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Mechanism of intermolecular dephasings on time-resolved anti-Stokes Raman scattering from a molecular ensemble

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Mechanisms of intermolecular dephasings revealed in the time-resolved coherent anti-Stokes Raman scattering (CARS) spectra of a molecular ensemble are theoretically studied by deriving the microscopical expression for the scattered photon intensity averaged over the heat-bath variables. The intermolecular dephasing means the decay of the intermolecular coherence created by the pumping process, i.e., a linear combination of the vibrational Raman transitions of the molecules at different sites. The intensity of the time-resolved CARS is expressed in terms of time-development matrix elements of the intermolecular coherence. An equation of motion for the intermolecular coherence is derived by using the projection operator method. The structure of the intermolecular-dephasing constant is clarified. The intermolecular-dephasing constant consists of the sum of population decay constants and the intermolecular pure dephasing constant that originates from an elastic interaction between the relevant molecules and a common heat-bath mode. The intermolecular pure dephasing constant is expressed in terms of the intramolecular pure dephasing constants and destructive interference of the intramolecular pure dephasings between the relevant two molecules. The intermolecular-dephasing constant is expressed as the sum of the intramolecular-dephasing constants of the relevant molecules when there is no common heat-bath mode. Inhomogeneous effects on the time-resolved CARS spectra are also investigated. A degree of the structural order is introduced to qualitatively express the inhomogeneity of local structures in the molecular ensemble. The microscopic expression derived in this paper has taken into account both incoherent and coherent optical processes in the thermally distributed molecular ensemble.

I. INTRODUCTION

Recently, with the development of ultrashort time-resolved coherent-scattering spectroscopy,[1-4] ultrafast dynamics in various molecular ensembles with random configuration have been studied both experimentally and theoretically with great interest.[5-9] The time evolution of two molecules interacting with each other at various positions can be directly observed by using such a coherent spectroscopy. For example, the time evolution of intermolecular vibrational coherence of the relevant molecules in liquids has been detected by time-resolved coherent anti-Stokes Raman scattering (CARS) in which terahertz quantum beats appears as a result of the creation of the intermolecular vibrational coherence.[10,11] By analyzing such a time-resolved spectrum, in principle, one can obtain information on the mechanism of the intermolecular dynamics.[12-14] However, in analyzing the time-resolved spectrum, there still remain several subjects to be clarified from the theoretical viewpoint. One of the main subjects is related to the mechanism of the vibrational dephasing of the intermolecular coherence: is the dephasing constant measured by the time-resolved CARS method simply given by a sum of the intramolecular dephasing constants of the relevant molecules, i.e.,

$$\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'} = \Gamma^{\alpha}_{ij:ij} + \Gamma^{\beta}_{i'j':i'j'} , \tag{1.1}$$

where $\Gamma^{\alpha\beta}_{ji,j'i':ji,i'j'}$ denotes the dephasing constant of the intermolecular vibrational coherence between vibrational transition ($i \leftrightarrow j$) of molecule α and that ($i' \leftrightarrow j'$) of β. Constant $\Gamma^{\alpha}_{ij:ij}$ ($\Gamma^{\beta}_{i'j':i'j'}$) represents the intramolecular-dephasing constant of the vibrational transition between i and j (i' and j') of individual molecule α (β). The intramolecular-dephasing constant consists of the population decay and pure dephasing constants. The former and the latter originate from the molecule–heat-bath inelastic- and elastic-scattering processes, respectively. We would like to know under what condition the expression for the intermolecular-dephasing constant denoted just above can be used. More rigorously speaking, we would like to know how the intermolecular pure dephasing constant which originates from the elastic interaction between the molecular pair of interest and the bath mode is involved in the intermolecular-dephasing processes.

The purpose of this paper is to theoretically study the mechanism of the intermolecular-dephasing processes which are reflected in the time-resolved CARS spectra, and to clarify the role of the bath modes in the intermolecular-dephasing processes. For this purpose, it should be noted that the conventional treatment for the CARS signal, which is based on the evaluation of the third-order nonlinear polarization averaged over the heat-bath variables, cannot be used. In other words, in taking account the intermolecular-dephasing effect on the time-resolved CARS spectra, the bath mode averaging procedure has to be carried out for the signal intensity but not for the amplitude of the CARS. Recently, Hanamura and Mukamel,[15] and Mukamel and Hanamura[16] have derived an expression for the photon-echo signal from an ensemble consisting of a two-level system with spatial correlations based on the stochastic theory. The signal intensity is averaged over the stochastic variables.

In the next section, we first derive an expression for the scattered photon intensity of the time-resolved nonresonant anti-Stokes Raman (ARS) processes of a multilevel molecular ensemble by using the perturbative density-matrix method. The density-matrix method is based on the quantum-mechanical theory. Each molecule in the molecular ensemble is assumed to consist of Raman active vibrational modes. The density operator for the scattered photon is given by tracing out the resulting expression over both the variables of the heat-heat modes and those of the incident radiation fields. In this derivation, effects of both incoherent and coherent photon-molecule scattering processes are taken into account. We call the incoherent component incoherent anti-Stokes Raman scattering (INARS) in this paper. The CARS process is expressed in terms of the time evolution of the molecular pair density matrix in the Markov approximation, and on the other hand, the INARS process is expressed in terms of the time evolution of a one-body molecular density matrix. These time evolutions are conveniently described on eight-time point Liouville space Feynman diagrams. Secondly, we derive an expression for the intermolecular-dephasing constant from the microscopic viewpoint. The equation of motion of the reduced, molecular pair density matrix is derived by using the projection operator method.[17,18] It is shown that the intermolecular-dephasing constant cannot be expressed as in Eq. (1.1) when the constituents interact with each other through a common bath mode.

In Sec. III, a qualitative discussion on the mechanism of the intermolecular-dephasing processes is given based on the time-resolved CARS expression derived in Sec. II. The structure of the intermolecular pure dephasing constant is evaluated in the Markov approximation. A molecular ensemble with one Raman active transition and that with two Raman active ones are treated. Effects of the environmental inhomogeneity of the molecular pairs on the time-resolved CARS spectra are discussed as well.

II. THEORY

In this section we first derive an expression for the intensity of the photons scattered from both incoherent and coherent fourth-order optical processes of a thermally distributed molecular ensemble, and secondly obtain the equation of motion for the intermolecular coherence within the second Born approximation.

A. Intensity of time-resolved ARS

We consider the time-resolved ARS from a molecular mixture which consists of two kinds of multimode molecules, α and β interacting with ensembles or perturbers, that is, a heat bath and radiation field as shown in Fig. 1.

In the CARS process, the radiation fields are assumed to create a linear combination of the Raman active vibrational transitions, that is, the intermolecular coherence between molecules α_l and β_m located at position $\mathbf{r}_l$ and $\mathbf{r}_m$ in the mixture, respectively. Two-coincident laser pulses (I,II) with central frequency (wave vector) $\omega_{\mathrm{I}}(\mathbf{k}_{\mathrm{I}})$ and $\omega_{\mathrm{II}}(\mathbf{k}_{\mathrm{II}})$ are sent into the molecules to create the intramolecular coherence between the initial states $\{a\}$ ($\{a'\}$) and vibrationally excited states $\{c\}$ ($\{c'\}$) in the electronic ground state via the virtual intermediate states $\{b\}$ ($\{b'\}$). This stimulated Raman scattering process creates the intermolecular coherence between the intramolecular coherences, $a \leftrightarrow c$ and $a' \leftrightarrow c'$. By applying the third pulse with $\omega_{\mathrm{I}}(\mathbf{k}_{\mathrm{III}})$, which is generated from the same source as pulse laser I, to the mixture after time delay τ, the photons with $\mathbf{k}_S$ are scattered.

On the other hand, in the INARS process the pumping pulses create the intramolecular coherence between the

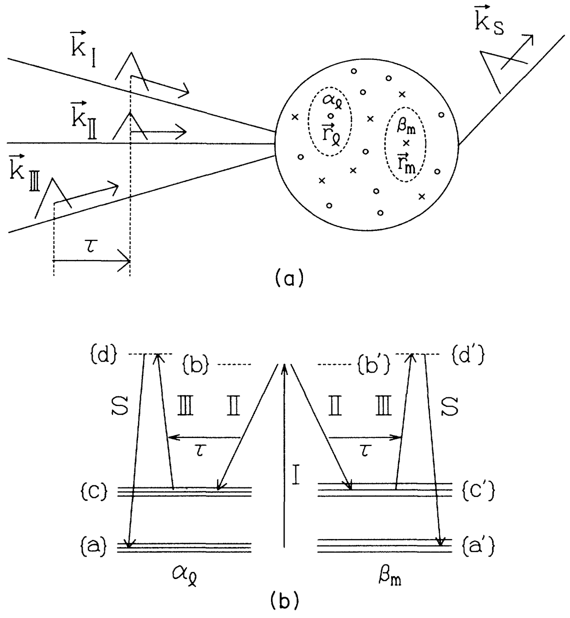

FIG. 1 (a) Model for the time-resolved anti-Stokes Raman scattering (ARS) from a molecular mixture with two kinds of multilevel molecules α and β. The circle at site $\mathbf{r}_l$ and cross at $\mathbf{r}_m$ encircled with dashed ellipses represent one of the molecular pairs reflected in the CARS spectra in the mixture. Two coincident laser pulses (I, II) with wave vectors ($\mathbf{k}_{\mathrm{I}}$,$\mathbf{k}_{\mathrm{II}}$) as pump pulses are driven through the molecular ensemble. The large circle represents the spatial coherence volume which is created by the pump lasers. After time delay τ, the third pulse (III) with $\mathbf{k}_{\mathrm{III}}$ is applied to the ensemble as the probe pulse. The coherent scattered photons with $\mathbf{k}_S$ are induced. (b) Schematic representation for the interaction between the molecules and the radiation fields in both nonresonant INARS and CARS processes. In the nonresonant CARS process, the pump pulses (I, II) create the intermolecular coherence between two Raman transitions, $a \leftrightarrow c$ and $a' \leftrightarrow c'$ at different sites l and m, respectively. In the INARS process the pumping pulses create the intramolecular coherence between two states associated with the Raman transition at each site. The real and virtual states are represented by the solid and dashed lines, respectively.

Raman active vibrational states $\{c\}$ ($\{c'\}$) of molecule α (β) via virtual intermediate states $\{b\}$ ($\{b'\}$).

The total Hamiltonian $\hat{H}$ is given as

$$\hat{H}=\hat{H}_{\mathrm{MB}}+\hat{H}_R+\hat{H}_{\mathrm{MR}} \ , \tag{2.1}$$

where $\hat{H}_{\mathrm{MB}}$ denotes the molecular Hamiltonian including the heat-bath variables, $\hat{H}_R$ the radiation field Hamiltonian, and $\hat{H}_{\mathrm{MR}}$ the molecule-radiation interaction Hamiltonian. We assume that there is no interaction between the heat bath and the radiation field. Within the dipole approximation and making use of the rotating-wave approximation, the interaction Hamiltonian is given as

$$\hat{H}_{\mathrm{MR}}=\sum_{l=1}^{n_\alpha}\hat{V}_l^\alpha+\sum_{m=1}^{n_\beta}\hat{V}_m^\beta+\mathrm{H.c.} \ , \tag{2.2}$$

where

$$\begin{aligned}\hat{V}_l^\alpha=&-\sum_b\sum_a M_{ba}^l\hat{T}_{ba}^l\hat{E}_{\mathrm{I}}^{(-)}\exp(i\mathbf{k}_{\mathrm{I}}\cdot\mathbf{r}_l)-\sum_c\sum_b M_{cb}^l\hat{T}_{cb}^l\hat{E}_{\mathrm{II}}^{(+)}\exp(-i\mathbf{k}_{\mathrm{II}}\cdot\mathbf{r}_l)\\&-\sum_d\sum_c M_{dc}^l\hat{T}_{dc}^l\hat{T}_{dc}^l\hat{E}_{\mathrm{III}}^{(-)}\exp(i\mathbf{k}_{\mathrm{III}}\cdot\mathbf{r}_l)-\sum_a\sum_d M_{ad}^l\hat{T}_{ad}^l\hat{E}_S^{(+)}\exp(-i\mathbf{k}_S\cdot\mathbf{r}_l) \ .\end{aligned} \tag{2.3}$$

The term $\hat{V}_m^\beta$ is obtained by exchanging subscripts of M, $\hat{T}$, and $\mathbf{r}$ between a and a', b and b', c and c', and l and m in Eq. (2.3). The suffix $l(m)$ denotes the numbering of molecule $\alpha(\beta)$. The term $M_{\nu\lambda}^l$ denotes the matrix element of the electric-dipole moment between states ν and λ of lth molecule. We have neglected the photon polarization effects in this paper. The term $\hat{T}_{\nu\lambda}^l(\equiv|\nu\rangle\langle\lambda|)$ is the transition operator from λ to ν states, and $\hat{E}_{\mathrm{II}}^{(+)}(\equiv c_{\mathrm{II}}b_{\mathrm{II}}^\dagger)$ and $\hat{E}_S^{(-)}$ refer to the radiation field operator of laser field II and scattering photon field S, respectively.

The density operator for the total system $\tilde{\rho}_T(t)$ is satisfied with the equation of motion,

$$i\hbar\frac{\partial}{\partial t}\tilde{\rho}_T(t)=[\hat{V}(t),\tilde{\rho}_T(t)] \ , \tag{2.4}$$

where the density operator with the overtilde denotes that in the interaction picture, and $\hat{V}(t)$, the dipole transition operator in the interaction representation is expressed by

$$\begin{aligned}\hat{V}(t)&=\exp[i(\hat{H}_{\mathrm{MB}}+\hat{H}_R)t/\hbar]\hat{H}_{\mathrm{MR}}\\&\quad\times\exp[-i(\hat{H}_{\mathrm{MB}}+\hat{H}_R)t/\hbar] \ . \qquad (2.5)\\&=\sum_{l=1}^{n_\alpha}\hat{V}_l^\alpha(t)+\sum_{m=1}^{n_\beta}\hat{V}_m^\beta(t)+\mathrm{H.c.} \qquad (2.6)\end{aligned}$$

In the perturbative density-matrix method, the total density operator for the ARS process, including the incoherent four-photon process $\tilde{\rho}_T^{(4)}(t)$, is given in expanding $\tilde{\rho}_T(t)$ in terms of photon number (4) as

$$\tilde{\rho}_T^{(4)}(t)=\left\{\int_{-\infty}^t dt^{(8)}\right\}[\hat{V}(t_1),[\hat{V}(t_2),\ldots,[\hat{V}(t_7),[\hat{V}(t_8),\tilde{\rho}_T(-\infty)]],\cdots]] \ , \tag{2.7}$$

where

$$\left\{\int_{-\infty}^t dt^{(8)}\right\}=(1/i\hbar)^8\int_{-\infty}^t dt_1\int_{-\infty}^{t_1}dt_2\cdots\int_{-\infty}^{t_6}dt_7\int_{-\infty}^{t_7}dt_8 \ , \tag{2.8}$$

and $\tilde{\rho}_T(-\infty)$ is the density operator for the total system at the initial time $t\rightarrow-\infty$, and is assumed to be given by

$$\tilde{\rho}_T(-\infty)=\tilde{\rho}_M(-\infty)\tilde{\rho}_B(-\infty)\tilde{\rho}_R(-\infty) \ . \tag{2.9}$$

$\tilde{\rho}_M(-\infty)$, $\tilde{\rho}_B(-\infty)$, and $\tilde{\rho}_R(-\infty)$ in Eq. (2.9) stand for the density matrices of the molecules, the heat bath, and the radiation field, respectively. We assume that the vibrational degrees of freedom of the molecule at each site in liquid are in thermal equilibrium before the excitations,[19] and $\tilde{\rho}_M(-\infty)$ is given as

$$\tilde{\rho}_M(-\infty)=\prod_{l=1}^{n_\alpha}\tilde{\rho}_{\alpha_l}(-\infty)\prod_{m=1}^{n_\beta}\tilde{\rho}_{\beta_m}(-\infty) \ . \tag{2.10}$$

The heat bath is in thermal equilibrium and the scattering photon field is in the vacuum state.

The density operator for the scattering field $\tilde{\rho}_S^{(4)}(t)$ can be derived from the total system density operator $\tilde{\rho}_T^{(4)}(t)$ by tracing out both the variables of the molecules and the heat-bath mode

$$\tilde{\rho}_S^{(4)}(\tau,\Delta\mathbf{k},t)=\langle\mathrm{Tr}_M[\mathrm{Tr}_{\mathrm{in}}\tilde{\rho}_T^{(4)}(t)]\rangle_{\mathrm{av}} \ , \tag{2.11}$$

where $\mathrm{Tr}_{\mathrm{in}}$ and $\langle\ \rangle_{\mathrm{av}}$ denote the averaging over the variables of the incident fields and those of the heat bath, respectively. Parameter τ represents the time interval between pumping and probing pulse lasers, and $\Delta\mathbf{k}=\mathbf{k}_{\mathrm{I}}-\mathbf{k}_{\mathrm{II}}+\mathbf{k}_{\mathrm{III}}-\mathbf{k}_s$. The population of the scattered photons $W_{\mathrm{ARS}}(\tau,\Delta\mathbf{k},\omega_S,t)$ with frequency ω_S at time t can be expressed using the Schrödinger picture of the density operator for the scattering field $\tilde{\rho}_S^{(4)}(\tau,\Delta\mathbf{k},t)$, as

$$\begin{aligned}W_{\mathrm{ARS}}(\tau,\Delta\mathbf{k},\omega_S,t)&=\langle\omega_S|\tilde{\rho}_S^{(4)}(\tau,\Delta\mathbf{k},t)|\omega_S\rangle \qquad (2.12)\\&=W_{\mathrm{INARS}}(\tau,\omega_S,t)\\&\quad+W_{\mathrm{CARS}}(\tau,\Delta\mathbf{k},\omega_S,t) \ , \qquad (2.13)\end{aligned}$$

where

$$W_{\mathrm{INARS}}(\tau,\omega_S,t)=\sum_{l=1}^{n_\alpha}\left\{\int_{-\infty}^{t}dt^{(8)}\right\}\sum_{\{P\}}\langle \hat{V}_l^{\alpha}(t_{P_1})\hat{V}_l^{\alpha}(t_{P_2})\hat{V}_l^{\alpha}(t_{P_3})\hat{V}_l^{\alpha}(t_{P_4})\tilde{\rho}_{\alpha_l}(-\infty)\tilde{\rho}_B(-\infty)\tilde{\rho}_R(-\infty)$$

$$\times\hat{V}_l^{\alpha}(t_{P'_4})\hat{V}_l^{\alpha}(t_{P'_3})\hat{V}_1^{\alpha}(t_{P'_2})\hat{V}_l^{\alpha}(t_{P'_1})\rangle_{\mathrm{AV}}$$

$$+\sum_{m=1}^{n_\beta}\left\{\int_{-\infty}^{t}dt^{(8)}\right\}\sum_{\{P\}}\langle \hat{V}_m^{\beta}(t_{P_1})\hat{V}_m^{\beta}(t_{P_2})\hat{V}_m^{\beta}(t_{P_3})\hat{V}_m^{\beta}(t_{P_4})\tilde{\rho}_{\beta_m}(-\infty)$$

$$\times\tilde{\rho}_B(-\infty)\tilde{\rho}_R(-\infty)\hat{V}_m^{\beta}(t_{P'_4})\hat{V}_m^{\beta}(t_{P'_3})\hat{V}_m^{\beta}(t_{P'_2})\hat{V}_m^{\beta}(t_{P'_1})\rangle_{\mathrm{AV}} \qquad (2.14\mathrm{a})$$

and

$$W_{\mathrm{CARS}}(\tau,\Delta\mathbf{k},\omega_S,t)=\sum_{\substack{l=1\\ l\neq l'}}^{n_\alpha}\sum_{l'=1}^{n_\alpha}\left\{\int_{-\infty}^{t}dt^{(8)}\right\}\sum_{\{P\}}\langle \hat{V}_l^{\alpha}(t_{P_1})\hat{V}_l^{\alpha}(t_{P_2})\hat{V}_l^{\alpha}(t_{P_3})\hat{V}_l^{\alpha}(t_{P_4})\tilde{\rho}_{\alpha_l}(-\infty)\tilde{\rho}_B(-\infty)\tilde{\rho}_R(-\infty)$$

$$\times\tilde{\rho}_{\alpha_{l'}}(-\infty)\hat{V}_{l'}^{\alpha}(t_{P'_4})\hat{V}_{l'}^{\alpha}(t_{P'_3})\hat{V}_{l'}^{\alpha}(t_{P'_2})\hat{V}_{l'}^{\alpha}(t_{P'_1})\rangle_{\mathrm{AV}}$$

$$+\sum_{\substack{m=1\\ m\neq m'}}^{n_\beta}\sum_{m'=1}^{n_\beta}\left\{\int_{-\infty}^{t}dt^{(8)}\right\}\sum_{\{P\}}\langle \hat{V}_m^{\beta}(t_{P_1})\hat{V}_m^{\beta}(t_{P_2})\hat{V}_m^{\beta}(t_{P_3})\hat{V}_m^{\beta}(t_{P_4})\tilde{\rho}_{\beta_m}(-\infty)\tilde{\rho}_B(-\infty)$$

$$\times\tilde{\rho}_R(-\infty)\tilde{\rho}_{\beta_{m'}}(-\infty)\hat{V}_{m'}^{\beta}(t_{P'_4})\hat{V}_{m'}^{\beta}(t_{P'_3})\hat{V}_{m'}^{\beta}(t_{P'_2})\hat{V}_{m'}^{\beta}(t_{P'_1})\rangle_{\mathrm{AV}}$$

$$+\sum_{l=1}^{n_\alpha}\sum_{m=1}^{n_\beta}\left\{\int_{-\infty}^{t}dt^{(8)}\right\}\sum_{\{P\}}[\langle \hat{V}_l^{\alpha}(t_{P_1})\hat{V}_l^{\alpha}(t_{P_2})\hat{V}_l^{\alpha}(t_{P_3})\hat{V}_l^{\alpha}(t_{P_4})\tilde{\rho}_{\alpha_l}(-\infty)\tilde{\rho}_B(-\infty)$$

$$\times\tilde{\rho}_R(-\infty)\tilde{\rho}_{\beta_m}(-\infty)\hat{V}_m^{\beta}(t_{P'_4})\hat{V}_m^{\beta}(t_{P'_3})\hat{V}_m^{\beta}(t_{P'_2})$$

$$\times\hat{V}_m^{\beta}(t_{P'_1})\rangle_{\mathrm{AV}}+\mathrm{c.c.}]\ , \qquad (2.14\mathrm{b})$$

where $\langle\ \rangle_{\mathrm{AV}}$ denotes the averaging over both variables of bath modes and radiation fields. Notation $\sum_{\{P\}}$ in Eqs. (2.14) means that we divide the time sequence $t_8<t_7<t_6<\cdots<t_1$ into any two pairs $(t_{P_4}<t_{P_3}<t_{P_2}<t_{P_1})$ and $(t_{P'_4}<t_{P'_3}<t_{P'_2}<t_{P'_1})$ and sum up all pairs. This procedure yields ${}_8C_4=70$ terms (35 terms plus the Hermite conjugate terms).

The intensity of time-resolved ARS is defined as

$$I_{\mathrm{ARS}}(\tau,\Delta\mathbf{k})=\int_{\Delta\Omega}d\omega_S\int_{\Delta T}dt\frac{\partial}{\partial t}W_{\mathrm{ARS}}(\tau,\Delta\mathbf{k},\omega_S,t) \qquad (2.15)$$

$$=I_{\mathrm{INARS}}(\tau)+I_{\mathrm{CARS}}(\tau,\Delta\mathbf{k})\ , \qquad (2.16)$$

where ΔT denotes the time range of observation of the scattered photons. The integration over ω_S means that we detect the photons without any frequency resolution, which allows us to adopt a δ function form for the time correlation function of the scattered photons. This reduces 70 terms in Eqs. (2.14) to 20 terms. Making use of Eqs. (2.3), (2.5), and (2.6), $I_{\mathrm{INARS}}(\tau)$ and $I_{\mathrm{CARS}}(\tau,\Delta\mathbf{k})$ are expressed as

$$I_{\mathrm{INARS}}(\tau)=\sum_{l=1}^{n_\alpha}I_l(\tau)+\sum_{m=1}^{n_\beta}I_m(\tau) \qquad (2.17\mathrm{a})$$

and

$$I_{\mathrm{CARS}}(\tau,\Delta\mathbf{k})$$

$$=\sum_{\substack{l=1\\ l\neq l'}}^{n_\alpha}\sum_{l'=1}^{n_\alpha}I_{ll'}(\tau)\exp(i\Delta\mathbf{k}\cdot\mathbf{r}_{ll'})$$

$$+\sum_{\substack{m=1\\ m\neq m'}}^{n_\beta}\sum_{m'=1}^{n_\beta}I_{mm'}(\tau)\exp(i\Delta\mathbf{k}\cdot\mathbf{r}_{mm'})$$

$$+\left[\sum_{l=1}^{n_\alpha}\sum_{m=1}^{n_\beta}I_{lm}(\tau)\exp(i\Delta\mathbf{k}\cdot\mathbf{r}_{lm})+\mathrm{c.c}\right] \qquad (2.17\mathrm{b})$$

respectively. The first and second terms in the right-hand side of Eq. (2.17a) represent the total populations of the photons emitted independently from molecules α and β, respectively, and independent of the incoming wave vector. The optical process associated with the two terms is an incoherent process. The magnitude of the two terms is proportional to the number of the excited molecules, that is, n_α and n_β, respectively. It should be noted that the incoherent optical process contains the microscopical information on the intramolecular dynamics induced by the heat-bath mode such as the intramolecular dephasing and coherence transfer.[20-22] The first, second, and third terms in the right-hand side of Eq. (2.17b) denote the total existence probabilities of the scattered photons due to the creation of the intermolecular coherence between the same kind molecules α (β) at different sites l (m) and l' (m'), and that between different kinds of molecules α and β, respectively.

In the case where $n_\alpha, n_\beta \gg 1$ within the laser spot, the magnitude of the three terms is approximately proportional to the square of the excited molecules number, namely, n_α^2, n_β^2, and $n_\alpha n_\beta$. We can see that the coherent optical process contains the information on the intermolecular dynamics induced by the interaction between two molecules through the heat-bath mode because each term $I_{ll'}(\tau)$, $I_{mm'}(\tau)$, and $I_{lm}(\tau)$ in Eq. (2.17b) depends on the states of two molecules at different sites. Terms $I_l(\tau)$ and $I_{lm}(\tau)$ can be expressed as

$$I_l(\tau)=2\,\mathrm{Re}\sum_{i=1}^{10} J_l^i(\tau) \tag{2.18a}$$

and

$$I_{lm}(\tau)=\sum_{i=1}^{10} K_{lm}^i(\tau)\ , \tag{2.18b}$$

respectively. After averaging Eqs. (2.18) over the heat-bath variables with the aid of the Liouville space Feynman diagram[23,24] as shown in Fig. 2 and within the factorization approximation,[25,26] we can easily reduce $J_l^i(\tau)$ and $K_{lm}^i(\tau)$ to, for example,

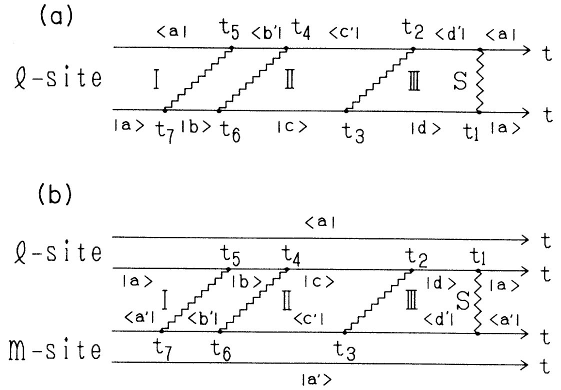

FIG. 2 Liouville space Feynman diagrams for time development of both intramolecular and intermolecular coherence in the ARS process. The diagram (a) which corresponds to Eq. (2.19a) represents time evolution of intramolecular coherence of a single molecule α_l in the time-resolved INARS process. The intramolecular coherence from the right- to left-hand side with initial condition $\bar{\rho}_{\alpha_l}(-\infty)$. The upper and lower lines represent the time development of the ket and bra vectors, respectively. Each wavy line represents the photon-molecule interaction. The intramolecular coherence between the c and c' states is created after the irradiation of pumping pulses (I, II) and evolves for period t_3-t_4. The diagram (b) which corresponds to Eq. (2.19b) represents the time evolution of the intermolecular coherence between two molecules α_l and $\beta_{m'}$ in the time-resolved CARS process. The upper and lower two lines are associated with representation for the time evolution of intramolecular coherence of the molecules α_l and β_m, respectively. These lines are connected through the incident laser fields (I, II, and III) indicated by wavy lines. In the case in which there exists the interaction between two molecules α_l and β_m through a common heat-bath mode, the four lines are connected with each other as well. The intermolecular coherence evolves from the right- to the left-hand side with initial condition $\bar{\rho}_{\alpha_l}(-\infty)\bar{\rho}_{\beta_m}(-\infty)$. The intermolecular coherence between $a\leftrightarrow c$ and $a'\leftrightarrow c'$ states is created after the irradation of pumping pulses (I, II) and evolves for the period t_3-t_4.

$$\begin{aligned}J_l^1(\tau)=&\int_{\Delta T}dt\frac{\partial}{\partial t}\sum_a\sum_{b'}\sum_b\sum_{c'}\sum_c\sum_{d'}\sum_d p_a^l M_{ad}^l M_{dc}^l M_{cb}^l M_{ba}^l M_{ab'}^l M_{b'c'}^l M_{c'd'}^l M_{d'a}^l\\&\times\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\int_{-\infty}^{t_3}dt_4\int_{-\infty}^{t_4}dt_5\int_{-\infty}^{t_6}dt_7\langle\hat{E}_{\mathrm{III}}^{(+)}(t_2)\hat{E}_{\mathrm{III}}^{(-)}(t_3)\rangle\langle\hat{E}_{\mathrm{II}}^{(-)}(t_4)\hat{E}_{\mathrm{II}}^{(+)}(t_6)\rangle\\&\times\langle\hat{E}_{\mathrm{I}}^{(+)}(t_5)\hat{E}_{\mathrm{I}}^{(-)}(t_7)\rangle[\langle\langle ba|G_l(t_6-t_7)|ba\rangle\rangle]_{\mathrm{av}}[\langle\langle ca|G_l(t_5-t_6)|ca\rangle\rangle]_{\mathrm{av}}\\&\times[\langle\langle cb'|G_l(t_4-t_5)|cb'\rangle\rangle]_{\mathrm{av}}[\langle\langle cc'|G_l(t_3-t_4)|cc'\rangle\rangle]_{\mathrm{av}}[\langle\langle dc'|G_l(t_2-t_3)|dc'\rangle\rangle]_{\mathrm{av}}[\langle\langle dd'|G_l(t_1-t_2)|dd'\rangle\rangle]_{\mathrm{av}}\end{aligned} \tag{2.19a}$$

and

$$\begin{aligned}K_{lm}^1(\tau)=&\int_{\Delta T}dt\frac{\partial}{\partial t}\sum_a\sum_b\sum_c\sum_d\sum_{a'}\sum_{b'}\sum_{c'}\sum_{d'} p_a^l p_{a'}^m M_{ad}^l M_{dc}^l M_{cb}^l M_{ba}^l M_{a'd'}^m M_{d'c'}^m M_{c'b'}^m M_{b'a'}^m\\&\times\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\int_{-\infty}^{t_3}dt_4\int_{-\infty}^{t_4}dt_5\int_{-\infty}^{t_5}dt_6\int_{-\infty}^{t_6}dt_7\langle\hat{E}_{\mathrm{III}}^{(-)}(t_2)\hat{E}_{\mathrm{III}}^{(+)}(t_3)\rangle\\&\times\langle\hat{E}_{\mathrm{II}}^{(+)}(t_4)\hat{E}_{\mathrm{II}}^{(-)}(t_6)\rangle\langle\hat{E}_{\mathrm{I}}^{(-)}(t_5)\hat{E}_{\mathrm{I}}^{(+)}(t_7)\rangle G^{lm}{}_{aa:a'b'}(t_6-t_7)G^{lm}{}_{aa:a'c'}(t_5-t_6)\\&\times G^{lm}{}_{ba:a'c'}(t_4-t_5)G^{lm}{}_{ca:a'c'}(t_3-t_4)G^{lm}{}_{ca:a'd'}(t_2-t_3)G^{lm}{}_{da:a'd'}(t_1-t_2)\ .\end{aligned} \tag{2.19b}$$

The terms p_a^l and $\langle \hat{E}_{\mathrm{I}}^{(-)}(t_i)\hat{E}_{\mathrm{I}}^{(+)}(t_j)\rangle$ in Eqs. (2.19a) and (2.19b) denote the population in the initial state a of the molecule α and the incident laser field correlation function, respectively. The matrix element $[\langle\langle \lambda v|G_l(t_i-t_j)|\lambda v\rangle\rangle]_{\mathrm{av}}$ in Eq. (2.19a) is that of the propagator of the intramolecular coherence between $\lambda\leftrightarrow v$ states of molecule α in the presence of the molecule–heat-bath interaction from time t_j to t_i, which is given under the Markov approximation as

$$[\langle\langle \lambda v|G_l(t_i-t_j)|\lambda v\rangle\rangle]_{\mathrm{av}} \\ =\exp[-(i\omega_{\lambda v}+\Gamma_{\lambda v:\lambda v})(t_i-t_j)] , \tag{2.20}$$

where $\omega_{\lambda v}$ and $\Gamma_{\lambda v:\lambda v}$ denote the transition frequency and the intramolecular-dephasing constant between the intramolecular coherence $\lambda\leftrightarrow v$, respectively.[12–14]

The term $G^{lm}{}_{\lambda v:\epsilon'\delta'}(t_i-t_j)$ in Eq. (2.19b) represents the time-development matrix element of the intermolecular coherence between $\nu_\alpha\leftrightarrow\lambda_\alpha$ and $\epsilon'_\beta\leftrightarrow\delta'_\beta$ from t_j to t_i in the presence of the molecule–heat-bath interaction and is defined by

$$G^{lm}{}_{\lambda v:\epsilon'\delta'}(t_i-t_j) \\ =[\langle\langle \nu_\alpha\epsilon'_\beta,\lambda_\alpha\delta'_\beta|\tilde{G}_{lm}(t_i-t_j)|\nu_\alpha\epsilon'_\beta,\lambda_\alpha\delta'_\beta\rangle\rangle]_{\mathrm{av}} , \tag{2.21}$$

where $\tilde{G}_{lm}(t_i-t_j)$, the propagator of the molecular pair of interest whose constituents are located at sites l and m, is given as

$$\tilde{G}_{lm}(t_i-t_j)=\exp[-i\hat{L}^{lm}_{\mathrm{MB}}(t_i-t_j)] , \tag{2.22}$$

with $\hat{L}^{lm}_{\mathrm{MB}}=[\hat{H}^{lm}_{\mathrm{MB}},\ ]/\hbar$. The equation of motion for $G^{lm}_{\lambda v:\epsilon'\delta'}(t_i-t_j)$ is given in the next section.

The diagram (a) shown in Fig. 2 is the Liouville space Feynman diagram representing the time evolution of the intramolecular coherence of molecule α in the INARS. The upper line (the lower line) stand for the time development of the bra(ket) vectors of the molecule α, and both lines are connected through the incident laser fields (I, II, and III) indicated by wavy lines and through the heat bath as well.

The diagram (b) in Fig. 2 stands for the time development of the intermolecular coherence between molecules α_l and β_m in the time-resolved CARS process. The upper and lower two lines are associated with representation for the time development of intramolecular coherence of molecules α_l and β_m, respectively. These lines are connected through the incident laser fields (I, II, and III) indicated by wavy lines. In the case in which there exists the interaction between two molecules α_l and β_m through a common heat-bath mode, the four lines are connected with each other as well.

The other diagrams are depicted in Figs. 3. The terms corresponding to these diagrams can be easily reduced by using the seven-time point Liouville space Feynamn diagrams as well.

B. Equation of motion for the intermolecular coherence

We are now in a position to find the equation of motion of the intermolecular coherence for pair molecules, i.e., coherence between the Raman transitions, $v\leftrightarrow\lambda$ and $\epsilon'\leftrightarrow\delta'$ at sites l and m, $G^{lm}{}_{\lambda v:\epsilon'\delta'}(t_i-t_j)$, in the presence of molecule–heat-bath interaction. This can easily be accomplished by applying the projection operator method[17,18] to the density-matrix equation of the total system in the absence of the radiation fields because both pumping and probing pulses are absent during time duration of t_i-t_j. For this purpose, in this subsection we consider a system which consists of two molecules α_l and β_m which interact with each other through the heat-bath mode. The total Hamiltonian without the radiation field ones $\hat{H}_{\mathrm{MB}}$ is given by

$$\hat{H}_{\mathrm{MB}}=\hat{H}_0+\hat{H}'_{\mathrm{MB}} \tag{2.23}$$

and

$$\hat{H}_0=\hat{H}_\alpha+\hat{H}_\beta+\hat{H}_B , \tag{2.24}$$

where $\hat{H}_\alpha$ $(\hat{H}_\beta)$ and $\hat{H}_B$ denote the Hamiltonian of the molecules α (β) and the heat bath, respectively. Hamiltonian $\hat{H}'_{\mathrm{MB}}$ represents the interaction between the molecules α (β) and the heat-bath mode.

The time evolution of the total system is determined by the Liouville equation for the density operator $\rho(t)$

$$-\frac{\partial}{\partial t}\rho(t)=i\hat{L}\rho(t) , \tag{2.25}$$

where $\hat{L}$ represents the Liouville operator of the total system.

Applying the Laplace transformation,

$$\rho(s)=\int_0^\infty dt\,\exp(-st)\rho(t) , \tag{2.26}$$

to Eq. (2.25), we obtain the equation for $\rho(s)$ in the s space

$$(s+i\hat{L})\rho(s)=\rho(0) , \tag{2.27}$$

where $\rho(0)$ $[\equiv\rho^{(\alpha)}(0)\rho^{(\beta)}(0)\rho^{(B)}(0)]$ is the density operator $\rho(t)$ at $t=0$. It is assumed that the molecules and heat bath are in thermal equilibrium.

Introducing projection operators

$$\hat{P}_B\equiv\rho^{(B)}(0)\mathrm{Tr}_B \tag{2.28}$$

and

$$\hat{Q}_B\equiv 1-\hat{P}_B \tag{2.29}$$

in which $\hat{P}_B^2=\hat{P}_B$, $\hat{Q}_B^2=\hat{Q}_B$, and $\hat{Q}_B\hat{P}_B=\hat{P}_B\hat{Q}_B=0$, Eq. (2.27) yields

$$[s+i(\hat{L}_\alpha+\hat{L}_\beta)+\langle\hat{\Sigma}(s)\rangle_{\mathrm{av}}]\rho_{\alpha\beta}(s)=\rho_{\alpha\beta}(0) , \tag{2.30}$$

where

$$\rho_{\alpha\beta}(s)=\mathrm{Tr}_B[\rho(s)] \tag{2.31a}$$

and

$$\langle\hat{\Sigma}(s)\rangle_{\mathrm{av}}=\mathrm{Tr}_B[\hat{\Sigma}(s)\rho^{(B)}(0)] . \tag{2.31b}$$

Operator $\hat{\Sigma}(s)$ in Eq. (2.30) represents the self-energy operator and satisfies

$$\hat{\Sigma}(s)=i\hat{L}'_{\mathrm{MB}}-i\hat{L}'_{\mathrm{MB}}\hat{Q}_B\frac{1}{s+i(\hat{L}_\alpha+\hat{L}_\beta+\hat{L}_B)}\hat{Q}_B\hat{\Sigma}(s)\,, \tag{2.32}$$

where $\hat{L}'_{\mathrm{MB}}=[\hat{H}'_{\mathrm{MB}},\ \ ]/\hbar$. Within the second Born approximation to the molecule–heat-bath interaction, Eq. (2.31b) can be expressed as

$$\langle\hat{\Sigma}(s)\rangle_{\mathrm{av}}\sim\mathrm{Tr}_B\left[\hat{L}'_{\mathrm{MB}}\frac{1}{s+i(\hat{L}_\alpha+\hat{L}_\beta+\hat{L}_B)}\hat{L}'_{\mathrm{MB}}\rho^{(B)}(0)\right]. \tag{2.33}$$

Performing the inverse Laplace transformation of Eqs. (2.30), we obtain

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}(t)=-i(\hat{L}_\alpha+\hat{L}_\beta)\rho_{\alpha\beta}(t)-\int_0^t d\mu\langle\hat{\Sigma}(\mu)\rangle_{\mathrm{av}}\rho_{\alpha\beta}(t-\mu)\,, \tag{2.34}$$

where

$$\langle\hat{\Sigma}(\mu)\rangle_{\mathrm{av}}=\frac{1}{2\pi i}\int_{-i\infty+c}^{i\infty+c}d\mu\langle\hat{\Sigma}(s)\rangle_{\mathrm{av}}\exp(s\mu)\,. \tag{2.35}$$

Making use of the displacement operator

$$\rho_{\alpha\beta}(t-\mu)=\exp\left(-\mu\frac{\partial}{\partial t}\right)\rho_{\alpha\beta}(t)\,, \tag{2.36}$$

we can rewrite Eq. (2.34) as

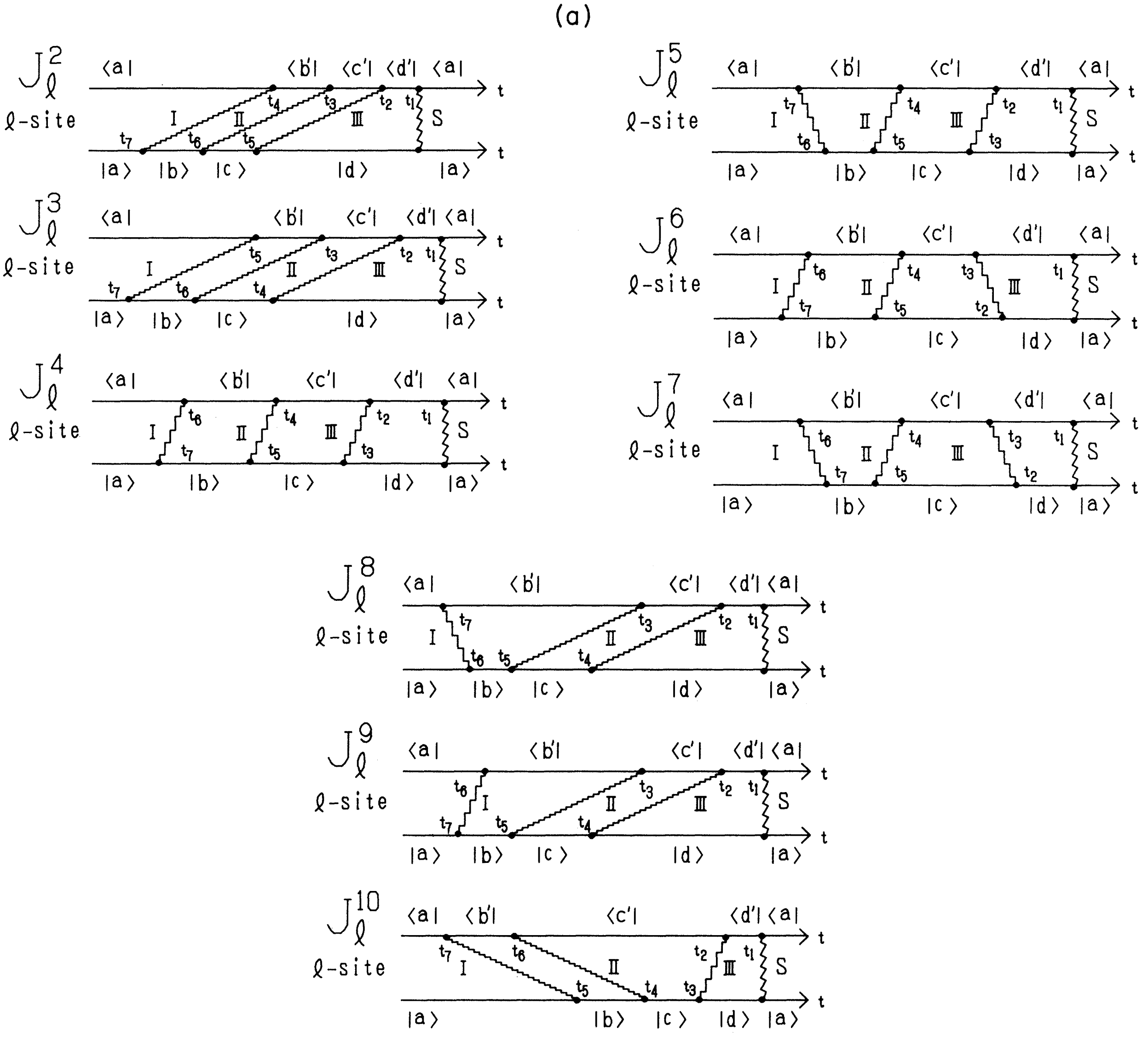

FIG. 3 (a) Other diagrams J_l^n for the time development of intramolecular coherence of the single molecule α_l. (b) Other diagrams K_{lm}^n for the time evolution of intermolecular coherence between two molecules α_l and β_m. The diagrams conjugate to those shown in Figs. 2 and 3 are omitted.

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}(t)=-i(\hat{L}_\alpha+\hat{L}_\beta)\rho_{\alpha\beta}(t)-\int_0^t d\mu\langle\hat{\Sigma}(\mu)\rangle_{\text{av}}\exp\left(-\mu\frac{\partial}{\partial t}\right)\rho_{\alpha\beta}(t) . \qquad (2.37)$$

Within the lowest order of $\langle\hat{\Sigma}(\mu)\rangle_{\text{av}}$, Eq. (2.36) can be expressed as

$$\rho_{\alpha\beta}(t-\mu)=\exp[-i(\hat{L}_\alpha+\hat{L}_\beta)\mu]\rho_{\alpha\beta}(t) . \qquad (2.38)$$

Substituting Eq. (2.38) into Eq. (2.37) yields

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}(t)=-[i(\hat{L}_\alpha+\hat{L}_\beta)+\hat{\Gamma}(t)]\rho_{\alpha\beta}(t) , \qquad (2.39)$$

where

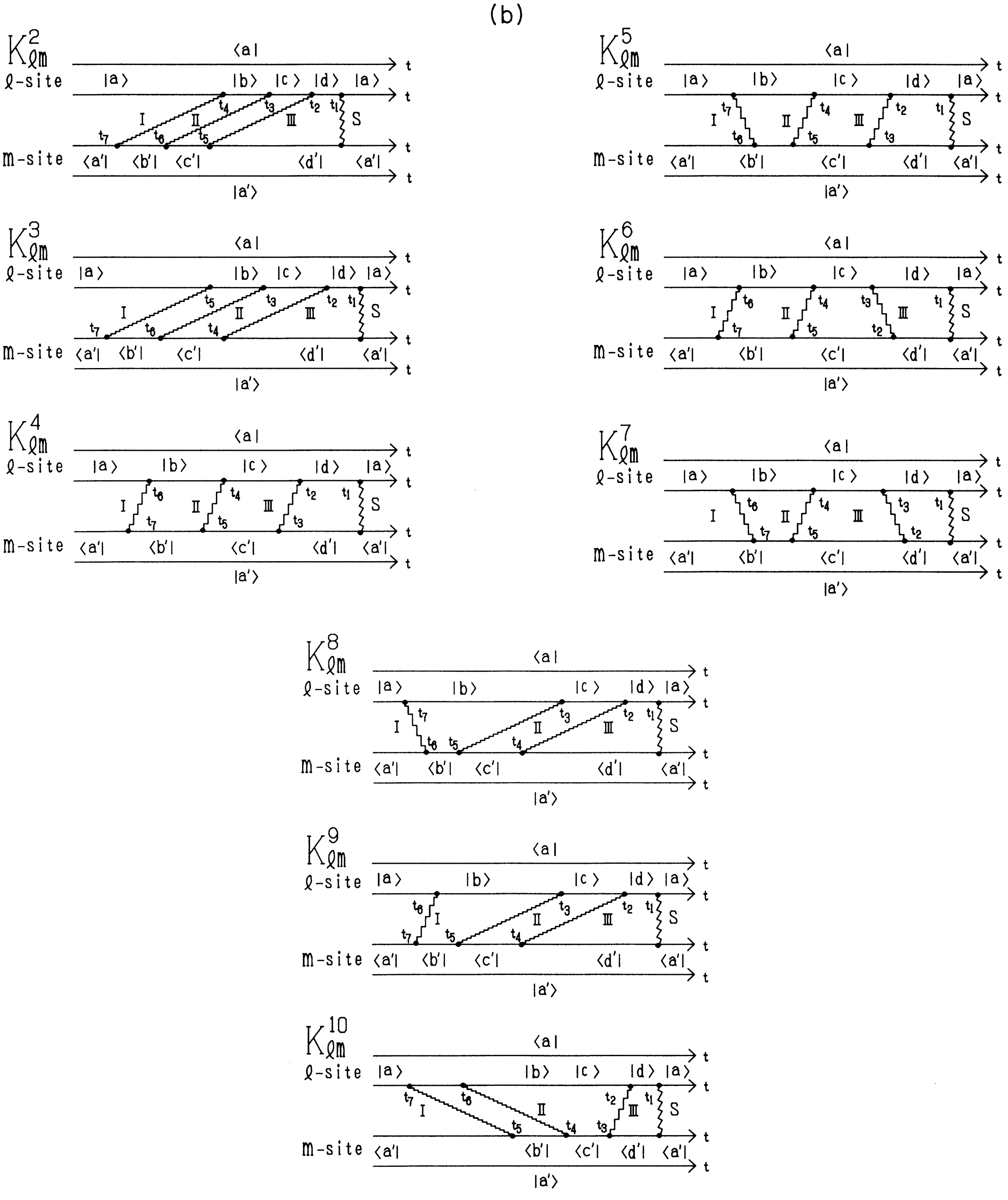

FIG. 3. (*Continued*).

$$\hat{\Gamma}(t)=\int_0^t d\mu \langle \hat{\Sigma}(\mu)\rangle_{\rm av} \exp[-i(\hat{L}_\alpha+\hat{L}_\beta)\mu] \ . \qquad (2.40)$$

The equation of motion for the intermolecular coherence between two transitions at sites α and β, $i_\alpha \leftrightarrow j_\alpha$ and $i'_\beta \leftrightarrow j'_\beta$,

$$G^{\alpha\beta}{}_{ji:i'j'}(t)=\langle\langle j_\alpha i'_\beta, i_\alpha j'_\beta | \rho_{\alpha\beta}(t)\rangle\rangle \ , \qquad (2.41)$$

is given as

$$\frac{d}{dt}G^{\alpha\beta}{}_{ji:i'j'}(t)=-[i\omega^{\alpha\beta}_{ji:i'j'}+\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'}(t)]G^{\alpha\beta}{}_{ji:i'j'}(t)+\sum_{(p_\alpha p'_\beta q_\alpha q'_\beta)\neq(j_\alpha i'_\beta i_\alpha j'_\beta)}\sum\sum\sum \Gamma^{\alpha\beta}_{ji,i'j':pq,p'q'}(t)G^{\alpha\beta}{}_{pq:p'q'}(t) \ , \qquad (2.42)$$

where

$$\omega^{\alpha\beta}_{ji:i'j'}=\omega_{j_\alpha}-\omega_{i_\alpha}+\omega_{i'_\beta}-\omega_{j'_\beta} \ , \qquad (2.43)$$

and the summations are carried out excluding the case $(p_\alpha \neq j_\alpha, p'_\beta \neq i'_\beta, q_\alpha \neq i_\alpha, q'_\beta \neq j'_\beta)$.

The second term in the right-hand side of Eq. (2.42), $\Gamma^{\alpha\beta}{}_{ji,i'j':ji,i'j'}(t)$, is expressed as

$$\begin{aligned}\Gamma^{\alpha\beta}{}_{ji,i'j':ji,i'j'}(t)&=\langle\langle j_\alpha i'_\beta, i_\alpha j'_\beta | \hat{\Gamma}(t) | j_\alpha i'_\beta, i_\alpha j'_\beta\rangle\rangle \\ &=\frac{1}{\hbar^2}\int_0^t d\mu \left[\sum_{m_\alpha}\sum_{m'_\beta} \exp(-i\omega_{m_\alpha m'_\beta : j_\alpha i'_\beta}\mu)\langle V'_{j_\alpha i'_\beta : m_\alpha m'_\beta}(\mu) V'_{m_\alpha m'_\beta : j_\alpha i'_\beta}\rangle_{\rm av} \right. \\ &\quad + \sum_{l_\alpha}\sum_{l'_\beta} \exp(-i\omega_{i_\alpha j'_\beta : l_\alpha l'_\beta}\mu)\langle V'_{i_\alpha j'_\beta : l_\alpha l'_\beta} V'_{l_\alpha l'_\beta : i_\alpha j'_\beta}(\mu)\rangle_{\rm av} \\ &\quad \left. -[\langle V'_{i_\alpha j'_\beta : i_\alpha j'_\beta}(\mu) V'_{j_\alpha i'_\beta : j_\alpha i'_\beta}\rangle_{\rm av} + \langle V'_{i_\alpha j'_\beta : i_\alpha j'_\beta} V'_{j_\alpha i'_\beta : j_\alpha i'_\beta}(\mu)\rangle_{\rm av}] \right] \ , \qquad (2.44)\end{aligned}$$

where

$$V'_{j_\alpha i'_\beta : m_\alpha m'_\beta}(\mu)=\langle j_\alpha i'_\beta | \exp(i\mu \hat{H}_B/\hbar)\hat{H}'_{\rm MB}\exp(-i\mu\hat{H}_B/\hbar)| m_\alpha m'_\beta\rangle \qquad (2.45a)$$

and

$$\omega_{j_\alpha i'_\beta : i_\alpha j'_\beta}=\omega_{j_\alpha}+\omega_{i'_\beta}-(\omega_{i_\alpha}+\omega_{j'_\beta}) \ . \qquad (2.45b)$$

The real part of the term $\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'}(t)$ represents the intermolecular-dephasing rate between two transitions, $i_\alpha \leftrightarrow j_\alpha$ and $i'_\beta \leftrightarrow j'_\beta$. The imaginary part of the matrix element refers to the time-dependent frequency shift.

The term $\Gamma^{\alpha\beta}_{ji,i'j':pq,p'q'}(t)$ in Eq. (2.42) is expressed as

$$\begin{aligned}\Gamma^{\alpha\beta}_{ji,i'j':pq,p'q'}(t)&=-\langle\langle j_\alpha i'_\beta, i_\alpha j'_\beta | \hat{\Gamma}(t) | p_\alpha p'_\beta, q_\alpha q'_\beta\rangle\rangle \\ &=-\frac{1}{\hbar^2}\int_0^t d\mu \left[\sum_{m_\alpha}\sum_{m'_\beta} \exp(-i\omega_{m_\alpha m'_\beta : p_\alpha p'_\beta}\mu)\langle V'_{j_\alpha i'_\beta : m_\alpha m'_\beta}(\mu) V'_{m_\alpha m'_\beta : p_\alpha p'_\beta}\rangle_{\rm av}\delta_{i_\alpha q_\alpha}\delta_{j'_\beta q'_\beta} \right. \\ &\quad + \sum_{l_\alpha}\sum_{l'_\beta} \exp(-i\omega'_{q_\alpha q'_\beta : l_\alpha l'_\beta}\mu)\langle V'_{q_\alpha q'_\beta : l_\alpha l'_\beta} V'_{l_\alpha l'_\beta : i_\alpha j'_\beta}(\mu)\rangle_{\rm av} \\ &\quad \times \delta_{j_\alpha p_\alpha}\delta_{i'_\beta p'_\beta} - [\exp(-i\omega_{j_\alpha i'_\beta : p_\alpha p'_\beta}\mu)\langle V'_{q_\alpha q'_\beta : i_\alpha j'_\beta}(\mu) V'_{j_\alpha i'_\beta : p_\alpha p'_\beta}\rangle_{\rm av} \\ &\quad \left. + \exp(-i\omega_{q_\alpha q'_\beta : i_\alpha j'_\beta}\mu)\langle V'_{q_\alpha q'_\beta : i_\alpha j'_\beta} V'_{j_\alpha i'_\beta : p_\alpha p'_\beta}(\mu)\rangle_{\rm av}] \right] \qquad (2.46)\end{aligned}$$

The real part of the term $\Gamma^{\alpha\beta}_{ji,i'j':pq,p'q'}(t)$ denotes the magnitude of transfer between two intermolecular coherences, $i_\alpha \leftrightarrow j_\alpha$ and $i'_\beta \leftrightarrow j'_\beta$, and $p_\alpha \leftrightarrow q_\alpha$ and $p'_\beta \leftrightarrow q'_\beta$ between two molecules, and is called the time-dependent intermolecular coherence transfer rate.

III. RESULTS AND DISCUSSION

In Sec. II, we have first shown how both the incoherent and coherent third-order nonlinear optical processes, that is, INARS and CARS, are taken into account on the same ground. This has been accomplished by expressing the intensities in terms of the scattered photon numbers in unit time. It is clear that only the CARS process can be treated by using the ordinary, semiclassical method by which the third-order nonlinear polarization is evaluated. Information on the intermolecular dynamics[26–29] such as intermolecular dephasing and intermolecular coherence transfer is directly reflected in the time-resolved CARS spectra.[12–14] Second, we have obtained the equation of motion for the intermolecular coherence that the self-energy operator of molecular pair of interest is derived under the weak molecule–heat-bath interaction.

In this section, first we clarify the structure of the intermolecular-dephasing constant within the Markov approximation. It is shown that the intermolecular-dephasing constant is not given by Eq. (1.1) when the molecular pairs are correlated with each other through a heat-bath mode. For this purpose, we consider two cases. In one case there exists a common heat-bath mode between the relevant two molecules, and in the other case two molecules are uncorrelated. In the former case, the interaction Hamiltonian $\hat{H}'_{\mathrm{MB}}$ is, for simplicity, assumed to be expressed as

$$\hat{H}'_{\mathrm{MB}}=\hat{H}'_{\alpha B}+\hat{H}'_{\beta B} , \tag{3.1}$$

where $\hat{H}'_{\alpha B}$ ($\hat{H}'_{\beta B}$) denotes the interaction Hamiltonian between molecule α (β) and heat-bath mode. We omit the direct interaction between molecules α and β through the heat-bath mode, i.e., $\hat{H}'_{\alpha\beta B}=0$.

In the latter case, $\hat{H}'_{\mathrm{MB}}$ is expressed as

$$\hat{H}'_{\mathrm{MB}}=\hat{H}'_{\alpha B}+\hat{H}'_{\beta B} . \tag{3.2}$$

It is assumed that $\hat{H}'_{\alpha B}$ is given by $\hat{V}_\alpha \hat{R}_B$ in which $\hat{V}_\alpha$ and $\hat{R}_B$ are operators of the molecule α and heat-bath mode.

A. Structure of the intermolecular-dephasing constant

Within the Markov approximation, the intermolecular-dephasing constant related to the coherence decay between $i_\alpha \leftrightarrow j_\alpha$ and $i'_\beta \leftrightarrow j'_\beta$ Raman transitions is given by taking the real part of Eq. (A4) and letting $t \longrightarrow \infty$ as

$$\begin{aligned}\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'}&=\mathrm{Re}\langle\langle j_\alpha i'_\beta, i_\alpha j'_\beta|\hat{\Gamma}(\infty)|j_\alpha i'_\beta, i_\alpha j'_\beta\rangle\rangle\\&=\tfrac{1}{2}(\Gamma^{\alpha}_{ii:ii}+\Gamma^{\alpha}_{jj:jj}+\Gamma^{\beta}_{i'i':i'i'}+\Gamma^{\beta}_{j'j':j'j'})\\&\quad+\Gamma^{\alpha\beta(d)}_{ji,i'j':ji,i'j'} ,\end{aligned} \tag{3.3}$$

where $\Gamma^{\alpha}_{ii:ii}$ and $\Gamma^{\alpha\beta(d)}_{ji,i'j':ji,i'j'}$ are the population decay and the intermolecular pure dephasing constants, respectively, which are given by

$$\Gamma^{\alpha}_{ii:ii}=\frac{2\pi}{\hbar^2}\sum_{B_i}\sum_{B_f}\sum_{m_\alpha\neq i_\alpha}p(B_i)|\langle i_\alpha,B_i|\hat{H}'_{\alpha B}|m_\alpha,B_f\rangle|^2 \times\delta(\omega_{m_\alpha B_f:i_\alpha B_i}) \tag{3.4}$$

and

$$\begin{aligned}\Gamma^{\alpha\beta(d)}_{ji,i'j':ji,i'j'}=\frac{2\pi}{\hbar^2}\sum_{B_i}\sum_{B_f}p(B_i)|(&\langle j_a,B_i|\hat{H}'_{\alpha B}|j_\alpha,B_f\rangle-\langle i_\alpha,B_i|\hat{H}'_{\alpha B}|i_\alpha,B_f\rangle)\\&+(\langle i'_\beta,B_i|\hat{H}'_{\beta B}|i'_\beta,B_f\rangle-\langle j'_\beta,B_i|\hat{H}'_{\beta B}|j'_\beta,B_f\rangle)|^2\delta(\omega_{B_iB_f}) .\end{aligned} \tag{3.5}$$

In terms of the intramolecular-dephasing constant defined as

$$\Gamma^{\alpha}_{ji:ji}=\tfrac{1}{2}(\Gamma^{\alpha}_{ii:ii}+\Gamma^{\alpha}_{jj:jj})+\Gamma^{\alpha(d)}_{ji:ji} , \tag{3.6}$$

where

$$\Gamma^{\alpha(d)}_{ji:ji}=\frac{2\pi}{\hbar^2}\sum_{B_i}\sum_{B_f}p(B_i)|(\langle j_\alpha,B_i|\hat{H}'_{\alpha B}|j_\alpha,B_f\rangle-\langle i_\alpha,B_i|\hat{H}'_{\alpha B}|i_\alpha,B_f\rangle)|^2\delta(\omega_{B_iB_f}) , \tag{3.7}$$

Eq (3.3) can be rewritten as

$$\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'}=\Gamma^{\alpha}_{ji:ji}+\Gamma^{\beta}_{i'j':i'j'}-\Gamma^{\alpha\beta(\mathrm{interfere})}_{ji,i'j':ji,i'j'} , \tag{3.8}$$

where the $\Gamma^{\alpha\beta(\mathrm{interfere})}_{ji,i'j':ji,i'j'}$ interference term of the intramolecular pure dephasings between molecules α and β is defined as

$$\begin{aligned}\Gamma^{\alpha\beta(\mathrm{interfere})}_{ji,i'j':ji,i'j'}=\frac{4\pi}{\hbar^2}\sum_{B_i}\sum_{B_f}p(B_i)&(\langle j_\alpha,B_i|\hat{H}'_{\alpha B}|j_\alpha,B_f\rangle-\langle i_\alpha,B_i|\hat{H}'_{\alpha B}|i_\alpha,B_f\rangle)\\&\times(\langle j'_\beta,B_i|\hat{H}'_{\beta B}|j'_\beta,B_f\rangle-\langle i'_\beta,B_i|\hat{H}'_{\beta B}|i'_\beta,B_f\rangle)\delta(\omega_{B_iB_f}) .\end{aligned} \tag{3.9}$$

Equation (3.8) indicates that in the presence of the common heat-bath mode the magnitude of the intermolecular-dephasing constant is less than that of the sum of the intramolecular-dephasing constant by the magnitude of the interference term $\Gamma^{\alpha\beta(\mathrm{interfere})}_{ji,i'j':ji,i'j'}$. We can say that the intermolecular-dephasing constant is not simply given by Equation (1.1) in the case in which the two molecules are correlated through the common heat bath. In other words, the fluctuations of the transition frequencies of the molecular pair interfere with each other through the common heat-bath mode.

We confine ourselves to the intermolecular-dephasing constants for the ensemble consisting of the same kind of molecules with one Raman active mode that with two Raman active ones as shown in Fig. 4. In the former case, the intermolecular-dephasing constant for the transitions $i \leftrightarrow j$ at site l and $i \leftrightarrow j$ at site l' is given by

$$\Gamma^{ll'}_{ji,ij:ji,ij} = \tfrac{1}{2}(\Gamma^{l}_{ii:ii} + \Gamma^{l}_{jj:jj} + \Gamma^{l'}_{ii:ii} + \Gamma^{l'}_{jj:jj}) \ . \tag{3.10}$$

In this case there exist no intramolecular and intermolecular pure dephasing effects in the dephasing constant.

In the latter case, the intermolecular-dephasing constant for $i \leftrightarrow j$ transition at site l and $i \leftrightarrow j$ at site l' is given by

$$\Gamma^{ll'}_{ji,ij:ji,ij} = \tfrac{1}{2}(\Gamma^{l}_{ii:ii} + \Gamma^{l}_{jj:jj} + \Gamma^{l'}_{ii:ii} + \Gamma^{l'}_{jj:jj}) \ , \tag{3.11}$$

and that for the transitions $i \leftrightarrow j$ at site l and $i \leftrightarrow k$ at site l' is expressed as

$$\Gamma^{ll'}_{ji,ik:ji,ik} = \tfrac{1}{2}(\Gamma^{l}_{ii:ii} + \Gamma^{l}_{jj:jj} + \Gamma^{l'}_{ii:ii} + \Gamma^{l'}_{kk:kk}) + \Gamma^{ll'(d)}_{ji,ik:ji,ik} \ . \tag{3.12}$$

In the case in which two molecules are uncorrected, the intermolecular pure dephasing constant reduces to

$$\Gamma^{\alpha\beta(d)}_{ji,i'j':ji,i'j'} = \Gamma^{\alpha(d)}_{ji:ji} + \Gamma^{\beta(d)}_{i'j':i'j'} \ . \tag{3.13}$$

From Eqs. (3.3), (3.6), and (3.13), we obtain

$$\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'} = \Gamma^{\alpha}_{ji:ji} + \Gamma^{\beta}_{i'j':i'j'} \ , \tag{3.14}$$

which is same as Eq. (1.1).

B. Inhomogeneity due to intermolecular-dephasing process

In this section we consider the inhomogeneous effects on the time-resolved CARS spectra from the molecular ensemble. The imaginary part of the diagonal matrix element of the intermolecular coherence, $\langle\langle j_\alpha i'_\beta, i_\alpha j'_\beta | \hat{\Gamma}(\infty) | j_\alpha i'_\beta, i_\alpha j'_\beta \rangle\rangle$, which represetns the frequency shift $\Delta^{\alpha\beta}_{ji,i'j':ji,i'j'}$ creates the inhomogeneity of the transition frequency shift $\omega^{\alpha\beta}_{ji:i'j'}$ between molecules α and β in the molecular ensemble. The frequency shift $\Delta^{\alpha\beta}_{ji,i'j':ji,i'j'}$ is expressed as

$$\begin{aligned}\Delta^{\alpha\beta}_{ji,i'j':ji,i'j'} &= \mathrm{Im}\langle\langle j_\alpha i'_\beta, i_\alpha j'_\beta | \hat{\Gamma}(\infty) | j_\alpha i'_\beta, i_\alpha j'_\beta \rangle\rangle \\ &= \Delta^{\alpha}_{jj:jj} + \Delta^{\beta}_{i'i':i'i'} - (\Delta^{\alpha}_{ii;ii} + \Delta^{\beta}_{j'j':j'j'}) \ ,\end{aligned} \tag{3.15}$$

where

$$\Delta^{\alpha}_{ii;ii} = \frac{2\pi}{\hbar^2} \sum_{B_i} \sum_{B_f} \sum_{m_\alpha \neq i_\alpha} p(B_i) |\langle i_\alpha, B_i | \hat{H}'_{\alpha B} | m_\alpha, B_f \rangle|^2 \times \mathrm{P} \frac{1}{\omega_{m_\alpha} + \omega_{B_f} - \omega_{i_\alpha} - \omega_{B_i}} \ , \tag{3.16}$$

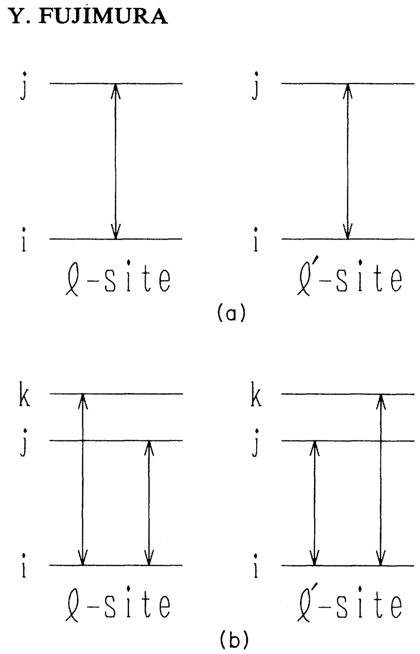

FIG. 4 (a) Model for the intermolecular-dephasing process in the case in which the ensemble consists of the same kind of molecules with one Raman active mode. After the pumping process, the intermolecular coherence $i \leftrightarrow j$ (l -site) and $i \leftrightarrow j$ (l' -site) is created. (b) Schematic diagram for the intermolecular-dephasing process in the case in which the ensemble consists of the same kind of molecules with two Raman active modes. After the pumping process, the intermolecular coherence between $i \leftrightarrow j$ (l site) and $i \leftrightarrow j$ (l' -site), $i \leftrightarrow k$ (l site) and $i \leftrightarrow j$ (l' site), and $i \leftrightarrow j$ (l site) and $i \leftrightarrow k$ (l' site) are created.

where P denotes Cauchy's principal value. From Eq. (3.15), we can see that the intermolecular pure dephasing process does not contribute to the frequency shift in our model for the molecule–heat-bath interaction. There exist various values of $\Delta^{\alpha\beta}_{ji,i'j':ji,i'j'}$ depending on the distance between the constituents of the molecular pairs ($\alpha\beta$). For the randomly distributed molecular ensemble, the inhomogeneity of $\Delta^{\alpha\beta}_{ji,i'j':ji,i'j'}$ is characterized by a Gaussian distribution function.

We consider two cases for the molecular ensemble. In case (1), the ensemble consists of only the same kind of molecule, α, and in case (2), two kinds of molecules α and β. In case (1), the time-resolved CARS spectra are approximately expressed from Eq. (2.17b) as

$$I_{\mathrm{CARS}}(\tau, \Delta\mathbf{k}) \sim \sum_{l \neq l'}^{n_\alpha} \sum^{n_\alpha} \exp[-(\Gamma^{ll'}_{ji,i'j':ji,i'j'} + i\Delta^{ll'}_{ji,i'j':ji,i'j'})\tau] \exp(i\Delta\mathbf{k}\cdot\mathbf{r}_{ll'}) \tag{3.17a}$$

$$= \sum_{l \neq l'}^{\Delta^l = \Delta^{l'}} \sum \exp(-\Gamma^{ll'}_{ji,i'j':ji,i'j'}\tau) \exp(i\Delta\mathbf{k}\cdot\mathbf{r}_{ll'}) + \sum_{l \neq l'}^{\Delta^l \neq \Delta^{l'}} \sum \exp[-(\Gamma^{ll'}_{ji,i'j':ji,i'j'} + i\Delta^{ll'})\tau] \exp(i\Delta\mathbf{k}\cdot\mathbf{r}_{ll'}) \ , \tag{3.17b}$$

where $\Delta^{ll'}$ $(=\Delta^{ll'}_{ji,i'j':ji,i'j'})$ is the difference of the Raman transition frequency shift between molecules at site l and l' and $\Delta^l = \Delta^{\alpha}_{jj:jj} - \Delta^{\alpha}_{ii:ii}$. The first term of the right-hand side in Eq. (3.17b) represents the contribution of the homogeneous subsystem in the molecular ensemble of the time-resolved CARS spectra. The second term refers to the contribution of the subsystem with local structures. We assume that $\Delta^{ll'}$ is distributed with Gaussian function

$$F_\alpha(\Delta^{ll'})=\frac{1}{(2\pi)^{1/2}\sigma_\alpha}\exp\left[-\frac{(\Delta^{ll'}-\Delta^0_\alpha)^2}{2\sigma^2_\alpha}\right], \tag{3.18}$$

where Δ^0_α and σ_α, which denote the mean value of $\Delta^{ll'}$ and its dispersion, respectively, are proper to the ensemble. The intermolecular coherence decay constant in Eqs. (3.17) is assumed to be given as $\Gamma^{ll'}_{ji,i'j':ji,i'j'}=\Gamma^{l}_{ji:ji}+\Gamma^{l'}_{i'j':i'j'}$, neglecting the intermolecular pure depending constant, for simplicity. After averaging Eq. (3.17) over $\Delta^{ll'}$, the intensity is given by

$$I_{\text{CARS}}(\tau,\Delta\mathbf{k})\sim\text{Re}\exp(-2\Gamma^{\alpha}_{ji:i'j'}\tau)\left\{A_\alpha+B_\alpha\exp\left[-\left\{i\Delta^0_\alpha\tau+\frac{\sigma^2_\alpha}{2}\tau^2\right\}\right]\right\}\delta(\Delta\mathbf{k})\ , \tag{3.19}$$

where A_α and B_α are the square of the number of molecules in the homogeneous subsystem and that in the subsystem with the local structures, respectively. We call $B_\alpha/(A_\alpha+B_\alpha)$ *the degree of the structural order* in the ensemble in this paper, which is a measure of the magnitude of the local structures in the molecular ensemble and can be determined from the time-resolved CARS spectra by extrapolation.

In case (2), the intensity is similarly given by

$$\begin{aligned}I_{\text{CARS}}(\tau,\Delta\mathbf{k})\sim{}&\text{Re}\exp(-2\Gamma^{\alpha}_{ji:ji}\tau)\left\{A_\alpha+B_\alpha\exp\left[-\left\{i\Delta^0_\alpha\tau+\frac{\sigma^2_\alpha}{2}\tau^2\right\}\right]\right\}\\&+\text{Re}\exp(-2\Gamma^{\beta}_{j'i':j'i'}\tau)\left\{A_\beta+B_\beta\exp\left[-\left\{i\Delta^0_\beta\tau+\frac{\sigma^0_\beta}{2}\tau^2\right\}\right]\right\}\\&+2\,\text{Re}\exp[-(i\omega^{\alpha\beta}_{ji:i'j'}+\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'})\tau]\left\{A_{\alpha\beta}+B_{\alpha\beta}\exp\left[-\left\{i\Delta^0_{\alpha\beta}\tau+\frac{\sigma^2_{\alpha\beta}}{2}\tau^2\right\}\right]\right\}\delta(\Delta\mathbf{k})\ .\end{aligned} \tag{3.20}$$

The first and second terms in the right-hand side of Eq. (3.20) refer to the contribution of molecular pairs $\alpha\alpha$ and $\beta\beta$ to the time-resolved CARS spectra, respectively. The third term represents the contribution of the molecular pair $\alpha\beta$. $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are the product of the number of molecules α and that of molecules β in the homogeneous subsystem of the molecular mixture and that in the subsystem with the local structure, respectively. We can determine the ratio $B_{\alpha\beta}/(A_{\alpha\beta}+B_{\alpha\beta})$ which represents the degree of the structural order in the molecular mixture from the time-resolved CARS experiment by extrapolating the amplitude of the quantum beat. Thus, analyzing the time-resolved CARS spectra for disordered systems such as the molecular liquids and liquid crystal, we can obtain the information on the inhomogeneity of the structure from the microscopic points of view.

Finally, it is interesting to apply the theory developed in this paper to studying the microscopic information on the laser-induced collective motions and that on the structure of the molecular ensembles in ultrashort time regions.

In summary, in this paper, to study the mechanism of the intermolecular-dephasing processes we have derived the expression for the intensity for the ARS from a thermally distributed molecular ensemble by taking into account both incoherent (INARS) and coherent (CARS) optical processes from a microscopic point of view. Our general expression for the intensity of the CARS is given in terms of the time-development matrix element of the intermolecular coherence of the two Raman transitions between molecules α and β. The diagonal and of-diagonal matrix elements represent the intermolecular coherence decays and transfer, respectively. The time development is conveniently expressed on the Liouville space Feynman diagram in which the basis set is given by four vibrational states associated with the two Raman transitions. We have derived the equation of motion for the time-development matrix element of the intermolecular coherence by using the projection operator method in the case in which the relevant two molecules interact with heat-bath modes. Within the Markov approximation, we have clarified the structure of the intermolecular-dephasing constant in the presence of the correlation between the relevant molecules through a common heat-bath mode. The intermolecular pure dephasing constant appeared in the intermolecular-dephasing constant as a result of the elastic interactions between the relevant molecules and common heat bath. The intermolecular-dephasing constant is expressed in terms of the intramolecular-dephasing constants and interference of the intramolecular pure dephasing between the two molecules of interest. On the other hand, if there is no correlation between the two molecules, the intermolecular-dephasing constant is equal to the sum of the intramolecular-dephasing constant associated with the relevant molecules. The inhomogeneous effects on the time-resolved CARS spectra are also considered. The degree of the structural order is introduced to qualitatively express the inhomogeneity of molecular ensemble.

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APPENDIX: STRUCTURE OF THE INTERMOLECULAR-DEPHASING RATE

In this appendix, we rewrite Eq. (2.44) in terms of Eq. (3.1). Making use of Eq. (2.45a), Eq. (2.44) becomes

$$\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'}(t)=\frac{1}{\hbar^2}\int_0^t d\mu\left[G_B(\mu)\left[\sum_{m_\alpha}\sum_{m'_\beta}\exp(-i\omega_{m_\alpha m'_\beta:j_\alpha i'_\beta}\mu)|V_{j_\alpha i'_\beta:m_\alpha m'_\beta}|^2-V_{i_\alpha j'_\beta:i_\alpha j'_\beta}V_{j_\alpha i'_\beta:j_\alpha i'_\beta}\right]\right.$$
$$\left.+G_B(-\mu)\left[\sum_{l_\alpha}\sum_{l'_\beta}\exp(-i\omega_{i_\alpha j'_\beta:l_\alpha l'_\beta}\mu)|V_{i_\alpha j'_\beta:l_\alpha l'_\beta}|^2-V_{i_\alpha j'_\beta:i_\alpha j'_\beta}V_{j_\alpha i'_\beta:j_\alpha i'_\beta}\right]\right], \tag{A1}$$

where $V_{j_\alpha i'_\beta:m_\alpha m'_\beta}=\langle j_\alpha i'_\beta|\hat{V}_M|m_\alpha m'_\beta\rangle$. $G_B(\mu)$ in Eq. (A1), the correlation function of the heat bath, is defined as

$$G_B(\mu)=\sum_{B_i}\sum_{B_f}p(B_i)|\langle B_i|\hat{R}_B|B_F\rangle|^2\exp(i\omega_{B_iB_f}\mu)\ . \tag{A2}$$

$p(B_i)$ represents the population in the initial state B_i of the heat bath and $\omega_{B_iB_f}=\omega_{B_i}-\omega_{B_f}$. Dividing the summation in Eq. (A1) into four parts,

$$\sum_{m_\alpha}\sum_{m'_\beta}=\sum_{m_\alpha\neq i_\alpha}\sum_{m'_\beta\neq i'_\beta}+\sum_{m_\alpha\neq i_\alpha}\sum_{m'_\beta=i'_\beta}+\sum_{m_\alpha=i_\alpha}\sum_{m'_\beta\neq i'_\beta}+\sum_{m_\alpha=i_\alpha}\sum_{m'_\beta=i'_\beta}\ , \tag{A3}$$

we finally obtain the structure of the intermolecular-dephasing rate as

$$\Gamma^{\alpha\beta}_{ji,i'j':ji,i'j'}(t)=\frac{1}{\hbar^2}\int_0^t d\mu\left[G_B(\mu)\left[\sum_{m_\alpha\neq j_\alpha}\sum_{m'_\beta\neq i'_\beta}\exp(-i\omega_{m_\alpha m'_\beta:j_\alpha i'_\beta}\mu)|V_{j_\alpha i'_\beta:m_\alpha m'_\beta}|^2\right.\right.$$
$$+\sum_{m_\alpha\neq j_\alpha}\exp(-i\omega_{m_\alpha j_\alpha}\mu)|V_{j_\alpha i'_\beta:m_\alpha i'_\beta}|^2$$
$$\left.+\sum_{m'_\beta\neq i'_\beta}\exp(-i\omega_{m'_\beta i'_\beta}\mu)|V_{i_\alpha i'_\beta:i_\alpha m'_\beta}|^2+|V_{j_\alpha i'_\beta:j_\alpha i'_\beta}|^2-V_{i_\alpha j'_\beta:i_\alpha j'_\beta}V_{j_\alpha i'_\beta:j_\alpha i'_\beta}\right]$$
$$+G_B(\mu)\left[\sum_{l_\alpha\neq i_\alpha}\sum_{l'_\beta\neq j'_\beta}\exp(-i\omega_{i_\alpha j'_\beta:l_\alpha l'_\beta}\mu)|V_{i_\alpha j'_\beta:l_\alpha l'_\beta}|^2+\sum_{l_\alpha\neq i_\alpha}\exp(-i\omega_{i_\alpha l_\alpha}\mu)|V_{i_\alpha j'_\beta:l_\alpha j'_\beta}|^2\right.$$
$$\left.\left.+\sum_{l'_\beta\neq j'_\beta}\exp(-i\omega_{j_\beta' l'_\beta}\mu)|V_{i_\alpha j'_\beta:i_\alpha l'_\beta}|^2+|V_{i_\alpha j'_\beta:i_\alpha j'_\beta}|^2-V_{j_\alpha i'_\beta:j_\alpha i'_\beta}V_{i_\alpha j'_\beta:i_\alpha j'_\beta}\right]\right]. \tag{A4}$$

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