

Unified time-path approach to the effect of anharmonicity on the molecular vibrational spectroscopy in solution

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(Received 19 December 1995; accepted 6 June 1996)

We obtain a closed expression for the response function for damped anharmonic vibrational modes using the Feynman rule obtained through the nonequilibrium generating functional derived in our previous paper [Phys. Rev. E **53**, 214 (1996)]. The linear absorption spectra are explicitly calculated through the Feynman diagrams for molecules with anharmonic potential in solution. The dependence of the spectra both on the temperature and on the solvent nature can be taken into account in our theory. The result is examined numerically for various dampings, anharmonicities, and temperatures. © 1996 American Institute of Physics. [S0021-9606(96)52634-6]

I. INTRODUCTION

Recent progress of ultrafast nonlinear spectroscopy such as infrared (IR) spectroscopy or Raman spectroscopy allows us to probe and characterize vibrational modes of molecules. These spectroscopies, including infrared photon echo,¹⁻³ Raman echo,⁴⁻⁷ and fifth order off-resonant⁸⁻¹² experiments, have been successful in studying the homogeneous and inhomogeneous broadening in liquids.

The electronically off-resonant coherent Raman experiments which contain only one time variable, such as the optical Kerr effects (OKE)¹³⁻¹⁷ and the coherent anti-Stokes Raman spectroscopies (CARS),^{18,19} are physically equivalent to the linear absorption experiment with infrared laser. These vibrational line shapes in solution contain the details of the interactions of normal modes with their environment. In order to explain the wide range of behaviors that have been observed experimentally, one can use a Brownian oscillator model that consists of primary modes and other environmental (the bath) modes.^{8,19-21} The OKE, CARS or linear absorption spectroscopy with the infrared laser is, then, related to the two-time autocorrelation functions $\langle Q(t)Q(t') \rangle$ of the primary nuclear coordinate Q in the quantum Brownian theory. Due to the assumption of the harmonic potential for nuclear degrees of freedom we are able to obtain a closed expression for the spectrum.⁸ The technique developed in the harmonic case can be applied to the intermolecular spectrum of liquid such as water.²²⁻²⁴ Though the assumption of the harmonic potential is reasonable for a number of realistic systems, there are still many exceptions. For example, the low frequency intermolecular modes of water are found to have fairly large anharmonicity.²² One of the purposes of this paper is to provide foundations for studying the anharmonicity for such systems.

The full quantum treatment of anharmonicity in the presence of the heat bath poses some difficult problems. Quantum vibrational transitions, in the absence of environment modes, can be studied by a wide variety of numerical methods based on the wave function.²⁵ When environment modes are important, these methods are not practical since the calculation requires the incorporation of many degrees of freedom (the bath). In such a case, it is convenient to integrate

out the bath degrees of freedom by using the projection-operator²⁶ or the path-integral²⁷ techniques.

Whether the projection-operator or the path-integral method is used, it is quite common to derive the equations of motion for the reduced density matrix (i.e. the master equation^{28,29} or the quantum Fokker-Planck equation³⁰) in order to calculate the physical observables numerically.³¹ The shortcomings of the reduced density matrix approach are as follows. First, the factorized initial conditions (i.e., $\rho_I = e^{-\beta H_S} e^{-\beta H_B}$) have to be assumed instead of the correlated ones (i.e., $\rho_I = e^{-\beta(H_S + H_B + H_{SB})}$). Here, ρ_I is the initial density matrix where H_S , H_B , and H_{SB} are the system, bath, and interaction Hamiltonians, respectively. Second, the interaction between the system and the bath has to be bilinear for the practical calculation.³² Third, either a high temperature Ohmic dissipative bath (a white noise bath) or a weak system-bath coupling has to be assumed. The white noise assumption leads to the quantum master equation or the quantum Fokker-Planck equation, whereas the weak coupling assumption leads to the generalized master equation. Due to these assumptions, however, the equation of motion approach is not applicable to a system coupled with a low temperature or non-Ohmic dissipative bath (a non-Markovian bath) with a strong system-bath interaction, although some improvement has been done (for example, Refs. 33-35).

The nonequilibrium generating functional for the correlation functions can be systematically calculated by use of the path integral. This approach through the generating functional is especially powerful for the harmonic system. As mentioned before, one can derive a closed form expression for the nuclear response function to an arbitrary order in the electric field for nuclear motions in the harmonic case.^{8,36}

Recently, the authors derived a nonequilibrium generating functional in a more general form and developed the Feynman rule from the generating functional.³⁷ By this rule we can systematically study the effects of anharmonicities of the potentials [both for molecules and the bath oscillators (solvent)] as well as the effects of nonbilinear molecular-solvent couplings in the presence of the bilinear system-bath coupling. This work can be regarded as an extension of the

work by Fukuda *et al.*³⁸ They dealt with a case of a nonbilinear system–bath coupling *in the absence of the bilinear system–bath coupling* and gave the microscopic expression for the damping constant through their Feynman rule. If one wants to take into account the bilinear coupling by using their rule, one has to deal with it by a perturbative expansion in the coupling constant.

Compared with the equation of motion approach, the present approach has the following advantages. First, we can incorporate the initial correlation between the system and the bath, namely we can start from $\rho_I = e^{-\beta(H_S + H_B + H_{SB})}$. Second, the system–bath coupling is not necessary to be bilinear in the practical calculation, though, in this paper, we only discuss the bilinear coupling case, where we can treat the system–bath interaction exactly. Third we can obtain the correlation functions (which is valid for the low temperature) by taking into account the memory effects of the noise produced from the non-Ohmic heat bath. Fourth, with the help of the graph rule, we can examine the effects of the anharmonicity of the system or the heat–bath potential.

In this paper, we present an explicit form for the two-time correlation function which enables us to calculate physical observables such as the linear absorption spectrum. This is obtained through the Feynman rule deduced from the nonequilibrium generating functional derived in our previous paper. Here, we take into account the anharmonicity of the system potential assuming the bilinear system–bath coupling, while analysis for the anharmonic oscillator bath or nonbilinear coupling are left for future study. We calculated the linear absorption spectrum and obtain modestly compact expressions through the diagrams [Eqs. (4.8)–(4.19) below] for an arbitrary spectral density of the heat bath. As an illustration, the result is further analyzed in the representative case of Ohmic dissipation [Eqs. (5.8)–(5.12) below]. The numerical results are also given for various parameters in the Ohmic case.

II. THE GENERAL SYSTEM AND THE LINEAR ABSORPTION SPECTRUM

Consider a molecular system whose electronic ground state is described by a single primary coordinate Q and its conjugate momentum P :

$$H_S = \frac{P^2}{2M} + \frac{M\Omega^2}{2}Q^2 + V_S(Q). \quad (2.1)$$

Here, Ω is of order of the frequency of the molecular vibrational modes in question and $V_S(Q)$ stands for the anharmonicity of the molecular potential $U(Q)$ [$= M\Omega^2 Q^2/2 + V_S(Q)$]. We consider infrared measurements conducted with laser fields far below any electronic transition. Thus, all the electronic excited states can be neglected unless we consider the case of considerably high temperature. The interaction between laser fields and the molecular system is expressed as

$$H_{SL}(t) = -\mu(Q)E(t), \quad (2.2)$$

where $E(t)$ is the classical electronic field and $\mu(Q)$ the dipole moment. Note that the present formulation applies also to experiments which use off-resonant laser pulses. In this case, we should replace the $\mu(Q)E(t)$ coupling by $E^2(t)\alpha(Q)$, where $\alpha(Q)$ is the electronic polarizability.^{8,19,20}

The molecular system is assumed to be coupled to the solvent (bath) degrees of freedom. We assume that these are described by a set of oscillators:

$$H_B = \sum_{i=1}^N \left(\frac{p_i^2}{2m_i} + \frac{m_i\omega_i^2}{2}q_i^2 \right) + V_B(q). \quad (2.3)$$

Here, $V_B(q)$ is the anharmonicity of the bath oscillators. The molecular system interacts with the oscillators:

$$H_{SB}(q, Q) = -\sum_{i=1}^N c_i q_i Q + V_{SB}(q, Q), \quad (2.4)$$

where $V_{SB}(q, Q)$ is the nonbilinear molecular–solvent coupling.³⁹ In order to describe dissipation from the molecular system the number N of the bath degrees of freedom will be taken to an infinity. The total Hamiltonian $H_T(t)$ governing the time evolution of the density matrix in the scheme based on the coupled Maxwell–Liouville equations⁴⁰ is now expressed as

$$H_T(t) = H + H_{SL}(t), \quad (2.5)$$

where

$$H = H_S^R + H_B + H_{SB}. \quad (2.6)$$

In order to compensate for the renormalization of the system potential due to the coupling to the bath (see, for example, Refs. 41 and 42), we have introduced the counter term: the renormalized system Hamiltonian H_S^R is the system Hamiltonian H_S with the frequency of the potential Ω^2 replaced by $\Omega^2 + \Delta\Omega^2$ where the frequency shift $\Delta\Omega^2$ is given by $\sum_i c_i^2 / (m_i \omega_i^2)$.

The physical observable in optical experiments is the polarization $P(t)$ or the expectation value of the dipole moment:

$$P(t) = \langle \mu(Q) \rangle = \text{Tr}[\rho(t)\mu(Q)], \quad (2.7)$$

where $\rho(t)$ is the density matrix at the observed time t . If we assume the total system is initially ($t=0$) in the equilibrium state at the temperature $1/\beta$, $\rho(t)$ is given by

$$\rho(t) = K_T(t)\rho_I K_T^\dagger(t), \quad (2.8)$$

where the initial distribution ρ_I is given by the following density matrix since the electric field is initially set to zero;

$$\rho_I = e^{-\beta H} / \text{Tr} e^{-\beta H}. \quad (2.9)$$

The time evolution operator for the total Hamiltonian $K_T(t)$ is defined as

$$K_T(t) = T \exp\left(-\frac{i}{\hbar} \int_0^t dt' H_T(t')\right), \quad (2.10)$$

where T is the time ordering operator. It has been shown that the quantity such as $P(t)$ can be estimated systematically by

using the Feynman rule on the unified time path.³⁷ In this paper we focus on the calculation of the first order in $E(t)$ of $P(t)$ to obtain the linear absorption spectrum $\sigma(\omega)$ as shown below.

The first order of the polarization $P^{(1)}(t)$ is given by

$$P^{(1)}(t) = \int_{-\infty}^{\infty} dt' E(t') S^{(1)}(t-t'). \quad (2.11)$$

The correlation function $S^{(1)}(t)$ independent of $E(t)$ is defined as

$$S^{(1)}(t) = \theta(t) \frac{i}{\hbar} (\text{Tr}[\mu(Q)K(t)\mu(Q)K(-t)\rho_I] - \text{c.c.}), \quad (2.12)$$

where c.c. stands for the complex conjugate and the time evolution operator with zero electric field $K(t)$ is given by

$$K(t) = K_T(t)|_{E(t)=0} = e^{-(i\hbar)Ht}. \quad (2.13)$$

The linear absorption spectrum $\sigma(\omega)$ is then expressed by the Laplace transform of $S^{(1)}(t)$ as

$$\sigma(\omega) = \text{Im}[\bar{S}^{(1)}(z = -i\omega)], \quad (2.14)$$

where

$$\bar{S}^{(1)}(z) = \mathcal{L}_z[S^{(1)}(t)] \equiv \int_0^{\infty} dt e^{-zt} S^{(1)}(t). \quad (2.15)$$

III. THE FEYNMAN RULE FOR AN ANHARMONIC POTENTIAL

We assume the following form of anharmonicity of the molecular potential and that of non-Condon dipole moment:

$$V_S(Q) = \frac{g_3}{3!} Q^3 + \frac{g_4}{4!} Q^4, \quad (3.1)$$

$$\mu(Q) = \mu_0 + \mu_1 Q, \quad (3.2)$$

while $V_B(q) = V_{SB}(q, Q) = 0$. In this case $S^{(1)}(t)$ is given by

$$S^{(1)}(t) = \theta(t) \mu_1^2 \frac{i}{\hbar} (\text{Tr}[\rho_I e^{(i\hbar)Ht} Q e^{-(i\hbar)Ht} Q] - \text{c.c.}). \quad (3.3)$$

The generating functional $W_J = W(J_1, J_2, J_3)$ is introduced by

$$\begin{aligned} e^{\frac{i}{\hbar} W_J} &= \text{Tr} \left[\text{T}_\tau \exp \left(-\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau [H - J_3(\tau) Q] \right) \right. \\ &\quad \times \left. \left\{ \text{T} \exp \left(-\frac{i}{\hbar} \int_0^{\infty} dt [H - J_2(t) Q] \right) \right\}^\dagger \right. \\ &\quad \times \left. \left. \text{T} \exp \left(-\frac{i}{\hbar} \int_0^{\infty} dt [H - J_1(t) Q] \right) \right] \right] \\ &= \text{Tr} \text{T}_C \exp \left(-\frac{i}{\hbar} \int_C dt [H - J(t) Q] \right), \end{aligned} \quad (3.4)$$

where T_C is the time ordering operator on the unified time path C and $\int_C dt$ implies the integration on the path (see Fig. 1). The step function on C is naturally defined:

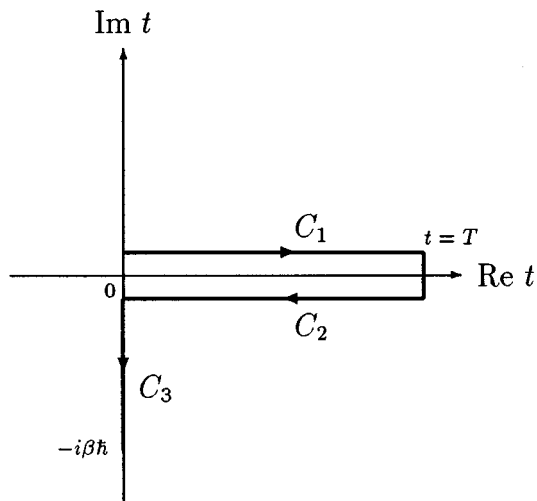


FIG. 1. The unified time-path $C = C_1 + C_2 + C_3$ on the complex t plane ($T \rightarrow \infty$). It starts from the origin up to an infinity along the real path (C_1), returns to the origin (C_2), and then goes to $-i\beta\hbar$ along the imaginary axis (C_3).

$\theta_C(t, t')$ takes the value unity if the time t appears later than t' along the unified time path when we follow the direction of the arrow; otherwise $\theta_C(t, t')$ is zero. The δ function on C is also defined accordingly.³⁷ If the system is in the equilibrium state or the ground state, only one component of the time path (C_3 for the equilibrium case and C_1 for the zero-temperature case) contributes to the calculation, while in the present nonequilibrium case the three components C_1 , C_2 , and C_3 take part in it. Accordingly, in our case, many kinds of propagators (which connect different time-path components, say $C_1 - C_3$, in addition to the same components, say $C_1 - C_1$) appear in the Feynman rule as we see below. On the other hand, in the case of the equilibrium system and the zero-temperature system, only one kind of propagator appears in the calculation which connects the same components ($C_3 - C_3$ and $C_1 - C_1$, respectively).

The correlation function is obtained as the derivative of the generating functional W_J :

$$\begin{aligned} S^{(1)}(t) &= \theta(t) \mu_1^2 \left(\frac{\partial^2 W_J}{\partial J_1(t) \partial J_1(0)} - \frac{\partial^2 W_J}{\partial J_2(t) \partial J_2(0)} \right)_{J_1=J_2=J_3=0} \\ &= \theta(t) \mu_1^2 \left(\frac{\partial^2 W_J}{\partial J^{(+)}(t) \partial J^{(-)}(0)} \right. \\ &\quad \left. + \frac{\partial^2 W_J}{\partial J^{(-)}(t) \partial J^{(+)}(0)} \right)_{J^{(+)}=J^{(-)}=J_3=0}, \end{aligned}$$

where $J^{(+)}$, $J^{(-)}$ are defined by

$$J^{(+)}(t) = \frac{J_1(t) + J_2(t)}{2}, \quad J^{(-)}(t) = J_1(t) - J_2(t). \quad (3.5)$$

The derivatives with respect to (J_1, J_2, J_3) pull out $(Q_1, -Q_2, Q_3)$, respectively, while those with respect to $(J^{(+)}, J^{(-)}, J_3)$ pull out $(Q_1 - Q_2, (Q_1 + Q_2)/2, Q_3)$, respectively. Here Q_i implies the operator Q on C_i .

By changing variables from (J_1, J_2, J_3) to $(J^{(+)}, J^{(-)}, J_3)$, we may decrease the number of the Feynman diagrams: we would have nine kinds of propagators $[D^{(ij)} (i, j = 1, 2, 3)]$ instead of the four $(D^{(-+)}, D^{(- -)}, D^{(-3)}, D^{(33)})$ in Eq. (3.6) below.

As shown in Appendix A, we have the following general formula for an arbitrary functional $\mathcal{O}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3]$ where $\varphi^{(+)}, \varphi^{(-)}$, and φ_3 correspond to the quantities $Q_1 - Q_2, (Q_1 + Q_2)/2$, and Q_3 , respectively,⁴³ in which Q_i implies the operator Q on C_i again,

$$\begin{aligned} \mathcal{O} \left[\frac{\hbar}{i} \frac{\partial}{\partial J^{(+)}} , \frac{\hbar}{i} \frac{\partial}{\partial J^{(-)}} , \hbar \frac{\partial}{\partial J_3} \right] i W_J |_{J=0} \\ = e^{\frac{\partial}{\partial \varphi} D \frac{\partial}{\partial \varphi}} \mathcal{O}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3] e^{V[\varphi]} |_{\varphi=0, \text{conn.}}, \end{aligned} \quad (3.6)$$

where

$$\begin{aligned} \frac{\partial}{\partial \varphi} D \frac{\partial}{\partial \varphi} \\ = \int_0^\infty dt \int_0^\infty ds \frac{\partial}{\partial \varphi^{(-)}(t)} D^{(-+)}(t, s) \frac{\partial}{\partial \varphi^{(+)}(s)} \\ + \frac{1}{2} \int_0^\infty dt \int_0^\infty ds \frac{\partial}{\partial \varphi^{(-)}(t)} D^{(- -)}(t, s) \frac{\partial}{\partial \varphi^{(-)}(s)} \\ + \int_0^\infty dt \int_0^{\beta\hbar} d\tau \frac{\partial}{\partial \varphi^{(-)}(t)} D^{(-3)}(t, \tau) \frac{\partial}{\partial \varphi_3(\tau)} \\ + \frac{1}{2} \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \frac{\partial}{\partial \varphi_3(\tau)} D^{(33)}(\tau, \tau') \frac{\partial}{\partial \varphi_3(\tau')} \end{aligned} \quad (3.7)$$

and

$$\begin{aligned} V[\varphi] = -\frac{i}{\hbar} \int_0^\infty dt [V_S(\varphi^{(+)}(t)/2 + \varphi^{(-)}(t)) \\ - V_S(-\varphi^{(+)}(t)/2 + \varphi^{(-)}(t))] - \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau V_S(\varphi_3(\tau)). \end{aligned} \quad (3.8)$$

Here, the subscript conn. implies that we keep only connected graphs. The Feynman rule is clear from this formula: propagators are given by $D^{(lm)}$ [$l, m = (+, -, 3)$] and vertices are determined by $V[\varphi]$ while $\mathcal{O}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3]$ corresponds to the external points. This can be seen as follows. For the moment, we employ a simple notation in which $D^{(lm)}(t, s)$ is denoted by D_{IJ} implying $I = (l, t), J = (m, s)$ for simplicity. Since \mathcal{O} and V in Eq. (3.6) are given as a polynomial of $\varphi_I, \varphi_J, \dots$, the quantity $\mathcal{O} e^V$ can also be expressed as a polynomial by expanding e^V in terms of V . Then the expressions needed for the calculation of the right-hand side of Eq. (3.6) (perturbatively in V) typically take the following form:

$$\exp \left(\sum_{IJ} \frac{\partial}{\partial \varphi_I} D_{IJ} \frac{\partial}{\partial \varphi_J} \right) \varphi_K \varphi_L \varphi_M \varphi_N \dots |_{\varphi=0}.$$

The system propagator $D^{(0)0}$: $-\text{---}^S\text{---}$

The Bath propagator $D^{(0)i}$: $-\text{---}^B\text{---}$

The bilinear vertex: $-\text{---}^S\text{---} \bullet \text{---}^B\text{---}$

FIG. 2. The bare propagators and the bilinear vertices.

If $\varphi_K \varphi_L \varphi_M \varphi_N \dots$ contains even number of φ 's, this expression reduces to the summation of the product of the propagators as follows:

$$D_{KL} D_{MN} \dots + D_{KM} D_{LN} \dots + \dots$$

Otherwise the expression is zero since we put $\varphi=0$ at the end. This process exactly coincides with making the Feynman diagram by taking the Wick contraction from the given vertices, external lines, and propagators (see Fig. 3 below).

$D^{(33)}$ is the Matsubara Green function, or the propagator connecting the imaginary time path components $C_3 - C_3$. $D^{(-+)}$ or $D^{(- -)}$ is a linear combination of the propagators on the real time path $D^{(11)}$ and $D^{(22)}$ which connect the components $C_1 - C_1$ and $C_2 - C_2$, respectively. $D^{(-3)}$ is the only propagator mixing the real and imaginary time path. [If we adopt the original (1, 2, 3)-representation instead of (+, -, 3)-representation, we have other mixing propagators such as $D^{(13)}$ and $D^{(23)}$.]

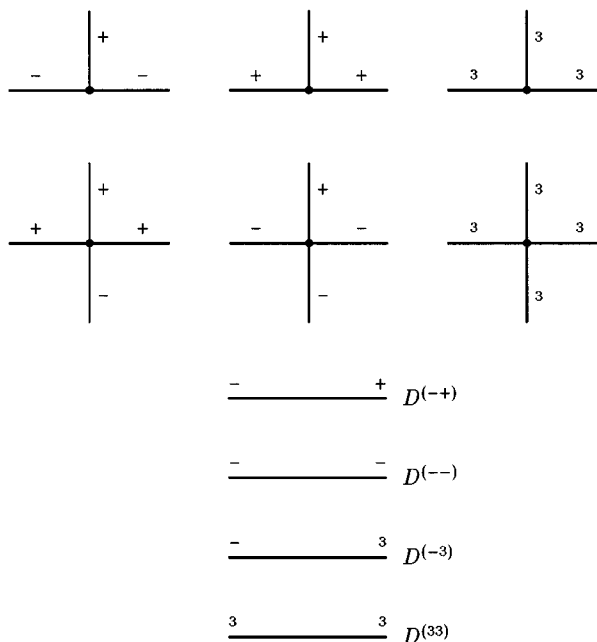


FIG. 3. Diagrammatic expressions for the Feynman rule: vertices and propagators.

These propagators are correlation functions for the bilinearly coupled system. If we introduce the cumulant part of the auto-correlation function $C(t+i\tau)$ for $0 < \tau < \beta\hbar$

$$C(t+i\tau) = \langle QQ(t+i\tau) \rangle_{\text{bilinear}}, \quad (3.9)$$

and call the real and imaginary part S and A , respectively ($C = S + iA$), then the propagators are expressed as follows:

$$D^{(-3)}(t, \tau) = C(t+i\tau), \quad (3.10)$$

$$D^{(-)}(t, s) = S(t-s), \quad (3.11)$$

$$D^{(-+)}(t, s) = -2i\theta(t-s)A(t-s), \quad (3.12)$$

$$D^{(33)}(\tau, \tau') = \theta(\tau - \tau')C(i\tau - i\tau') + \theta(\tau' - \tau)C(i\tau' - i\tau). \quad (3.13)$$

The bilinearly corrected propagators $D^{(lm)}$ which completely take into account the general bilinear system-bath coupling (see Ref. 39), have been derived in Ref. 37. Originally the formula (3.6) or the corresponding Feynman rule is written in terms of the bare propagators (of both the system and the

bath) and bilinear vertices (see Fig. 2) in addition to the anharmonic or nonbilinear vertices. The bare propagators are denoted as $D_{IJ}^{(0)i}$ where the $D_{IJ}^{(0)0}$ is the bare system propagator and $D_{IJ}^{(0)i}$ ($i \neq 0$) are the bare bath propagators. That is, the right-hand side of Eq. (3.6) originally takes the following form (with suppression of the I, J indices)

$$\exp\left(\sum_{i=0}^N \frac{\partial}{\partial \varphi_i} D^{(0)i} \frac{\partial}{\partial \varphi_i}\right) \mathcal{O}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3] \exp(V[\varphi_i]),$$

where $V[\varphi_i]$ contains the bilinear vertex in addition to the vertices due to the anharmonicity and nonbilinearity. The correction originating from the bilinear vertices is not included in the system propagators at all in the above expression. The corrections are, however, always made to the system propagator and thus the bilinear coupling correction is fully taken into account. Namely, the system propagators with the full correction of the bilinear bath is graphically expressed as [with suppression of the (lm) indices in the diagrams]

$$D_{IJ}^0 = \begin{array}{c} \text{---} \text{---} \text{---} + \text{---} \text{---} \bullet \text{---} \text{---} \bullet \text{---} \text{---} + \text{---} \text{---} \bullet \text{---} \text{---} \bullet \text{---} \text{---} \bullet \text{---} \text{---} + \dots \\ \text{---} \text{---} \text{---} \end{array} = \frac{1}{\left(\text{---} \text{---} \text{---}\right)^{-1} - \left(\bullet \text{---} \text{---} \bullet\right)}, \quad (3.14)$$

where the broken lines denote the bare propagators and the black dots the bilinear vertices. In the specific case of the bilinear coupling [the first term in Eq. (2.4)],⁴⁴ $D^{(lm)}$ are explicitly given by

$$D^{(-+)}(t, 0) = \int_{C_z} \frac{dz}{2\pi i} e^{zt} D^{(-+)}(z), \quad (3.15)$$

$$D^{(-)}(t, 0) = \int_{C_z} \frac{dz}{2\pi i} [\theta(t)e^{zt} + \theta(-t)e^{-zt}] D^{(-)}(z), \quad (3.16)$$

$$D^{(-3)}(t, \tau) = \frac{1}{\beta\hbar} \sum_{n=-\infty}^{\infty} e^{i\nu_n\tau} \int_{C_z} \frac{dz}{2\pi i} e^{zt} D^{(-3)}(z), \quad (3.17)$$

$$D^{(33)}(\tau, 0) = \frac{1}{\beta\hbar} \sum_{n=-\infty}^{\infty} e^{i\nu_n\tau} D^{(33)}(z), \quad (3.18)$$

where

$$D^{(-+)}(z) = \frac{\hbar}{i} F(z), \quad (3.19)$$

$$D^{(-)}(z) = \frac{-\hbar}{\beta\hbar} \sum_n \frac{z}{z^2 - \nu_n^2} [F(z) - F(\nu_n)], \quad (3.20)$$

$$D^{(-3)}(z) = \frac{-\hbar}{z - \nu_n} [F(z) - F(\nu_n)], \quad (3.21)$$

$$D^{(33)}(z) = \hbar F(\nu_n), \quad (3.22)$$

with

$$F(x) = \frac{1}{1/f(x) - \sum_{i=1}^N c_i^2 f_i(x)} = \frac{1}{M} \frac{1}{\Omega^2 + x^2 + x\gamma(x)}, \quad (3.23)$$

$$f(x) = \frac{1}{M} \frac{1}{\Omega^2 + \Delta\Omega^2 + x^2}, \quad f_i(x) = \frac{1}{m_i} \frac{1}{\omega_i^2 + x^2}, \quad (3.24)$$

$$\gamma(x) = \frac{1}{Mx} \left[\Delta\Omega^2 - \sum_{i=1}^N c_i^2 f_i(x) \right], \quad (3.25)$$

$$\nu_n = \frac{2\pi n}{\beta\hbar}. \quad (3.26)$$

Here the contour C_z on the complex z plane runs parallel to the imaginary axis where the real part of the path is chosen such that there are no poles on the left side of the path.

We notice here that the characteristic function $F(x)$ for the bilinearly corrected propagator reflects the structure shown in Eq. (3.14): $f(x)$ is the characteristic function for the system bare propagator and $f_i(x)$ is that for the bath bare propagator.

Once we use the bilinearly corrected propagators, we have to neglect the bilinear vertices altogether since it is taken into account already. In addition, since we do not assume the bath anharmonicity and the nonbilinear system–bath coupling, we can omit the bare bath propagators, too. In this way we obtain Eq. (3.6), which is expressed only through the propagators and vertices of the system: no propagators and vertices of the bath appear.

In our theory all the bath parameters (c_i, m_i, ω_i) appear only through the auxiliary function $F(x)$. In what follows, we follow the conventional arguments (for example, see Refs. 41 and 42) to clarify our points. In the above expression for $F(x)$, we rewrite the summation into the integral form as

$$\sum_{i=1}^N c_i^2 f_i(z) = \int_0^\infty \frac{d\omega}{\pi} I(\omega) \frac{2\omega}{\omega^2 + z^2}, \quad (3.27)$$

where the spectral distribution function $I(\omega)$, which characterizes the solvent nature, is defined by

$$I(\omega) = \pi \sum_{i=1}^N \frac{c_i^2}{2m_i\omega_i} \delta(\omega - \omega_i). \quad (3.28)$$

We may consider $I(\omega)$ as a continuous function of ω since we tacitly assume $N \rightarrow \infty$ to realize the dissipation. We introduced the counter term $M\Delta\Omega^2 Q^2/2$ to the Hamiltonian in Eq. (2.6) where

$$\Delta\Omega^2 = \frac{1}{M} \int_0^\infty \frac{d\omega}{\pi} I(\omega) \frac{2}{\omega},$$

in order to compensate for the coupling-induced re-normalization of the potential. Then the classical equation of motion for Q has the friction term proportional to the velocity \dot{Q} ;

$$\int_0^t dt' \gamma(t-t') \dot{Q}(t').$$

The Laplace transform of the damping kernel $\gamma(t)$ is nothing but $\gamma(z)$ appearing in Eq. (3.25). By use of $I(\omega)$, this can be rewritten as

$$\gamma(z) = \frac{1}{M} \int_0^\infty \frac{d\omega}{\pi} \frac{I(\omega)}{\omega} \frac{2z}{\omega^2 + z^2}.$$

Thus, in our propagator, all the bilinear bath effect is completely contained through this damping kernel.

If we assume the Ohmic dissipation, $I(\omega) = M\gamma\omega$, we obtain $\gamma(t) = \gamma\delta(t)$. In this case $\gamma(x)$ in Eq. (3.23) or (3.25) is replaced by a constant γ and $F(\nu_n)$ in Eqs. (3.19)–(3.22) by $F(|\nu_n|)$.⁴⁵ Here, $|x|$ is the absolute value of x . In the case of a memory damping kernel, say $\gamma(t) = \gamma\omega_D e^{-\omega_D t}$ (Durdy model), $\gamma(x)$ is replaced by

$$\gamma(x) = \frac{\gamma\omega_D}{\omega_D + x}.$$

The Durdy model approaches the Ohmic model as $\omega_D \rightarrow \infty$.

In our special case of the cubic and quadratic interactions (anharmonicity) the vertex part $V[\varphi]$ in Eq. (3.6) is given as follows:

$$\begin{aligned} V[\varphi] = & -\frac{i}{\hbar} \int_0^\infty dt \left(\frac{g'_3}{3!} [\varphi^{(+)}(t)]^3 + \frac{g_3}{2!} \varphi^{(+)}(t) [\varphi^{(-)}(t)]^2 \right) - \frac{i}{\hbar} \int_0^\infty dt \left(\frac{g'_4}{3!} [\varphi^{(+)}(t)]^3 \varphi^{(-)}(t) + \frac{g_4}{3!} \varphi^{(+)}(t) [\varphi^{(-)}(t)]^3 \right) \\ & - \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left(\frac{g_3}{3!} [\varphi_3(\tau)]^3 + \frac{g_4}{4!} [\varphi_3(\tau)]^4 \right), \end{aligned} \quad (3.29)$$

where $g'_3 = g_3/4$ and $g'_4 = g_4/4$. For any polynomial interaction, a vertex contains an odd number of $\varphi^{(+)}$, which is clear from the expression $V(\varphi^{(+)}/2 + \varphi^{(-)}) - V(-\varphi^{(+)}/2 + \varphi^{(-)})$ in Eq. (3.8). The graphical elements for our Feynman rule are given in Fig. 3. The rule is more closely explained in the next section.

Since higher order correlation functions required for calculation of higher order polarization (corresponding to non-

linear optical processes) can always be cast into the form of Eq. (3.6), they can also be estimated systematically by our Feynman rule.

IV. AN ANALYTICAL EXPRESSION FOR THE LINEAR ABSORPTION SPECTRUM THROUGH THE FEYNMAN DIAGRAM

By using the above Feynman rule we have the diagrammatic expansion of $S^{(1)}(t)$:

$$S^{(1)}(t) = \theta(t)\mu_1^2 e^{\frac{\partial}{\partial \varphi} D \frac{\partial}{\partial \varphi} \frac{i}{\hbar}} \left[\varphi^{(-)}(t)\varphi^{(+)}(0) + \varphi^{(+)}(t)\varphi^{(-)}(0) \right] e^{V[\varphi]} \Big|_{\varphi^{(+)}=\varphi^{(-)}=\varphi=0, \text{conn.}} \quad (4.1)$$

$$= \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \begin{array}{c} \text{---} \text{+} \\ \text{---} \text{+} \end{array} + \dots \quad (4.2)$$

All the graphs up to the order of g^2 for $g_3 \sim g_4 \sim g$ are presented in the above. Let us illustrate the Feynman diagrams more closely by considering an example: the first order contribution [the second graph in diagram (4.2)]. The first order correction term should be made up of two external points $-$ and $+$ and one of the three 4-point vertices given in Fig. 3. The graphs with a single 3-point vertex need not be considered, since such graphs always have an uncontracted φ (which should be set to zero) and their contributions vanish. First consider the $\varphi^{(+)}[\varphi^{(-)}]^3$ vertex (depicted in the lower center in Fig. 3) as the 4-point vertex to be contracted with the two external points. Considering that the point $+$ always has to be contracted with the point $-$ (see Fig. 3: $D^{(++)}$, $D^{(3)}$ etc., do not exist in the rule) and that $D^{(-+)}$ is non-zero only for $t > 0$, we obtain the second diagram whose analytical expression is given by

$$\theta(t)\mu_1^2 \frac{i}{\hbar} \frac{1}{2} \left(\frac{-ig_4}{\hbar} \right) \int_0^\infty dt' D^{(-+)}(t, t') \times D^{(-)}(t', t') D^{(-+)}(t', 0). \quad (4.3)$$

The symmetry factor $1/2$ is easily understood if we consider that this is coming from the following expression:

$$\theta(t)\mu_1^2 e^{\frac{\partial}{\partial \varphi} D \frac{\partial}{\partial \varphi} \frac{i}{\hbar}} \varphi^{(-)}(t)\varphi^{(+)}(0) \times \left(\frac{-ig_4}{3!\hbar} \right) \int_0^\infty dt' \varphi^{(+)}(t') [\varphi^{(-)}(t')]^3 \Big|_{\varphi=0, \text{conn.}} \quad (4.4)$$

The other two 4-point vertices in Fig. 3 (except $\varphi^{(+)} \times [\varphi^{(-)}]^3$) do not contribute in this expression, since propagators like $D^{(++)}$ and $D^{(3)}$ do not exist in our rule. The absence of $D^{(++)}$ and $D^{(3)}$ in our rule (Fig. 3) decreases the number of diagrams in general. This is one of the advantages of the $(+, -, 3)$ -representation instead of the original

$(1, 2, 3)$ -representation. In this way we confirm that only one diagram appears from the first order calculation.

In a similar manner we can construct the diagrams starting from the given vertices, external points, and propagators. Then the corresponding analytical expression to the diagram is obtained from the following rule.

- (1) In one specific way (as you like), assign n labels t_1, t_2, \dots, t_n and n' labels t'_1, t'_2, \dots, t'_n to all the vertices (internal points) and external points, respectively, where n is the total number of the vertices and n' is that of external points. In our case of the $S^{(1)}$ the external points is always two or $n' = 2$ (while we set $t'_1 = t$ and $t'_2 = 0$ in the above).
- (2) Associate a propagator $D^{(lm)}(t, t')$ with each line whose ends carry indices (l, m) and the time indices (t, t') where $l, m = +, -, 3$. Factors $-ig'_3/\hbar$, $-ig'_4/\hbar$, $-ig_3/\hbar$, $-ig_4/\hbar$, $-g_3/\hbar$, and $-g_4/\hbar$ are assigned to the vertices corresponding to $[\varphi^{(+)}]^3$, $\varphi^{(+)}[\varphi^{(-)}]^2$, $\varphi^{(-)}[\varphi^{(+)}]^3$, $\varphi^{(+)}[\varphi^{(-)}]^3$, $[\varphi_3]^3$, $[\varphi_3]^4$, respectively.
- (3) Associate the symmetry factor $1/S$ with the diagram.
- (4) Integrate the product of all factors in rules (2)–(3) over the internal time t_1, t_2, \dots, t_n .

The symmetry number S is an integer easily obtained from the symmetric property of the graph while we can always obtain the factor by looking at the original expression like Eq. (4.4).

The analytical expression for the third term is, for example, given by

$$\theta(t)\mu_1^2 \frac{i}{\hbar} \left(\frac{-ig_3}{\hbar} \right)^2 \int_0^\infty dt' \int_0^\infty dt'' D^{(-+)}(t, t') \times D^{(-)}(t', t'') D^{(-+)}(t', t'') D^{(-+)}(t'', 0). \quad (4.5)$$

Noting, for example, that the Laplace transform of Eq. (4.5) is given by

$$\theta(t)\mu_1^2 \frac{i}{\hbar} D^{(-+)}(z)\Sigma_A(z)D^{(-+)}(z), \quad (4.6)$$

where

$$\Sigma_A(z) = \left(\frac{-ig_3}{\hbar}\right)^2 \mathcal{L}_z[D^{(-)}(t,0)D^{(+)}(t,0)], \quad (4.7)$$

the Laplace transform of the two-time correlation function $S^{(1)}(t)$ [Eq. (2.12)] is then expressed as

$$\bar{S}^{(1)}(z) \equiv \mu_1^2 \frac{i}{\hbar} D_C^{(-+)}(z) \quad (4.8)$$

$$D_C^{(-+)}(z) = D^{(-+)}(z) + D^{(-+)}(z)\Sigma(z)D^{(-+)}(z) + \dots \quad (4.9)$$

$$= \frac{1}{[D^{(-+)}(z)]^{-1} - \Sigma(z)}, \quad (4.10)$$

where

$$\Sigma(z) = \begin{array}{c} \text{---} \circ \text{---} \\ | \\ t \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} \\ + \mathcal{L}_z \left[\begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ \text{---} \circ \text{---} \\ | \\ t \end{array} + \dots \right] \quad (4.11)$$

All the graphs appearing in $\Sigma(z)$ up to the second order in g are presented on the right-hand side of Eq. (4.11). Though the second and the third graphs on the right-hand side of Eq. (4.11) explicitly depend on t , the sum of the two graphs is independent of t . The sum of the fourth and fifth graphs also becomes a constant. These properties are expected to be general and actually proved in Appendix B without assuming Ohmic damping.

The final expression for the linear absorption is then given by $\sigma(\omega) = \text{Im}[\bar{S}^{(1)}(z = -i\omega)]$ with $\bar{S}^{(1)}(z)$ given in the above. Explicit analytical expressions corresponding to the Feynman diagrams are given as follows. The first five graphs on the right-hand side of Eq. (4.11) are given by

$$\Sigma_{01} = -\frac{i}{\hbar} \frac{g_4}{2} D^{(-)}(0,0), \quad (4.12)$$

$$\Sigma_{02}(t) = \frac{i}{2} \left(\frac{-g_3}{\hbar}\right)^2 D^{(33)}(0,0) \int_0^{\beta\hbar} d\tau D^{(-3)}(t,\tau), \quad (4.13)$$

$$\Sigma_{03}(t) = \frac{1}{2} \left(\frac{-ig_3}{\hbar}\right)^2 D^{(-)}(0,0) \int_0^t dt' D^{(+)}(t,t'), \quad (4.14)$$

$$\Sigma_{04}(t) = \frac{1}{2 \cdot 2} \left(\frac{-ig_4^2}{\hbar}\right)^2 D^{(33)}(0,0) \int_0^{\beta\hbar} d\tau [D^{(-3)}(t,\tau)]^2, \quad (4.15)$$

$$\Sigma_{05}(t) = \frac{1}{2} \left(\frac{-ig_4^2}{\hbar}\right)^2 D^{(-)}(0,0) \int_0^\infty dt' \times D^{(-+)}(t,t') D^{(-)}(t,t'), \quad (4.16)$$

respectively. The graphs in the bracket of \mathcal{L}_z are expressed as

$$\Sigma_A(t) = \left(\frac{-i}{\hbar}\right)^2 g_3^2 D^{(-+)}(t,0) D^{(-)}(t,0), \quad (4.17)$$

$$\Sigma_B(t) = \left(\frac{-i}{\hbar}\right)^2 \frac{g_4 g_4'}{3!} [D^{(-+)}(t,0)]^3, \quad (4.18)$$

$$\Sigma_C(t) = \left(\frac{-i}{\hbar}\right)^2 \frac{g_4^2}{2} D^{(-+)}(t,0) [D^{(-)}(t,0)]^2. \quad (4.19)$$

The physical interpretation of Eqs. (4.9) or (4.10) goes as follows. For the harmonic system, between the two external points $(-, +)$ runs a single propagator $D^{(-+)}$ which has a fundamental resonance around at the energy $\hbar\Omega$ (if the damping is weak). Due to the anharmonicity, the mass operator $\Sigma(z)$ appears between $(-, +)$. The z -dependent part of $\Sigma(z)$ causes the other resonances while the z -independent part makes the shift of the resonances. In other words, the particle (system) dressed with the heat bath undergoes the interaction with the dressed particle (system) and thus with the thermal bath again and again due to the anharmonicity.

V. ANALYTICAL RESULTS FOR THE OHMIC DAMPING

In order to clarify the physical interpretation given in the above, here we consider the representative case of the Ohmic damping. An analytical expression for the linear absorption spectrum $\sigma(\omega)$ in this case will be presented in this section. The series expansion of $\Sigma(z)$ up to the second order in g [all the graphs on the right-hand side of Eq. (4.11)] is fully included in the calculation. The detailed calculations are given in Appendix B. Though we truncate the series expansion of $\Sigma(z)$, an infinite series in g is partially included in $D_C^{(-+)}(z)$ or $\sigma(\omega)$, as clearly seen from Eq. (4.9). Indeed the result (5.8) below contains g_3 and g_4 in nonperturbative ways. The system bath coupling c_i or γ is treated exactly since we use the bilinearly corrected propagators as mentioned in Sec. III.

We introduce dimensionless quantities \tilde{X}

$$Q = \sqrt{\frac{\hbar}{M\Omega}} \tilde{Q}, \quad z = \Omega \tilde{z}, \quad \gamma = \Omega \tilde{\gamma}, \quad \beta \hbar \Omega = \tilde{\beta}. \quad (5.1)$$

Then the molecular Hamiltonian takes the form

$$H_S = \hbar \Omega \left(-\frac{1}{2} \frac{\partial^2}{\partial \tilde{Q}^2} + \frac{1}{2} \tilde{Q}^2 + \frac{1}{3!} \tilde{g}_3 \tilde{Q}^3 + \frac{1}{4!} \tilde{g}_4 \tilde{Q}^4 \right) \\ \equiv \hbar \Omega \tilde{H}_S, \quad (5.2)$$

where

$$g_3 = \sqrt{\frac{M^3 \Omega^5}{\hbar}} \tilde{g}_3, \quad g_4 = \frac{M^2 \Omega^3}{\hbar} \tilde{g}_4. \quad (5.3)$$

Dimensionless propagators and self energy are introduced as

$$D^{(lm)}(z) = \frac{\hbar}{i} \frac{1}{M\Omega^2} \tilde{D}^{(lm)}(\tilde{z}) \quad [l, m = (+, -, 3)] \quad (5.4)$$

and

$$\Sigma(z) = \frac{i}{\hbar} M\Omega^2 \tilde{\Sigma}(\tilde{z}), \quad (5.5)$$

respectively. The dimensionless absorption spectrum is then given by [see Eq. (4.8)]

$$\tilde{\sigma}(\tilde{\omega}) = \text{Im}[\tilde{D}^{(-+)}(\tilde{z})]_{\tilde{z} = -i\tilde{\omega}}, \quad \tilde{\omega} = \omega/\Omega \quad (5.6)$$

besides the trivial factor $\mu_1^2/(M\Omega^2)$.

In the following, we omit tildes for dimensionless quantities introduced in the above if it causes no ambiguity. By noting the dimensionless expression for $D^{(-+)}(z)$

$$D^{(-+)}(z) = \frac{1}{1+z^2+z\gamma} = \frac{1}{(z+\lambda_1)(z+\lambda_2)}, \quad (5.7)$$

we have the following analytical result:

$$\sigma(\omega) = \text{Im} \left[\frac{1}{(z+\lambda_1)(z+\lambda_2) - \Sigma(z)} \right]_{z = -i\omega}, \quad (5.8)$$

where

$$\Sigma(z) = -g_4 A + g_3^2 A + g_4^2 A \left[\zeta B - \frac{1}{16\zeta i} \left\{ C_1 \left(\frac{1}{2\lambda_1} - \frac{1}{\gamma} \right) + C_2 \left(\frac{1}{2\lambda_2} - \frac{1}{\gamma} \right) \right\} \right] + \frac{g_3^2}{4\zeta} \frac{1}{z+\gamma} \left(-\frac{C_1}{z+2\lambda_1} + \frac{C_2}{z+2\lambda_2} \right) \\ + \frac{g_4^2}{32\zeta^2} \left[\frac{1}{(z+3\lambda_1)(z+3\lambda_2)} - \frac{1+2C_1C_2}{(z+\gamma+\lambda_1)(z+\gamma+\lambda_2)} + \frac{C_1^2}{(z+3\lambda_1)(z+\gamma+\lambda_1)} + \frac{C_2^2}{(z+3\lambda_2)(z+\gamma+\lambda_2)} \right] \\ + 2g_3^2 \sum_{n=1}^{\infty} \frac{A_n}{(z+\nu_n+\lambda_1)(z+\nu_n+\lambda_2)} + \frac{g_4^2}{2\zeta} \sum_{n=1}^{\infty} \frac{A_n}{z+\gamma+\nu_n} \left(\frac{C_1}{z+2\lambda_1+\nu_n} - \frac{C_2}{z+2\lambda_2+\nu_n} \right) \\ + 2g_4^2 \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{A_n A_m}{(z+\lambda_1+\nu_n+\nu_m)(z+\lambda_2+\nu_n+\nu_m)}. \quad (5.9)$$

Here, we have introduced the following dimensionless parameters:

$$\zeta = \sqrt{1 - \frac{\gamma^2}{4}}, \quad \lambda_1 = \frac{\gamma}{2} + i\zeta, \quad \lambda_2 = \frac{\gamma}{2} - i\zeta, \quad C_j = \coth \frac{i\beta\lambda_j}{2}, \quad (5.10)$$

$$A = \frac{1}{\beta} \left[\sum_{n=1}^{\infty} \frac{1}{(\nu_n+\lambda_1)(\nu_n+\lambda_2)} + \frac{1}{2} \right], \quad B = \sum_{n=1}^{\infty} \frac{A_n}{(\nu_n+\lambda_1)(\nu_n+\lambda_2)}, \quad (5.11)$$

$$A_n = \frac{1}{\beta} \frac{\gamma\nu_n}{(\nu_n+\lambda_1)(\nu_n+\lambda_2)(\nu_n-\lambda_1)(\nu_n-\lambda_2)} = \frac{1}{\beta} \frac{\gamma\nu_n}{(1+\nu_n^2)^2 - \nu_n^2\gamma^2}. \quad (5.12)$$

The first three terms (proportional to A) on the right-hand side of Eq. (5.9), which is independent of $z = -i\omega$, corresponds to the first five graphs on the right-hand side of Eq. (4.11). The other terms proportional to g_3^2 (g_4^2) come from the first (second and third) term(s) in the bracket of \mathcal{L}_z in Eq. (4.11). From the definition, $\sigma(\omega)$ is zero at $z = -i\omega = 0$, which implies that $\Sigma(0)$ should be real. It is easy to make sure that $\Sigma(0)$ is real in the expression (5.9). The numerical estimations of this expression will be presented in the next section. In this section we discuss qualitative features of the above analytical expression for the spectrum, which confirms our previous physical interpretation. First, we note that, in general, the imaginary part of the function

$$f(\omega) = \frac{1}{(z+a)(z+b)\cdots(z+c)} \Big|_{z=-i\omega} \quad (5.13)$$

shows peaks around $\omega = \text{Im}(a), \text{Im}(b), \dots, \text{Im}(c)$, if the real parts of a, b, \dots, c are small. Next, it is important to notice the fact that

$$\text{Im}\lambda_j \rightarrow \pm\Omega \quad (\text{Im}\tilde{\lambda}_j \rightarrow \pm 1), \quad \text{as } \gamma \rightarrow 0, \quad (5.14)$$

since the dimensional expression for ζ is given by [see Eq. (5.10)]:

$$\zeta = \sqrt{\Omega^2 - \gamma^2/4}. \quad (5.15)$$

Thus, from Eq. (5.8), $\sigma(\omega)$ is expected to have a peak around $\omega = \Omega$ in the weakly damped case ($1 \gg \gamma$), if $\Sigma(z) = 0$ (the harmonic case). This implies the fact that our molecular system can absorb only one quantum (with frequency Ω) in the first order optical process since we assumed that $\mu(Q)$ is a linear function of Q .

For a small value of g_3 in the weakly damped case, a new peak around $\omega = 2\Omega$ is expected as seen from the fourth term (proportional to g_3^2) on the right-hand side of Eq. (5.9). The intensity of this peak is temperature dependent through C_1 and C_2 . At the same time the intensity of the peak around $\omega = \Omega$ may be modified due to the sixth term on the right-hand side of Eq. (5.9) because of the cubic interaction.

For a small value of g_4 in the weakly damped case, a similar consideration is possible. There will be another new peak around $\omega = 3\Omega$ and various temperature dependent corrections of intensities are expected.

At the zero temperature, the above expression is simplified significantly

$$\begin{aligned} \Sigma(z)|_{\beta=\infty} &= \frac{g_3^2}{4\zeta} \frac{1}{z+\gamma} \left(\frac{1}{z+2\lambda_1} + \frac{1}{z+2\lambda_2} \right) + \frac{g_4^2}{32\zeta^2} \\ &\times \left[\frac{1}{(z+3\lambda_1)(z+3\lambda_2)} + \frac{1}{(z+\gamma+\lambda_1)(z+\gamma+\lambda_2)} \right. \\ &\left. + \frac{1}{(z+3\lambda_1)(z+\gamma+\lambda_1)} + \frac{1}{(z+3\lambda_2)(z+\gamma+\lambda_2)} \right]. \end{aligned} \quad (5.16)$$

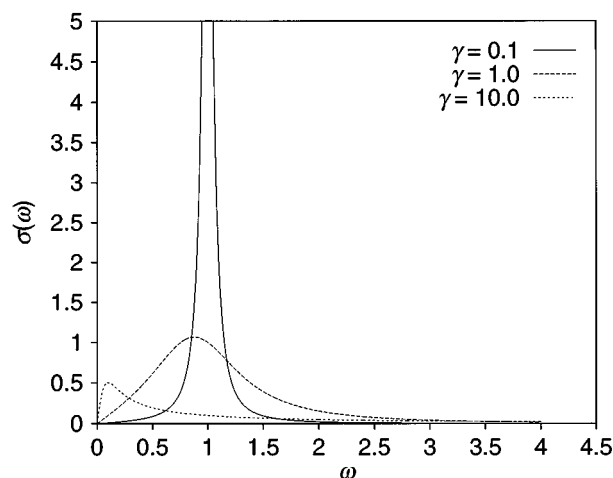


FIG. 4. The linear absorption spectra of the harmonic system in: (1) the underdamped case $\gamma=0.1$; (2) the intermediate case $\gamma=1$; (3) the overdamped case $\gamma=10$. Here, we normalized γ and ω by the unit Ω . In the harmonic case the spectra are temperature independent.

VI. NUMERICAL RESULTS

A. The harmonic system (Fig. 4)

From Eq. (5.8), the spectrum for the harmonic potential ($\Sigma(z) = 0$) shows a single temperature-independent peak at $\omega = \Omega$ for weak damping ($\gamma \ll 1$). This peak is shifted and broadened as the damping constant γ increases (see Fig. 4). In all the graphs below, the unit of ω (the frequency of the laser field) is chosen to be the characteristic frequency of the system oscillator Ω .

B. The anharmonic system (Figs. 5–7)

We now present numerically the linear absorption spectra for anharmonic potentials [$V_S(Q) \neq 0$] given in the previous section. The anharmonic parameters used in the following numerical estimations are $g_3 = g_4 = 0.2, 0.5$ and 7 . The corresponding potentials are shown in Figs. 5(a)–5(c), respectively. We set $g_3 = g_4$ in the above choices, since we truncate the series in $\Sigma(z)$ up to the second order in g regarding $g_3 \sim g_4 \sim g$. The strongly anharmonic case (c) is also examined since our calculation includes an infinite number of diagrams and it is interesting to see the validity of our expression.

Figure 6 shows the absorption spectra at the low temperature $\tilde{T} = k_B T / \hbar \Omega = 0.05$ together with the corresponding logarithmic plots. At the initial equilibrium, the population of the first excited state is about $e^{-1/\tilde{T}} \sim 10^{-9}$ if that of the ground state is 1 for the harmonic system. This temperature corresponds to 36[K] if $\Omega = 500[\text{cm}^{-1}]$. As mentioned in the previous section, for a weak damping case [Figs. 6(a) and 6(b)], we observe new peaks around $\omega = 2\Omega$ and $\omega = 3\Omega$ due to Q^3 and Q^4 anharmonicities, respectively. The naive consideration for weak anharmonicity given in Sec. V is clearly not true of the strongly anharmonic case in Fig. 6(c).

Our approximation may deteriorate as anharmonicity increases since we take unperturbative contributions into ac-

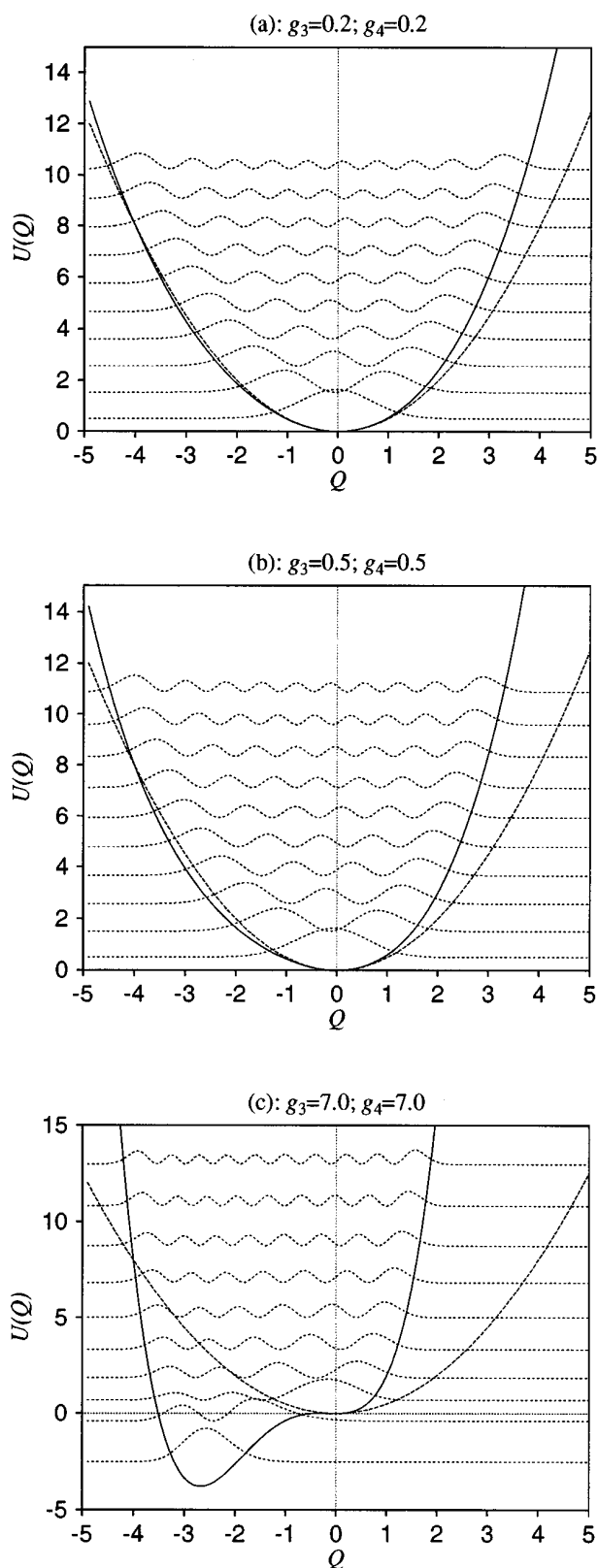


FIG. 5. The potential surfaces $U(Q)$ (in the unit $\hbar\Omega$) for different anharmonic parameters; (a) $g=0.2$; (b) $g=0.5$; (c) $g=7$. Here, we set $g=g_3=g_4$. We also display the n th eigenvalues E_n and eigenfunctions $|\Psi_n\rangle$ of the system Hamiltonian H_S (for some values of n) by the quantities $E_n + c|\Psi_n|^2$, where we chose $c=20$ to superpose them on the potentials. The broken line represents the unperturbed harmonic potential ($g=g_3=g_4=0$).

count only partially. However, the first peak in Fig. 6(c) seems to correspond to the transition between the ground state and the first excited state while the second peak to the transition between the ground and second excited states, which is consistent with our physical intuition [see Fig. 5(c)]. This implies that our inclusion of unperturbative contributions is enough at least to describe the qualitative physics, though, in this case, due to the strong anharmonicity, the ground state is critically changed—the minimum of the potential $U(Q)$ is no longer at $Q=0$.

At the higher temperature $\tilde{T}=0.5$ the spectra look different (see Fig. 7). At the initial equilibrium, the population of the first excited state is about $e^{-1/\tilde{T}} \sim 0.1$ if that of the ground state is 1 for the harmonic system. This temperature corresponds to 360[K] if $\Omega=500[\text{cm}^{-1}]$. In Figs. 7(a) and 7(b) we notice the splitting of the peak around $\omega=1$ (Ω). This is quite natural since the occupation probability of the first excited state becomes higher as the temperature increases. At $\tilde{T}=0.05$ only the transition between the ground and the first excited states may be observed while, at $\tilde{T}=0.5$, in addition to this, the transition between the first and second states may start to be observed (for the weak harmonic cases). The energies of these two transitions are slightly different due to the anharmonicity and thus we observe the splittings of the peaks.

The relative intensities of all peaks are also changed as temperature varies. This tendency is stronger as the anharmonicity increases as seen from both analytical and numerical results. Especially the change between the two temperatures in the strongly anharmonic case (c) may be easily noticed—large intensity correction and appearance of a new peak around $\omega=\Omega$. This new peak may reflect the transition from the first to the second excited states.

In Fig. 7 (b.2), the spectrum $\sigma(\omega)$ may not seem to go toward zero as $\omega \rightarrow 0$ for $\gamma=0.001$, while the analytical expression tells $\sigma(0)=0$ as mentioned before. We made sure, however, that $\sigma(\omega)$ really goes to zero $\omega \rightarrow 0$ ($\omega \lesssim 0.001$).

VII. CONCLUDING REMARKS

The appearance of new peaks due to the anharmonicity has been well known for an isolated molecular system from the Schrödinger equation approach (e.g. Ref. 46). Our results include effects of a bath system (of any strength of dissipation) and allows us to study an interplay between anharmonicity and dissipation. Using the expression we analyzed the effects of the third and fourth order anharmonicity [g_3Q^3 and g_4Q^4 in $V_S(Q)$] at various temperatures with different strengths of dissipation.

Our results can be applied for a non-Ohmic distribution case, but here we restricted our analysis to the Ohmic one to illustrate main qualitative features. We should notice, however, that even in the simple Ohmic case, the effects of anharmonicity at the low temperature have not been well studied, since the reduced equation of motion approach fails at this range as mentioned before. As shown in Sec. III, the generalization to a non-Ohmic case is straightforward.

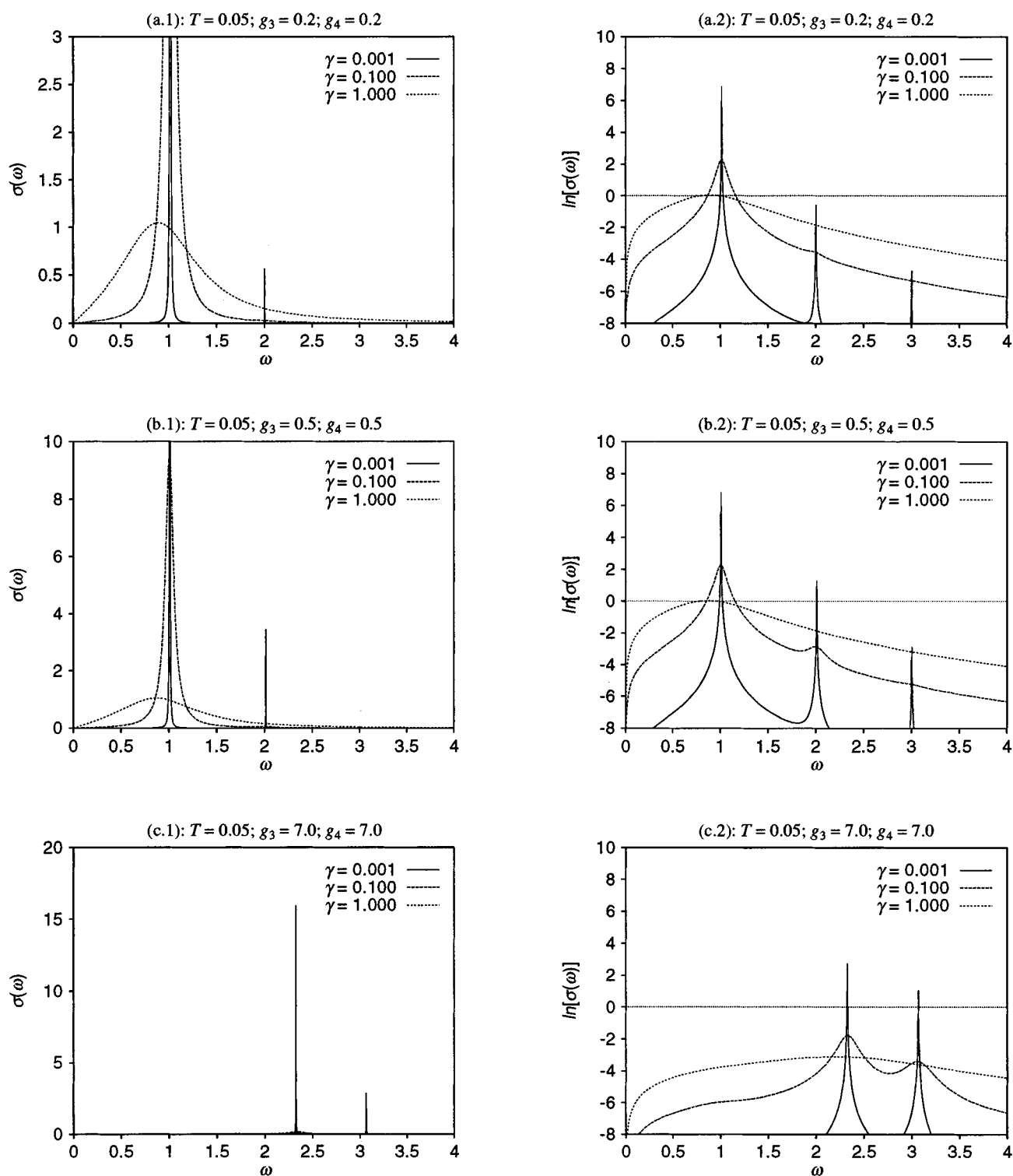


FIG. 6. The linear absorption spectra $\sigma(\omega)$ of the anharmonic system for the different damping constants $\gamma=0.001, 0.1, 1$ at the low temperature $\tilde{T}=0.05$. The graphs (a), (b), and (c) correspond to the spectra from the different potentials in Figs. 5(a), 5(b), and 5(c), respectively. The logarithmic plots of each spectrum are given on the right-hand side [(a.2), (b.2), and (c.2)].

As shown in the numerical calculations, when the temperature varies, the peaks not only change their intensity but also shift because of anharmonicity. Our expression seems to be good even for the strong anharmonicity where the minimum of the potential $U(Q)$ is shifted from $Q=0$. This result

suggests that all the terms dropped in the approximation do not play a significant role. In order to make this point clearly, it is desired to include unperturbative contributions more precisely.

One possible way to systematically include the unpertur-

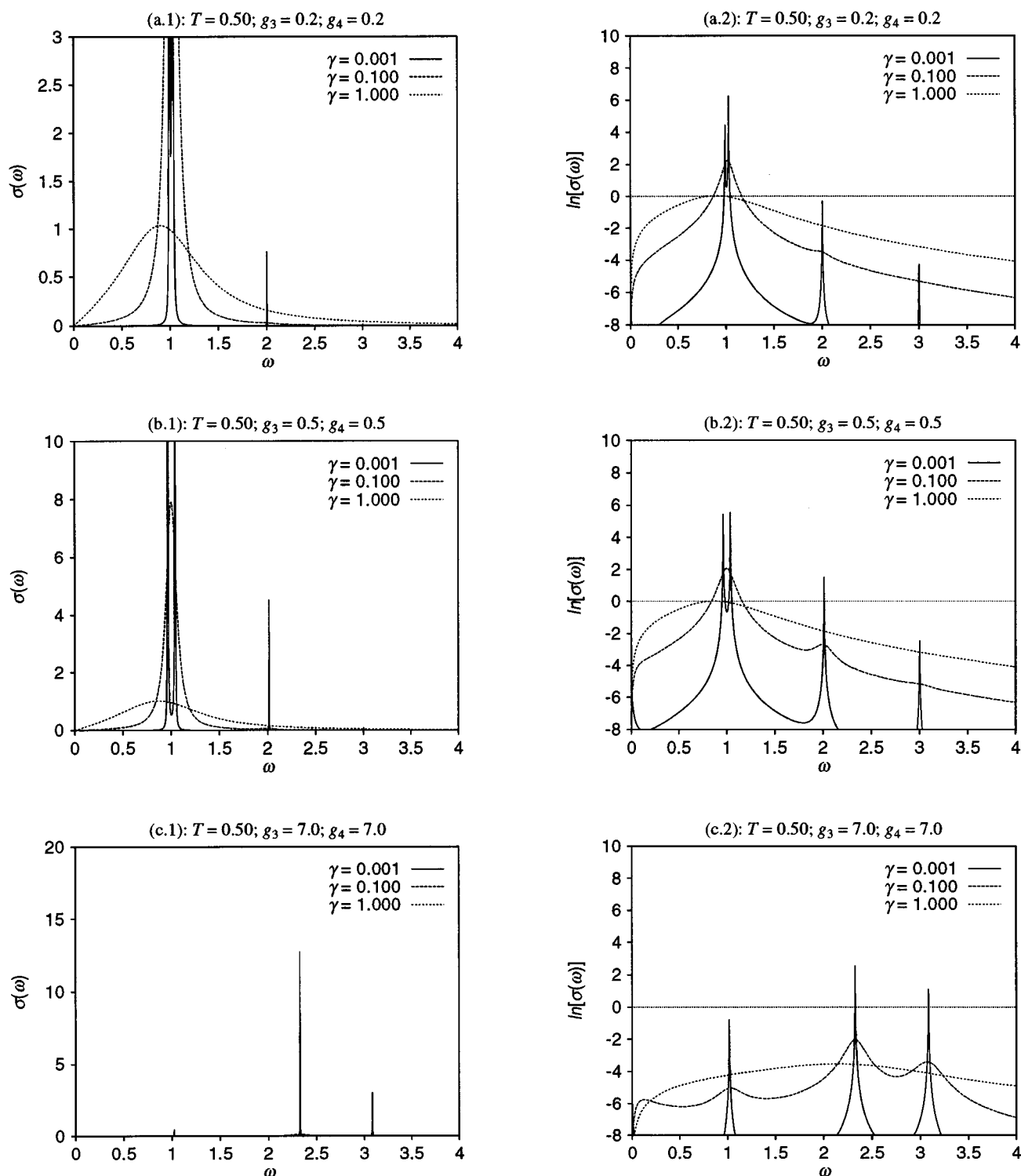


FIG. 7. The linear absorption spectra of the anharmonic system at the high temperature $\bar{T}=0.5$. The other parameters are the same as in Fig. 6.

bative contributions is Fukuda's method which consists of the inversion method and the on-shell expansion.⁴⁷⁻⁴⁹ They are originally applied to the problems in high energy physics and have proved their wide applicability in various fields.⁵⁰⁻⁵⁵ By this method one can rewrite the theory in terms of the physical observable in question by using the Legendre transformation. The unperturbative contributions

are systematically taken into account by perturbative calculations in this method (though it may sound paradoxical). The application of this method to the present problem of the molecular spectra should be studied in the future.

At the very high temperature our perturbation scheme may become worse since in that case the initial wave packet is spreading out so that higher energy eigenstates are well

populated and the effect of the anharmonicity will appear strongly. This can be seen if we look at the temperature dependent propagators, say, in the Ohmic case. Both $D^{(-)}$ and $D^{(-3)}$ proportional to $C_i = \coth(i\beta\lambda_i/2)$ become large as $T \rightarrow \infty$. However, in the temperature range of the experiment or in our numerical calculation, we may not need to care about it. Since in this region C_i is of order unity.

It is emphasized here that our theory can be used to investigate the form of anharmonic adiabatic potential surfaces.

The formalism employed in the present paper can be easily generalized to study the anharmonicity of the bath oscillators and the nonbilinear system–bath coupling by adapting the Feynman rule. These are also important issues to be studied in a separate paper.

In the present paper, we limited our study to a system with a single potential surface. Many systems in nonlinear optical response as well as nonadiabatic transition and tunneling are, however, characterized by two or three potential surfaces with dipole or nonadiabatic couplings between them. For a displaced (two-state) harmonic oscillator system, one can obtain response functions by using the generating functional.³⁶ In the same way, we can extend the present results to the multi-anharmonic potentials.

In our calculation of the spectrum or the response function, we assumed that the dipole moment is expressed in the

linear function of the coordinate as $\mu(Q) = \mu_0 + \mu_1 Q$. Our diagrammatic approach, however, makes it possible to include the higher-order coordinate dependence of $\mu(Q)$ as well. For the harmonic case, the response functions for a general $\mu(Q)$ had been obtained in a compact form (see Appendix E of Ref. 8). It is also possible to extend our results to study the fifth order optical process related to three time correlation functions, such as $\langle Q(t)Q(t')Q(t'') \rangle$. Fifth order optical measurements may be useful in distinguishing the spectrum of anharmonic origin from that of the other origins, since this measurement has two-time evolution period and the time dependencies on the anharmonic and other origins are expected to be different. By using this measurement, for example, we should be able to tell the effects of anharmonicity from those of higher order coordinate dependence of $\mu(Q)$. On the other hand, it may be difficult to distinguish those two effects in the linear absorption spectrum. This direction of study is also useful to investigate the homogeneous and inhomogeneous nature of the spectrum.³⁶ We leave these problems for future study.⁵⁶

ACKNOWLEDGMENT

One of the authors (K.O.) thanks S. Yokojima for fruitful discussions.

APPENDIX A: DERIVATION OF THE GENERAL FORMULA (3.6)

The generating functional obtained in Ref. 37 is expressed as

$$\exp\left(\frac{i}{\hbar} W_J\right) = \exp\left(\bar{V}\left[\frac{\hbar}{i} \frac{\partial}{\partial J^{(+)}}\right], \frac{\hbar}{i} \frac{\partial}{\partial J^{(-)}}, \hbar \frac{\partial}{\partial J_3}\right) \exp(\Phi[J^{(+)}, J^{(-)}, J_3]), \quad (\text{A1})$$

where \bar{V} and Φ are given by

$$\begin{aligned} \bar{V}\left[\frac{\hbar}{i} \frac{\partial}{\partial J^{(+)}}\right], \frac{\hbar}{i} \frac{\partial}{\partial J^{(-)}}, \hbar \frac{\partial}{\partial J_3} &= -\frac{i}{\hbar} \int_0^\infty dt \left[V\left(\frac{\hbar}{i} \frac{\partial}{\partial J_1(t)}\right) - V\left(-\frac{\hbar}{i} \frac{\partial}{\partial J_2(t)}\right) \right] - \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau V\left(\hbar \frac{\partial}{\partial J_3(\tau)}\right) \\ &= -\frac{i}{\hbar} \int_0^\infty dt \left[V\left(\frac{\hbar}{2i} \frac{\partial}{\partial J^{(+)}(t)} + \frac{\hbar}{i} \frac{\partial}{\partial J^{(-)}(t)}\right) - V\left(-\frac{\hbar}{2i} \frac{\partial}{\partial J^{(+)}(t)} + \frac{\hbar}{i} \frac{\partial}{\partial J^{(-)}(t)}\right) \right] \\ &\quad - \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau V\left(\hbar \frac{\partial}{\partial J_3(\tau)}\right), \end{aligned} \quad (\text{A2})$$

$$\begin{aligned} \Phi[J^{(+)}, J^{(-)}, J_3] &= \left(\frac{i}{\hbar}\right)^2 \int_0^\infty dt \int_0^\infty ds J^{(-)}(t) D^{(-+)}(t,s) J^{(+)}(s) + \frac{1}{2} \left(\frac{i}{\hbar}\right)^2 \int_0^\infty dt \int_0^\infty ds J^{(-)}(t) D^{(--)}(t,s) J^{(-)}(s) \\ &\quad + \frac{i}{\hbar^2} \int_0^\infty dt \int_0^{\beta\hbar} d\tau J^{(-)}(t) D^{(-3)}(t,\tau) J_3(\tau) + \frac{1}{2\hbar^2} \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' J_3(\tau) D^{(33)}(\tau,\tau') J_3(\tau'). \end{aligned} \quad (\text{A3})$$

We insert the right hand-side of the following identity at the end of Eq. (A1):⁴³

$$1 = \exp\left(\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau J_3(\tau) \varphi_3(\tau) + \int_0^\infty dt [J^{(+)}(t) \varphi^{(+)}(t) + J^{(-)}(t) \varphi^{(-)}(t)]\right) \Bigg|_{\varphi^{(+)} = \varphi^{(-)} = \varphi_3 = 0}. \quad (\text{A4})$$

Using the simple relation

$$e^{f(\frac{\partial}{\partial x})} e^{g(x)} e^{ax} = e^{ax} e^{g(\frac{\partial}{\partial a} + x)} e^{f(a)}, \quad (\text{A5})$$

we have

$$\exp\left(\frac{i}{\hbar} W_J\right) = \exp\left(\Phi\left[\frac{\hbar}{i} \frac{\partial}{\partial \varphi^{(+)}} + J^{(+)}, \frac{\hbar}{i} \frac{\partial}{\partial \varphi^{(-)}} + J^{(-)}, \frac{\hbar}{i} \frac{\partial}{\partial \varphi_3} + J_3\right]\right) \exp(\bar{V}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3])|_{\varphi=0}. \quad (\text{A6})$$

In the same way we have

$$\begin{aligned} \mathcal{O}\left[\frac{\hbar}{i} \frac{\partial}{\partial J^{(+)}} + J^{(+)}, \frac{\hbar}{i} \frac{\partial}{\partial J^{(-)}} + J^{(-)}, \frac{\hbar}{i} \frac{\partial}{\partial J_3} + J_3\right] e^{(i/\hbar)W_J}|_{J=0} \\ = \exp\left(\Phi\left[\frac{\hbar}{i} \frac{\partial}{\partial \varphi^{(+)}} + J^{(+)}, \frac{\hbar}{i} \frac{\partial}{\partial \varphi^{(-)}} + J^{(-)}, \frac{\hbar}{i} \frac{\partial}{\partial \varphi_3} + J_3\right]\right) \\ \times \mathcal{O}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3] \exp(\bar{V}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3])|_{\varphi=0}. \end{aligned} \quad (\text{A7})$$

Since $\Phi[\hbar/i \partial/\partial \varphi^{(+)}, \hbar/i \partial/\partial \varphi^{(-)}, \hbar \partial/\partial \varphi_3] = \partial/\partial \varphi D \partial/\partial \varphi$ and $\bar{V}[\varphi^{(+)}, \varphi^{(-)}, \varphi_3] = V[\varphi]$, we have the general formula (3.6) which keeps only connected graphs as is clear from the Goldstone theorem of the Feynman graph.

APPENDIX B: ESTIMATION OF GRAPHS

In this appendix we explicitly calculate the Laplace transforms of each diagrams of the mass operator $\Sigma(z)$ in the Ohmic case. For later convenience, we present propagators in terms of time variable in the Ohmic case.

$$D^{(-+)}(t, 0) = \frac{\hbar}{iM\zeta} e^{-\gamma t/2} \sin \zeta t, \quad (\text{B1})$$

$$D^{(--)}(t, 0) = \frac{\hbar}{4M\zeta} (-C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t}) - \Gamma(t), \quad (\text{B2})$$

$$D^{(-3)}(t, \tau) = -a_1 e^{-\lambda_1(t+i\tau)} + a_2 e^{-\lambda_2(t+i\tau)} - \Gamma(t+i\tau), \quad (\text{B3})$$

with

$$a_j = \frac{\hbar}{4M\zeta} (1 + C_j), \quad \Gamma(x) = \frac{2\gamma}{M\beta} \sum_{n=1}^{\infty} \frac{\nu_n e^{-\nu_n x}}{(\Omega^2 + \nu_n^2)^2 - \gamma^2 \nu_n^2}. \quad (\text{B4})$$

Here, λ_j, C_j are defined in Sec. V. The expressions for the first two propagators have already been derived in a rather different context.⁴² Owing to the initial value theorem of the Laplace transform, we have

$$\begin{aligned} D^{(-+)}(0, 0) &= zD^{(-+)}(z)|_{z \rightarrow 0} \\ &= \frac{1}{M\beta} \sum_{n=-\infty}^{\infty} \frac{1}{\Omega^2 + \nu_n^2 + |\nu_n| \gamma} = D^{(33)}(0, 0). \end{aligned} \quad (\text{B5})$$

Let us first consider the Laplace transform of $\Sigma_B(t)$. In terms of the dimensionless quantities it is expressed as:

$$\tilde{\Sigma}_B(\tilde{z}) \equiv \frac{\hbar}{i} \frac{1}{M\Omega^2} \Sigma_B(z) = -\frac{\tilde{g}_4^2}{4!} \int_0^{\infty} d\tilde{t} e^{-\tilde{z}\tilde{t}} [\tilde{D}^{(-+)}(\tilde{t}, 0)]^3. \quad (\text{B6})$$

We should notice here that the dimensionless propagators in terms of time variable is defined by [compare with Eq. (5.4)]

$$D^{(lm)}(t, 0) = \frac{\hbar}{i} \frac{1}{M\Omega} \tilde{D}^{(lm)}(\tilde{t}, 0) \quad [l, m = (+, -, 3)]. \quad (\text{B7})$$

In what follows we use the dimensionless expressions but with no tildes. From Eq. (B1) and the simple relation

$$\int_0^{\infty} dt e^{-xt} \sin \zeta t = \frac{\zeta}{x^2 + \zeta^2} \quad (\text{Re } x > 0), \quad (\text{B8})$$

we have

$$\begin{aligned} \Sigma_B(z) &= -\frac{g_4^2}{4!} \frac{3}{4\zeta^2} \left[\frac{1}{(z + \gamma + \lambda_1)(z + \gamma + \lambda_2)} \right. \\ &\quad \left. - \frac{1}{(z + 3\lambda_1)(z + 3\lambda_2)} \right]. \end{aligned} \quad (\text{B9})$$

Next we consider the Laplace transform of dimensionless function $\Sigma_A(t)$

$$\Sigma_A(z) = g_3^2 \int_0^{\infty} dt e^{-zt} D^{(-+)}(t, 0) D^{(-+)}(t, 0). \quad (\text{B10})$$

From Eqs. (B1), (B2), and (B8), we have

$$\Sigma_A(z) = -\Sigma_1(z) + \Sigma_2(z) - \Sigma_{\Gamma}(z), \quad (\text{B11})$$

where

$$\Sigma_i(z) = \frac{g_3^2}{4\zeta} \frac{C_i}{(z + \gamma)(z + 2\lambda_i)}, \quad (\text{B12})$$

$$\Sigma_{\Gamma}(z) = 2g_3^2 \sum_{n=1}^{\infty} \frac{A_n}{(z + \nu_n + \lambda_1)(z + \nu_n + \lambda_2)}. \quad (\text{B13})$$

Here, C_i and A_n were defined in Sec. V.

In a similar manner, the Laplace transform of dimensionless function Σ_C is calculated as

$$\begin{aligned} \Sigma_C(z) &= \frac{g_4^2}{2} \int_0^{\infty} dt e^{-zt} D^{(-+)}(t, 0) [D^{(-+)}(t, 0)]^2 \\ &= \frac{g_4^2}{32\zeta^2} \left[\frac{C_1^2}{(z + 3\lambda_1)(z + \gamma + \lambda_1)} \right. \\ &\quad \left. + \frac{C_2^2}{(z + 3\lambda_2)(z + \gamma + \lambda_2)} - \frac{2C_1 C_2}{(z + \gamma + \lambda_1)(z + \gamma + \lambda_2)} \right] \\ &\quad + \frac{g_4^2}{2\zeta} \sum_{n=1}^{\infty} \frac{A_n}{z + \gamma + \nu_n} \left(\frac{C_1}{z + 2\lambda_1 + \nu_n} - \frac{C_2}{z + 2\lambda_2 + \nu_n} \right) \\ &\quad + 2g_4^2 \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{A_n A_m}{(z + \lambda_1 + \nu_n + \nu_m)(z + \lambda_2 + \nu_n + \nu_m)}. \end{aligned} \quad (\text{B14})$$

Finally we calculate the first five terms on the right-hand

side of Eq. (4.11) or $\Sigma_{01}-\Sigma_{05}$, given in Eqs. (4.12) to (4.16). The dimensionless expression of Σ_{01} reduces to $-g_4A$ through Eq. (B.5). The sum of $\Sigma_{02}(t)$ and $\Sigma_{03}(t)$ can be directly calculated from Eqs. (B1) to (B3). After tedious but straightforward calculations, we find that the (dimensionless) sum is g_3^2A , which is independent of t . Instead we can use the fact that the sum is equal to $\Sigma_{02}(t=0)$ since the sum is independent of t and $\Sigma_{03}(t=0)=0$ in order to alleviate the tedious calculation. The independence on t can be proved generally (by not assuming the Ohmic damping) as follows. Since $D^{(33)}(0,0)=D^{(-)}(0,0)=S(0)$, the sum is expressed as

$$\frac{1}{2}\left(\frac{-g_3}{\hbar}\right)^2 S(0)G(t),$$

where

$$G(t)=2i\int_0^t dt' A(t')+i\int_0^{\beta\hbar} d\tau C(t+i\tau).$$

By noting the periodicity relations

$$S(t+i\beta\hbar)=S(t), \quad A(t+i\beta\hbar)=-A(t),$$

we conclude that the time derivative of $G(t)$ which is $2iA(t)+C(t+i\beta\hbar)-C(t)$ becomes zero. Thus the sum is truly time independent.

In the same way, the sum of $\Sigma_{04}(t)$ and $\Sigma_{05}(t)$ is proved to be independent of t and the dimensionless quantity $\hbar/(iM\Omega^2)[\Sigma_{04}(t)+\Sigma_{05}(t)]$ reduces to the third terms on the right-hand side of Eq. (5.9).

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⁴⁵Note the relation

$$M\Delta\Omega^2 - \sum_i c_i^2 f_i(x) = \int_0^\infty \frac{d\omega I(\omega)}{\pi} \frac{2x^2}{\omega^2 + x^2} = \begin{cases} M\gamma x & (\text{Re}x > 0) \\ -M\gamma x & (\text{Re}x < 0) \end{cases}$$

and the fact that we can assume $\text{Re}z > 0$ without losing generality since the inverse Laplace transform of the bare propagator $(\hbar/i)f(z)$ has to exist.

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