Secular Dynamics in Intramolecular Vibrational Energy Redistribution and Secular Increase of Relative Entropy

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An irreversible character of the intramolecular vibrational energy redistribution (IVR) is discussed, and a novel definition of entropy of molecular vibration is proposed. A generalized master equation having a non-Markovian memory kernel for the occupation probability (squared modulus of the probablity amplitude) is derived from the Schrödinger equation. Long-time behavior of the occupation probability is analyzed by the renormalization-group method. The occupation probability exhibits secular motion when recurrences of the memory kernel are suppressed by an exponential-damping factor $e^{-\epsilon t}$. The secular motion obeys a Markovian master equation and represents quasi-irreversible dynamics, which is embedded in the reversible quantum dynamics and caused by the suppression of the recurrences. Transition rates of the quasi-irreversible dynamics are discussed in connection with molecular absorption spectra. The ϵ-dependence of the transition matrix clarifies the mechanism giving rise to the quasi-irreversibility. The irreversible character of the secular dynamics can be utilized to estimate the entropy, which indicates the extent of the IVR proceeded up to a given time.

1. Introduction

The study of molecular reaction dynamics has shown that the energy transfer among vibrational degrees of freedom takes a crucial role in dynamical processes, such as chemical reaction and molecular dissociation, particularly when polyatomic molecules are involved.[1,2] This energy transfer is called intramolecular vibrational energy redistribution (IVR) and has long been a target of many experimental and theoretical studies.[2−4]

The simplest classical picture of IVR is uniform distribution of the energy among the vibrational degrees of freedom. In this sense, IVR can be interpreted as randomization caused in the approach to the microcanonical equilibrium. From the quantum mechanical point of view, IVR is a diffusion of probablity amplitudes over the quantum states under conservation of the total energy. The wave function is continuously deformed in the course of IVR and finally acquires a very complicated shape. In this context, IVR has often been discussed in connection with quantum chaos.[5−8] Several attempts to define a measure that indicates the complexity of wave function have been reported.[9−11] The main problem in these studies originates from the fact that IVR is strictly reversible pure-state dynamics. In consequence, the von Neumann entropy of the pure-state densty operator is always zero and not very useful as a measure of IVR. Heller proposed a measure on the basis of a volume of the classical phase space swept by the distribution function up to a given time.[9] Although the measure of Heller is a good measure for ergodicity, it does not represent the complexity of wave function. On the other hand, Remacle and Levine proposed a kind of relative entropy on the basis of the maximum entropy formalism.[11] The relative entropy (or conditional entropy) is defined as

$$S(t) = -\sum_j p_j(t) \ln \frac{p_j(t)}{n_j} \tag{1}$$

where $p_j(t)$ is the occupation probablity of a quantum state or of a group of quantum states:

$$p_j(t) \equiv \sum_{\mu=1}^{n_j} |\langle j\mu|\Psi(t)\rangle|^2 \tag{2}$$

Here, $|\Psi(t)\rangle$ is the wave function of the system and $|j\mu\rangle$ is a basis state, where j is the index of group and μ specifies the member of group. Remacle and Levine discussed the case in which $p_1 = |\langle\Psi(0)|\Psi(t)\rangle|^2$. The entropy of Remacle and Levine oscillates in accordance with the oscillation of $|\langle\Psi(0)|\Psi(t)\rangle|^2$ as shown in section 5 of the present paper. This oscillation is quantum dephasing caused by motion of a wave packet traveling to and fro in the configuration space.

The purpose of the present study is to define a measure of IVR that does not increase with the reversible dephasing but does increase monotonically with the irreversible approach to the equilibrium. For this purpose we need to extract irreversibility from the dynamics of $p_j(t)$ and to clarify the condition to encounter the irreversibility.

Irreversible dynamics in molecular processes, such as internal conversion and intersystem crossing, has successfully been described by the theory of radiationless transition.[12,13] The basic assumption of the latter theory is the existence of densely located energy levels giving rise to a quasicontinuum. This assumption is equivalent to disregard of recurrences. It is valid when the recurrence time is much longer than the time scale of chemical interest. A nonstationary state prepared, for example, by a pulsed-laser excitation undergoes exponential decay when it is coupled with a quasicontinuum. In the present paper we name such decay "quasi-irreversibility" because it is the irreversibility caused by the disregard of recurrences. Recent studies have shown that IVR sometimes consists of several different molecular motions, each having a different time scale.[3,14−23] The dynamics of the longest time scale can be regarded as irrevers-

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ible decay like radiationless transition upon disregard of the reccurences. In this case, extraction of quasi-irreversible dynamics can be achieved by disregarding the recurrences of the longest time scale.

Irreversible time evolution can be described by master equations. It is known that the relative entropy increases monotonically when the time evolution of $p_j(t)$ obeys a Markovian master equation satisfying the detailed balance condition.[24] The Markovian master equation is a fundamental tool for describing rate processes in macroscopic chemical kinetics[2] and photochemistry.[25] All these chemical processes are results of molecular motions governed by the Schrödinger equation. To discuss the connection between the Schrödinger equation and the master equation is a fundamental issue in statistical physics as well as physical chemistry.[26]

The study on the microscopic foundation of master equations has a long history. Van Kampen derived the master equation under the assumption of cancellation of phase factors caused by "molecular chaos".[27] The validity of this assumption, however, was left to be an open question. Van Hove presented a different derivation without assuming the phase cancellation.[28] He assumed, however, that the system has a continuous energy spectrum. Zwanzig discussed a generalized master equation satisfied by density operator.[29] In his theory the memory kernel of the generalized master equation is assumed to decline with time. There are several variations of master equations.[30−34] For example, Robertson presented a generalized version of Zwanzig's equation.[35,36] All of these master equations are not Markovian as far as they are equivalent to the Schrödinger equation. Pursuits have been continued in order to derive dissipative dynamics from quantum and classical mechanics.[37] The most fundamental study concerning the origin of irreversibility has continuously been pursued by Prigogine and coworkers.[38]

In the present paper, we derive the Markovian master equation without postulating a quasicontinuum nor a decline of memory kernel, and we define a measure of IVR that monotonically increases with time. In section 2, a generalized master equation for $p_j(t)$ is derived from the Schrödinger equation. In section 3, we analyze long-time behavior of $p_j(t)$ by use of the renormalization-group method.[39] When the recurrences of the memory kernel are suppressed by the damping factor $e^{-\epsilon t}$, the secular motion of $p_j(t)$ appears, and it obeys a Markovian master equation. The relative entropy of the secular motion is a monotonically increasing function of time and is a desirable measure of IVR. In section 4, we examine the transition matrix of the master equation, and particularly analyze its dependence on the damping parameter ϵ. The finite ϵ is shown to give rise to a nonzero transition matrix. This implies that quasi-irreversibility arises in a generic situation. Numerical examples are shown in section 5. The ϵ-dependence of the transition matrix clarifies the mechanism causing the quasi-irreversibility. The numerical results illustrate that the present formalism successfully describes the secular dynamics of IVR.

2. Generalized Master Equation Derived from the Schrödinger Equation

The goal of this section is to derive the equation of motion for occupation probability, $p_j(t)$, from the Schrödinger equation. In order to handle $p_j(t)$ in quantum mechanical formalism, it is useful to define the projection operator:

$$P_j \equiv \sum_{\mu=1}^{n_j} |j\mu\rangle\langle j\mu| \tag{3}$$

The occupation probablity can be expressed by expectation value of P_j as $p_j(t) = Tr\{\rho(t)P_j\}$, where $\rho(t)$ is the density operator. Mori discussed equations of motion for expectation values in his well-known formalism.[40,41] Here, we obey his prescription, in which we need an inner product and a projection operator in the Liouville space. We define the inner product as $(A|B) \equiv Tr\{A^\dagger B\}$, and the projection operator as

$$\mathcal{P} \equiv \sum_j \frac{|P_j)(P_j|}{(P_j|P_j)} = \sum_j \frac{1}{n_j}|P_j)(P_j| \tag{4}$$

Here, $(\cdot|$ and $|\cdot)$ represent bra and ket in the Liouville space, and we used the property $(P_j|P_j) = Tr\{P_j\} \equiv n_j$. The time-dependent ket is defined as

$$|P_j(t)) \equiv e^{i\mathcal{L}t/\hbar}|P_j) = e^{iHt/\hbar}P_j e^{-iHt/\hbar} \tag{5}$$

where $\mathcal{L}X \equiv [H, X]$. The starting point of our formalism is the operator identity

$$e^{i(A+B)t/\hbar} = e^{iAt/\hbar} + \frac{i}{\hbar}\int_0^t dt'\, e^{i(A+B)(t-t')/\hbar}Be^{iAt'/\hbar} \tag{6}$$

The proof is given in Appendix A. By choosing the operators as $A \equiv (1 - \mathcal{P})\mathcal{L}$ and $B \equiv \mathcal{P}\mathcal{L}$, eq 6 is written as

$$e^{i\mathcal{L}t/\hbar} = e^{i(1-\mathcal{P})\mathcal{L}t/\hbar} + \frac{i}{\hbar}\int_0^t dt'\, e^{i\mathcal{L}(t-t')/\hbar}\mathcal{P}\mathcal{L}e^{i(1-\mathcal{P})\mathcal{L}t'/\hbar} \tag{7}$$

which immediately leads to

$$e^{i\mathcal{L}t/\hbar}|P_j) = e^{i(1-\mathcal{P})\mathcal{L}t/\hbar}|P_j) + \frac{i}{\hbar}\sum_l \int_0^t dt'\, e^{i\mathcal{L}(t-t')/\hbar}|P_l)\frac{1}{n_l}(P_l|\mathcal{L}\, e^{i(1-\mathcal{P})\mathcal{L}t'/\hbar}|P_j) \tag{8}$$

Multiplying $(P_k|$ from the left, we obtain

$$(P_k|P_j(t)) = \frac{i}{\hbar}\sum_l \int_0^t ds\, (P_k|e^{i\mathcal{L}s/\hbar}|P_l)\frac{1}{n_l}(P_l|\mathcal{L}e^{i(1-\mathcal{P})\mathcal{L}(t-s)/\hbar}|P_j) \tag{9}$$

Here, we used $(P_k|(1 - \mathcal{P}) = 0$ and changed the integration variable to $s \equiv t - t'$. Differentiating both sides with respect to t, we obtain

$$\frac{d}{dt}(P_k|P_j(t)) = -\frac{1}{\hbar^2}\sum_l \int_0^t ds\, (P_k|P_l(s))\frac{1}{n_l}(P_l|\mathcal{L}\, e^{i(1-\mathcal{P})\mathcal{L}(t-s)/\hbar}(1 - \mathcal{P})\mathcal{L}\,|P_j) \tag{10}$$

Here, we used the property

$$(P_l|\mathcal{L}|P_j) = Tr\{P_l[H,P_j]\} = Tr\{P_lHP_j - P_lP_jH\} = 0 \tag{11}$$

By using the notation $P_{jk}(t) \equiv (P_k|P_j(t))$ and changing the integration variable back to $t' = t - s$, eq 10 can be written in the matrix notation as

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}(t) = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t'\, \mathbf{K}(t')\mathbf{n}^{-1}\mathbf{P}(t-t') \tag{12}$$

where the element of the memory-kernel matrix, $\mathbf{K}(t)$, is defined as

$$K_{jl}(t) \equiv (P_j|L\, \mathrm{e}^{i(1-P)Lt/\hbar}(1-P)L\,|P_j) \tag{13}$$

and $\mathrm{n} \equiv diag(n_1,n_2,...,n_N)$. Equation 12 is the basic equation of the present formalism. It is derived from the Schrödinger equation without any approximation. In the following sections, we analyze the behavior of the memory kernel $\mathbf{K}(t)$ on the basis of eq 12.

We proceed to the next step to obtain equations of motion for $p_j(t)$. By use of the inner product in Liouville space, $p_j(t)$ can be expressed as $p_j(t) = (\rho(0)|p_j(t))$. If we assume that the initial density operator $\rho(0)$ is in P space, i.e., $P|\rho(0)) = |\rho(0))$, then $p_j(t)$ can be written as

$$p_j(t) = \sum_k \frac{1}{n_k}(\rho(0)|P_k)(P_k|P_j(t)) \tag{14}$$

An elementary manipulation on eq 10 leads to the equations of motion:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{p}(t) = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t'\, \mathbf{K}(t')\mathbf{n}^{-1}\mathbf{p}(t-t') \tag{15}$$

This is a generalized master equation with memory. The non-Markovness originates from the coherency of quantum dynamics. The memory retains the information carried in the phase of quantum probability amplitudes. There is a parallelism between eq 15 and Zwanzig's equation.[29] They differ, however, in that eq 15 is a set of finite number of equations for scalar functions in contrast to Zwanzig's equation for the operator.

It is useful to carry out the Fourier transform when we handle eqs 12 and 15. We define the Fourier transforms of $\mathbf{P}(t)$ and $\mathbf{K}(t)$ as

$$\mathbf{\Pi}_\epsilon(\omega) \equiv \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\epsilon t}\mathrm{e}^{i\omega t}\mathbf{P}(t) \tag{16}$$

and

$$\mathbf{X}_\epsilon(\omega) \equiv \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\epsilon t}\mathrm{e}^{i\omega t}\mathbf{K}(t) \tag{17}$$

respectively. The factor $\mathrm{e}^{-\epsilon t}$ is the convergence factor. In the usual situation, the limit $\epsilon \to 0$ is taken. In the present paper, however, we retain ϵ to be finite in order to suppress the recurrences. The physical meaning and role of the damping factor $\mathrm{e}^{-\epsilon t}$ is discussed in section 4. It follows from eq 12 that $\Pi_\epsilon(\omega)$ and $\mathbf{X}_\epsilon(\omega)$ satisfy (see Appendix B)

$$\mathbf{X}_\epsilon(\omega) = \hbar^2[i(\omega + i\epsilon)\mathbf{n} + \mathbf{n}\mathbf{\Pi}_\epsilon(\omega)^{-1}\mathbf{n}] \tag{18}$$

3. Long-Time Behavior

3.A. Van Hove Limit. Zwanzig discussed the Markovian limit of his generalized master equation.[29] He considered long-time behavior of a weakly perturbed system assuming that his memory kernel declines as $t \to \infty$. We follow Zwanzig in that we also discuss long-time behavior of a system with weak perturbation, but we do not assume that our memory kernel, $\mathbf{K}(t)$, decays as $t \to \infty$.

We consider the Hamiltonian that consists of the unperturbed part H_0 and the perturbation λV as $H = H_0 + \lambda V$. We examine the limit, known as the van Hove limit,[29] $\lambda \to 0$ and $t \to \infty$, retaining $\lambda^2 t$ to be finite. In other words, we consider the limit of weak perturbation, but we examine the long-time limit, in which even very weak perturbation gives rise to a nontrivial effect. We assume $\mathrm{p}(t)$ to be stationary if the perturbation is turned off, i.e., $[H_0, P_j] = 0$. The memory kernel $\mathbf{K}(t)$ is shown to be on the order of magnitude of λ^2 (see Appendix C). Hereafter, we write $\mathbf{K}(t)$ as $\lambda^2\mathbf{K}(t)$ so as to indicate explicitly that $\mathbf{K}(t) \sim o(\lambda^2)$. Thus, we can write as

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{p}(t) = -\frac{\lambda^2}{\hbar^2}\int_0^t \mathrm{d}t'\, \mathbf{K}(t')\mathrm{n}^{-1}\mathbf{p}(t-t') \tag{19}$$

The naive perturbation expansion leads to

$$\mathbf{p}(t) = \left[1 - \frac{\lambda^2}{\hbar^2}\mathbf{J}(t)\mathrm{n}^{-1}\right]\mathbf{p}(0) + o(\lambda^4) \tag{20}$$

where

$$\mathbf{J}(t) \equiv \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \mathbf{K}(t_2) \tag{21}$$

The derivation is given in Appendix D. In the limit of $t \to \infty$, $\mathbf{J}(t)$ may diverge or oscillate. The perturbation expansion is valid only when the term $(\lambda/\hbar)^2\mathbf{J}(t)\mathrm{n}^{-1}$ is much smaller than unity. In order to examine the behavior in long time when $\mathbf{J}(t)$ may diverge, we need a singular perturbation treatment.

3.B. Renormalization-Group Method. In this section, we analyze long-time behavior of $\mathbf{p}(t)$ on the basis of the renormalization-group method, a powerful tool of singular perturbation.[39] In order to carry out the renormalization, we need to know the asymptotic behavior of $\mathbf{J}(t)$ in the limit of $t \to \infty$. We begin with an intuitive argument. The memory kernel $\mathbf{K}(t)$ is presumably an oscillatory function of time. The indefinite integral of $\mathbf{K}(t)$ has, as $t \to \infty$, a constant baseline, around which certain oscillation is added. The second indefinite integral, i.e., $\mathbf{J}(t)$, should exhibit divergence proportional to t. In other words, the limit

$$\bar{\mathbf{K}} \equiv \lim_{t\to\infty}\frac{1}{t}\mathbf{J}(t) \tag{22}$$

exists. The existence of the limit is further discussed in section 4. We can write $\mathbf{J}(t) = \bar{\mathbf{K}}t + \tilde{\mathbf{K}}(t)$, where $\tilde{\mathbf{K}}(t)$ is an oscillatory function. Substitution of this into eq 20 leads to

$$\mathbf{p}(t) = \left[1 - \frac{\lambda^2}{\hbar^2}t\bar{\mathbf{K}}\mathrm{n}^{-1} - \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}(t)\mathrm{n}^{-1}\right]\mathbf{p}_0 + o(\lambda^4) \tag{23}$$

where $\mathbf{p}_0 = \mathbf{p}(0)$. We follow the renormalization-group prescription.[39] By inserting the counter term $(\lambda^2/\hbar^2)\tau\bar{\mathbf{K}}\mathrm{n}^{-1}$, we obtain

$$\mathbf{p}(t) = \left[1 - \frac{\lambda^2}{\hbar^2}(t-\tau)\bar{\mathbf{K}}\mathrm{n}^{-1} - \frac{\lambda^2}{\hbar^2}\tau\bar{\mathbf{K}}\mathrm{n}^{-1} - \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}(t)\mathrm{n}^{-1}\right]\mathbf{p}_0 + o(\lambda^4)$$

$$= \left[1 - \frac{\lambda^2}{\hbar^2}(t-\tau)\bar{\mathbf{K}}\mathrm{n}^{-1} - \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}(t)\mathrm{n}^{-1}\right]\mathbf{q}_0(\tau) + o(\lambda^4) \tag{24}$$

where τ is an arbitrary and artificial parameter. In the second equality, we introduced the renormalized initial condition $\mathbf{q}_0(\tau)$ to which the counter term is absorbed. According to the

renormalization-group theory, we determine $\mathbf{q}_0(\tau)$ so as to satisfy the renormalization-group equation

$$\left(\frac{\partial \mathbf{p}(t)}{\partial \tau}\right)_{\tau=t} = 0 \tag{25}$$

i.e., the condition that the artificial parameter τ does not affect $\mathbf{p}(t)$. From eq 24 the renormalization-group equation can be written as

$$\left[1 - \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}(t)\mathrm{n}^{-1}\right]\left(\frac{\mathrm{d}\mathbf{q}_0(\tau)}{\mathrm{d}\tau}\right)_{\tau=t} + \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}\mathrm{n}^{-1}\mathbf{q}_0(t) + o(\lambda^4) = 0 \tag{26}$$

which immediately leads to

$$\begin{aligned}\frac{\mathrm{d}\mathbf{q}_0(t)}{\mathrm{d}t} &= -\left[1 - \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}(t)\mathrm{n}^{-1}\right]^{-1}\frac{\lambda^2}{\hbar^2}\bar{\mathbf{K}}\mathrm{n}^{-1}\mathbf{q}_0(t) + o(\lambda^4) \\ &= -\frac{\lambda^2}{\hbar^2}\bar{\mathbf{K}}\mathrm{n}^{-1}\mathbf{q}_0(t) + o(\lambda^4)\end{aligned} \tag{27}$$

Since $\mathbf{q}_0(t)$ coincides with $\mathbf{p}_0$ at $t = 0$, we obtain

$$\mathbf{q}_0(t) = \exp\left[-\frac{\lambda^2}{\hbar^2}\bar{\mathbf{K}}\mathrm{n}^{-1}t + o(\lambda^4 t)\right]\mathbf{p}_0 \tag{28}$$

Returning to eq 24, we obtain (notice that we put $\tau = t$)

$$\mathbf{p}(t) = \left[1 - \frac{\lambda^2}{\hbar^2}\tilde{\mathbf{K}}(t)\mathrm{n}^{-1}\right]\exp\left[-\frac{\lambda^2}{\hbar^2}\bar{\mathbf{K}}\mathrm{n}^{-1}t + o(\lambda^4 t)\right]\mathbf{p}_0 + o(\lambda^4) \tag{29}$$

We retain the term on the order of magnitude $\lambda^2 t$. The above equation, therefore, holds good for the time satisfying $1 \ll t \sim \lambda^{-2} \ll \lambda^{-4}$. Time t should be sufficiently large so as to satisfy $\bar{\mathbf{K}} \simeq \mathbf{J}(t)/t$. In short, eq 29 represents the long-time behavior of $\mathbf{p}(t)$.

3.C. Secular Part. Equation 29 indicates that $\mathbf{p}(t)$ contains the part whose time dependence is represented by a matrix exponential. We call it the secular part; i.e., the secular part is defined as

$$\bar{\mathbf{p}}(t) \equiv \exp\left[-\frac{\lambda^2}{\hbar^2}\bar{\mathbf{K}}\mathrm{n}^{-1}t\right]\mathbf{p}_0 \tag{30}$$

We divide $\mathbf{p}(t)$ into the secular part $\bar{\mathbf{p}}(t)$ and the rest $\tilde{\mathbf{p}}(t)$ as $\mathbf{p}(t) = \bar{\mathbf{p}}(t) + \tilde{\mathbf{p}}(t)$. The term $\tilde{\mathbf{p}}(t)$ represents oscillatory behavior of $\mathbf{p}(t)$. It is noteworthy that $\tilde{\mathbf{p}}(t)$ is "proportional" to $\bar{\mathbf{p}}(t)$, i.e., $\tilde{\mathbf{p}}(t) \propto \tilde{\mathbf{K}}(t)\bar{\mathbf{p}}(t)$. If $\tilde{\mathbf{K}}(t)$ is diagonal, eq 29 is parallel to the Hilbert and Chapman−Enskog expansion of the solution to the Boltzmann equation.[26]

As can easily be seen, the secular part $\bar{\mathbf{p}}(t)$ obeys the Markovian master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{\mathbf{p}}(t) = \mathbf{W}\bar{\mathbf{p}}(t) \tag{31}$$

where $\mathbf{W} \equiv -(\lambda^2/\hbar^2)\bar{\mathbf{K}}\mathrm{n}^{-1}$. It can be shown that the transition matrix, $\mathbf{W}$, satisfies the detailed balance relation $W_{jk}n_k = W_{kj}n_j$ (see Appendix E). As eq 30 indicates, the time evolution of $\bar{\mathbf{p}}(t)$ is irreversible. It represents irreversible character embedded in the reversible quantum dynamics. The secular part $\bar{\mathbf{p}}(t)$ is meaningful only if $\bar{\mathbf{K}} \neq 0$. This condition is discussed in section 4.

On the basis of the secular part $\bar{\mathbf{p}}(t)$, we define the secular entropy as

$$\bar{S}(t) \equiv -\sum_j \bar{p}_j(t) \ln \frac{\bar{p}_j(t)}{n_j} \tag{32}$$

It can be shown that $\bar{S}(t)$ increases monotonically with t when $\bar{p}_j(t)$ obeys a Markovian master equation satisfying the detailed balance condition.[24] Therefore, eq 31 guarantees that $\bar{S}(t)$ increases monotonically.

4. Analysis of $\bar{\mathbf{K}}$

4.A. Basic Equation for Estimating $\bar{\mathbf{K}}$ In this section we derive a relation between $\bar{\mathbf{K}}$ and $\mathbf{X}_\epsilon(\omega)$, which is useful in estimating $\bar{\mathbf{K}}$. By the use of the Fourier representation, $\mathbf{J}(t)$ can be written as

$$\begin{aligned}\mathbf{J}_\epsilon(t) &\equiv \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \mathrm{e}^{-\epsilon t_2}\mathbf{K}(t_2) = \\ &\qquad \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega \int_0^t \mathrm{d}t_1 \int_0^{t_1}\mathrm{d}t_2\, \mathrm{e}^{-i\omega t_2}\mathbf{X}_\epsilon(\omega) \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\, \frac{1 - i\omega t - \mathrm{e}^{-i\omega t}}{\omega^2}\mathbf{X}_\epsilon(\omega) \\ &= -i\sum_k \frac{1 - i(\omega_k - i\epsilon)t - \mathrm{e}^{-i(\omega_k - i\epsilon)t}}{(\omega_k - i\epsilon)^2}\mathbf{x}_k\end{aligned} \tag{33}$$

where $\omega_k - i\epsilon$ is the pole of $\mathbf{X}_\epsilon(\omega)$ and $\mathbf{x}_k$ is its residue. From eq 18 we can see that the pole ω_k satisfies the equation $det\Pi_\epsilon(\omega_k) = 0$. In eq 33, the damping factor $\mathrm{e}^{-\epsilon t_2}$ is multiplied to $\mathbf{K}(t_2)$ in order to suppress the recurrences of the memory. To analyze the effect of this artificial damping factor is the main subject of the present section. From eq 33, we obtain

$$\bar{\mathbf{K}}_\epsilon \equiv \lim_{t\to\infty}\frac{\mathbf{J}_\epsilon(t)}{t} = -\sum_k \frac{\mathrm{x}_k}{\omega_k - i\epsilon} \tag{34}$$

If all the poles of $\mathbf{X}_\epsilon(\omega)$ are of the first order, i.e., if all the roots of $det\Pi_\epsilon(\omega_k) = 0$ are nondegenerate, $\mathbf{X}_\epsilon(\omega)$ can be expressed, according to the Mittag−Leffler theorem,[42] by the partial fraction expansion

$$\mathbf{X}_\epsilon(\omega) = \sum_k \frac{\mathrm{x}_k}{\omega - \omega_k + i\epsilon} \tag{35}$$

which contains only the principal part due to the property (see Appendix F)

$$\lim_{\omega\to\infty}\mathbf{X}_\epsilon(\omega) = 0 \tag{36}$$

From eqs 34 and 35, we obtain the relation

$$\bar{\mathbf{K}}_\epsilon = \mathbf{X}_\epsilon(0) \tag{37}$$

On the basis of this relation, we estimate the magnitude of $\bar{\mathbf{K}}_\epsilon$ in the next subsection. Although the derivation of $\bar{\mathbf{K}}_\epsilon$ in section 3 is based on the perturbation, eq 37 does not explicitly contain the unperturbed Hamiltonian H_0. By virtue of it, we can apply the present formalism without specifying H_0 explicitly.

4.B. Estimation of $\bar{\mathbf{K}}_\epsilon$ from Spectroscopic Data. There have been reported several attempts to obtain the dynamical

information from spectra experimentally observed. We can obtain autocorrelation functions from optical absorption spectra[43−45] and mutual-correlation functions from Raman excitation profiles.[46,47] The attempts to define the measure of IVR by several authors[9−11] are also along this direction. In this section we show that information contained in absorption spectra enables us to estimate $\bar{\mathbf{K}}_\epsilon$ under a particular choice of the projection operators.

An absorption spectrum with infinitely fine resolution is given by

$$I(E) = \sum_n a_n \delta(E - E_n) \tag{38}$$

where E_n represents the energy eigenvalue and a_n is the intensity of the spectral line. Under the Condon approximation, a_n is given by the Franck−Condon factor $a_n = |\langle\phi_n|\psi_0\rangle|^2$, where ϕ_n represents the eigenstate and ψ_0 is the initial state of the absorption transition. We choose the projection operators $P_1 \equiv |\phi_0\rangle\langle\phi_0|$, and $P_2 \equiv 1 - P_1$. In this case, $P_{11}(t)$ is written as

$$P_{11}(t) = |\langle\phi_0|\mathrm{e}^{-iHt/\hbar}|\phi_0\rangle|^2 = |\sum_n a_n \mathrm{e}^{-iE_n t/\hbar}|^2 \tag{39}$$

By the Fourier transform, we obtain

$$\Pi_{\epsilon 11}(\omega) = \sum_n \frac{i{a_n}^2}{\omega + i\epsilon} + \sum_{n\neq m} \frac{i a_n a_m}{\omega - \omega_{nm} + i\epsilon} \tag{40}$$

where $\omega_{nm} \equiv (E_n - E_m)/\hbar$. In the limit of $\epsilon \to 0$, the imaginary part of $\Pi_{\epsilon 11}(\omega)$ is known to result in the spectral correlation function.[48] In the present paper, however, ϵ is retained to be finite. It is useful to notice that sum rules

$$\sum_k P_{jk}(t) = \sum_k \mathrm{Tr}\{P_k P_j(t)\} = Tr\{(\sum_k P_k) P_j(t)\} = n_j \tag{41}$$

and

$$\sum_j P_{jk}(t) = \mathrm{Tr}\{P_k(\sum_j P_j(t))\} = n_k \tag{42}$$

hold. These sum rules and the present choice of the projection operators lead to

$$\mathbf{P}(t) = \begin{pmatrix} P_{11}(t) & 1 - P_{11}(t) \\ 1 - P_{11}(t) & P_{11}(t) + N - 2 \end{pmatrix} \tag{43}$$

where N is the total number of quantum states. It follows that $\Pi_\epsilon(\omega)$ is written as

$$\Pi_\epsilon(\omega) = \begin{pmatrix} \Pi_{\epsilon 11}(\omega) & \dfrac{i}{\omega + i\epsilon} - \Pi_{\epsilon 11}(\omega) \\ \dfrac{i}{\omega + i\epsilon} - \Pi_{\epsilon 11}(\omega) & \dfrac{i(N-2)}{\omega + i\epsilon} - \Pi_{\epsilon 11}(\omega) \end{pmatrix} \tag{44}$$

From eqs 37 and 44, $\bar{\mathbf{K}}_\epsilon$ is given by

$$\bar{\mathbf{K}}_\epsilon = \mathbf{X}_\epsilon(0) = -\hbar^2\epsilon\mathrm{n} + \hbar^2\mathrm{n}\Pi_\epsilon(0)^{-1}\mathrm{n} = \hbar^2 k_\epsilon \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \tag{45}$$

where $k_\epsilon \equiv \epsilon(N-1)(1 - \epsilon\Pi_0)/(N\epsilon\Pi_0 - 1)$ and $\Pi_0 \equiv \Pi_{\epsilon 11}(0)$. It follows from eq 40 that

$$\Pi_0 = \frac{1}{\epsilon}\sum_n {a_n}^2 + \sum_{n\neq m} \frac{i a_n a_m}{i\epsilon - \omega_{nm}} = \frac{1}{\epsilon}\sum_n {a_n}^2 + \sum_{n\neq m} \frac{\epsilon a_n a_m}{\epsilon^2 + \omega_{nm}^2} \tag{46}$$

In the second equality we used the property $\omega_{nm} = -\omega_{mn}$. Since $\sum_n a_n = 1$ holds, the spectral intensity, a_n, can be written as

$$a_n = N^{-1} + \delta_n \tag{47}$$

where δ_n represents fluctuation of a_n satisfying $\sum_n \delta_n = 0$. This leads to

$$\sum_n {a_n}^2 = N^{-1} + N^{-1}{\sigma'}^2 \tag{48}$$

where σ' represents the standard deviation divided by the mean value:

$$\sigma' \equiv \left(\frac{1}{N}\sum_n {\delta_n}^2\right)^{1/2} / N^{-1} \tag{49}$$

In consequence, we obtain

$$k_\epsilon = \epsilon \frac{(N-1)\{1 - N^{-1}(1 + {\sigma'}^2) - \Sigma_\epsilon\}}{{\sigma'}^2 + N\Sigma_\epsilon} \tag{50}$$

where

$$\Sigma_\epsilon \equiv \sum_{n\neq m} \frac{\epsilon^2 a_n a_m}{\epsilon^2 + \omega_{nm}^2} \tag{51}$$

By use of eq 50, we can estimate the value of k_ϵ from the spectroscopic data, i.e., the spectral intensity, a_n, and the energy position, E_n.

We examine the behavior of k_ϵ in the limits of $\epsilon \to 0$ and $\epsilon \to \infty$. The Taylor expansion of k_ϵ in eq 50 with respect to ϵ leads to the expression of k_ϵ for small ϵ:

$$k_\epsilon = \epsilon \frac{1}{{\sigma'}^2}(N-1)\left(1 - \frac{1 + {\sigma'}^2}{N}\right) + o(\epsilon^3) \tag{52}$$

In order to examine the limit of $\epsilon \to \infty$, $\epsilon\Pi_0$ is expanded in $1/\epsilon$ as

$$\epsilon\Pi_0 = \sum_n {a_n}^2 + \sum_{n\neq m} \frac{a_n a_m}{1 + (\omega_{nm}/\epsilon)^2} = 1 - \sum_{n\neq m} a_n a_m \left(\frac{\omega_{nm}}{\epsilon}\right)^2 + o\left(\frac{1}{\epsilon^2}\right) \tag{53}$$

where we used the normalization of the spectral intensities, $\sum_n a_n = 1$. It follows that

$$k_\epsilon = \frac{1}{\epsilon}\sum_{n\neq m} a_n a_m {\omega_{nm}}^2 + o\left(\frac{1}{\epsilon^3}\right) \tag{54}$$

Equations 52 and 54 indicate that k_ϵ takes a nonzero value when ϵ is finite. In short, the secular part is shown to exist when the convergence parameter ϵ is retained to be finite. In the next section, the ϵ dependence of $\bar{\mathbf{K}}_\epsilon$ is discussed on the basis of model systems.

5. Examples

5.A. Hierarchical Picket Fence Model. In the present subsection, we consider the level structure

$$E_{n_1 n_2} = \hbar D_1 n_1 + \hbar D_2 n_2 \tag{55}$$

where $n_1 = 1, 2, ..., N_1$ and $n_2 = 1, 2, ..., N_2$, and we assume that $N_1 D_1 \ll D_2$. This level structure involves two different level spacings, D_1 and D_2. Such structure is called hierarchical structure and is known to give rise to dynamics involving motions of two different time scales.[15]

In order to obtain k_ϵ (eq 50), it suffices to estimate Σ_ϵ (eq 51). We assume that the contributions from δ_n terms (see eq 47) approximately cancel with each other. Under this approximation we obtain

$$\Sigma_\epsilon^P = \frac{1}{(N_1 N_2)^2} \sum_{(n_1 m_1) \neq (n_2 m_2)} \frac{\epsilon^2}{\epsilon^2 + \{D_1(n_1 - m_1) + D_2(n_2 - m_2)\}^2}$$

$$\simeq \frac{N_2}{(N_1 N_2)^2} \sum_{n_1 \neq m_1} \frac{\epsilon^2}{\epsilon^2 + D_1^2 (n_1 - m_1)^2} + \frac{N_1^2}{(N_1 N_2)^2} \sum_{n_2 \neq m_2} \frac{\epsilon^2}{\epsilon^2 + D_2^2 (n_2 - m_2)^2} \tag{56}$$

Here, we used $N_1 D_1 \ll D_2$, $N_1 \gg 1$, and $N_2 \gg 1$. It is useful to define a function

$$s_N(x) \equiv \frac{2}{N^2} \sum_{n=1}^{N} \sum_{m=1}^{n-1} \frac{1}{1 + (n-m)^2/x^2} \tag{57}$$

Approximating the sum by integration (see Appendix G), we obtain

$$s_N(x) \simeq \frac{2x}{N} \tan^{-1}\left(x \frac{N-1}{x^2 + N}\right) - \left(\frac{x}{N}\right)^2 \ln\left(\frac{x^2 + N^2}{x^2 + 1}\right) \tag{58}$$

The function $s_N(x)$ can be approximated as

$$s_N(x) \simeq \begin{cases} (2/N)x^2 & x \ll 1 \\ (\pi/N)x & 1 \ll x \ll N \\ 1 - (N^2/6x^2) & N \ll x \end{cases} \tag{59}$$

By substituting eqs 56 and 58 into eq 50, we obtain

$$k_\epsilon = \epsilon \frac{1 - (N_1 N_2)^{-1}(1 + \sigma'^2) - \left\{\frac{1}{N_2} s_{N_1}\left(\frac{\epsilon}{D_1}\right) + s_{N_2}\left(\frac{\epsilon}{D_2}\right)\right\}}{\frac{\sigma^{1/2}}{N_1 N_2} + \frac{1}{N_2} s_{N_1}\left(\frac{\epsilon}{D_1}\right) + s_{N_2}\left(\frac{\epsilon}{D_2}\right)} \tag{60}$$

By the use of eq 59, the ϵ-dependence of k_ϵ can be summarized as

$$k_\epsilon \simeq \begin{cases} (N_1 N_2/\sigma'^2)\epsilon & \epsilon \ll (1/\pi) D_1 \sigma'^2 < D_1 \\ (N_1 N_2/\pi) D_1 & D_1 \ll \epsilon \ll N_1 D_1 \\ N_2 \epsilon & N_1 D_1 \ll \epsilon \ll D_2 \\ N_2 D_2 & D_2 \ll \epsilon \ll N_2 D_2 \\ (N_1 D_1)^2/6\epsilon & N_2 D_2 \ll \epsilon \end{cases} \tag{61}$$

A significant point is that k_ϵ can be regarded as constant in the regions of $D_1 \ll \epsilon \ll N_1 D_1$ and $D_2 \ll \epsilon \ll N_2 D_2$. In other words, k_ϵ is insensitive to the artificial parameter ϵ. This indicates that the master equation has a robust physical meaning. In Figure 1a, k_ϵ (eq 60) is plotted, in which the parameters $N_1 = 50$, $N_2 = 500$, $D_1 = 1.0$, $D_2 = 5.0 \times 10^2$, and $\sigma' = 1.0$ are adopted.

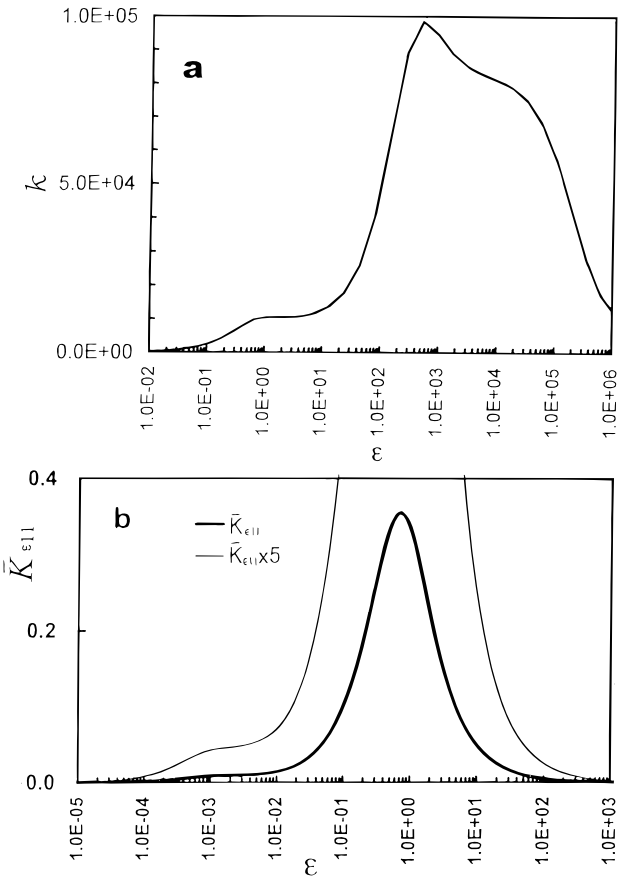

Figure 1. (a) k_ϵ given in eq 60. The graph exhibits a plateau in the region of $1 < \epsilon < 50$. (b) $\bar{K}_{\epsilon 11}$<equation:some202>> of the model in section 5B. The graph exhibits a plateau in the region of $0.001 < \epsilon < 0.005$.

The graph exhibits a plateau in the region of $\epsilon = 1.0 \sim 10.0$. This agrees with the prediction of eq 61 that k_ϵ is constant in the region of $D_1 \ll \epsilon \ll N_1 D_1$. In the region of $D_2 < \epsilon < N_2 D_2$, however, k_ϵ does not completely become constant. This is because the approximations used in eqs 59 and 61 are not sufficiently good for the present choice of the parameters.

The ϵ dependence of k_ϵ and its physical contents can be summarized as follows: In the limit of $\epsilon \rightarrow 0$, the dynamics strictly follows the reversible quantum mechanics, and therefore, k_ϵ vanishes. In short, no secular part exists in the limit of $\epsilon \rightarrow 0$. When ϵ is as large as the smallest energy-level spacing D_1, the bunches of quantum states work as quasicontinua, and the recurrences of the longest time scale are suppressed. In consequence, $\mathbf{p}(t)$ comes to have the secular part $\bar{\mathbf{p}}(t)$. Particularly when the energy level has a hierarchical structure, there exists the regime where the magnitude of k_ϵ is insensitive to ϵ. In this regime, $\bar{\mathbf{p}}(t)$ and the master equation have a robust physical meaning, and we can define the entropy $\bar{S}(t)$ (eq 32) as a measure of IVR. When ϵ is so large that the damping factor $e^{-\epsilon t}$ affects the dynamics of short time scales, the information carried in the memory kernel is lost, and k_ϵ looses its physical meaning as is implied by vanishing k_ϵ in the limit of $\epsilon \rightarrow \infty$.

5.B. Coupled Harmonic Oscillator Model. In this subsection, we examine $\bar{\mathbf{p}}(t)$ and $\bar{S}(t)$ as well as the ϵ dependence of $\bar{\mathbf{K}}_\epsilon$ on the basis of a coupled harmonic oscillator model. The Hamiltonian is given by

$$H = 2a^\dagger a + b^\dagger b + \zeta(a^\dagger + a)(b^\dagger + b)^2 \tag{62}$$

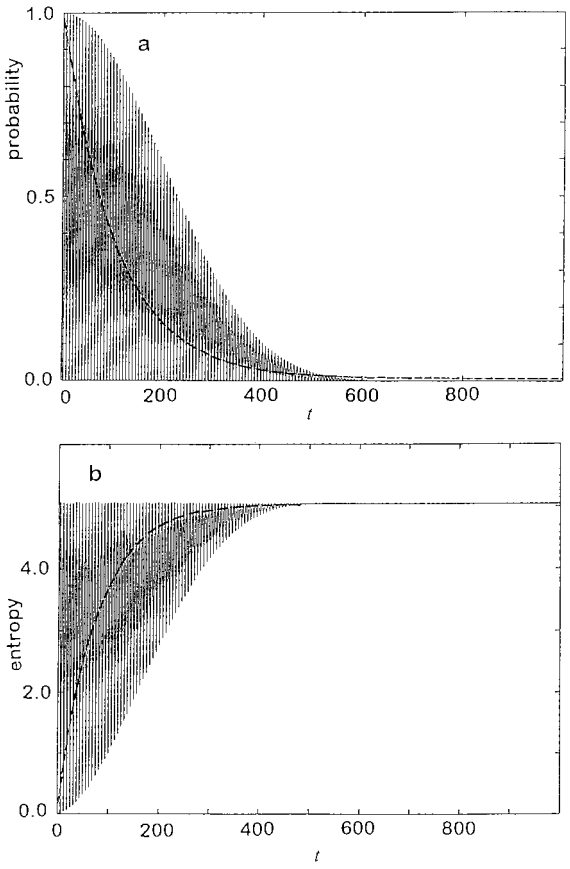

Figure 2. (a) Occupation probability $p_1(t)$ (thin line) and secular part $\bar{p}_1(t)$ (broken line) of the model in section 5B. (b) Relative entropy $S(t)$ (solid line) and secular entropy $\bar{S}(t)$ (broken line) of the model in section 5.B.

where a and b are boson annihilation operators. The parameter $\zeta = 0.0002$ is adopted. The energy level of the present Hamiltonian has a hierarchical structure.[49] The initial state is chosen as $|\phi_0\rangle = 2^{-1/2}(|0, 18\rangle + |0, 19\rangle)$, where $|\upsilon_a, \upsilon_b\rangle$ denotes the eigenstate of the uncoupled two-dimensional harmonic oscillator, $H_0 = 2a^\dagger a + b^\dagger b$. The projection operators are chosen as $P_1 = |\phi_0\rangle\langle\phi_0|$ and $P_2 = 1 - P_1$. By numerical calculation using 156 basis states, $\mathbf{P}(t)$, $\Pi_\epsilon(\omega)$, $\mathbf{X}_\epsilon(\omega)$, $\bar{\mathbf{K}}_\epsilon$, $\bar{\mathbf{p}}(t)$, and $\bar{S}(t)$ are obtained.

Figure 1b shows $\bar{K}_{\epsilon 11}$ as a function of ϵ. A plateau is seen in the region of $\epsilon = 0.001 \sim 0.01$. By setting $\epsilon = 0.002$ (at the middle of the plateau), $\bar{\mathbf{p}}(t)$ is calculated. Figure 2a shows $\bar{p}_1(t)$ as a function of t together with $p_1(t)$. It can be seen that the secular decrease of $p_1(t)$ is nicely represented by $\bar{p}_1(t)$. Figure 2b shows the relative entropy $S(t)$ (eq 1) and the secular entropy $\bar{S}(t)$ (eq 32). Although $S(t)$ exhibits oscillation originating from quantum dephasing, $\bar{S}(t)$ increases monotonically so as to represent the secular increase of $S(t)$.

Figure 1b shows that $\bar{K}_{\epsilon 11}$ reaches a maximum at $\epsilon = 0.9$. The maximum value of $\bar{K}_{\epsilon 11}$ also has a physical meaning. It is the maximum possible decay rate of $\bar{p}_1(t)$. If we choose $\epsilon = 0.9$ (at the maximum of $\bar{K}_{\epsilon 11}$), $\bar{p}_1(t)$ decays quickly, mimicking the fast fall-down of $p_1(t)$ in the shortest time scale. In this choice of ϵ, even the fastest dephasing is treated as a recurrence to be disregarded. In short, the maximum of $\bar{K}_{\epsilon 11}$ is also physically meaningful, although it is practically useless in this particular example from the chemical point of view. The existence of the plateau indicates the existence of dynamics of long time scale other than the fastest dephasing.

5.C. Model of Sequential IVR. In this subsection, a prototypical model of sequential dynamics is discussed. The initial bright state, $|\phi_b\rangle$, is coupled to a doorway state, $|\phi_d\rangle$, with a coupling matrix element, $\langle\phi_b|H|\phi_d\rangle = 2.0$. The zeroth-order energies of $|\phi_b\rangle$ and $|\phi_d\rangle$ are set equal to zero; i.e., $\langle\phi_b|H|\phi_b\rangle = \langle\phi_d|H|\phi_d\rangle = 0$. The doorway state is coupled with 250 dark states, $|\phi_n\rangle$ ($n = 1, 2, ..., 250$), which are distributed with equal spacing, i.e., $\langle\phi_n|H|\phi_n\rangle = 0.04(n - 124.5)$. We adopt the coupling matrix element, $\langle\phi_d|H|\phi_n\rangle = 0.05$, which is independent of n. The interaction between $|\phi_b\rangle$ and $|\phi_n\rangle$ ($n = 1, 2, ..., 250$) is set equal to zero. We adopt the projection operators, $P_1 = |\phi_b\rangle\langle\phi_b|$, $P_2 = |\phi_d\rangle\langle\phi_d|$, and $P_3 = \sum_n |\phi_n\rangle\langle\phi_n|$.

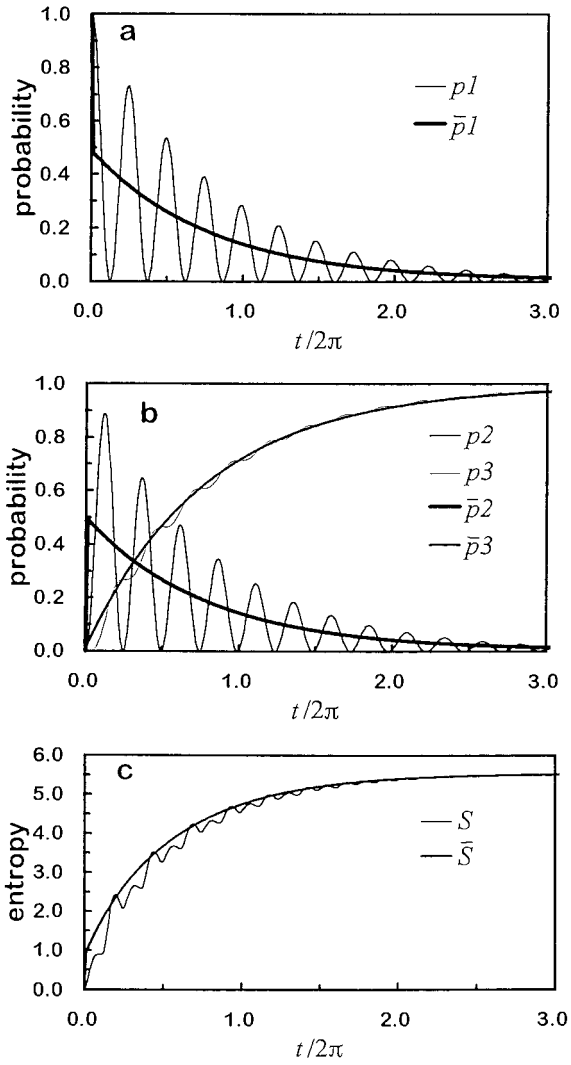

Figure 3. (a) Occupation probability $p_1(t)$ (thin line) and secular part, $\bar{p}_1(t)$ (thick line) of the model in section 5C. (b) $p_2(t)$, $\bar{p}_2(t)$, $p_3(t)$, and $\bar{p}_3(t)$ of the model in section 5C. (c) Relative entropy $S(t)$ (thin line) and secular entropy $\bar{S}(t)$ (thick line) of the model in section 5C.

By numerical calculation, $\bar{K}_{\epsilon 11}$ is found to have a maximum at $\epsilon = 0.025$, to which the value of ϵ is fixed in the following calculation. In the present model, $\bar{K}_\epsilon$ is a 3×3 matrix and is capable of describing the decay containing two different components, i.e., from $|\phi_b\rangle\langle\phi_d|$ and from $|\phi_d\rangle$ to the dark states. This is a reason why $\bar{K}_{\epsilon 11}$ does not have any plateau in contrast to the example in the preceding subsection. The secular part $\bar{\mathbf{p}}(t)$ is plotted in Figures 3a,b and 4a together with $\mathbf{p}(t)$. The former successfully extracts the long time behavior of the latter. The secular parts, $\bar{p}_1(t)$, $\bar{p}_2(t)$, and $\bar{p}_3(t)$, exhibit typical time dependence of "successive reaction". The population of the initial state ($|\phi_b\rangle$) is transmitted to the "reaction intermediate" ($|\phi_d\rangle$) and then the "final product" (the dark states) gradually

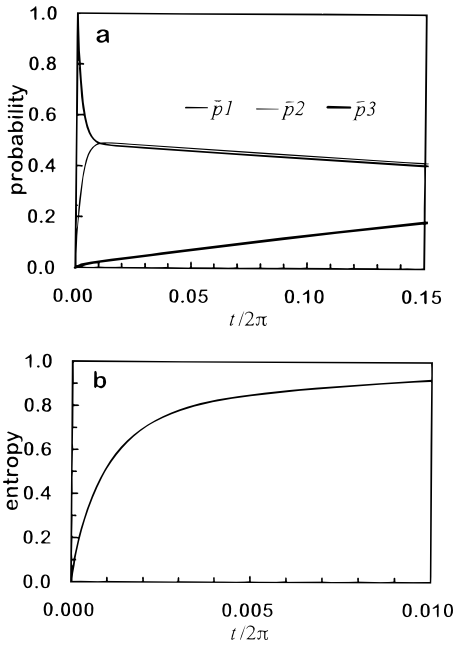

Figure 4. (a) $\bar{p}_1(t)$ and $\bar{p}_2(t)$ of the model in section 5C. in the short time scale. (b) $\bar{S}(t)$ of the model in section 5C. in the short time scale.

grows. The secular motion of quantum dynamics is shown to result in the behavior well-known in the macroscopic chemical kinetics.

The relative entropy, $S(t)$, and the secular part, $\bar{S}(t)$, are shown in Figures 3c and 4b. The latter nicely describes the secular increase of the former. In the short time scale, $t = 0 \sim 0.003$, $\bar{S}(t)$ increases quickly. It represents the fast transition from $|\phi_b\rangle$ to $|\phi_d\rangle$. The gradual increase of $\bar{S}(t)$ in the long time scale corresponds to the slow dissipation into the dark states. In short, the secular entropy increases by two different production rates, each of which corresponds to each step of the sequential dynamics of the present model, i.e., from $|\phi_b\rangle$ to $|\phi_d\rangle$ and from $|\phi_d\rangle$ to the dark states.

6. Discussion

In sections 4 and 5, $\bar{\mathbf{K}}_\epsilon$ is estimated on the basis of the spectral positions and intensities, both of which can be obtained experimentally. It should be noted that $\bar{\mathbf{K}}_\epsilon$ is obtained from the zero-frequency part of $\Pi(\omega)$. As can be seen in eq 46, small spacing ω_{nm} has a larger contribution to Π_0 and thus to $\bar{\mathbf{K}}_\epsilon$. The data based on the spectrum of less than perfect resolution are, therefore, liable to cause error. The circumstance is parallel to the case of radiationless transition, where the rate is determined by the density of states. In short, missing peaks may harm the accuracy of the estimation even if their intensities are weak.

No mathematical reasoning can lead to a criterion for the choice of the damping parameter ϵ. The criterion should be derived on the basis of physical insight. An important point is that $\bar{\mathbf{K}}_\epsilon$ has a maximum as a function of ϵ (see Figure 1) in all the cases discussed in section 5. The maximum value of $\bar{\mathbf{K}}_\epsilon$ corresponds to the maximum possible decay rate and has a robust physical meaning. In the case of section 5C, where the Hilbert space is partitioned into three subspaces, the maximum value of $\bar{\mathbf{K}}_\epsilon$ is shown to describe correctly the sequential dynamics of the system. In the cases of sections 5A and 5B, where the Hilbert space is partitioned into two subspaces, the maximum value of $\bar{\mathbf{K}}_\epsilon$ corresponds to the time scale of the fastest dephasing. In these cases, the time scale of interest concerning IVR can be obtained at the plateau of $\bar{\mathbf{K}}_\epsilon$. The behavior of $\bar{\mathbf{K}}_\epsilon$ depends on both the dynamics of the system and the choice of projection. The appropriate value of ϵ can be obtained at either maximum point or plateau part, i.e., at nearly stationary point, depending on the cases.

Such stationary points arise from the hierarchical structure of molecular spectra as demonstrated in section 5A. The hierarchical structure gives rise to the separation of time scales of different dynamics, and the latter enables us to neglect the recurrence, i.e., the dynamics of the longest time scale, without affecting the IVR dynamics of interest. If there is no hierarchical structure, $\bar{\mathbf{K}}_\epsilon$ indicates merely the time scale of the shortest dephasing. In short, the neglect of recurrence is justifiable when the IVR is stepwise and the molecular spectrum possesses a hierarchical structure.

7. Summary

For the purpose of acquiring a measure of IVR, the quasi-irreversibility in the quantum dynamics is discussed. It is shown in the present paper that the quantum-mechanical time evolution of the occupation probability, $\mathbf{p}(t)$, obeys a generalized master equation (eq 15) having a non-Markovian memory kernel.

A Markovian limit of the generalized master equation is discussed by analyzing the long-time behavior of $\mathbf{p}(t)$ on the basis of the renormalization-group method. We define the secular part $\bar{\mathbf{p}}(t)$, which obeys a Markovian master equation (eq 31). The secular entropy $\bar{S}(t)$ (eq 32) is defined by use of $\bar{\mathbf{p}}(t)$. It follows that $\bar{S}(t)$ is a monotonically increasing function of time. It is a property desirable for a measure of IVR.

The Markovian master equation for $\bar{\mathbf{p}}(t)$ has a physical meaning when the quantum recurrences in the memory kernel are suppressed by the damping factor $e^{-\epsilon t}$. In the limit of $\epsilon \rightarrow 0$, in which the strictly reversible quantum mechanics governs, the transition matrix of the master equation is shown to vanish. Also in the limit of $\epsilon \rightarrow \infty$, the master equation looses its meaning simply because the dynamical information carried in the memory kernel is lost in this limit.

The ϵ dependence is analyzed on the basis of model calculations. It is found that the system exhibiting a hierarchical level structure gives rise to a master equation insensitive to the value of ϵ. The ϵ dependence clarifies the mechanism giving rise to the quasi-irreversibility. Numerical calculation based on model Hamiltonians is carried out, and $\bar{\mathbf{p}}(t)$ and $\bar{S}(t)$ are found to represent successfully the secular bahavior of $\mathbf{p}(t)$ and $S(t)$, respectively, when the damping parameter ϵ is kept finite. The retention of the damping parameter is best justified in the case of sequential IVR. A model of sequential IVR (section 5C) shows that the secular motion of quantum dynamics follows the macroscopic chemical kinetics. The secular entropy monotonically increases by different production rates, indicating two different time scales of IVR. In conclusion, the secular dynamics derived on the basis of the renormalization-group method well describes quasi-irreversible dynamics embedded in IVR, and thereby, the measure of IVR is obtained.

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Appendix A: Proof of Equation 6

The left-hand side of eq 6 satisfies the differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{i(A+B)t/\hbar} = \frac{i}{\hbar}(A+B)\mathrm{e}^{i(A+B)t/\hbar} \tag{63}$$

and the boundary condition $\mathrm{e}^{i(A+B)t/\hbar}|_{t=0} = 1$. On the other hand, the right-hand side of eq 6 is also shown to satisfy the same differential equation as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\Big[\mathrm{e}^{iAt/\hbar} + \frac{i}{\hbar}\int_0^t \mathrm{d}t'\, \mathrm{e}^{i(A+B)(t-t')/\hbar}B\mathrm{e}^{iAt/\hbar}\Big] \\ = \frac{i}{\hbar}A\mathrm{e}^{iAt/\hbar} + \frac{i}{\hbar}B\mathrm{e}^{iAt/\hbar} + \\ \frac{i}{\hbar}\int_0^t \mathrm{d}t'\, \frac{i}{\hbar}(A+B)\mathrm{e}^{i(A+B)(t-t')/\hbar}B\mathrm{e}^{iAt'/\hbar} \\ = \frac{i}{\hbar}(A+B)\Big[\mathrm{e}^{iAt/\hbar} + \frac{i}{\hbar}\int_0^t \mathrm{d}t'\, \mathrm{e}^{i(A+B)(t-t')/\hbar}B\mathrm{e}^{iAt'/\hbar}\Big]\end{aligned} \tag{64}$$

At $t = 0$ the right-hand side of eq 64 results in 1. Accordingly, the left- and right-hand sides of eq 6 both satisfy the same first-order differential equation with the same boundary condition, and hence, they are identical with each other.

Appendix B: Derivation of Equation 18

By use of the relation

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{-\epsilon t}\theta(t)\mathbf{P}(t) = \delta(t)\mathbf{P}(0) - \epsilon\mathrm{e}^{-\epsilon t}\theta(t)\mathrm{P(t)} + \mathrm{e}^{-\epsilon t}\theta(t)\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}(t) \tag{65}$$

eq 12 multiplied with $\mathrm{e}^{-\epsilon t}\theta(t)$ in both sides leads to

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{-\epsilon t}\theta(t)\mathbf{P}(t) = \delta(t)\mathbf{P}(0) - \epsilon\mathrm{e}^{-\epsilon t}\theta(t)\mathbf{P}(\mathrm{t}) - \\ \frac{1}{\hbar^2}\int_{-\infty}^{\infty}\mathrm{d}t'\, \mathrm{e}^{-\epsilon t'}\theta(t')\mathbf{K}(t')\mathrm{n}^{-1}\mathrm{e}^{-\epsilon(t-t')}\theta(t-t')\mathbf{P}(t-t')\end{aligned} \tag{66}$$

By use of the inverse transformation of eqs 16 and 17, eq 66 can be written as

$$\begin{aligned}\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\, \mathrm{e}^{-i\omega t}(-i\omega)\Pi_\epsilon(\omega) = \\ \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\, \mathrm{e}^{-i\omega t}\Big[\mathbf{P}(0) - \epsilon\Pi_\epsilon(\omega) - \frac{1}{\hbar^2}\mathbf{X}_\epsilon(\omega)\mathrm{n}^{-1}\Pi_\epsilon(\omega)\Big]\end{aligned} \tag{67}$$

which leads to

$$-i\omega\Pi_\epsilon(\omega) = \mathbf{P}(0) - \epsilon\Pi_\epsilon(\omega) - \frac{1}{\hbar^2}\mathbf{X}_\epsilon(\omega)\mathrm{n}^{-1}\Pi_\epsilon(\omega) \tag{68}$$

From the definition, it follows that $\mathbf{P}(0) = \mathrm{n}$. Elementary algebra leads to eq 18.

Appendix C: Derivation of Equation 19

The assumption $[H_0,P_j] = 0$ leads to $\mathcal{L}|P_j) = [H_0 + \lambda V,P_j] = \lambda[V,P_j] \equiv \lambda\mathcal{L}_1|P_j)$ and that $(P_j|\mathcal{L}|X) = Tr\{P_j[H_0 + \lambda V,X]\} = \lambda Tr\{X[P_j,V]\} = \lambda(P_j|\mathcal{L}_1|X)$, where X is an arbitrary operator. By use of above relations, we obtain

$$\begin{aligned}K_{jl}(t) = (P_l/\mathcal{L}\ \mathrm{e}^{-i(1-\mathcal{P})\mathcal{L}\, t/\hbar}(1-\mathcal{P})\mathcal{L}\ |P_j) \\ = \lambda^2(P_l|\mathcal{L}_1\mathrm{e}^{-i(1-\mathcal{P})\mathcal{L}\, t/\hbar}(1-\mathcal{P})\mathcal{L}_1|P_j)\end{aligned} \tag{69}$$

Thus, it is shown that $\mathbf{K}(t) \sim o(\lambda^2)$.

Appendix D: Derivation of Equation 20

We expand $\mathbf{p}(t)$ in the power series of λ^2 as $\mathbf{p}(t) = \mathbf{p}^{(0)}(t) + \lambda^2\mathbf{p}^{(2)}(t) + o(\lambda^4)$. Substituting this into eq 19, we obtain

$$\begin{aligned}\dot{\mathbf{p}}^{(0)}(t) + \lambda^2\dot{\mathbf{p}}^{(2)}(t) + \mathrm{o}(\lambda^4) = \\ -\frac{\lambda^2}{\hbar^2}\int_0^t \mathrm{d}t_1\, \mathbf{K}(t_1)\mathrm{n}^{-1}\mathbf{p}^{(0)}(t-t_1) + o(\lambda^4)\end{aligned} \tag{70}$$

From the terms on the order of λ^0, we obtain $\dot{\mathbf{p}}^{(0)}(t) = 0$, which immediately leads to $\mathbf{p}^{(0)}(t) = \mathbf{p}^{(0)}$. From the term on the order of λ^2, we obtain

$$\begin{aligned}\dot{\mathbf{p}}^{(2)}(t) = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t_1\, \mathbf{K}(t_1)\mathrm{n}^{-1}\mathbf{p}^{(0)}(t-t_1) \\ = -\frac{1}{\hbar^2}\{\int_0^t \mathrm{d}t_1\, \mathbf{K}(t_1)\}\mathrm{n}^{-1}\mathbf{p}(0)\end{aligned} \tag{71}$$

which leads to

$$\mathbf{p}^{(2)}(t) = -\frac{1}{\hbar^2}\{\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \mathbf{K}(t_2)\}\mathrm{n}^{-1}\mathbf{p}(0) \tag{72}$$

From this and $\mathbf{p}^{(0)}(t) = \mathbf{p}^{(0)}$ obtained above, we obtain eq 20.

Appendix E: Proof of the Detailed Balance Condition of Equation 31

We begin with showing the symmetry of the matrix $\mathbf{P}(t)$. By definition $P_{jk}(t)$ is given by

$$\begin{aligned}P_{jk}(t) = \sum_{\lambda=1}^{n_k}\sum_{\mu=1}^{n_j}|\langle k\lambda|\mathrm{e}^{-iHt/\hbar}|j\mu\rangle|^2 = \\ \sum_{\lambda=1}^{n_k}\sum_{\mu=1}^{n_j}|\sum_n\langle k\lambda|n\rangle\langle j\mu|n\rangle^*\mathrm{e}^{-iE_n/\hbar}|^2\end{aligned} \tag{73}$$

where $|n\rangle$ is the eigenstate of H and E_n is the corresponding eigenvalue. When H is real symmetric, we can choose the basis states so that $\langle j\mu|n\rangle$ is real. It can easily be seen from eq 73 that $P_{jk}(t) = P_{kj}(t)$ when $\langle j\mu|n\rangle$ is real. Symmetry of $\mathbf{P}(t)$ leads to symmetric $\Pi(\omega)$ (see eq 16), symmetric $\mathbf{X}(\omega)$ (see eq 18), symmetric $\mathbf{K}(t)$ (see eq 17), symmetric $\mathbf{J}(t)$ (see eq 21), and finally symmetric $\bar{\mathbf{K}}$ (see eq 22). The symmetry of $\bar{\mathbf{K}}$ gives rise to the detailed balance condition as

$$W_{jk}n_k = -\frac{\lambda^2}{\hbar^2}\bar{K}_{jk} = -\frac{\lambda^2}{\hbar^2}\bar{K}_{kj} = W_{kj}n_j \tag{74}$$

Appendix F: Proof of Equation 36

By definition $\Pi_{kj}(\omega)$ is expressed as

$$\Pi_{\epsilon kj}(\omega) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\epsilon t}\mathrm{e}^{i\omega t}P_{kj}(t)$$

$$= i\sum_{\lambda=1}^{n_k}\sum_{\mu=1}^{n_j}\left[\sum_n \frac{|\langle k\lambda|n\rangle\langle j\mu|n\rangle^*|^2}{\omega + i\epsilon} + \sum_{n\neq m}\frac{\langle k\lambda|n\rangle\langle j\mu|n\rangle^*\langle k\lambda|m\rangle^*\langle j\mu|m\rangle}{\omega - \omega_{nm} + i\epsilon}\right] \quad (75)$$

It follows that

$$\lim_{\omega\to\infty}\omega\Pi_{\epsilon kj}(\omega) = i\sum_{\lambda=1}^{n_k}\sum_{\mu=1}^{n_j}[\sum_n|\langle k\lambda|n\rangle\langle j\mu|n\rangle^*|^2 + \sum_{n\neq m}\langle k\lambda|n\rangle\langle j\mu|n\rangle^*\langle k\lambda|m\rangle^*\langle j\mu|m\rangle]$$

$$= i\sum_{\lambda=1}^{n_k}\sum_{\mu=1}^{n_j}\sum_n\sum_m\langle k\lambda|n\rangle\langle j\mu|n\rangle^*\langle k\lambda|m\rangle^*\langle j\mu|m\rangle$$

$$= n_k\delta_{kj} \quad (76)$$

which leads to

$$\lim_{\omega\to\infty}\mathbf{X}_\epsilon(\omega) = \lim_{\omega\to\infty}\hbar^2[i(\omega - i\epsilon)\mathrm{n} + \omega\mathrm{n}(\omega\Pi_\epsilon(\omega))^{-1}\mathrm{n}]$$

$$= \hbar^2[i\omega\mathrm{n} + \omega\mathrm{n}(i\mathrm{n})^{-1}\mathrm{n}] = 0 \quad (77)$$

Appendix G: Derivation of Equation 58

After rearrangement of the running suffixes to $n_+ \equiv n + m$ and $n_- \equiv n - m$, the summation is approximated by an integral as

$$s_N(x) \equiv \frac{2}{N^2}\sum_{n=1}^{N}\sum_{m=1}^{n-1}\frac{1}{1 + (n-m)^2/x^2}$$

$$= \frac{2}{N^2}\sum_{n_-=1}^{N-1}\frac{1}{1 + (n_-^2/x^2)}\frac{2N - 2n_-}{2}$$

$$= 2\sum_{n_-=1}^{N-1}\frac{1}{N}\frac{1 - (n_-/N)}{1 + (N/x)^2\,(n_-/N)^2}$$

$$\simeq 2\int_{1/N}^1 \mathrm{d}\xi\frac{1-\xi}{1 + (N/x)^2\xi^2}$$

$$= 2\left[\frac{x}{N}\left(\tan^{-1}\frac{N}{x} - \tan^{-1}\frac{1}{x}\right) - \frac{x^2}{2N^2}\ln\frac{x^2 + N^2}{x^2 + 1}\right] \quad (78)$$

Further reduction by elementary algebra leads to eq 58.

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