(g^0_{\mathbf{x}}|C)$ rather than $\chi(\mathbf{x}|C)$ in expressions since one discerns more easily that this value remains unchanged as long as $\mathbf{x}$ is placed on an identical segment. Generally,

$$\chi(\mathbf{x}_t|C) = \chi(g^0_{\mathbf{x}_t}|C) = \chi(g^{\nu(\mathbf{x},t)}_{\mathbf{x}}|C). \tag{30}$$

Let $f_C(\tau,t)$ be the distribution of age τ in a cell $C \in \mathcal{C}_{\mathrm{exist}}$, and $N_C(t)$ be the population in C

$$f_C(\tau,t) := \langle \delta[\tau(\mathbf{x}) - \tau]\chi(g^0_{\mathbf{x}}|C)\rho(\mathbf{x},t)\rangle, \tag{31}$$

$$N_C(t) := \langle \chi(g^0_{\mathbf{x}}|C)\rho(\mathbf{x},t)\rangle = \int_0^\infty d\tau\, f_C(\tau,t). \tag{32}$$

The total population is given by $N(t) = \Sigma_{C \in \mathcal{C}_{\mathrm{exist}}} N_C(t)$.

On constructing the kinetic theory we suppose the following two approximations. (i) The phase space distribution within an isoage hypersurface in a cell $C \in \mathcal{C}_{\mathrm{exist}}$, defined by

$$i_C(\tau) := \{\mathbf{x} \in C \,|\, \tau(\mathbf{x}) = \tau\}, \tag{33}$$

is regarded as microcanonical. In other words, we directly consider nonstatistical distribution with only one dimension along segments. (ii) An occurrence of a transition $V_A \to V_R$ of a phase point $\mathbf{x}$ is delayed until the next passage of $\mathbf{x}$ across Σ^+; that is, we replace transition time $t^\xi_n(\mathbf{x})$ with $t^{\Sigma^+}_m(\mathbf{x})$ such that $t^{\Sigma^+}_{m-1}(\mathbf{x}) < t^\xi_n(\mathbf{x}) \leqslant t^{\Sigma^+}_m(\mathbf{x})$ without change of the transition probability. A typical τ_{seg} (or a typical $t^{\Sigma^+}_m - t^{\Sigma^+}_{m-1}$) is so short compared to the time scale of reaction that the error caused by this approximation is negligible in the kinetic model.

Under these conditions, the time evolution of an age distribution function is provided by (see Appendix A)

$$f_C(\tau, t+\Delta t) = f_C(\tau - \Delta t, t)\frac{S_C(\tau)}{S_C(\tau - \Delta t)} \quad \text{for } 0 \leqslant \Delta t \leqslant \tau, \tag{34}$$

$$f_{C'}(0,t) = \sum_{C \in \mathrm{par}C'} \int_0^\infty d\tau\, B^{C'}_C(\tau) f_C(\tau,t), \tag{35}$$

with

$$S_C(\tau) := \frac{\langle \delta[\tau(\mathbf{x})]\chi(g^0_{\mathbf{x}}|C)\,\theta[\tau_{\mathrm{seg}}(g^0_{\mathbf{x}}) - \tau]\rangle}{\langle \delta[\tau(\mathbf{x})]\chi(g^0_{\mathbf{x}}|C)\rangle}, \tag{36}$$

$$B^{C'}_C(\tau) := \frac{\langle Q_{\mathrm{seg}}(g^0_{\mathbf{x}})\,\delta[\tau_{\mathrm{seg}}(g^0_{\mathbf{x}}) - \tau]\,\delta[\tau(\mathbf{x})]\chi(g^1_{\mathbf{x}}|C')\chi(g^0_{\mathbf{x}}|C)\rangle}{\langle \delta[\tau(\mathbf{x})]\chi(g^0_{\mathbf{x}}|C)\,\theta[\tau_{\mathrm{seg}}(g^0_{\mathbf{x}}) - \tau]\rangle}, \tag{37}$$

$$Q_{\mathrm{seg}}(g) := \prod_{\substack{t \in \{t^\xi_n(\mathbf{x})\} \\ t^{\Sigma^+}_0(\mathbf{x}) \leqslant t < t^{\Sigma^+}_1(\mathbf{x})}} [1 - P_{\mathrm{hop}}(\mathbf{x}_t)], \tag{38}$$

where $\mathbf{x}$ in Eq. (38) is an arbitrary point in g, and $\theta(x)$ is the unit step function

$$\theta(x) := \begin{cases} 1 & \text{if } x > 0, \quad (39) \\ 0 & \text{if } x \leqslant 0. \quad (40) \end{cases}$$

It is evident from the definition that

$$S_C(0) = 1, \tag{41}$$

$$S_C(\tau_a) \geqslant S_C(\tau_b) \quad \text{when } \tau_a < \tau_b, \tag{42}$$

and that $f_C(\tau,t)$ must be zero for all τ such that $S_C(\tau) = 0$. $B^{C'}_C(\tau)$ is defined for a pair of C and C' such that C' is a child of C. $Q_{\mathrm{seg}}(g)$ is a probability that a phase point passing through the segment g will not result in a transition $V_A \to V_R$ within g. All fractional expressions in Eqs. (34), (36), and Eq. (37) satisfy the condition that when a denominator

vanishes, the corresponding numerator also vanishes. We define 0/0 to be 0 for the fractions. Equations (34) and (35) describe the kinetics of our statistical model.

The physical meaning of $S_C(\tau)$ is shown by the following consideration. Assume the simple situation where no transition $V_A \to V_R$ occurs; then $Q_{\mathrm{seg}}(g)$ is settled unity for all $g \in G$. Let $f_C^{\mathrm{eq}}(\tau)$ denote the stationary distribution of $f_C(\tau,t)$ with the normalization condition

$$\sum_{C \in \mathcal{C}_{\mathrm{exist}}} \int_0^\infty d\tau\, f_C^{\mathrm{eq}}(\tau) = 1. \tag{43}$$

Namely, $f_C^{\mathrm{eq}}(\tau)$ is the age distribution in C when a microcanonical distribution is achieved in Γ. From Eqs. (34) and (35), we have

$$f_C^{\mathrm{eq}}(\tau) = \alpha_C S_C(\tau), \tag{44}$$

$$F_{C'}^{\mathrm{eq}}(0) = \sum_{C \in \mathrm{par}C'} \int_0^\infty d\tau\, \overline{B}_C^{C'}(\tau) f_C^{\mathrm{eq}}(\tau), \tag{45}$$

where

$$\alpha_C := f_C^{\mathrm{eq}}(0), \tag{46}$$

$$\overline{B}_C^{C'}(\tau) := \frac{\langle \delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0) - \tau]\delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^1|C')\chi(g_{\mathbf{x}}^0|C)\rangle}{\langle \delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^0|C)\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0) - \tau]\rangle}. \tag{47}$$

Equation (44) shows that $S_C(\tau)$ is equal to the equilibrium age distribution function, except for a constant factor. The factor α_C, is found from the simultaneous equations (43), (44), (45), (46), and (47).

C. Computational method

Hereafter, we stipulate that a range of an integral contains the lower limit but does not contain the upper limit. This is essential for integrals with the Dirac delta function; for arbitrary a and b such that $a < b$ and an arbitrary function $F(x)$

$$\int_a^b dx\, F(x)\delta(x-c) = \theta_a^b(c)F(c), \tag{48}$$

where

$$\theta_a^b(c) := \begin{cases} 1 & \text{if } a \leqslant c < b \\ 0 & \text{otherwise} \end{cases}. \tag{49}$$

The following relation will be used several times:

$$\int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})} dt\, F(g_{\mathbf{x}_t}^j)\delta[\tau(\mathbf{x}_t)] = \theta_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})}[t_i^{\Sigma^+}(\mathbf{x})]F[g_{\mathbf{x}}^{j+\nu(\mathbf{x},t_i^{\Sigma^+}(\mathbf{x}))}] = F[g_{\mathbf{x}}^{i+j}]. \tag{50}$$

It is more convenient to numerically solve the kinetic equations (34) and (35) for the following $W_C(\tau,t)$ than $f_C(\tau,t)$:

$$f_C(\tau,t) = S_C(\tau)W_C(\tau,t). \tag{51}$$

The value of $W_C(\tau)$ is meaningless for τ such that $S_C(\tau)$ is zero, since $f_C(\tau,t)$ vanishes whenever $S_C(\tau)$ is zero. Substituting Eq. (51) into Eqs. (34) and (35), we obtain

$$W_C(\tau+\Delta t, t+\Delta t) = W_C(\tau,t) \quad \text{for} \quad \tau > 0,\ \Delta t > 0, \tag{52}$$

$$W_{C'}(0,t) = \sum_{C \in \mathrm{par}C'} \int_0^\infty d\tau\, B_C^{C'}(\tau)S_C(\tau)W_C(\tau,t). \tag{53}$$

To apply numerical integration in Eq. (53), we shall discretize both τ and t with a constant step $\Delta t > 0$. W_C is approximated with respect to τ by rectangular strips with the same width Δt

$$\tilde{W}_C(\tilde{\iota},t) :\approx W_C(\tau,t), \tag{54}$$

where $\tilde{\iota}$ is an integer such that

$$(\tilde{\iota} - 1/2)\Delta t \leqslant \tau < (\tilde{\iota} + 1/2)\Delta t. \tag{55}$$

From Eqs. (52), (53), and (54),

$$\tilde{W}_C(\tilde{\iota}+1, t+\Delta t) = \tilde{W}_C(\tilde{\iota},t), \tag{56}$$

$$\tilde{W}_{C'}(0,t) = \sum_{C \in \mathrm{par}C'} \sum_{\tilde{\iota}=0}^{n_{\max}} D_C^{C'}(\tilde{\iota})\tilde{W}_C(\tilde{\iota},t), \tag{57}$$

where $n_{\max}$ is an integer such that $D_C^{C'}(\tilde{\iota}) = 0$ for all $\tilde{\iota} > n_{\max}$, and $D_C^{C'}(\tilde{\iota})$ is

$$D_C^{C'}(\tilde{\iota}) := \int_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t} d\tau\, B_C^{C'}(\tau)S_C(\tau). \tag{58}$$

The functions $S_C(\tau)$ and $D_C^{C'}(\tilde{\iota})$ should be found to solve the kinetic equations. Since we have assumed that Γ is ergodic, a phase space average may be rewritten into a time average for almost everywhere $\mathbf{x} \in \Gamma$.[20]

$$\langle F(\mathbf{x})\rangle = \lim_{t' \to \infty} \frac{1}{t'} \int_0^{t'} dt\, F(\mathbf{x}_t), \tag{59}$$

where $F(\mathbf{x})$ is an arbitrary function. This may be rewritten as a segment average (which is more useful for us)

$$\langle F(\mathbf{x})\rangle = \lim_{n \to \infty} \frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x}) - t_0^{\Sigma^+}(\mathbf{x})} \sum_{i=0}^{n} \int_{t_n^{\Sigma^+}(\mathbf{x})}^{t_{n+1}^{\Sigma^+}(\mathbf{x})} dt\, F(\mathbf{x}_t). \tag{60}$$

Substituting Eq. (60) into Eq. (36), we obtain

$$S_C(\tau) = \lim_{n \to \infty} \frac{\sum_{i=0}^n \int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})} \delta[\tau(\mathbf{x}_t)]\chi(g_{\mathbf{x}_t}^0|C)\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}_t}^0) - \tau]dt}{\sum_{i=0}^n \int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})} \delta[\tau(\mathbf{x}_t)]\chi(g_{\mathbf{x}_t}^0|C)dt} = \lim_{n \to \infty} \frac{\sum_{i=0}^n \theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^i) - \tau]\chi(g_{\mathbf{x}}^i|C)}{\sum_{i=0}^n \chi(g_{\mathbf{x}}^i|C)}, \tag{61}$$

where the last step comes from Eqs. (10), (30), and (50). Let C be $(s_{m_\triangleleft} \cdots s_1 . s_0 \cdots s_{m_\triangleright})$. If and only if a segment g is contained in a cell A, then $u^m g$ is contained in $u^m A$. Thus

$$\chi(g_{\mathbf{x}}^{i}|C)=\prod_{j=m_{\triangleright}}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i}|R_{s_j}^{j})$$

$$=\prod_{j=m_{\triangleright}}^{m_{\triangleleft}}\chi(u^{-j}g_{\mathbf{x}}^{i}|u^{-j}R_{s_j}^{j}) \tag{62}$$

$$=\prod_{j=m_{\triangleright}}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^{0}).$$

Substituting Eq. (62) into Eq. (61), we obtain

$$S_C(\tau)=\lim_{n\to\infty}\frac{\Sigma_{i=0}^{n}\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^{i})-\tau]\Pi_{j=m_{\triangleright}}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^{0})}{\Sigma_{i=0}^{n}\Pi_{j=m_{\triangleright}}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^{0})}. \tag{63}$$

From Eqs. (58) and (60)

$$D_C^{C'}(\tilde{\iota})=\frac{\int_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t}d\tau\langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^{0})\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^{0})-\tau]\delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^{0}|C)\chi(g_{\mathbf{x}}^{1}|C')\rangle}{\langle\delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^{0}|C)\rangle}$$

$$=\lim_{n\to\infty}\frac{\int_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t}d\tau\Sigma_{i=0}^{n}\int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})}dt\ Q_{\mathrm{seg}}(g_{\mathbf{x}_t}^{0})\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}_t}^{0})-\tau]\delta[\tau(\mathbf{x}_t)]\chi(g_{\mathbf{x}_t}^{0}|C)\chi(g_{\mathbf{x}_t}^{1}|C')}{\Sigma_{i=0}^{n}\int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})}dt\ \delta[\tau(\mathbf{x}_t)]\chi(g_{\mathbf{x}_t}^{0}|C)}$$

$$=\lim_{n\to\infty}\frac{\int_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t}d\tau\Sigma_{i=0}^{n}Q_{\mathrm{seg}}(g_{\mathbf{x}}^{i})\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^{i})-\tau]\chi(g_{\mathbf{x}}^{i}|C)\chi(g_{\mathbf{x}}^{i+1}|C')}{\Sigma_{i=0}^{n}\chi(g_{\mathbf{x}}^{i}|C)}$$

$$=\lim_{n\to\infty}\frac{\Sigma_{i=0}^{n}Q_{\mathrm{seg}}(g_{\mathbf{x}}^{i})\chi(g_{\mathbf{x}}^{i}|C)\chi(g_{\mathbf{x}}^{i+1}|C')\theta_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t}[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^{i})]}{\Sigma_{i=0}^{n}\chi(g_{\mathbf{x}}^{i}|C)}. \tag{64}$$

Let C be $(s_{m_{\triangleleft}}\cdots s_1.s_0\cdots s_{m_{\triangleright}})$ and C' be $(s_{m_{\triangleleft}-1}\cdots s_0.s_{-1}\cdots s_{m_{\triangleright}-1})$ (remember that C must be a parent of C'). Then, we have

$$\chi(g_{\mathbf{x}}^{i}|C)\chi(g_{\mathbf{x}}^{i+1}|C')=\chi[g_{\mathbf{x}}^{i}|(s_{m_{\triangleleft}}\cdots s_1.s_0\cdots s_{m_{\triangleright}}s_{m_{\triangleright}-1})]=\prod_{j=m_{\triangleright}-1}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^{0}). \tag{65}$$

From Eqs. (62), (64), and (65)

$$D_C^{C'}(\tilde{\iota})=\lim_{n\to\infty}\frac{\Sigma_{i=0}^{n}Q_{\mathrm{seg}}(g_{\mathbf{x}}^{i})\theta_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t}[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^{i})]\Pi_{j=m_{\triangleright}-1}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^{0})}{\Sigma_{i=0}^{n}\Pi_{j=m_{\triangleright}}^{m_{\triangleleft}}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^{0})}. \tag{66}$$

Taking n as a large integer, one can determine S_C and $D_C^{C'}$ from Eqs. (63) and (66) using trajectory calculations. This method would be inefficient when a passage process of $\mathbf{x}$ across ξ is rare. We now propose a dynamical and statistical hybrid method to efficiently determine S_C and $D_C^{C'}$.

In this method, we suppose two primitive cells: R_1^0 is theset of all segments that pass across the crossing seam ξ, and R_0^0 is the complement. Consider a narrow volume $\Xi\subset\Gamma$ such that $\xi\subset\Xi$, and let Ξ^* be $\Xi\cap R_1^0$. It is evident from the definitions that *all* segments in R_1^0 and *few* segments in R_0^0 must pass through Ξ, and that *all* segments in R_1^0 and *no* segments in R_0^0 must pass through Ξ^*. We have (see Appendix B)

$$S_C(\tau)=\frac{\Sigma_{m\in\{1^{m_\triangleleft}_{m_\triangleright}\}}\langle w(\mathbf{x})\theta[\tau_{\mathrm{seg}}(g^m_{\mathbf{x}})-\tau]\Pi_{j=m_\triangleright}^{m_\triangleleft}\chi(g^{m-j}_{\mathbf{x}}|R^0_{s_j})\rangle_{\Xi*}}{\Sigma_{m\in\{1^{m_\triangleleft}_{m_\triangleright}\}}\langle w(\mathbf{x})\Pi_{j=m_\triangleright}^{m_\triangleleft}\chi(g^{m-j}_{\mathbf{x}}|R^0_{s_j})\rangle_{\Xi*}}, \tag{67}$$

$$D_C^{C'}(\tilde{\imath})=\frac{\#\{1^{m_\triangleleft}_{m_\triangleright}\}\Sigma_{m\in\{1^{m_\triangleleft}_{m_\triangleright-1}\}}\langle w(\mathbf{x})Q_{\mathrm{seg}}(g^m_{\mathbf{x}})\,\theta^{(\tilde{\imath}+1/2)\Delta t}_{(\tilde{\imath}-1/2)\Delta t}[\tau_{\mathrm{seg}}(g^m_{\mathbf{x}})]\Pi_{j=m_\triangleright-1}^{m_\triangleleft}\chi(g^{m-j}_{\mathbf{x}}|R^0_{s_j})\rangle_{\Xi*}}{\#\{1^{m_\triangleleft}_{m_\triangleright-1}\}\Sigma_{m\in\{1^{m_\triangleleft}_{m_\triangleright}\}}\langle w(\mathbf{x})\Pi_{j=m_\triangleright}^{m_\triangleleft}\chi(g^{m-j}_{\mathbf{x}}|R^0_{s_j})\rangle_{\Xi*}}, \tag{68}$$

where $w(\mathbf{x})$ is the reciprocal of a temporal length of $g^0_{\mathbf{x}}\cap\Xi$

$$w(\mathbf{x}):=\left[\int_{t_0^{\Sigma^+}(\mathbf{x})}^{t_1^{\Sigma^+}(\mathbf{x})}dt\;\chi(\mathbf{x}_t|\Xi)\right]^{-1}, \tag{69}$$

$\langle\cdots\rangle_{\Xi*}$ is the phase space average restricted in $\Xi*$

$$\langle F(\mathbf{x})\rangle_{\Xi*}:=\frac{\int_{\Xi*}d\mathbf{x}F(\mathbf{x})}{\int_{\Xi*}d\mathbf{x}}, \tag{70}$$

$\#S$ denotes the number of elements of the set S, and $\{1^j_i\}$ is a set of indices depending on $\{s_i,s_{i+1},\ldots,s_j\}$ defined to be

$$\{1^j_i\}:=\{m|s_m=1,m\in\{i,i+1,\ldots,j\}\}, \tag{71}$$

e.g., if $C=(\cdots011.001\;001\cdots)$, $\{1^3_{-5}\}=\{2,1,-2,-5\}$.

Here, we employ the following abbreviation:

$$\underline{0}:=(\overbrace{0\cdots0}^{m_\triangleleft}\cdot\overbrace{0\cdots0}^{1-m_\triangleright})_l, \tag{72}$$

$$\underline{1}:=(\overbrace{0\cdots0}^{m_\triangleleft}\cdot\overbrace{0\cdots1}^{1-m_\triangleright})_l, \tag{73}$$

$$\underline{01}:=(\overbrace{00\cdots0}^{m_\triangleleft+1}\cdot\overbrace{0\cdots1}^{1-m_\triangleright})_{l+1}, \tag{74}$$

where a "$\cdots$" denotes sequence of 0's. $\underline{01}$ is a subset of $\underline{1}$ into which a flux from $\underline{0}$ flows directly. The remainder $\underline{1}-\underline{01}=(10\cdots0.0\cdots1)$ is occupied by a region into which a flux from $(1\cdots0.0\cdots0)$ flows directly.

Since Eqs. (67) and (68) are inapplicable for $C=\underline{0}$, this cell must be specially dealt with. Cell $\underline{0}$ has two children, $\underline{0}$ itself and $\underline{1}$. We treat the transport process from $\underline{0}$ to $\underline{0}$ implicitly, and approximately consider that the process from $\underline{0}$ to $\underline{1}$ obeys the first-order rate law; that is, the distribution function of time required in which phase points go through $\underline{0}$ to $\underline{1}$ is described by $1/k_{01}\exp(-k_{01}t)k_{01}$ is the rate coefficient for the process. The rate coefficient k_{01} is determined by a similar manner as the conventional RRKM theory,[2–4] i.e.,

$$k_{01}:=\frac{\langle\chi(g^0_{\mathbf{x}_{-\varepsilon}}|\underline{0})\chi(g^0_{\mathbf{x}_\varepsilon}|\underline{1})\delta[q_\diamond(\mathbf{x})-q^0_\diamond]\dot{q}_\diamond(\mathbf{x})\rangle}{\langle\chi(g^0_{\mathbf{x}}|\underline{0})\rangle}, \tag{75}$$

where ε is a sufficiently short time. The numerator signifies the flux from $\underline{0}$ to $\underline{1}$ across Σ^+, and the denominator is the normalized density of states (NDOS), of $\underline{0}$, i.e., the ratio of density of states of $\underline{0}$ to density of states of Γ. A factor of 1/2 and an absolute value sign $|\cdots|$ appearing in the original RRKM expression is unnecessary for Eq. (75) since the reverse flux from $\underline{1}$ to $\underline{0}$ has already been excluded.

The numerator of Eq. (75) is reduced to

$$\langle\chi(g^0_{\mathbf{x}_{-\varepsilon}}|\underline{0})\chi(g^0_{\mathbf{x}_\varepsilon}|\underline{1})\delta[q_\diamond(\mathbf{x})-q^0_\diamond]\dot{q}_\diamond(\mathbf{x})\rangle$$
$$=\langle\chi(\mathbf{x}|\Xi*)\rangle\left\langle w(\mathbf{x})\prod_{j=m_\triangleright}^{m_\triangleleft}\chi(g^{m_\triangleright-1-j}_{\mathbf{x}}|R^0_0)\right\rangle_{\Xi*}. \tag{76}$$

The denominator of Eq. (75) can be obtained indirectly by subtracting the sum of the NDOSs of the other cells from unity. The NDOS of a cell $C\neq\underline{0}$ is obtained from

$$\langle\chi(g^0_{\mathbf{x}}|C)\rangle=\frac{\langle\chi(\mathbf{x}|\Xi*)\rangle}{\#\{1^{m_\triangleleft}_{m_\triangleright}\}}\times\sum_{m\in\{1^{m_\triangleleft}_{m_\triangleright}\}}\left\langle w(\mathbf{x})\tau_{\mathrm{seg}}(g^m_{\mathbf{x}})\prod_{j=m_\triangleright}^{m_\triangleleft}\chi(g^{m-j}_{\mathbf{x}}|R^0_{s_j})\right\rangle_{\Xi*}, \tag{77}$$

where $(s_{m_\triangleleft}\cdots s_1.s_0\cdots s_{m_\triangleright}):=C$. See Appendix B for the derivation of Eqs. (76) and (77).

All phase space integrals in Eqs. (67) and (68) take the form of $\langle w(\mathbf{x})F(\mathbf{x})\rangle_{\Xi*}$, and Eqs. (76) and (77) have integrals $\langle w(\mathbf{x})F(\mathbf{x})\rangle_{\Xi*}$ and $\langle\chi(\mathbf{x}|\Xi*)\rangle$. These integrals can be evaluated using Monte Carlo phase space integration involving short-time trajectory calculations. On the standard Monte Carlo integration, these are evaluated by

$$\langle\chi(\mathbf{x}|\Xi*)\rangle\simeq\frac{1}{\#\mathcal{X}}\sum_{\mathbf{x}\in\mathcal{X}}\chi(\mathbf{x}|\Xi*)=\frac{\#\mathcal{X}*}{\#\mathcal{X}}, \tag{78}$$

$$\langle w(\mathbf{x})F(\mathbf{x})\rangle_{\Xi*}\simeq\frac{1}{\#\mathcal{X}*}\sum_{\mathbf{x}\in\mathcal{X}*}w(\mathbf{x})F(\mathbf{x}), \tag{79}$$

where $\mathcal{X}$ is a finite set of phase points drawn uniformly from Γ, and $\mathcal{X}*$ is the intersection of $\mathcal{X}$ and $\Xi*$. To reduce the required trajectory calculations effectively, we use the fol-

lowing algorithm for the evaluation: The following four sets are assembled from $\mathcal{X}$: (i) $\mathcal{X}_{\mathrm{I}} := \mathcal{X} \cap \Xi$, (ii) $\mathcal{X}_{\mathrm{II}}$, assembled by thinning out $\mathcal{X}_{\mathrm{I}}$ randomly; (iii) $\mathcal{X}_{\mathrm{III}} := \mathcal{X}_{\mathrm{II}} \cap \Xi^*$; (iv) $\mathcal{X}_{\mathrm{IV}}$, assembled by drawing from $\mathcal{X}_{\mathrm{III}}$ with a probability proportional to $w(\mathbf{x})$. Note that $\mathcal{X} \supset \mathcal{X}_{\mathrm{I}} \supset \mathcal{X}_{\mathrm{II}} \supset \mathcal{X}_{\mathrm{III}} \supset \mathcal{X}_{\mathrm{IV}}$. Then, the integrals are evaluated by

$$\langle \chi(\mathbf{x}|\Xi^*) \rangle \simeq \frac{\#\mathcal{X}_{\mathrm{III}} \#\mathcal{X}_{\mathrm{I}}}{\#\mathcal{X}_{\mathrm{II}} \#\mathcal{X}}, \tag{80}$$

$$\langle w(\mathbf{x}) F(\mathbf{x}) \rangle_{\Xi^*} \simeq \frac{\langle w(\mathbf{x}) \rangle_{\Xi^*}}{\#\mathcal{X}_{\mathrm{IV}}} \sum_{\mathbf{x} \in \mathcal{X}_{\mathrm{IV}}} F(\mathbf{x}), \tag{81}$$

where Eq. (81) is based on an importance sampling technique.[22] The average $\langle w(\mathbf{x}) \rangle_{\Xi^*}$ on the right-hand side of Eq. (81) can be obtained by

$$\langle w(\mathbf{x}) \rangle_{\Xi^*} \simeq \frac{1}{\#\mathcal{X}_{\mathrm{III}}} \sum_{\mathbf{x} \in \mathcal{X}_{\mathrm{III}}} w(\mathbf{x}). \tag{82}$$

Another trajectory-economizing technique which we employed in use of time reversal trajectories based on the time reversal symmetry of classical dynamics and adiabatic transition probability of our model.

In addition, we consider the improvement of the Monte Carlo integration of $\langle \chi(\mathbf{x}|\Xi^*) \rangle$ obtained from Eq. (80). The convergence of $\#\mathcal{X}_{\mathrm{I}}/\#\mathcal{X}$ is slow because of the small NDOS ratio of Ξ to Γ. To bring about a rapid convergence, we can use an importance sampling technique:[22] an ensemble enhancing the distribution in Ξ is employed for the Monte Carlo sampling of $\mathcal{X}$. Equation (80) is changed into the following equations:

$$\langle \chi(\mathbf{x}|\Xi^*) \rangle \simeq \frac{\#\mathcal{X}_{\mathrm{III}} \Sigma_{\mathbf{x} \in \mathcal{X}_{\mathrm{I}}} \Omega^{-1}(\mathbf{x})}{\#\mathcal{X}_{\mathrm{II}} \Sigma_{\mathbf{x} \in \mathcal{X}} \Omega^{-1}(\mathbf{x})}, \tag{83}$$

where $\Omega(\mathbf{x})$ is a weight function of the Monte Carlo sampling and we impose $\Omega(\mathbf{x})$ that the distribution is microcanonical within $\mathbf{x} \in \Xi$. Note that Eq. (81) is kept intact so long as the relative distribution within $\mathbf{x} \in \Xi$ is unchanged.

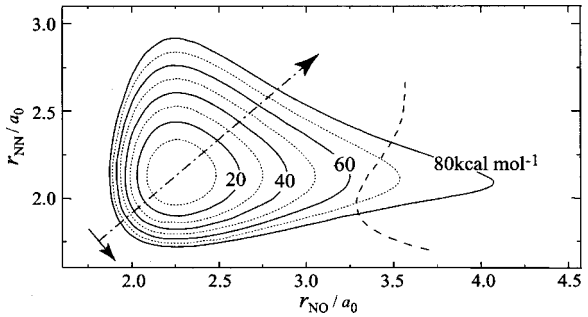

FIG. 2. The contour plot of potential energy surfaces used in this study, the crossing seams ξ (dashed line), and the surface of section Σ^+ (dot-dashed line) of the collinear N_2O. The dot-dashed line corresponds to the normal mode of the symmetric stretching. The abscissa and the ordinate express the lengths of N(center)–O and N–N, respectively, where a_0:=Bohr radius.

The concrete algorithm of the Monte Carlo integration and short-time trajectory calculations for the SM*l*-PST are described in Appendix C.

III. APPLICATION

A. Model system

As a test calculation, the statistical model is applied to a model system of collinear N_2O with a potential energy surface defined by Zahr *et al.*[23] at total energies $E = 64,65,\ldots,80$ kcal mol^{-1}. A contour plot of the potential energy surface is shown in Fig. 2.

The Landau–Zener formula[24] is utilized as the transition probability

$$P_{\mathrm{LZ}}(\mathbf{x}) := 1 - \exp\left[\frac{-2\pi V_{12}^2}{\hbar |\Delta \mathbf{F}(\mathbf{q}) . \mathbf{v}(\mathbf{x})|}\right], \tag{84}$$

TABLE I. Values of parameters used in the calculations.

Method	Parameter	Value
EMS (common)	Number of incubation steps	5×10^4
	Number of atoms moved in each step	3
Trajectory calculations	Number of trajectories, N_T	5×10^3
	EMS steps between successive two trajectories	1×10^4
	Step size/fs[a]	0.50
NMC-TST	Number of sampled states, N	4×10^8
	Critical surface width in potential energy difference, 2ε/kcal mol^{-1}	0.20
	Number of momenta set generated at critical surface, N_{mon}	10
SM*l*-PST	Number of sampled states, N_{MC}	2×10^7
	Number of trajectories, N_{IV}	5×10^3
	Width of Ξ in potential energy difference, 2ε/kcal mol^{-1}	1.0
	Factor for importance sampling, F_w	4.0
	Step size for integration of kinetic equations, Δt/fs	1.0

[a]This is common to *l*th-order semi-Markov model.

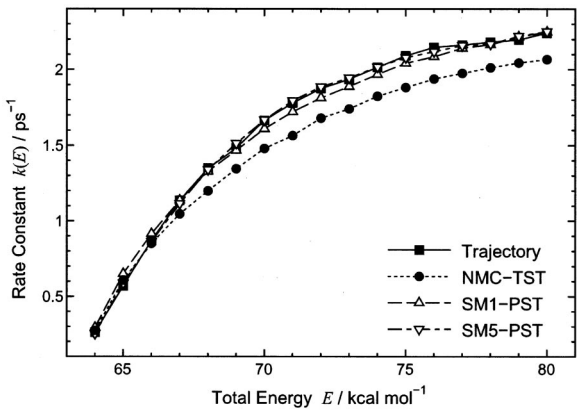

FIG. 3. Comparison of rate coefficients for the model system calculated with four methods.

where $\mathbf{x}$ is a point in the crossing seam, $\mathbf{q}$ is the coordinate of $\mathbf{x}$ in configuration space, $\Delta\mathbf{F}(\mathbf{q})$ is the difference in the forces of the two states, evaluated at the crossing point, $\mathbf{v}(\mathbf{x})$ is the nuclear velocity, and V_{12} is the interaction term that couples the two states. We assume V_{12} to be a somewhat greater value, 400 cm^{-1}, to highlight nonstatistical behavior; this trick was presented by Marks and Thompson.[19]

We calculated the population decay of the system using standard trajectory calculations, the nonadiabatic Monte Carlo transition state theory (NMC-TST), and the SM*l*-PST

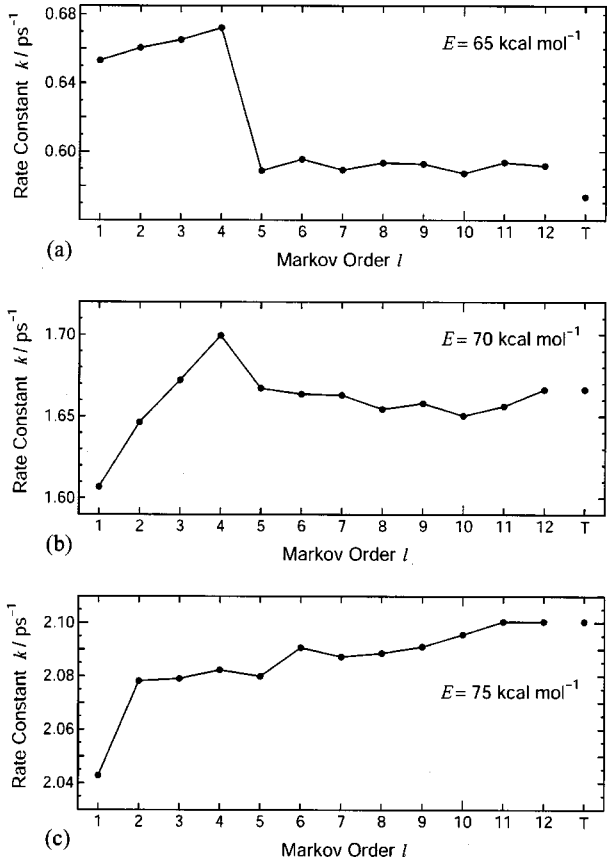

FIG. 4. The Markov-order dependence of rate coefficients for (a) $E=65$ kcal mol^{-1}; (b) $E=70$ kcal mol^{-1}; and (c) $E=75$ kcal mol^{-1}. The extreme right points indicate the trajectory rate coefficients.

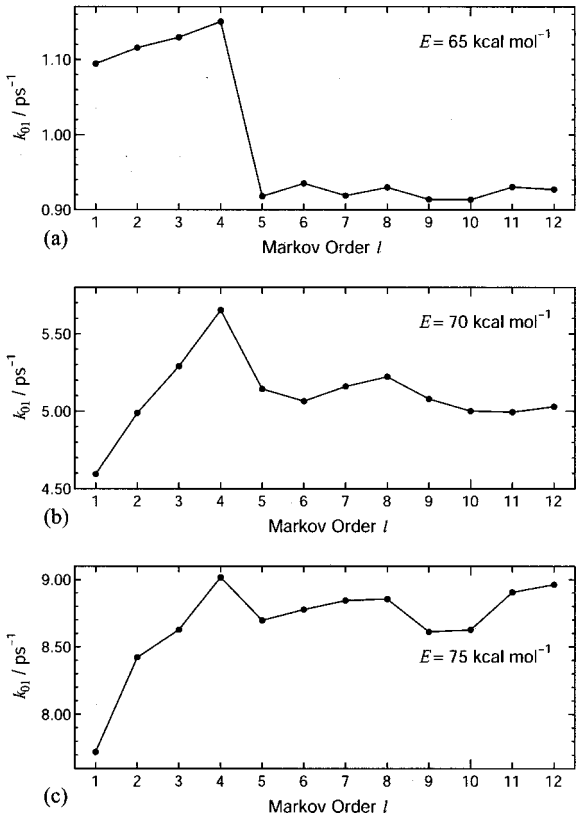

FIG. 5. The Markov-order dependence of k_{01}, rate coefficients from $\underline{0}$ to $\underline{1}$, for (a) $E=65$ kcal mol^{-1}; (b) $E=70$ kcal mol^{-1}; and (c) $E=75$ kcal mol^{-1}.

with two primitive cells. The initial reactant distribution was settled to be microcanonical for trajectory calculations and the SM*l*-PST. We explain the computational details for trajectory calculations and the SM*l*-PST in the next subsection. The values of parameters used in the calculations are given in Table I.

B. Computational details

1. Trajectory calculations

The standard trajectory calculations are carried out as follows. The initial phase points are selected using the efficient microcanonical sampling (EMS) method.[25] The EMS method comprises two stages, sampling from configuration space and momentum space. The configuration sampling procedure involves a Markov walk. The maximum step size of the Markov walk was chosen to keep the acceptance/rejection ratio between 0.3–0.7. The weight function of the configuration sampling for this system with two degrees of freedom is

$$\omega_{\mathrm{EMS}}(\mathbf{q}) := \begin{cases} 1 & V_A(\mathbf{q}) < E \\ 0 & \text{otherwise} \end{cases}, \tag{85}$$

where E is the total energy of the system.

Each initial point obtained from the EMS was propagated until 5 ps by Candy and Rozmus' fourth-order symplectic integrator.[26] The energy difference between two potential surfaces, $\Delta V := V_A - V_R$, was monitored. The change in sign of ΔV indicates a passage across the seam. When this

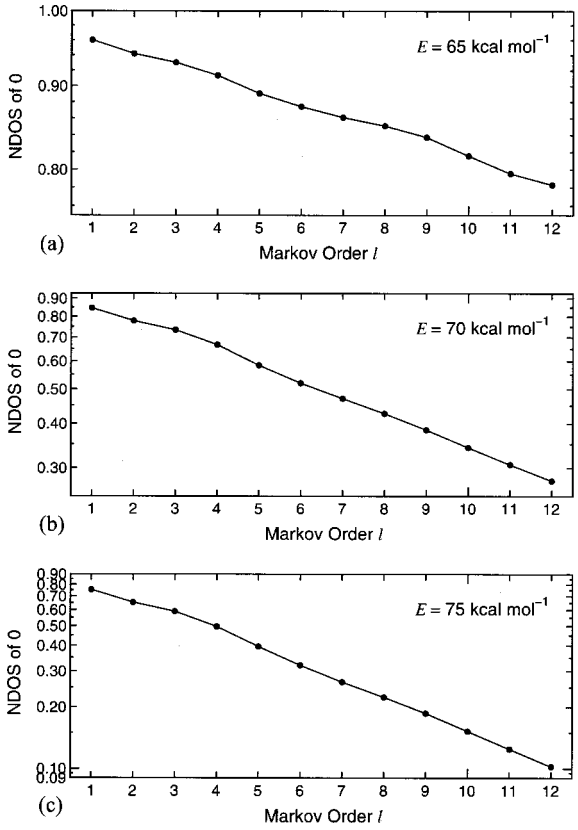

FIG. 6. The Markov-order dependence of the normalized density of states of the region $\underline{0}$ for (a) $E=65$ kcal mol^{-1}; (b) $E=70$ kcal mol^{-1}; and (c) $E=75$ kcal mol^{-1}. The vertical axes are log scaled.

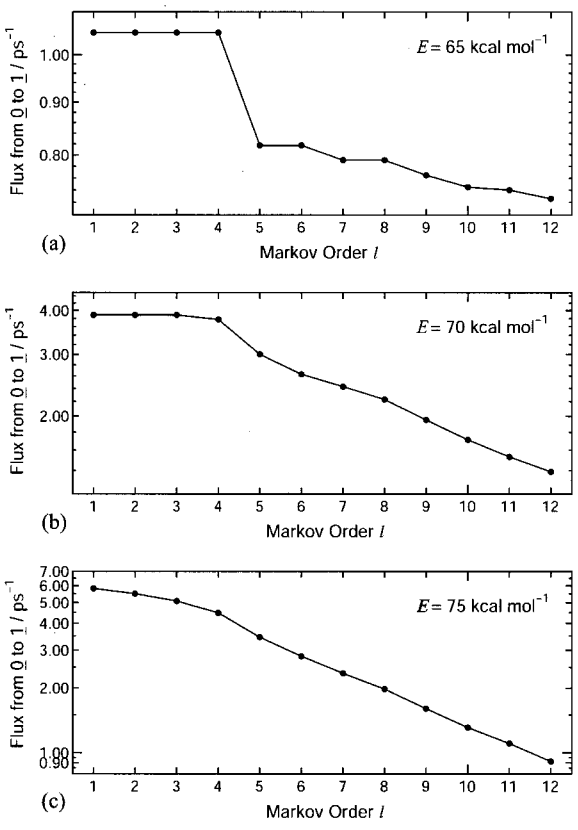

FIG. 7. The Markov-order dependence of the flux from $\underline{0}$ to $\underline{1}$ for (a) $E=65$ kcal mol^{-1}; (b) $E=70$ kcal mol^{-1}; and (c) $E=75$ kcal mol^{-1}. The vertical axes are log scaled.

occurs, we judge the trajectory reached the crossing point. Then, it is necessary to locate the phase space coordinate of the crossing point and to determine the time at the point. A first-order approximation for ΔV and $\mathbf{x}_t$ at t is used to determine the corresponding crossing point $\mathbf{x}^{\xi}$ such that $\Delta V=0$ and the crossing time t^{ξ}.[27]

The population decay evaluated from the trajectories is given by

$$N(t)=\frac{1}{N_T}\sum_{i=1}^{N_T}\prod_{j=1}^{t^{\xi}(i,j)<t}[1-P_{\mathrm{LZ}}(i,j)], \tag{86}$$

where N_T is the number of the trajectories, $t^{\xi}(i,j)$ and $P_{\mathrm{LZ}}(i,j)$ are the crossing time and the transition probability at the jth crossing point on the ith trajectory, respectively. Equation (86) corresponds to the evaluation of Eq. (22) by Monte Carlo integration using EMS.

2. Ith-order semi-Markov phase space theory

Let (q_1,q_2) be the representation of $\mathbf{q}$ by the components with normal coordinates. We approximately adopt the surface $q_1=0$ and $\dot{q}_1>0$ as Σ^+ (see Fig. 2) because it is difficult to find Poincaré surface of sections in general Hamiltonian systems. The number of primitive cells are two: $R_0^0:=\{g\in G|g\cap\xi=\varnothing\}$ and $R_0^1:=G-R_0^0$. We settle $\Xi:=\{\mathbf{x}|-\varepsilon<\Delta V(\mathbf{q})<\varepsilon,\mathbf{x}\in\Gamma\}$, and $\eta:=\{\mathbf{x}|\Delta V(\mathbf{q})=-1.5\varepsilon,\mathbf{x}\in\Gamma\}$ (η is explained in Appendix C). The configuration sampling weight is $\Omega(\mathbf{q}):=\omega_{\mathrm{EMS}}(\mathbf{q})\phi(\mathbf{q})$, where $\omega_{\mathrm{EMS}}(\mathbf{q})$ is the EMS configuration sampling weight, and $\phi(\mathbf{q})$ is the importance sampling weight, which we defined as

$$\phi(\mathbf{q}):=\begin{cases}1 & \text{if } |\Delta V(\mathbf{q})|\leqslant\varepsilon\\ [a(|\Delta V(\mathbf{q})|-\varepsilon)+1]^{-1} & \text{if } \varepsilon<|\Delta V(\mathbf{q})|<b,\\ [a(b-\varepsilon)+1]^{-1} & \text{if } b\leqslant|\Delta V(\mathbf{q})|\end{cases} \tag{87}$$

where $a:=1.6$ kcal mol^{-1} and $b:=40$ kcal mol^{-1}.

The whole-energy hypersurfaces of the model molecule for $E=64,65,\ldots,80$ kcal mol^{-1} are approximately considered to be ergodic. This was ascertained by observation of the Poincaré maps.

C. Results and discussion

The population decay was calculated for the model reaction system using trajectory calculations, NMC-TST, SM1-PST, and SM5-PST. In Fig. 3 we compare the rate coefficients for population decay, $k(E)$. For the trajectory calculations and the SM1-PST, the rate coefficients were evaluated by least-square fits for calculated population decay curves. The NMC-TST rates are smaller than the trajectory rates for $E\geqslant 66$ kcal mol^{-1}, and the discrepancy is especially remarkable at $E\gtrsim 70$ kcal mol^{-1}. On the other hand, the discrepancy of the SM1-PST rates is small, and the SM5-PST rates show excellent agreement with the trajectory rates.

TABLE II. The total flux into a region (ps^{-1}).

(1)							65 kcal mol^{-1}	
1.05								
(01)	(10)							
1.05	1.05							
(001)	(010)	(100)						
1.05	1.05	1.05						
(000 1)	(001 0)	(010 0)	(100 0)					
1.05	1.05	1.05	1.05					
(000 01)	(000 10)	(001 00)	(010 00)	(100 00)				
1.05	1.05	1.05	1.05	1.05				
(000 001)	(000 010)	(000 100)	(001 000)	(010 000)	(100 000)	(100 001)		
0.82	1.05	1.05	1.05	1.05	0.82	0.23		
							70 kcal mol^{-1}	
(1)								
3.88								
(01)	(10)							
3.88	3.88							
(001)	(010)	(100)						
3.88	3.88	3.88						
(000 1)	(001 0)	(010 0)	(100 0)					
3.88	3.88	3.88	3.88					
(000 01)	(000 10)	(001 00)	(010 00)	(100 00)	(100 01)			
3.77	3.88	3.88	3.88	3.77	0.11			
(000 001)	(000 010)	(000 100)	(001 000)	(010 000)	(010 001)	(100 000)	(100 001)	(100 010)
3.00	3.77	3.88	3.88	3.77	0.11	3.00	0.77	0.11
(1)							75 kcal mol^{-1}	
5.82								
(01)	(10)							
5.82	5.82							
(001)	(010)	(100)	(101)					
5.82	5.82	5.50	0.32					
(000 1)	(001 0)	(010 0)	(010 1)	(100 0)	(100 1)	(101 0)		
5.09	5.50	5.50	0.32	5.09	0.42	0.32		

Next, we investigate the dependence on l for the SMl-PST rate coefficients for $E=65$, 70, and 75 kcal mol^{-1}. In Fig. 4, the numbers on the abscissa indicate l, and the points on the extreme right indicate the trajectory rate coefficients. Although the SMl-PST rates roughly approach the trajectory rates with an increase of l, the variations of the rate coefficients at $E=65$ and 70 kcal mol^{-1} are not monotonous; that is, the rate coefficients increase for $l\leqslant 4$, fall at $l=5$, and then retain nearly constant values for $l\geqslant 6$.

The behavior is qualitatively explained as follows. Once a phase point has entered the region of $\underline{1}$, the point will be transported to the crossing seam within a short time. That is, the transport process from $\underline{0}$ to $\underline{1}$ is expected to be rate limiting when the NDOS of $\underline{0}$ is the greater part of Γ. Figure 5 shows the values of the k_{01}, or rate coefficients of the process from $\underline{0}$ to $\underline{1}$. It can be seen from Fig. 5 that k indeed correlated with k_{01}. The correlation at $E=75$ kcal mol^{-1} is slightly poor. This can be explained by the fact that the NDOS of $\underline{0}$ is smaller at $E=75$ kcal mol^{-1} than at $E=65$ kcal mol^{-1}. k_{01} is determined by Eq. (75); that is, the flux from $\underline{0}$ to $\underline{1}$, shown in Fig. 7, divided by the NDOS of $\underline{0}$, shown in Fig. 6. Although the NDOSs of $\underline{0}$ decay nearly exponentially, the fluxes of $\underline{0}$ deviate from exponential decays for small l region. Thus, the remarkable behavior of k_{01} arises mainly from the behavior of the flux from $\underline{0}$ to $\underline{1}$. Table II shows the total flux into each cell, $\langle \chi(g^0_{\mathbf{x}}|C)\delta[g_\diamond(\mathbf{x})-q^0_\diamond]\dot{q}_\diamond(\mathbf{x})\rangle$. Note that a total flux into $(s_1 \ldots s_n)$ is equal to the flux from $(s_1 \ldots s_{n-1})$ to $(s_2 \ldots s_n)$. At $E=65$ kcal mol^{-1}, there is no sequence including two or more "1" for $l\leqslant 5$; i.e., cells R_1^m and R_1^n have no overlap if $|m-n|<5$ and $m\neq n$. For $l=6$, a overlapping sequence (100 001) appears for the first time. Whereas all the fluxes from (0) to (1), from (00) to (01), from (000) to (001), and from (0000) to (0001) are 1.05 ps^{-1}, the flux from (000 00) to (000 01) decreases to 0.82 ps^{-1}, because the total flux into (000 01) must be shared between fluxes from (000 00) and from (100 00). De Leon called this effect "clogging."[18] At $E=70$ kcal mol^{-1}, there exists (100 01) with $l=5$; however, the flux, or clogging, is small (0.11 out of 3.77 ps^{-1}) and the dominant clogging arises from (100 001). At $E=80$ kcal mol^{-1}, the first clogging occurs from (101); the flux decreases nearly exponentially with increasing l. The situations of clogging are confirmed intuitively in Fig. 8, which shows the shapes of $R_1^n(n=-3,-2,\ldots,2)$ on Σ^+. The area of each region expresses the corresponding flux.[17,18]

The computational efficiency for obtaining $k(E)$ was investigated in the trajectory calculations and the SMl-PST. In Fig. 9, the coefficients of variation in $k(E)$ (i.e., the quotient of the standard deviation to the arithmetic mean) at $E=65$, 70, and 75 kcal mol^{-1} by the trajectory calculations and the SM5-PST are plotted as a function of the total temporal length of calculated trajectories. Each data point was estimated from 20 runs using different random seeds with $N_T=25-2500$ for the trajectory calculations and with N_{IV}

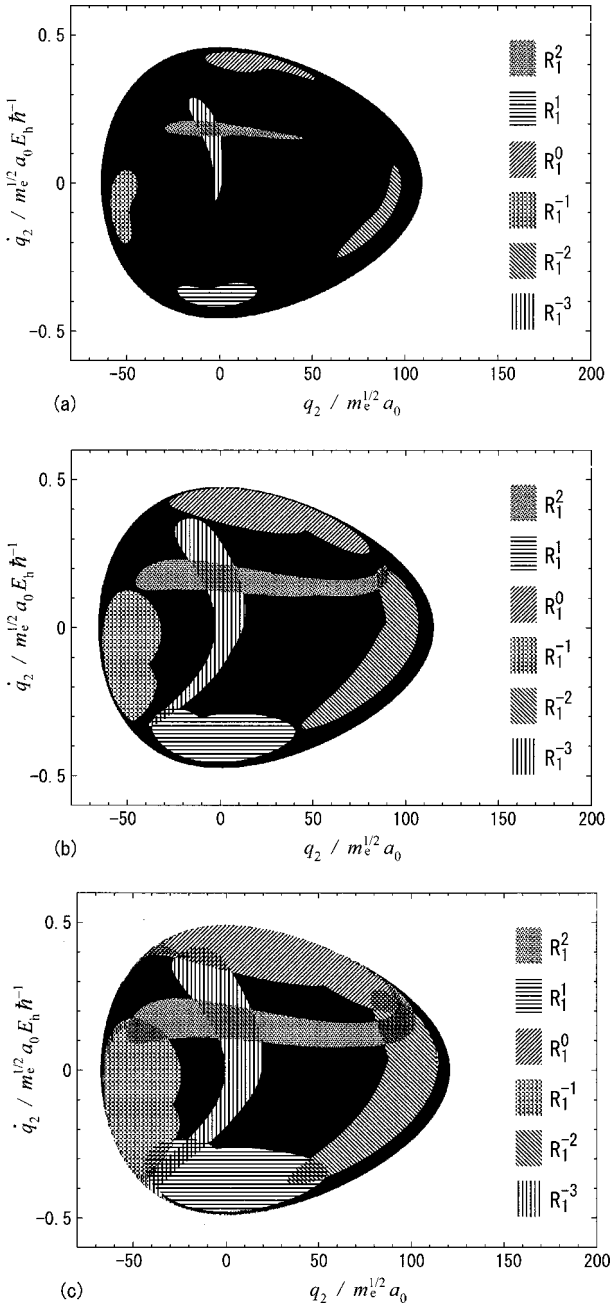

FIG. 8. The shapes of regions R_n^1 on Σ^+ at (a) $E=65$; (b) $E=70$; and (c) $E=75$ kcal mol^{-1}. The black-filled areas denote (000.000). The abscissa and the ordinate express the normal coordinate of q_2 and the time derivative of q_2, respectively, where m_e:=electron mass, a_0:=Bohr radius, and E_h:=1 hartree.

$=100-5000$ for the SM5-PST, under the conditions same as in Table I. The arithmetic means of the 20 runs were used for a total length for the SM5-PST since there is a slight difference in the total length for each run. From this plot, it is found that the evaluation by the SM5-PST gives more precise $k(E)$ for the three energies under the same length of the trajectory. Although our method includes a Monte Carlo integration, the computational time for the Monte Carlo integration is minor when N_{IV} is larger than 1000. In the trajectory calculations extra time is also needed for sampling of initial phase points.

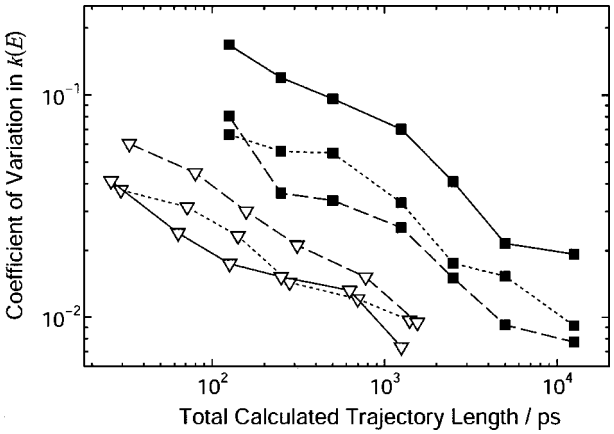

FIG. 9. The coefficients of variation in $k(E)$ at $E=65$ (solid line), 70 (short-dashed line), and 75 kcal mol^{-1} (long-dashed line) by trajectory calculations (square) and SM5-PST (triangle) vs the total temporal length of calculated trajectories.

Although the results of the test calculation are successful, there are still some problems. First, it is necessary to develop a procedure to determine practically optimum l without large computational effort. We expect that this will be possible by successive elongation for l with judgment whether l is sufficiently long by means of inspection of clogging effects. Second, we must resolve the problem that the number of cells in $\mathcal{C}_{\mathrm{exist}}$ increases exponentially with increasing l. This problem arises from the fact that our statistical model contains cells with constant $s_{m_\triangleleft}$ and $s_{m_\triangleright}$ only. We are going to resolve this problem by loosening restriction of cells in the model. Work along these lines is currently in progress.

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APPENDIX A: DERIVATIONS OF KINETIC EQUATIONS

In this Appendix we derive Eqs. (34) and (35).

If $0 \leqslant \tau_2 \leqslant \tau_1$, the following relation holds:

$$\langle F_1(\mathbf{x}, g_{\mathbf{x}}^m)\, \delta[\tau(\mathbf{x}) - \tau_1] \rangle = \langle F_1(\mathbf{x}_{\tau_1-\tau_2}, g_{\mathbf{x}}^m)\, \delta[\tau(\mathbf{x}) - \tau_2]\, \theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0) - \tau_1] \rangle, \quad \text{(A1)}$$

where m is an arbitrary integer, and $F_1(\mathbf{x}, g)$ are an arbitrary function. When $\tau_2 = 0$, we have

$$\langle F_1(\mathbf{x}, g_{\mathbf{x}}^m)\, \delta[\tau(\mathbf{x}) - \tau_1] \rangle = \langle F_1(\mathbf{x}_{\tau_1}, g_{\mathbf{x}}^m)\, \delta[\tau(\mathbf{x})]\, \theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0) - \tau_1] \rangle. \quad \text{(A2)}$$

A proof of Eq. (A1) runs as follows. We may change the variable $\mathbf{x}$ of the phase space integral on the left-hand side of

Eq. (A1) to $\mathbf{x}_{\tau_1-\tau_2}$ with a Jacobian of unity because of Liouville's theorem

$$\begin{aligned}
&\langle F_1(\mathbf{x},g_{\mathbf{x}}^m)\,\delta[\tau(\mathbf{x})-\tau_1]\rangle \\
&\quad=\langle F_1(\mathbf{x}_{\tau_1-\tau_2},g_{\mathbf{x}_{\tau_1-\tau_2}}^m)\,\delta[\tau(\mathbf{x}_{\tau_1-\tau_2})-\tau_1]\rangle \\
&\quad=\sum_{\nu\in\mathbf{Z}}\langle F_1(\mathbf{x}_{\tau_1-\tau_2},g_{\mathbf{x}}^{m+\nu})\,\delta[-t_\nu^{\Sigma^+}(\mathbf{x})-\tau_2] \\
&\qquad\times I[t_\nu^{\Sigma^+}(\mathbf{x})\leqslant\tau_1-\tau_2<t_{\nu+1}^{\Sigma^+}(\mathbf{x})]\rangle, \qquad \text{(A3)}
\end{aligned}$$

where $I(\mathcal{E})$ is the indicator function defined to be unity if event $\mathcal{E}$ holds and zero otherwise, and the second step follows from Eqs. (24) and (25). A requirement for $\delta[-t_\nu^{\Sigma^+}(\mathbf{x})-\tau_2]I[t_\nu^{\Sigma^+}(\mathbf{x})\leqslant\tau_1-\tau_2<t_{\nu+1}^{\Sigma^+}(\mathbf{x})]$ to be nonzero is that $-t_\nu^{\Sigma^+}(\mathbf{x})-\tau_2=0$ and $t_\nu^{\Sigma^+}(\mathbf{x})\leqslant\tau_1-\tau_2<t_{\nu+1}^{\Sigma^+}(\mathbf{x})$. Since we suppose that $0\leqslant\tau_2\leqslant\tau_1$, the value of $t_\nu^{\Sigma^+}(\mathbf{x})$ must be nonpositive because of the former condition, and the latter condition forces $t_{\nu+1}^{\Sigma^+}(\mathbf{x})$ to be positive. This implies that all the terms except for $\nu=0$ in the summation must vanish. Thus, from Eqs. (26) and (27)

$$\begin{aligned}
&\langle F_1(\mathbf{x},g_{\mathbf{x}}^m)\,\delta[\tau(\mathbf{x})-\tau_1]\rangle \\
&\quad=\langle F_1(\mathbf{x}_{\tau_1-\tau_2},g_{\mathbf{x}}^m)\,\delta[\tau(\mathbf{x})-\tau_2] \\
&\qquad\times I[\tau_1-\tau_2+\tau(\mathbf{x})<\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)]\rangle \\
&\quad=\langle F_1(\mathbf{x}_{\tau_1-\tau_2},g_{\mathbf{x}}^m)\,\delta[\tau(\mathbf{x})-\tau_2]I[\tau_1<\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)]\rangle, \qquad \text{(A4)}
\end{aligned}$$

with $0\leqslant\tau_2\leqslant\tau_1$. Therefore, we obtain Eq. (A1).

We introduce a statistical approximation that $\rho(\mathbf{x},t)$ is regarded as constant within an isoage hypersurface in a cell. Let $\overline{\rho}_C(\tau,t)$ be the average of $\rho(\mathbf{x},t)$ on the isopage hypersurface $i_C(\tau)$

$$\begin{aligned}
\overline{\rho}_C(\tau,t)&:=\frac{\langle\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C\rangle\rho(\mathbf{x},t)\rangle}{\langle\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle} \\
&=\frac{f_C(\tau,t)}{\langle\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle}. \qquad \text{(A5)}
\end{aligned}$$

We define $\overline{\rho}_C(\tau,t)$ to be zero when $\langle\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle$ vanishes [i.e., $f_C(\tau,t)$ also vanishes]. The approximation allows us to replace $\rho(\mathbf{x},t)$ with the corresponding $\overline{\rho}_C(\tau,t)$; thus, the following relation holds:

$$\begin{aligned}
&\langle F_2(\mathbf{x})\,\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rho(\mathbf{x},t)\rangle \\
&\quad=\langle F_2(\mathbf{x})\,\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\overline{\rho}_C(\tau,t)\rangle \\
&\quad=f_C(\tau,t)\frac{\langle F_2(\mathbf{x})\,\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle}{\langle\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle}, \qquad \text{(A6)}
\end{aligned}$$

where $F_2(\mathbf{x})$ is an arbitrary function. In addition, the following approximation is also adopted: transition time $t_n^{\xi}(\mathbf{x})$ is replaced with $t_m^{\Sigma^+}(\mathbf{x})$ such that $t_{m-1}^{\Sigma^+}(\mathbf{x})\leqslant t_n^{\xi}(\mathbf{x})<t_m^{\Sigma^+}(\mathbf{x})$. This implies that Eq. (20) is replaced with

$$\rho(\mathbf{x}_{\Delta t},t+\Delta t)=\rho(\mathbf{x},t)\overline{Q}(\mathbf{x},\Delta t), \qquad \text{(A7)}$$

where

$$\overline{Q}(\mathbf{x},\Delta t):=\prod_{\substack{t\in\{t_n^{\xi}(\mathbf{x})\}\\ t_0^{\Sigma^+}(\mathbf{x})\leqslant t<t_{\nu(\mathbf{x},\Delta t)}^{\Sigma^+}(\mathbf{x})}}[1-P_{\mathrm{hop}}(\mathbf{x}_t)], \qquad \text{(A8)}$$

or [cf. Eqs. (10) and (38)]

$$\overline{Q}(\mathbf{x},\Delta t):=\begin{cases}1 & \text{if } 0\leqslant\Delta t<t_1^{\Sigma^+}(\mathbf{x})\\ Q_{\mathrm{seg}}(g_{\mathbf{x}}^0) & \text{if } t_1^{\Sigma^+}(\mathbf{x})\leqslant\Delta t<t_2^{\Sigma^+}(\mathbf{x})\\ Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)Q_{\mathrm{seg}}(g_{\mathbf{x}}^1) & \text{if } t_2^{\Sigma^+}(\mathbf{x})\leqslant\Delta t<t_3^{\Sigma^+}(\mathbf{x})\\ \vdots & \vdots\end{cases}. \qquad \text{(A9)}$$

Consider an age distribution function at $t+\Delta t$ with $\Delta t\geqslant 0$

$$f_C(\tau,t+\Delta t)=\langle\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rho(\mathbf{x},t+\Delta t)\rangle. \qquad \text{(A10)}$$

Substituting Eq. (A1) with $\tau_1=\tau$, $\tau_2=\tau-\Delta t$, and $F_1(\mathbf{x},g_{\mathbf{x}}^m)=\chi(g_{\mathbf{x}}^0|C)\rho(\mathbf{x},t)$ into Eq. (A10), we obtain

$$\begin{aligned}
&f_C(\tau,t+\Delta t) \\
&\quad=\langle\delta[\tau(\mathbf{x})-(\tau-\Delta t)]\chi(g_{\mathbf{x}}^0|C)\rho(\mathbf{x}_{\Delta t},t+\Delta t) \\
&\qquad\times\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau|\rangle \\
&\quad=\langle\delta[\tau(\mathbf{x})-(\tau-\Delta t)]\chi(g_{\mathbf{x}}^0|C\rangle\rho(\mathbf{x},t)\overline{Q}(\mathbf{x},\Delta t) \\
&\qquad\times\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]\rangle. \qquad \text{(A11)}
\end{aligned}$$

A requirement for $\delta[\tau(\mathbf{x})-(\tau-\Delta t)]\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]$ to be nonzero is that $-t_0^{\Sigma^+}(\mathbf{x})-\tau+\Delta t=0$ and $\tau<t_1^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})$; that is, $t_1^{\Sigma^+}(\mathbf{x})>\Delta t$. Thus, the factor $\overline{Q}(\mathbf{x},\Delta t)$ in the integrand may be eliminated. From Eq. (A6), we have

$$\begin{aligned}
&f_C(\tau,t+\Delta t) \\
&\quad=f_C(\tau-\Delta t,t) \\
&\qquad\times\frac{\langle\delta[\tau(\mathbf{x})-(\tau-\Delta t)]\chi(g_{\mathbf{x}}^0|C)\,\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]\rangle}{\langle\delta[\tau(\mathbf{x})-(\tau-\Delta t)]\chi(g_{\mathbf{x}}^0|C)\rangle}.
\end{aligned} \qquad \text{(A12)}$$

Suppose $\tau-\Delta t\geqslant 0$. Using Eq. (A1) reversely for the numerator with $\tau_1=\tau$, $\tau_2=\tau-\Delta t$, and $F_1(\mathbf{x},g_{\mathbf{x}}^0)=\chi(g_{\mathbf{x}}^0|C)$, we have

$$\begin{aligned}
&f_C(\tau,t+\Delta t) \\
&\quad=f_C(\tau-\Delta t,t)\frac{\langle\delta(\tau(\mathbf{x})-\tau)\chi(g_{\mathbf{x}}^0|C)\rangle}{\langle\delta[\tau(\mathbf{x})-(\tau-\Delta t)]\chi(g_{\mathbf{x}}^0|C)\rangle}. \qquad \text{(A13)}
\end{aligned}$$

We introduce a function

$$S_C(\tau) := \frac{\langle \delta(\tau(\mathbf{x})-\tau)\chi(g_{\mathbf{x}}^0|C)\rangle}{\langle \delta(\tau(\mathbf{x}))\chi(g_{\mathbf{x}}^0|C)\rangle}. \tag{A14}$$

The use of Eq. (A2) provides an alternative expression

$$S_C(\tau) := \frac{\langle \delta(\tau(\mathbf{x}))\chi(g_{\mathbf{x}}^0|C)\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]\rangle}{\langle \delta(\tau(\mathbf{x}))\chi(g_{\mathbf{x}}^0|C)\rangle}. \tag{A15}$$

From Eqs. (A13) and (A14)

$$f_C(\tau,t+\Delta t) = f_C(\tau-\Delta t,t)\frac{S_C(\tau)}{S_C(\tau-\Delta t)} \quad \text{for } \tau-\Delta t\geqslant 0,\ \Delta t\geqslant 0. \tag{A16}$$

Equation (A16) is devoid of treatment for $\tau=0$. To incorporate it, we consider

$$f_{C'}(\Delta\tau,t+\Delta t) = \langle \delta[\tau(\mathbf{x})-\delta\tau]\chi(g_{\mathbf{x}}^0|C')\rho(\mathbf{x},t+\Delta t)\rangle, \tag{A17}$$

with $\Delta\tau\to+0$, $\Delta t\to+0$, and $\Delta\tau<\Delta t$. One can rewrite this as

$$\begin{aligned} f_{C'}(\Delta\tau,t+\Delta t) &= \langle \delta[\Delta\tau-\tau(\mathbf{x}_{\Delta t})]\chi(g_{\mathbf{x}_{\Delta t}}^0|C')\rho(\mathbf{x}_{\Delta t},t+\Delta t)\rangle \\ &= \sum_{\nu\in\mathbf{Z}} \langle \delta[\Delta\tau-t_\nu^{\Sigma^+}(\mathbf{x})]\chi(g_{\mathbf{x}}^\nu|C')\rho(\mathbf{x},t) \\ &\quad \times \overline{Q}(\mathbf{x},\Delta t) I[t_\nu^{\Sigma^+}(\mathbf{x})\leqslant\Delta t<t_{\nu+1}^{\Sigma^+}(\mathbf{x})]\rangle \\ &= \sum_{\nu\in\mathbf{Z}} \langle \delta[\Delta\tau-t_\nu^{\Sigma^+}(\mathbf{x})]\chi(g_{\mathbf{x}}^\nu|C')\rho(\mathbf{x},t)\overline{Q}(\mathbf{x},\Delta t)\rangle, \end{aligned} \tag{A18}$$

where the last step comes from the fact that $\delta[t_\nu^{\Sigma^+}(\mathbf{x})-\Delta\tau]I[t_\nu^{\Sigma^+}(\mathbf{x})\leqslant\Delta t<t_{\nu+1}^{\Sigma^+}(\mathbf{x})]$ may be reduced to $\delta[t_\nu^{\Sigma^+}(\mathbf{x})-\Delta\tau]$ when $\Delta\tau\leqslant\Delta t\ll 1$. It is evident that if $\Delta\tau$ is unequal to $t_\nu^{\Sigma^+}(\mathbf{x})$ then $\delta[\Delta\tau-t_\nu^{\Sigma^+}(\mathbf{x})]$ vanishes. Thus, all terms in the summation corresponding to $\nu\neq 1$ vanish when $\Delta\tau\to+0$. Moreover, if $t_1^{\Sigma^+}(\mathbf{x})$ is equal to $\Delta\tau$, $\overline{Q}(\mathbf{x},\Delta t)$ may be replaced by $Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)$. Hence

$$\begin{aligned} f_{C'}(\Delta\tau,t+\Delta t) &= \langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[t_1^{\Sigma^+}(\mathbf{x})-\Delta\tau]\rho(\mathbf{x},t)\chi(g_{\mathbf{x}}^1|C')\rangle \\ &= \langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\Delta\tau-\tau(\mathbf{x})]\rho(\mathbf{x},t)\chi(g_{\mathbf{x}}^1|C')\rangle. \end{aligned} \tag{A19}$$

Disintegrating the integrals into contributions from all isoage hypersurfaces in the cell, we obtain

$$f_{C'}(\Delta\tau,t+\Delta t) = \int_0^\infty d\tau \langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\Delta\tau-\tau(\mathbf{x})\delta[\tau(\mathbf{x})-\tau]\rho(\mathbf{x},t)\chi(g_{\mathbf{x}}^1|C')\rangle. \tag{A20}$$

Since a phase point $\mathbf{x}$ satisfying $\chi(g_{\mathbf{x}}^1|C')=1$ must be contained in a parent of C', we may disintegrate the right-hand side of Eq. (A20) further into contributions from all parents of C'

$$\begin{aligned} f_{C'}(\Delta\tau,t+\Delta t) &= \sum_{C\in \mathrm{par}C'} \int_0^\infty d\tau \langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\Delta\tau-\tau(\mathbf{x})] \\ &\quad \times \delta[\tau(\mathbf{x})-\tau]\rho(\mathbf{x},t)\chi(g_{\mathbf{x}}^0|C)\chi(g_{\mathbf{x}}^1|C')\rangle. \end{aligned} \tag{A21}$$

From Eq. (A6)

$$\begin{aligned} f_{C'}(\Delta\tau,t+\Delta t) &= \sum_{C\in \mathrm{par}C'} \int_0^\infty d\tau\, f_C(\tau,t)\langle \delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle^{-1} \\ &\quad \times \langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\Delta\tau-\tau] \\ &\quad \times \delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\chi(g_{\mathbf{x}}^1|C')\rangle. \end{aligned} \tag{A22}$$

Therefore

$$f_{C'}(0,t) = \sum_{C\in \mathrm{par}\ C'} \int_0^\infty d\tau\, B_C^{C'}(\tau) f_C(\tau,t), \tag{A23}$$

where

$$\begin{aligned} B_C^{C'}(\tau) &:= \lim_{\Delta\tau\to+0} \frac{\langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\Delta\tau-\tau]\delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\chi(g_{\mathbf{x}}^1|C')\rangle}{\langle \delta[\tau(\mathbf{x})-\tau]\chi(g_{\mathbf{x}}^0|C)\rangle} \\ &= \lim_{\Delta\tau\to+0} \frac{\langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\Delta\tau-\tau]\delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^0|C)\chi(g_{\mathbf{x}}^1|C')I[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]\rangle}{\langle \delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^0|C\rangle\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]\rangle} \\ &= \frac{\langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^0)\delta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0)-\tau]\delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^0|C)\chi(g_{\mathbf{x}}^1|C')\rangle}{\langle \delta[\tau(\mathbf{x})]\chi(g_{\mathbf{x}}^0|C\rangle\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^0(-\tau]\rangle}. \end{aligned} \tag{A24}$$

APPENDIX B: DERIVATIONS FOR COMPUTATIONAL METHOD

In this Appendix we derive Eqs. (67), (68), (76), and (77).

Let us consider the following segment average:

$$\lim_{n\to\infty}\frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})}\sum_{i=0}^{n}F(g_{\mathbf{x}}^i)\prod_{j=m'}^{m''}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^0), \quad \text{(B1)}$$

where $F(g)$ is an arbitrary function for a segment $g\in G$, and $\{s_{m'},s_{m'+1},\ldots,s_{m''}\}$ is a set of symbols, 0 or 1. We shall rewrite Eq. (B1) as a phase space average restricted in Ξ.

Suppose that $\{1_{m'}^{m''}\}$ is not empty. Then

$$\begin{aligned}
&\lim_{n\to\infty}\frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})}\sum_{i=0}^{n}F(g_{\mathbf{x}}^i)\prod_{j=m'}^{m''}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^0)\\
&=\lim_{n\to\infty}\frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})}\sum_{i=0}^{n}F(g_{\mathbf{x}}^i)\chi(g_{\mathbf{x}}^{i-m}|R_1^0)\\
&\quad\times\prod_{j=m'}^{m''}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^0), \quad \text{(B2)}
\end{aligned}$$

where m is an index contained in $\{1_{m'}^{m''}\}$. Since if and only if $g\in R_1^0$ then g passes through Ξ^*, the following equation holds for an arbitrary integer n:

$$\chi(g_{\mathbf{x}}^0|R_1^0)=I\left\{\left[\int_{t_n^{\Sigma^+}(\mathbf{x})}^{t_{n+1}^{\Sigma^+}(\mathbf{x})}dt\ \chi(\mathbf{x}_t|\Xi^*)\right]\neq 0\right\}, \quad \text{(B3)}$$

or

$$\chi(g_{\mathbf{x}}^n|R_1^0)=J\left[\int_{t_n^{\Sigma^+}(\mathbf{x})}^{t_{n+1}^{\Sigma^+}(\mathbf{x})}dt\ \chi(\mathbf{x}_t|\Xi)\right]\int_{t_n^{\Sigma^+}(\mathbf{x})}^{t_{n+1}^{\Sigma^+}(\mathbf{x})}dt\ \chi(\mathbf{x}_t|\Xi^*), \quad \text{(B4)}$$

where $J(a)$ is a function defined to be

$$J(a):=\begin{cases}1/a & \text{if } a\neq 0\\ 0 & \text{if } a=0\end{cases}. \quad \text{(B5)}$$

Then, we obtain

$$\begin{aligned}
\chi(g_{\mathbf{x}}^n|R_1^0)&=J[\tau_\Xi(g_{\mathbf{x}}^n)]\int_{t_n^{\Sigma^+}(\mathbf{x})}^{t_{n+1}^{\Sigma^+}(\mathbf{x})}dt\ \chi(\mathbf{x}_t|\Xi^*)\\
&=\int_{t_n^{\Sigma^+}(\mathbf{x})}^{t_{n+1}^{\Sigma^+}(\mathbf{x})}dt\ J[\tau_\Xi(g_{\mathbf{x}_t}^0)]\chi(\mathbf{x}_t|\Xi^*), \quad \text{(B6)}
\end{aligned}$$

where $\tau_\Xi(g)$ is a temporal length of $g\cap\Xi$

$$\tau_\Xi(g):=\int_{t_0^{\Sigma^+}(\mathbf{x})}^{t_1^{\Sigma^+}(\mathbf{x})}dt\ \chi(\mathbf{x}_t|\Xi), \quad \text{(B7)}$$

where $\mathbf{x}$ is an arbitrary point on g. From Eqs. (B2) and (B6)

$$\begin{aligned}
&\lim_{n\to\infty}\frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})}\sum_{i=0}^{n}F(g_{\mathbf{x}}^i)\prod_{j=m'}^{m''}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^0)\\
&=\lim_{n\to\infty}\frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})}\sum_{i=0}^{n}F(g_{\mathbf{x}}^i)\\
&\quad\times\left[\int_{t_{i-m}^{\Sigma^+}(\mathbf{x})}^{t_{i-m+1}^{\Sigma^+}(\mathbf{x})}dt\ J[\tau_\Xi(g_{\mathbf{x}_t}^0)]\chi(\mathbf{x}_t|\Xi^*)\right]\\
&\quad\times\prod_{j=m'}^{m''}\chi(g_{\mathbf{x}}^{i-j}|R_{s_j}^0)\\
&=\lim_{n\to\infty}\frac{1}{t_{n+1}^{\Sigma^+}(\mathbf{x})-t_0^{\Sigma^+}(\mathbf{x})}\sum_{i=0}^{n}\int_{t_{i-m}^{\Sigma^+}(\mathbf{x})}^{t_{i-m+1}^{\Sigma^+}(\mathbf{x})}dt\ F(g_{\mathbf{x}_t}^m)\\
&\quad\times J[\tau_\Xi(g_{\mathbf{x}_t}^0)]\chi(\mathbf{x}_t|\Xi^*)\prod_{j=m_1}^{m_2}\chi(g_{\mathbf{x}_t}^{m-j})|R_{s_j}^0)\\
&=\left\langle F(g_{\mathbf{x}}^m)J[\tau_\Xi(g_{\mathbf{x}}^0)]\chi(\mathbf{x}|\Xi^*)\prod_{j=m_1}^{m_2}\chi(g_{\mathbf{x}}^{m-j}|R_{s_j}^0)\right\rangle\\
&=\left[\int_{\Xi^*}d\mathbf{x}\frac{f(g_{\mathbf{x}}^m)}{\tau_\Xi(g_{\mathbf{x}}^0)}\prod_{j=m_1}^{m_2}\chi(g_{\mathbf{x}}^{m-j}|R_{s_j}^0)\right]\Big/\left[\int_\Gamma d\mathbf{x}\right]\\
&=\langle\chi(\mathbf{x}|\Xi^*)\rangle\left\langle\frac{F(g_{\mathbf{x}}^m)}{\tau_\Xi(g_{\mathbf{x}}^0)}\prod_{j=m_1}^{m_2}\chi(g_{\mathbf{x}}^{m-j}|R_{s_j}^0)\right\rangle_{\Xi^*}. \quad \text{(B8)}
\end{aligned}$$

From Eqs. (63) and (B8)

$$S_C(\tau)=\frac{\langle\theta[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^m)-\tau]/\tau_\Xi(g_{\mathbf{x}}^0)\Pi_{j=m_\triangleright}^{m_\triangleleft}\chi(g_{\mathbf{x}}^{m-j}|R_{s_j}^0)\rangle_{\Xi^*}}{\langle 1/\tau_\Xi(g_{\mathbf{x}}^0)\Pi_{j=m_\triangleright}^{m_\triangleleft}\chi(g_{\mathbf{x}}^{m-j}|R_{s_j}^0)\rangle_{\Xi^*}}, \quad \text{(B9)}$$

where $(s_{m\triangleleft}\cdots s_1.s_0\cdots s_{m_\triangleright}):=C$, and m is an integer contained in $\{1_{m_\triangleright}^{m_\triangleleft}\}$.

From Eqs. (66) and (B8)

$$D_C^{C'}(\tilde{\iota})=\frac{\langle Q_{\mathrm{seg}}(g_{\mathbf{x}}^{m_1})\theta_{(\tilde{\iota}-1/2)\Delta t}^{(\tilde{\iota}+1/2)\Delta t}[\tau_{\mathrm{seg}}(g_{\mathbf{x}}^{m_1})]/\tau_\Xi(g_{\mathbf{x}}^0)\Pi_{j=m_\triangleright-1}^{m_\triangleleft}\chi(g_{\mathbf{x}}^{m_1-j}|R_{s_j}^0)\rangle_{\Xi^*}}{\langle 1/\tau_\Xi(g_{\mathbf{x}}^0)\Pi_{j=m_\triangleright}^{m_\triangleleft}\chi(g_{\mathbf{x}}^{m_2-j}|R_{s_j}^0)\rangle_{\Xi^*}}, \quad \text{(B10)}$$

where $(s_{m_\triangleleft}\cdots s_1.s_0\cdots s_{m_\triangleright}):=C$, $(s_{m_\triangleleft-1}\cdots s_0.s_{-1}\cdots s_{m_\triangleright-1}):=C'$, and m_1 and m_2 are integers contained in $\{1^{m_\triangleleft}_{m_\triangleright-1}\}$ and $\{1^{m_\triangleleft}_{m_\triangleright}\}$, respectively.

The numerator on the right-hand side of Eq. (75) is

$$\begin{aligned}
&\langle\chi(g^0_{\mathbf{x}_{-\varepsilon}}|\underline{0})\chi(g^0_{\mathbf{x}_\varepsilon}|\underline{1})\delta[q_\diamond(\mathbf{x})-q^0_\diamond]\dot{q}_\diamond(\mathbf{x})\rangle\\
&=\lim_{n\to\infty}\frac{1}{t^{\Sigma^+}_{n+1}(\mathbf{x})-t^{\Sigma^+}_0(\mathbf{x})}\sum_{i=0}^{n}\int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})}\\
&\quad\times dt\ \chi(g^0_{\mathbf{x}_{-\varepsilon+1}}|\underline{0})\chi(g^0_{\mathbf{x}_{\varepsilon+1}}|\underline{1})\delta[q_\diamond(\mathbf{x}_t)-q^0_\diamond]\dot{q}_\diamond(\mathbf{x}_t)\\
&=\lim_{n\to\infty}\frac{1}{t^{\Sigma^+}_{n+1}(\mathbf{x})-t^{\Sigma^+}_0(\mathbf{x})}\sum_{i=0}^{n}\chi(g^i_{\mathbf{x}}|\underline{01})\\
&=\lim_{n\to\infty}\frac{1}{t^{\Sigma^+}_{n+1}(\mathbf{x})-t^{\Sigma^+}_0(\mathbf{x})}\sum_{i=0}^{n}\prod_{j=m_\triangleright}^{m_\triangleleft+1}\chi(g^{i-j}_{\mathbf{x}}|R^0_{s_j})\\
&=\langle\chi(\mathbf{x}|\Xi^*)\rangle\left\langle\frac{1}{\tau_\Xi(g^0_{\mathbf{x}})}\prod_{j=m_\triangleright}^{m_\triangleleft+1}\chi(g^{m_\triangleright-j}_{\mathbf{x}}|R^0_{s_j})\right\rangle_{\Xi^*},
\end{aligned}\tag{B11}$$

where the second step comes from

$$\int_{t_i^{\Sigma^+}}^{t_{i+1}^{\Sigma^+}}dt\ \delta[q_\diamond(\mathbf{x}_t)-q^0_\diamond]\dot{q}_\diamond(\mathbf{x}_t)=1.\tag{B12}$$

Rearranging this equation, we obtain

$$\begin{aligned}
&\langle\chi(g^0_{\mathbf{x}_{-\varepsilon}}|\underline{0})\chi(g^0_{\mathbf{x}_\varepsilon}|\underline{1})\delta[q_\diamond(\mathbf{x})-q^0_\diamond]\dot{q}_\diamond(\mathbf{x})\rangle\\
&=\langle\chi(\mathbf{x}|\Xi^*)\rangle\\
&\quad\times\left\langle\frac{1}{\tau_\Xi(g^0_{\mathbf{x}})}\chi(g^{m_\triangleright-m_\triangleright}_{\mathbf{x}}|R^0_1)\prod_{j=m_\triangleright+1}^{m_\triangleleft+1}\chi(g^{m_\triangleright-j}_{\mathbf{x}}|R^0_0)\right\rangle_{\Xi^*}\\
&=\langle\chi(\mathbf{x}|\Xi^*)\rangle\left\langle\frac{1}{\tau_\Xi(g^0_{\mathbf{x}})}\prod_{j=m_\triangleright}^{m_\triangleleft}\chi(g^{m_\triangleright-1-j}_{\mathbf{x}}|R^0_0)\right\rangle_{\Xi^*}.
\end{aligned}\tag{B13}$$

The NDOS of a cell $(s_{m_\triangleleft}\cdots s_1.s_0\cdots s_{m_\triangleright}):=C\neq\underline{0}$ is obtained from

$$\begin{aligned}
&\langle\chi(g^0_{\mathbf{x}}|C)\rangle\\
&=\lim_{n\to\infty}\frac{1}{t^{\Sigma^+}_{n+1}(\mathbf{x})-t^{\Sigma^+}_0(\mathbf{x})}\sum_{i=0}^{n}\int_{t_i^{\Sigma^+}(\mathbf{x})}^{t_{i+1}^{\Sigma^+}(\mathbf{x})}dt\ \chi(g^0_{\mathbf{x}_t}|C)\\
&=\lim_{n\to\infty}\frac{1}{t^{\Sigma^+}_{n+1}(\mathbf{x})-t^{\Sigma^+}_0(\mathbf{x})}\sum_{i=0}^{n}\chi(g^i_{\mathbf{x}}|C)\tau_{\mathrm{seg}}(g^i_{\mathbf{x}})\\
&=\langle\chi(\mathbf{x}|\Xi^*)\rangle\left\langle\frac{\tau_{\mathrm{seg}}(g^m_{\mathbf{x}})}{\tau_\Xi(g^0_{\mathbf{x}})}\prod_{j=m_\triangleleft}^{m_\triangleright}\chi(g^{m-j}_{\mathbf{x}}|R^0_{s_j})\right\rangle_{\Xi^*},
\end{aligned}\tag{B14}$$

where m is an integer contained in $\{1^{m_\triangleleft}_{m_\triangleright}\}$.

Although the values of phase space integrals contained in Eqs. (B9), (B10), and (B14) should not depend on the choice of m [or m_1 and m_2 for $D_C^{C'}(\tilde{\tau})$], theoretically, they are not so for numerical calculations owing to errors. Then, we regard the arithmetic mean values among available m (or m_1 and m_2) as the estimators of the integrals. Therefore, we obtain Eqs. (67), (68), and (77).

APPENDIX C: PSEUDOCODE

The Monte Carlo integration and trajectory calculations for SM*l*-PST can be expressed in pseudocode as follows:

```
(1)  Draw a point x by Monte Carlo sampling procedure;
(2)  If (x∈Ξ){
(3)      y_I:=y_I+1/Ω(x);
(4)      c:=c+1.0;
(5)      If (c>d_skip and n_IV<N_IV){
(6)          c:=c−d_skip;
(7)          n_II:=n_II+1;
(8)          Evolve x until the passage across a hypersurface
               η in both the forward and the backward time
               directions, and let x^+ and x^− be the two end
               points x^+=x_{t^+} and x^−=x_{t^−}(t^−<0<t^+);
(9)          If (x∈Ξ*){
(10)             w_current:=w(x);
(11)             w_sum:=w_sum+w_current
(12)             n_III:=n_III+1;
(13)             If (n_III<N_0){
(14)                 If (w_max<w_current)w_max:=w_current;
(15)             } else if (w_current>F_w.w_max.Rand){
(16)                 n_IV:=n_IV+1;
(17)                 Evolve x^+ during 2l+1 times passage
                       across Σ^± in the forward time direc-
                       tion;
(18)                 Evolve x^− during 2l+1 times passage
                       across Σ^± in the backward time di-
                       rection;
(19)                 Store the trajectory data (w_current, a set
                       of times at which it passes across
                       Σ^±, a set of times at which it passes
                       across ξ, and the corresponding tran-
                       sition probabilities) in a storage;
(20)             }
(21)         }
(22)     }
(23) }
(24) y:=y+1/Ω(x);
```

In this code, N_{IV}, N_0, F_w, and I are constants (N_0 must be much smaller than N_{IV}, typically $N_0=N_{\mathrm{IV}}/100$). Rand is a uniform random fraction generator within zero to one, and $\Sigma^\pm:=\{\mathbf{x}\in\Gamma|q_0(\mathbf{x})=q_0^0\}$. The hypersurface η in line 8 is decided empirically so that $\{\mathbf{x}_t|t_-<t<t_-^{\Sigma^\pm}\}\cap\xi=\varnothing$ and $\{\mathbf{x}_t|t_+<t<t_+^{\Sigma^\pm}\}\cap\xi=\varnothing$ for all phase point $\mathbf{x}\in\Xi$, where t_+ and t_- is defined in the pseudo code, $t_+^{\Sigma^\ddagger}:=\min\{t>0|\mathbf{x}_t\in\Sigma^\ddagger\}$, and $t_-^{\Sigma^\pm}:=\max\{t<0|\mathbf{x}_t\in\Sigma^\pm\}$. The hypersurface η is used for an efficient decision whether a phase point $\mathbf{x}\in\Xi$ is contained in Ξ^*: if and only if $\{\mathbf{x}_t|t_-<t<t_+\}\cap\neq\varnothing$ then $\mathbf{x}$ is contained in Ξ^*. The variables y, y_1, n_{II}, n_{III}, n_{IV}, c, $w_{\max}$, and w_{sum} are initialized as zero beforehand. The code is repeated N_{MC} times. For the repetition, the variable d_{skip} is occasionally regulated so that the predicted value of n_{IV} at

the end of the loop exceeds N_{IV} by only a small amount. After completion of the loop, the integrals $\langle \chi(\mathbf{x}|\Xi^*)\rangle$ and $\langle w(\mathbf{x})F(\mathbf{x})\rangle$ are estimated as

$$\langle \chi(\mathbf{x}|\Xi^*)\rangle \simeq \frac{n_{\mathrm{III}} y_{\mathrm{I}}}{n_{\mathrm{II}} y}, \tag{C1}$$

$$\langle w(\mathbf{x})F(\mathbf{x})\rangle \simeq \frac{w_{\mathrm{sum}}}{2n_{\mathrm{IV}} n_{\mathrm{III}}} \sum_{\mathbf{x}\in\mathcal{X}_{\mathrm{IV}}} [F(\mathbf{x})+F(\mathbf{x}')], \tag{C2}$$

where $\mathbf{x}'$ denotes the time reversal of $\mathbf{x}$, and $F(\mathbf{x})$ and $F(\mathbf{x}')$ are calculated from the stored data.

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