Modeling vibrational dephasing and energy relaxation of intramolecular anharmonic modes for multidimensional infrared spectroscopies

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Starting from a system-bath Hamiltonian in a molecular coordinate representation, we examine an applicability of a stochastic multilevel model for vibrational dephasing and energy relaxation in multidimensional infrared spectroscopy. We consider an intramolecular anharmonic mode nonlinearly coupled to a colored noise bath at finite temperature. The system-bath interaction is assumed linear plus square in the system coordinate, but linear in the bath coordinates. The square-linear system-bath interaction leads to dephasing due to the frequency fluctuation of system vibration, while the linear-linear interaction contributes to energy relaxation and a part of dephasing arises from anharmonicity. To clarify the role and origin of vibrational dephasing and energy relaxation in the stochastic model, the system part is then transformed into an energy eigenstate representation without using the rotating wave approximation. Two-dimensional (2D) infrared spectra are then calculated by solving a low-temperature corrected quantum Fokker-Planck (LTC-QFP) equation for a colored noise bath and by the stochastic theory. In motional narrowing regime, the spectra from the stochastic model are quite different from those from the LTC-QFP. In spectral diffusion regime, however, the 2D line shapes from the stochastic model resemble those from the LTC-QFP besides the blueshifts caused by the dissipation from the colored noise bath. The preconditions for validity of the stochastic theory for molecular vibrational motion are also discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2244558]

I. INTRODUCTION

Ultrafast nonlinear spectroscopy plays a pivotal role in investigating inter- and intramolecular motions in complex molecular systems.1 Over the last decade, extensive theoretical,2–20 computational,21–25 and experimental26–35 efforts have been made for multidimensional vibrational spectroscopy to have a variety of information for molecular motion and interactions.

Owing to recent technological progresses in the generation of stable ultrashort infrared (IR) laser pulses, third-order spectroscopic experiments have been extended in the IR region and can, therefore, be utilized to investigate intramolecular vibrational transition rather than electronic one. As an intramolecular vibrational motion is sensitive to local fluctuation of surroundings, it provides an important window to insight into the structure and dynamics of complex molecules, solvents, and protein environments. While the line shapes observed in IR absorption spectroscopy are broadened due to static inhomogeneity, we can separate the contribution of homogeneous vibrational motion, which contains important microscopic dynamics, by third-order IR spectroscopy such as an IR photon echo measurement.36 Theoretically, static inhomogeneity has been treated by using the slow modulation limit of the stochastic theory, and homogeneity by the fast modulation limit. However, there is also a wide intermediate range of modulation times between the inhomogeneous and homogeneous limits, which gives rise to what is called vibrational spectral diffusion. The spectral diffusion process was analyzed by means of three-pulse photon echo measurement. Hamm et al.37 performed the first femtosecond IR three-pulse echo experiment on a mode of the azide ion N3− in deuterium water. Employing the stochastic theory of frequency fluctuation,38,39 they quantified the magnitudes and time scales of dynamic solvent fluctuations that cause spectral diffusion. Hamm et al.40 also achieved the first two-dimensional infrared (2D-IR) measurement by means of double-resonance or dynamic hole burning experiments on the amide I bands of N-methylacetamide and small globular peptides, and gained access to the detailed information on the structures of peptides that could not be obtained from linear absorption spectra. These works stimulated many experimental and theoretical studies41–48 and sparked off the pulsed Fourier transform 2D-IR spectroscopy by means of the heterodyne-detected photon echo experiments.49–52 Objects under study of 2D-IR spectroscopic experiments have definitely spread very wide: conformational fluctuations of small peptides53–57 and dipptides,58,59 conformational changes in proteins,60–63 hydrogen-bonded complexes,64–67 and water dynamics.68 In the immediate past, heterodyned fifth-order 2D-IR measurements69 were reported on ions in glasses.70,71

In this paper, we explore roles of vibrational dephasing and energy relaxation involved in the multidimensional IR spectroscopy to establish a reasonable system-bath model to discuss these dissipative processes from a microscopic point of view. To study vibrational dephasing, the stochastic theory of transition frequencies was introduced72 and intensively used to analyze the signals from IR echo and 2D-IR spectroscopy. The stochastic model was extensively utilized in...
the nuclear magnetic resonance (NMR) or electronically resonant spectroscopy.\(^{39}\) The character of spectroscopic experiments is, however, different for vibrational and electronic transitions. While the decay time of population in electronically excited state is invariably long compared with the dephasing of optical transitions, that in vibrational excited states is sometimes comparable to the time scale of vibrational dephasing; the system relaxes toward the thermal equilibrium on time scale comparable with the vibrational dephasing. Nonetheless, the stochastic theory involves only frequency fluctuations without any accounts of the contributions from temperature and dissipation. Then, the effects of vibrational energy relaxation were sometimes included in a phenomenological manner independently from the stochastic theory. A simple one is a Bloch picture which accounts for the effects of energy relaxation and dephasing by a longitudinal relaxation time constant \(T_1\), a transversal relaxation time constant \(T_2\), and a pure dephasing time \(T_2'\), i.e., \(1/T_2 = 1/2T_1 + 1/T_2'\). The validity of such phenomenological approach is an open question, since such simple relation is based on the assumption of a weak coupling or a white noise bath within the rotating wave approximation (RWA). The stochastic theory and Bloch-Redfield theory also have inherent difficulty to treat a finite temperature system.

To clarify the above-mentioned problems, here, we start from a Hamiltonian consisting of an anharmonic molecular system coupled to a heat bath. The bath degrees of freedom are described by an ensemble of oscillators, which correspond to optically inactive modes such as solvent modes. The key to the relation between the coordinate and energy-level pictures is on a form of a system-bath interaction. To make our discussion more concrete, here, we denote the interaction potential as

\[
\mathcal{H}_{\text{int}} = q \hat{v} + \hat{p} \hat{q} + \sum_j \frac{1}{2} m_j \omega_j^2 \hat{x}_j^2 + \frac{1}{4} \sum_{j<k} \frac{1}{2} m_j m_k \omega_{jk}^2 \hat{x}_j \hat{x}_k.
\]

As we will show below, the primary contribution of 2D-IR signals arises from the transitions between the lowest three internal modes or solvent modes, are optically inactive and therefore, the system is regarded as in a low temperature where the quantum description of the system becomes important. For this purpose, we extended the quantum Fokker-Planck equation and included low-temperature correction terms.\(^{76}\) We show how one can handle low-temperature system using this formalism. For the interaction potential in Eq. (1.1), we include terms up to the second order in \(q\) and take into account only the linear dependence on \(\{x_j\}\), i.e., \(F_1(\{x_j\}) = -v_{11} \sum_j \hat{c}_j \hat{x}_j\) and \(F_2(\{x_j\}) = -v_{21} \sum_j \hat{c}_j \hat{x}_j^2\). Integrating the reduced equation of motion, we calculate signals for the system-bath Hamiltonian with bath coupling and temperatures. The major difficulty to calculate signals for the system-bath Hamiltonian with interaction potential [Eq. (1.1)] is on the derivation of the equation of motion for a reduced density matrix. If temperature is high compared with vibrational excitation energy, one can use the quantum Fokker-Planck equation for nearly Markovian noise bath.\(^{75}\) The case we want to discuss here is, however, the intramolecular vibrational modes, where the temperature is much lower than vibrational excitation energy; therefore, the system is regarded as in a low temperature where the quantum description of the system becomes important. For this purpose, we extended the quantum Fokker-Planck equation and included low-temperature correction terms.\(^{76}\) We show how one can handle low-temperature system using this formalism. For the interaction potential in Eq. (1.1), we include terms up to the second order in \(q\) and take into account only the linear dependence on \(\{x_j\}\), i.e., \(F_1(\{x_j\}) = -v_{11} \sum_j \hat{c}_j \hat{x}_j\) and \(F_2(\{x_j\}) = -v_{21} \sum_j \hat{c}_j \hat{x}_j^2\). Integrating the reduced equation of motion, we calculate 2D-IR signals and discuss the importance of dissipative and anharmonic effects which arise from the first term in Eq. (1.1) by comparison to the results from the energy-level picture with stochastic modulation.

This paper is organized as follows: In Sec. II we give a brief review of nonlinear optical responses and the stochastic theory. In Sec. III we introduce the quantum dissipative equation applicable to a low-temperature coordinate system, low-temperature corrected quantum Fokker-Planck (LT-CQFP) equation to analyze vibrational dephasing and energy relaxation in an intramolecular mode. In Sec. IV numerical results are presented as 2D-IR correlation spectra and are discussed. Finally, Sec. V is devoted to concluding remarks.

II. NONLINEAR RESPONSE FUNCTIONS

We consider a system consisting of a single intramolecular vibrational mode described by the Hamiltonian

\[
\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{q}),
\]

where \(m, q, p, \) and \(U(\hat{q})\) denote the effective mass, the coordinate, the conjugate momentum, and the potential of the vibrational mode, respectively. Using the energy eigenstates of the system \(|\{v\}\rangle, \langle v|\) (\(v=0,1,...,v_{\text{max}}\)), we can rewrite Eq. (2.1) as

\[
\hat{H} = \sum_{v=0}^{v_{\text{max}}} \hbar \omega_v |v\rangle \langle v|,
\]

where \(\hbar \omega_v\) is the energy of the \(v\)th eigenstate \(|v\rangle\). We introduce transition frequencies between levels as \(\omega_{jk} = \omega_j - \omega_k\). As we will show below, the primary contribution of 2D-IR signals arises from the transitions between the lowest three energy levels. Then, the anharmonicity of the mode is expressed as

\[
\Delta_{\text{anh}} = \omega_{10} - \omega_{21}.
\]

We assume that all other degrees of freedom, e.g., other internal modes or solvent modes, are optically inactive and
treat as a heat bath. The Hamiltonian of the system plus bath is denoted by $\hat{H}_{\text{tot}}$.

The first-order IR response function $R^{(1)}(t_1)$ is defined by

$$R^{(1)}(t_1) = \frac{1}{\hbar} \langle \mu(t_1), \mu(0) \rangle, \tag{2.4}$$

where $\mu(t) = e^{i(\hat{p}/\hbar)t} \mu(0) e^{-i(\hat{p}/\hbar)t}$ is the Heisenberg representation of the dipole-moment operator and $\langle \cdots \rangle = \text{Tr}(\cdots \hat{\rho}_{\text{tot}})$, with $\hat{\rho}_{\text{tot}} = e^{-\beta \hat{H}_{\text{tot}}}/\text{Tr} e^{-\beta \hat{H}_{\text{tot}}}$. Using the hyper-operator notations,

$$\hat{O}^\times \hat{f} = \hat{O} \hat{f} - i \hat{f} \hat{O}, \quad \hat{O} \hat{\hat{f}} = \hat{O} \hat{f} + i \hat{f} \hat{O} \tag{2.5}$$

for any operator $\hat{O}$ and operand operator $\hat{f}$, we can recast Eq. (2.4) into

$$R^{(1)}(t_1) = \text{Tr} \left\{ \mu(\hat{f}) \hat{G}(t_1) - i \hat{\mu}(\hat{f}) \right\}, \tag{2.6}$$

where $\hat{G}(t)$ is the Liouville space propagator defined by $\hat{G}(t) = e^{-i(\hat{p}/\hbar)t} \hat{T} e^{i(\hat{p}/\hbar)t}$ for any operator $\hat{f}$.

For resonant 2D-IR experiments, we consider the three pulses, tuned to the molecular vibration of interest, with wave vectors $k_1$, $k_2$, and $k_3$ which are sequentially applied to samples. These pulses cross in a sample to generate a third-order polarization, which radiates a signal field in the phase-matched directions. The rephasing (echo) response detected in the direction $k_1 = +k_3 + k_2 - k_1$ is described by the following correlation function:

$$R^{(3)}_R(t_3, t_2, t_1) = \text{Tr} \left\{ \hat{\mu}_{-} \hat{G}(t_3) \hat{\mu}_{+} \hat{G}(t_2) \hat{\mu}_{+} \hat{G}(t_1) \right\}, \tag{2.7}$$

where $\hat{\mu}_{-}$ and $\hat{\mu}_{+}$ are defined by

$$\hat{\mu}_{-} = \sum_v \langle v \mid u+1 \rangle \mu_{v+1,u} \langle u \mid, \tag{2.8a}$$

$$\hat{\mu}_{+} = \sum_v \langle v \mid u \rangle \mu_{v,u+1} \langle u+1 \mid, \tag{2.8b}$$

with the abbreviation $\mu_{v,k} = \langle \hat{f} \mu(\hat{q}) k \rangle$. The nonrephasing (virtual echo) response detected in the direction $k_1 = +k_3 - k_2 + k_1$ is described by

$$R^{(3)}_N(t_3, t_2, t_1) = \text{Tr} \left\{ \hat{\mu}_{-} \hat{G}(t_3) \hat{\mu}_{+} \hat{G}(t_2) \hat{\mu}_{+} \hat{G}(t_1) \hat{\mu}_{-} \right\}. \tag{2.9}$$

Note that the directions of the subscript arrows in Eqs. (2.7)–(2.9) correspond to those of the arrows depicted in Fig. 1.

These expressions provide us an intuitive picture upon the response function. For instance, the right-hand side of Eq. (2.6) can be read from right to left as follows. The thermal equilibrium state is modified by the first interaction with a laser pulse via the dipole moment at time $t=0$, and then it evolves in time for the interval $t_1$ by the propagator $\hat{G}(t)$.

![FIG. 1. The double-sided Feynman diagrams contributing to the (a) rephasing and (b) nonrephasing Liouville space pathways. The variables $t_i$ ($i = 1, 2, 3$) represent the delays between the three input pulses to generate a third-order nonlinear polarization.](image)
\[ C_{\text{nw}}(t) = \langle \delta \omega_{10}(t) \delta \omega_{10}(0) \rangle_0, \]  
\[ \text{and } f(t_3, t_2, t_1) \text{ is the auxiliary function given by} \]
\[ f(t_3, t_2, t_1) = g(t_2) - g(t_2 + t_1) - g(t_3 + t_2) + g(t_3 + t_2 + t_1). \]

Due to this handiness, the stochastic approach has been employed to study not only the electronic dephasing but also vibrational dephasing. We should notice that the above-mentioned formalism involves only frequency fluctuation without any accounts of excited energy relaxation. In contrast with the electronic case, the vibrational modes in molecules strongly coupled to the bath modes that often relax excitation energy on a time scale comparable with the vibrational dephasing. In addition, as we will show in Sec. IV, if the mode is anharmonic, the energy relaxation process also induces vibrational dephasing, which may not be separated from the other dephasing effects. The interplay between the energy relaxation and dephasing is also nontrivial. To take into account the effect of energy relaxation, one often employs a simple Bloch picture. However, it is an open question that the phenomenological treatment of energy dissipation is valid, because the Bloch picture assumes a white noise bath and a weak system-bath coupling with the RWA. Such treatments cannot overcome the difficulty inherent in the stochastic approach; the stochastic theory itself does not account for energy relaxation and dephasing is also nontrivial. To take into account the effect of energy relaxation, one often employs the Anderson-Kubo process \( \Delta^2 \langle \hat{x}(t) \hat{x}(0) \rangle \) and \( \Delta^2 \langle \hat{p}(t) \hat{p}(0) \rangle \) respectively. In Eq. (2.13), we refer to the terms proportional to 2! in the second order in \( \hat{q} \) as follows:

\[ V(\hat{q}) = \frac{\nu_{\text{LL}}}{!} \hat{q} + \frac{\nu_{\text{SL}}}{2!} \hat{q}^2. \]

In Eq. (3.1), we refer to the terms proportional to \( \nu_{\text{LL}} \) and \( \nu_{\text{SL}} \) as the linear-linear (LL) and square-linear (SL) couplings, respectively. For anharmonic vibrational modes, the LL coupling term deforms the potential curve and induces frequency fluctuation. The SL coupling \( \nu_{\text{SL}} \) mainly modulates the curvature of the Hamiltonian for \( U(\hat{q}) = 0 \). We expand \( V(\hat{q}) \) up to the second order in \( \hat{q} \) as follows:

\[ \hat{H}_{\text{tot}} = \hat{H} + \sum_j \left[ \frac{\hat{x}_j^2}{2m_j} + \frac{m_j \omega_j^2}{2} \left( \hat{x}_j - \frac{c_j V(\hat{q})}{m_j \omega_j^2} \right)^2 \right]. \]
The reduced description of the system can be introduced for computational purposes only; the expression shown in Ref.76, dynamics of the reduced density operator denoted by tracing over the optically inactive bath degrees of freedom denoted by \( \{ x_i \} \) from the total density operator.\(^7\) As shown in Ref. 76, dynamics of the reduced density operator for the system equation (3.1) with Eq. (3.3) is described by the LTC-QFP equation expressed as

\[
\mathcal{L} = \frac{d}{dt} \rho_{1\ldots K}(t) = -\frac{i}{\hbar} \mathcal{L} + \sum_{k=1}^{\infty} \left( j_k \mathcal{V}_k + \Phi \mathcal{V}_{k}^+ + \Xi \right) \mathcal{R}_{1\ldots K}(t) - \sum_{k=1}^{\infty} \Phi \mathcal{V}_{k} \mathcal{R}_{1\ldots K}(t) - \sum_{k=1}^{\infty} j_k \mathcal{V}_k \mathcal{R}_{1\ldots K}(t)
\]

for non-negative integers \( n, j_1, \ldots, j_K \), where we determine the value of \( K \) so as to satisfy

\[
v_K \gg \omega_c,
\]

for bosonic Matsubara frequencies \( n=2\pi k/\hbar \). In Eq. (3.8), \( \mathcal{L} = (i/\hbar) \mathcal{H}^\times \) is the quantal Liouvillian of the system and \( \Phi, \hat{\Phi}, \mathcal{V}_k, \) and \( \Xi \) are the bath-induced relaxation operators defined by

\[
\hat{\Phi} = \frac{i}{\hbar} \mathcal{V}^\times(\hat{q}),
\]

\[
\hat{\Theta} = \frac{m \xi}{\hbar^2} \left[ -i \frac{\beta \hbar \gamma}{2} \mathcal{V}^\times(\hat{q}) + \frac{\beta \hbar \gamma}{2} \cot \left( \frac{\beta \hbar \gamma}{2} \right) \mathcal{V}^\times(\hat{q}) \right],
\]

In Eq. (3.10d), the second term is derived from the counter-term mentioned above. Note that only \( \rho_0(0)(t) = \rho(t) \) has a physical meaning, and the other elements \( \rho_j(0)(t) \) for \( j \neq 0 \) are the auxiliary operators being introduced for computational purposes only; the expression of \( \rho_j(0)(t) \) is given by the Appendix. The \( K+1 \) dimensional hierarchy equations given by Eq. (3.8) continue to infinity, which is not easy to solve numerically. To terminate Eq. (3.8) at finite stages, we solve Eq. (3.8) formally as

\[
\rho_{1\ldots K}(t) = \int_{0}^{t} \frac{d s e^{-[i \mathcal{L} + \gamma \mathcal{L}^\times \rho_{1\ldots K}(s)] \Xi (0, t)]}}{i} \left[ - \Phi \rho_{1\ldots K}(t) - n \gamma \Phi \rho_{1\ldots K}(t) \right]
\]

\[
- \rho_{1\ldots K}^{(n)}(t) + \sum_{k=1}^{\infty} j_k \mathcal{V}_k \rho_{1\ldots K}(t) - \sum_{k=1}^{\infty} \Phi \rho_{1\ldots K}(t)
\]

\[
\rho_{1\ldots K}(t) = \int_{0}^{t} \frac{d s e^{-[i \mathcal{L} + \gamma \mathcal{L}^\times \rho_{1\ldots K}(s)] \Xi (0, t)]}}{i} \left[ - \Phi \rho_{1\ldots K}(t) - n \gamma \Phi \rho_{1\ldots K}(t) \right]
\]

\[
- \rho_{1\ldots K}^{(n)}(t) + \sum_{k=1}^{\infty} j_k \mathcal{V}_k \rho_{1\ldots K}(t) - \sum_{k=1}^{\infty} \Phi \rho_{1\ldots K}(t)
\]
If \( n \gamma + \sum_{k=1}^{K} j_k v_k \) is large enough compared with \( \omega_c \), the kernel of time integral can be replaced by Dirac’s delta function as

\[
\left( n \gamma + \sum_{k=1}^{K} j_k v_k \right) e^{-\left(n \gamma + \sum_{k=1}^{K} j_k v_k \right)(t-s)} \approx \delta(t-s),
\]

and then Eq. (3.8) becomes

\[
\frac{\partial}{\partial t} \hat{\rho}^{(n)}_{j_1,\ldots,j_K}(t) = -\left( i \hat{L} + \sum_{k=1}^{K} \Phi \hat{\Psi}_k + \Xi \right) \hat{\rho}^{(n)}_{j_1,\ldots,j_K}(t),
\]

which works as the terminator for Eq. (3.8). This termination is valid for the integers \( n, j_1, \ldots, j_K \), satisfying

\[
N = n + \sum_{k=1}^{K} j_k \gg \frac{\omega_c}{\min(\gamma, v_1)},
\]

because \( n \gamma + \sum_{k=1}^{K} j_k v_k \approx (n + \sum_{k=1}^{K} j_k) \min(\gamma, v_1) \). This termination is simple and easy to utilize in numerical calculations. In practice, as demonstrated numerically in Ref. 76, we may use the lower values of \( K \) and \( N \) which do not satisfy Eqs. (3.9) and (3.14), respectively. This formalism has applicability to a low-temperature system \((\beta \omega_1/2 \gg 1)\) strongly coupled to the heat bath without employing RWA for the system-bath interaction. Namely, Eq. (3.8) with Eqs. (3.10) and (3.13) is free from the positivity problem, 86 where the populations of the excited states calculated from the reduced equations of motion such as the quantum master equation and the Redfield equation without RWA become negative at low temperatures. The advantage of Eq. (3.8) deserves explicit emphasis.

To calculate the optical responses [Eqs. (2.6) and (2.7)] from the equation of motion approach, we adopt the procedure presented in Ref. 39. We first have to generate the initial equilibrium state by integrating the equations of motion, Eqs. (2.10) and (2.13), until all hierarchical elements attain steady-state values. To have the equilibrium state, we set a temporally initial condition for the integration by

\[
\hat{\rho}^{(0)}_{0,\ldots,0}(t=t_i) = \frac{\exp(-\beta \hat{H})}{\text{Tr} \exp(-\beta \hat{H})} = \hat{\rho}^{(\text{eq})},
\]

and \( \hat{\rho}^{(n)}_{j_1,\ldots,j_K}(t=t_i) = 0 \) for \( (n, j_1, \ldots, j_K) \neq (0, 0, \ldots, 0) \). The generated initial state is then modified by the first laser pulse via the dipole operator as \((i/\hbar) \mu(\hat{q}) \hat{\rho}^{(n)}_{j_1,\ldots,j_K} \). The perturbed density operator then evolves in time for the \( t_1 \) period following the equations of motion [Eqs. (3.8) and (3.13)]. First-order IR response function, Eq. (2.4), is then obtained by calculating the trace of \( \mu(\hat{q}) \). The third-order IR response functions [Eqs. (2.7) and (2.9)] can also be calculated in a similar manner.

The connection between the present approach and the stochastic approach can be seen as follows. When the temperature effects and vibrational energy relaxation are ignored, the LTC-QFP equation [Eq. (3.8)] reduces to

\[
\frac{\partial}{\partial t} \hat{\rho}^{(n)}(t) = -\left( i \hat{L} + n \gamma \right) \hat{\rho}^{(n)}(t) - \frac{i}{\hbar} \hat{W} \hat{\rho}^{(n+1)}(t)
\]

\[
- m \frac{\hbar}{\beta \hbar} \hat{W} \hat{\rho}^{(n-1)}(t),
\]

where \( \hat{W} \) is the adiabatic component of \( V(\hat{q}) \) defined by

\[
\hat{W} = \sum_{v} |v\rangle \langle v| V(\hat{q}) |v\rangle \langle v|.
\]

Equation (3.16) is the extension of the stochastic Liouville equation to a potential system (see Fig. 6). The comparison between Eq. (3.16) and the original stochastic Liouville equation tells us that the amplitude of the fluctuation \( \delta \omega_{01}(t) \) is expressed as

\[
\Delta = | \text{Tr} (\hat{W} \hat{\rho}^{(1)}(0)|0\rangle \rangle | \sqrt{m \xi \gamma \beta \hbar^2} |
\]

\[
= \text{abs} \left[ | \text{sgn}(\xi_{11} \epsilon_{SL}) (Q_{11} - Q_{00}) \sqrt{\xi_{11} \gamma \beta \hbar \omega_c} \right. \right.

\[
\left. \left. + \frac{1}{2} (Q_{11}^2 - Q_{00}^2) \sqrt{\xi_{SL} \gamma \beta \hbar \omega_c} \right] \right]
\]

From Eq. (3.18), we can estimate the amplitude of the frequency fluctuation in the system in accordance with the LTC-QFP [Eq. (3.8)].

IV. 2D-IR SPECTRA FOR MORSE POTENTIAL WITH LL+SL COUPLING

We present the numerical results for Morse potential defined by

\[
U(\hat{q}) = D_e (1 - e^{-\alpha \hat{q}})^2,
\]

where \( D_e \) denotes the dissociation energy. The \( v \)th eigenenergy for the Hamiltonian with the potential Eq. (4.1) is expressed as

\[
\hbar \omega_v = \hbar \omega_c \left[ (v + \frac{1}{2}) - \frac{\hbar}{2m \omega_c} \alpha^2 \left( v + \frac{1}{2} \right) \right],
\]

where \( \omega_c = \sqrt{2D_e \alpha^2 / m} \). Then, the anharmonicity \( \Delta_{\text{anh}} = \omega_{10} - \omega_{21} \) and the fundamental frequency \( \omega_0 \) are given by \( \Delta_{\text{anh}} = \hbar \omega_c^2 / m \) and \( \omega_{10} = \omega_c - \Delta_{\text{anh}} \), respectively. The fundamental frequency and the anharmonicity of the system are set to be \( \omega_{10} = 1600 \text{ cm}^{-1} \) (2\pi/\omega_{10} = 20.8 fs) and \( \Delta_{\text{anh}} = 16 \text{ cm}^{-1} \) \( \Delta_{\text{anh}}/\omega_{10} = 0.01 \), which are in the typical range for intramolecular vibrational motion. We consider a room temperature heat bath, \( T = 300 \text{ K} \) \( \beta \hbar \omega_{10} = 7.67 \). To carry out calculations, we employ the lowest six energy eigenstates to represent the system. The fourth-order Runge-Kutta method is used to numerically integrate the equation of motion. The time step for the finite difference expression for \( \partial \hat{\rho}^{(n)}_{j_1,\ldots,j_K}/\partial t \) is \( \Delta t = (1 / \times \omega_{10}) 0.01 \). We chose the depth of the hierarchy and the number of the Matsubara frequencies \( N = 3 - 25 \) and
\( K = 1–4 \), respectively. The accuracy of the calculations is checked by changing the number of the energy eigenstates and the values of \( \delta t \), \( N \), and \( K \). The dipole moment is assumed to be \( \mu(\hat{q}) = \mu \hat{q} \), and we set \( \mu_1 = 1 \) to calculate the 2D-IR signals. Under these conditions, we calculate 2D-IR correlation spectrum \(^87\) defined as

\[
S_C(\omega_3, \omega_1; t_2) = S_R(\omega_1, -\omega_1; t_2) + S_{NR}(\omega_3, \omega_1; t_2),
\]

where

\[
S_R(\omega_3, \omega_1; t_2) = \text{Im} \int_0^\infty dt_3 e^{i\omega_3 t_3} \int_0^\infty dt_1 e^{i\omega_1 t_1} R^{(3)}(t_3, t_2, t_1)
\]

is 2D rephasing spectrum and

\[
S_{NR}(\omega_3, \omega_1; t_2) = \text{Im} \int_0^\infty dt_3 e^{i\omega_3 t_3} \int_0^\infty dt_1 e^{i\omega_1 t_1} R^{(3)}(t_3, t_2, t_1)
\]

is 2D nonrephasing spectrum.

### A. Motional narrowing regime

Figure 3 presents 2D-IR correlation spectra \( S_C(\omega_3, \omega_1; t_2=0) \) for \( \gamma/\omega_{10}=0.5 \) (\( \gamma = 6.6 \text{ fs} \)). In the figure, the panels (a) are calculated by integrating the LTC-QFP equation, Eq. (3.8), while the panels (b) by the stochastic model, Eq. (2.11). The system-bath coupling (\( k_{\text{LL}}, k_{\text{SL}}/\omega_{10} \) for panels (a) are chosen to be (i) \( +0.05, 0 \), (ii) \( 0, +0.05 \), (iii) \( +0.05, +0.05 \), and (iv) \( -0.05, +0.05 \), respectively. The parameters for the stochastic case shown in (b) are evaluated from those in (a) using Eq. (3.18) and the values of \( Q_{10} = 0.074, Q_{11} = 0.226, Q_{10}^2 = 0.509, \) and \( Q_{11}^2 = 1.567 \). The amplitude of frequency fluctuation \( \Delta \) for each panel are calculated as (i) \( 13.7 \text{ cm}^{-1} \) (\( \Delta/\gamma = 0.01 \)), (ii) \( 48.1 \text{ cm}^{-1} \) (\( \Delta/\gamma = 0.06 \)), (iii) \( 61.8 \text{ cm}^{-1} \) (\( \Delta/\gamma = 0.08 \)), and (iv) \( 34.3 \text{ cm}^{-1} \) (\( \Delta/\gamma = 0.04 \)). As seen from the gradient of the 2D line shapes, these are in the motional narrowing regime without the inhomogeneity.

In this large \( \gamma \) case, the spectra calculated by the LTC-QFP equation are quite different from the stochastic results due to energy relaxation missing in the stochastic approach. The linewidth of the spectra from the stochastic approach (b-i) is very small in this motional narrowing regime, whereas the spectra from the LTC-QFP equation case (a-i) are broad because vibrational dephasing is dominated by energy relaxation rather than elastic pure dephasing.

We now consider the SL coupling case [(a-ii) and (b-ii)]. As mentioned in Fig. 2, the SL coupling term, \( q^2 \sum_j \hat{x}_j \), mainly induces the two-quantum transition as well as the curvature modulation of the potential. The population relaxations \( 1 \rightarrow 0 \) and \( 2 \rightarrow 1 \) are almost prohibited, whereas the relaxation \( 2 \rightarrow 0 \) is allowed. (The one-quantum relaxations are not completely prohibited because of the anharmonicity of potential.) As a result, energy relaxation destroys only the \( 1 \rightarrow 2 \) coherence. Hence, the positive-going peaks (1–2 transition) in the two panels are different, while the negative-going peaks (0–1 transition) have similar characteristics.

Next, we discuss the difference between the +LL+SL and −LL+SL coupling cases. As is evident from Eq. (3.18), the +LL+SL coupling reinforces the amplitude of frequency fluctuation, while the −LL+SL coupling diminishes the amplitude. The amplitude of fluctuation affects the strength of pure dephasing in the stochastic case. Therefore the line shapes from the stochastic approach [(b-iii) and (b-iv)] are different. The primary relaxation processes in the LTC-QFP equation case shown in (a-iii) and (a-iv) are, however, energy relaxation rather than pure dephasing; therefore, the profiles in (a-iii) and (a-iv) are also different from those in (b-iii) and (b-iv). The difference between (a-iii) and (a-iv) is caused.
from the cross term contribution between the LL and SL couplings.\textsuperscript{18,82} To explain this, we consider the classical generalized Langevin equation (GLE) for the Hamiltonian equation (3.1),\textsuperscript{74}

\[
m\ddot{q}_i = -U'(q_i) - m \int_0^t ds V'(q_s) \eta(t-s) V'(q_s) \dot{q}_i + V'(q_i) \dot{q}_i(t),
\]

where the fluctuation \(\dot{q}(t)\) and the dissipation \(\eta(t)\) are related by the fluctuation-dissipation theorem \(\langle \dot{q}(t)\dot{q}(s) \rangle_0 = \frac{m}{\Delta} \langle \eta(t)\eta(s) \rangle_0 \), in which \(\langle \cdot \rangle_0\) denotes the statistical average. For +LL+SL coupling \(V(q) = +v_{11} q + v_{22} q^2 / 2\), the integral kernel \(\Gamma(t-s) = V(q) \eta(t-s) V'(q_s)\) in Eq. (4.6) is expressed as

\[
\Gamma(t-s) = \left[ v_{11}^2 + \frac{v_{22}^2}{4} q_s^2 \right] \eta(t-s) + \frac{v_{11} v_{22}}{2} [q_s + \frac{v_{22}}{v_{11}} q_i] \eta(t-s),
\]

whereas for −LL+SL coupling \(V(q) = -v_{11} + v_{22} q^2 / 2\), \(\Gamma(t-s)\) is given by

\[
\Gamma(t-s) = \left[ v_{11}^2 + \frac{v_{22}^2}{4} q_s^2 \right] \eta(t-s) - \frac{v_{11} v_{22}}{2} [q_s + \frac{v_{22}}{v_{11}} q_i] \eta(t-s).
\]

The difference between Eqs. (4.7) and (4.8) is on the sign of the term proportional to \(v_{11} v_{22} q_s^2 / 2\); the difference between the panels (a-iii) and (a-iv) arises only from the cross term contribution between the LL and SL couplings.

In the stochastic case (b), the negative-going peaks (0–1 coherence) and the positive-going peaks (1–2 coherence) are located on \(\omega_0 = \omega_0 = \omega_1\) and \(\omega_0 = \omega_0 = \omega_0 - \Delta_{\text{mb}}\), respectively. In the LTC-QFP equation case (a), however, we can see that the spectral peak locations shift toward the upper right. These 2D blueshifts arise purely from the dissipation with the finite noise correlation time. To illustrate this, we consider a harmonic potential \(U(q) = m \omega_q^2 q^2 / 2\) in the presence of only the LL coupling \(V(q) = q\) with the Markovian noise bath \(\eta(t) = \xi(t) e^{-\gamma t}\) and depict linear absorption spectra. The analytic expression of the absorption spectrum (first-order response) for this system is obtained as

\[
I(\omega) = \text{Im} \int_0^\infty dt e^{i\omega t} \left[ -\beta \frac{d}{dt} \langle \dot{q}(t) q(0) \rangle \right],\tag{4.9a}
\]

\[
= \frac{\omega_{10}^2(\omega(0))^2 \beta \omega_l \omega_{10}}{(\omega^2 - \omega_{10}^2)^2 + \frac{\omega_{10}^2}{\gamma^2} G_\omega(\omega)}, \tag{4.9b}
\]

with

\[
G_\omega(\omega) = \left( \frac{\omega^2 - \omega_{10}^2}{\xi \gamma} - 1 \right)^2. \tag{4.9c}
\]

If \(\gamma \rightarrow \infty\), the result reduces to the white noise case with \(G_\omega(\omega) \rightarrow 1\). We show the linear absorption spectra calculated for Markovian noise and white noise cases in Fig. 4. Here, we set \(\gamma / \omega_{10} = 0.5\) and \(\xi / \omega_{10} = 0.05\), which are the same values as in Fig. 3. As clearly seen from the figure, the dissipation with the finite noise correlation time causes the blueshift of the spectral peak position. We cannot obtain such analytic expression for the SL coupling case as Eq. (4.9b). Notice, however, that the SL coupling induces the dissipation involving two-quantum relaxation, and then causes the blueshift. Since characters of 2D-IR spectra and linear absorption are both determined from the time propagator as illustrated in Eqs. (2.7) and (2.6), the spectral peaks in 2D-IR spectra also exhibit the blueshifts.

B. Spectral diffusion regime

Figure 5 presents 2D-IR correlation spectra \(S_c(\omega_1, \omega_2; t_2 = 0)\) for small \(\gamma\). In the figure, the panels (a) are calculated by integrating the LTC-QFP equation [Eq. (3.8)], while the panels (b) by the stochastic result [Eq. (2.11)]. The inverse noise correlation time is set to be \(\gamma / \omega_{10} = 0.005 (\gamma^2 = 0.66)\) ps. The system-bath coupling strengths \(\omega_1 / \omega_{10}\) for panels (a) are chosen to be (i) \((2 + 0, 0)\), (ii) \((0, +0.5)\), (iii) \((+2, +0.5)\), and (iv) \((-2, +0.5)\), respectively. As in the motional narrowing cases, we can evaluate the amplitude of frequency fluctuation \(\Delta\) for (b) as follows: (i) \(8.7\) cm\(^{-1}\) (\(\Delta / \gamma = 1.1\)), (ii) \(15.2\) cm\(^{-1}\) (\(\Delta / \gamma = 1.9\)), (iii) \(23.9\) cm\(^{-1}\) (\(\Delta / \gamma = 3.0\)), and (iv) \(6.5\) cm\(^{-1}\) (\(\Delta / \gamma = 0.8\)). As seen from the profiles of the 2D line shapes, these are in the spectral diffusion regime with moderate inhomogeneity.

In this small \(\gamma\) case, the spectra calculated by the LTC-QFP equation resemble those from the stochastic approach. This similarity indicates that vibrational dephasing processes in the present situation are dominated by elastic pure dephasing rather than by energy relaxation; hence, the stochastic theory is a good description for 2D line shapes. However, compared with the cases in (b), the peak positions for the LTC-QFP equation case in (a) slightly shift toward the upper right. The cause of the blueshifts is the dissipation with finite noise correlation time, as mentioned in Sec. IV A. This fact indicates that although the effect of vibrational energy relaxation in comparison to that of frequency fluctuation process is small, still there exist effects of dissipation caused by the system-bath coupling. The stochastic theory, which neglects any dissipation, cannot explain the 2D blueshifts.
To estimate the strength of dissipation, we utilize the correlation function of the collective bath coordinate [Eq. (3.4)],

$$\langle \hat{X}(t)\hat{X}(0) \rangle_b = C'(t) + iC''(t),$$

(4.10)

where $C'(t)$ is the real part of $\langle \hat{X}(t)\hat{X}(0) \rangle_b$ that relates to fluctuation and $C''(t)$ is the imaginary part that relates to dissipation.\(^{39,83}\) For Eq. (3.3), they are expressed as

$$C'(t) = \frac{m}{\beta} \zeta e^{-\gamma t},$$

(4.11)

$$C''(t) = -\frac{\beta h \gamma m}{2} \zeta e^{-\gamma t},$$

(4.12)

where we assumed that $\beta h \gamma / 2 \ll 1$ in Eq. (4.11), and therefore we have

$$\left| \frac{C''(t)}{C'(t)} \right| \ll 1.$$  

(4.13)

This indicates that the dissipation is negligible relative to the fluctuation for $\beta h \gamma / 2 \ll 1$.

Summarizing two conditions, we have

$$\gamma \ll \omega_c, \quad \beta h \gamma / 2 \ll 1.$$  

(4.14)

As long as the above conditions are satisfied, the energy relaxation plays a minor role compared with the elastic pure dephasing, and the vibrational dephasing is dominated by the pure dephasing caused by the frequency fluctuation rather than the energy relaxation. In such cases, the stochastic theory may be applied to analyze 2D line shapes although the theory cannot account such dissipative effects as the blueshifts.

V. CONCLUDING REMARKS

In this paper, we considered an anharmonic potential system coupled to a colored noise bath with linear-linear (LL) and square-linear (SL) system-bath interactions. For the system, we introduced the low-temperature corrected quantum Fokker-Planck (LTC-QFP) equation, which can describe an anharmonic intramolecular vibration at temperature much lower than vibrational excitation energy (a low-temperature system). It is noteworthy that the equation is based on the vibrational coordinate and is not afflicted with the positivity problem that occurs in a low-temperature system without the rotating wave approximation, as opposed to the conventional quantum master equation or Bloch-Redfield equation. By utilizing the equation we calculated 2D-IR correlation spectra for various system-bath parameters. Our formalism, LTC-QFP equation, can treat a dissipation-dominated regime (Fig. 3) and a fluctuation-dominated regime (Fig. 5) in a unified framework. We found the profiles of 2D-IR spectra change dramatically with a form and strength of system-bath coupling and a noise correlation time. In this anharmonic system, the LL coupling leads to not only one-quantum relaxation but also the deformation of a potential curve, whereas the SL coupling gives rise to a curvature modulation of the potential curve in addition to two-quantum relaxation.

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**FIG. 5.** (Color) 2D-IR correlation spectra $S_2(\omega_1, \omega_2; t_2=0)$ of the Morse oscillator ($\omega_0=1600$ cm$^{-1}$, $\Delta \omega_0=16$ cm$^{-1}$) in the spectral diffusion regime. The spectra were calculated from (a) the LTC-QFP approach with Eq. (3.8) and (b) the stochastic approach with Eq. (2.11). The panels from the top to bottom show the spectra for (i) LL, (ii) SL, (iii) +LL+SL, and (iv) -LL+SL system-bath coupling cases, respectively. The inverse noise correlation time is $\gamma/\omega_0=0.005$ ($\gamma'=0.66$ ps). The negative-going peaks arise from the 0-1 transition, whereas the positive-going peaks from the 1-2 transition.
Through 2D-IR spectra, we clarify the details of the system-bath coupling as follows: (1) the difference between one- and two-quantum relaxations, (2) a cross term contribution between the LL and SL couplings, and (3) the interplay between the LL and SL mechanisms of frequency fluctuation (Fig. 2).

We also discussed the precondition for validity of the stochastic approach. Since the stochastic theory breaks down for a system where the energy relaxation is significant because the theory neglects any dissipative effects, we focus on the case where energy dissipative effects can be ignored. Then we found that if the noise correlation time $\tau = \gamma^{-1}$ satisfies the following two conditions, (a) $\gamma \ll \omega$, for the characteristic frequency of the system oscillator $\omega$, and (b) $\beta \hbar \gamma / 2 \ll 1$ for the inverse temperature $\beta$, we may disregard energy dissipation processes in comparison with dephasing processes (see Fig. 6). Within the two conditions, the stochastic theory can explain the line shapes of the multidimensional vibrational spectra, regardless of the characteristic frequency of the system such as $\beta \hbar \omega / 2 \gg 1$ or $\beta \hbar \omega / 2 \ll 1$, besides the blueshifts caused by the dissipation from colored noise bath.

In this paper, we restricted our discussions to a single anharmonic mode in a bath characterized by a single decay constant $\gamma$. Extension to multimodal anharmonic systems in more realistic bath is left for future studies.

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APPENDIX: DERIVATION OF LOW-TEMPERATURE CORRECTED QUANTUM FOKKER-PLEANCK EQUATION

In this appendix, we outline a derivation of the quantal equation of motion for a reduced density matrix, which has applicability to a low-temperature system ($\beta \hbar \omega / 2 \gg 1$) that can be used to analyze an intramolecular vibrational mode.$^{39,76}$

The reduced density matrix element for the system is expressed in the path integral form with the factorized initial condition as

$$
\rho(q, q'; t) = \int dq_i \int dq' \int Dq \int Dq' \exp \left[ \frac{i}{\hbar} (S[q] - S[q']) \right] F_{\text{FV}}(q, q') \rho(q_i, q'_i; t_i).
$$

(A1)

Here, $S[q]$ is the action of the system and $F_{\text{FV}}(q, q')$ is the Feynman-Vernon influence functional given by$^{84}$

$$
F_{\text{FV}}(q, q') = \exp \left[ -\frac{1}{\hbar} \int_0^\infty d\omega J(\omega) \int_{t_i}^{t_f} ds \int_{t_i}^{s} ds' V^\omega(s) \times \left[ V^\omega(s') \coth \left( \frac{\beta \hbar \omega}{2} \right) \cos(\omega(s - s')) \right] \right. 
$$

$$
\left. \left. - i V^\omega(s') \sin(\omega(s - s')) \right] \right] \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t_f} ds \left[ \Delta U(q_i) - \Delta U(q'_i) \right] \right),
$$

(A2)

where we have introduced the abbreviations $V^\omega(t) = V(q) - V(q_i)$ and $V^\omega(t) = V(q) + V(q'_i)$. The counterterm $\Delta U(q) = \int_0^\omega d\omega J^2(\omega) V^2(\omega)/\omega$ found in Eq. (3.1) is taken into account as the second exponential on the right-hand side of Eq. (A2).

For the distribution Eq. (3.3), we can rewrite Eq. (A2) as

$$
F_{\text{FV}}[q, q'] = \exp \left( \int_{t_i}^{t_f} ds \int_{t_i}^{s} ds' \Phi(t) \Theta(s) \psi_1(s) \psi_2(s') e^{-\frac{i}{\hbar} V^\omega(s)} \right) \times \prod_{k=1}^\infty \exp \left( \int_{t_i}^{t_f} ds \int_{t_i}^{s} ds' \Phi(s) \Theta_2(s') \psi_1(s') \psi_2(s) e^{-\frac{i}{\hbar} V^\omega(s')} \right) \times \exp \left( -\frac{i}{\hbar} \int_{t_i}^{t_f} ds \frac{m_G \gamma}{2} V^\omega(s) V^\omega(s') \right),
$$

(A3)

with

$$
\Phi(t) = \frac{i}{\hbar} V^\omega(t),
$$

(A4)

$$
\Theta(t) = \frac{m_G \gamma}{\beta \hbar} \left[ -i \frac{\beta \hbar \gamma}{2} V^\omega(t) + \frac{\beta \hbar \gamma}{2} \cot \left( \frac{\beta \hbar \gamma}{2} V^\omega(t) \right) \right],
$$

(A5)

$$
\psi_1(t) = \frac{i}{\beta \hbar} \frac{2 \gamma^2}{v_k^2 - \gamma^2} V^\omega(t),
$$

(A6)

where $v_k = 2\pi k/(\beta)$ is a bosonic Matsubara frequency.

If we choose $K$ so as to satisfy $\nu_k \gg \omega$, the factor $e^{-\nu_k(s-s')} in Eq. (A3) can be replaced by Dirac’s delta function as

$$
\nu_k e^{-\nu_k(s-s')} \approx \delta(s - s') \quad (k \gg K + 1).
$$

(A7)

Thus, by choosing the relevant $K$, Eq. (A3) can be reduced to
In order to derive the equation of motion, we introduce the auxiliary operator $\rho^{(0)}(t)$ defined by its matrix element as

$$\rho^{(0)}(q, q'; t) = \sum_{j_1, \ldots, j_K} e^{-i q_j^2} \left[ - \int_{t_i}^{t_f} ds \gamma(s) e^{i q_j^2} \right]_{j_1, \ldots, j_K}$$

for non-negative integers $n, j_1, \ldots, j_K$. Note that only $\rho^{(0)}(t) = \rho^{(0)}(t)$ has a physical meaning, and the other elements $\rho_n^{(0)}(q, q'; t)$ for $(n; j_1, \ldots, j_K) \neq (0; 0, \ldots, 0)$ are introduced for computational purposes only. The differentiation of $\rho_n^{(0)}(q, q'; t)$ with respect to $t$ gives rise to the factors from the time differentiation of the left- and right-hand side actions and the influence functional. The terms with these factors constitute the hierarchy members of Eq. (A9) with different $n$ and $\{j\}$. As a result, we obtain the hierarchy of equations, Eq. (3.8).

References: