PHYSICAL REVIEW E VOLUME 50, NUMBER 1 JULY 1994

Time-resolved optical spectrum for transient resonant light scattering

Toshihico Arimitsu and Naoko Arimitsu*
Institute of Physics, University of Tsukuba, Tsukuba 305, Japan
(Received 18 January 1994)

A general formula of the time-resolved optical spectrum for transient resonant light scattering is derived systematically by means of the operator algebra within the formalism of nonequilibrium thermo field dynamics (NETFD). The formula is applied to an analytically solvable model of the localized electron and phonon system, i.e., second-order light scattering due to the optically active three electronic states whose intermediate state is dynamically modulated by the phonon interaction mode. The derivation of the analytical expression for a four-point function, needed to obtain the spectrum, is performed with the help of the algebraic manipulations in NETFD, which showed the advantage of its methodology with respect to nonequilibrium transient phenomena. The three-dimensional profiles of the Raman and luminescence components in the time-resolved spectrum in the model are presented to show how the stochastic character comes out in the fast modulation limit, and how the dynamical behavior of the phonon system causing the modulation of the intermediate electronic state comes out in the slow modulation limit.

PACS number(s): 05.30.−d, 42.50.Ct

I. INTRODUCTION

The time-resolved optical spectrum of transient resonant light scattering was extensively examined first by Takagawara, Hanamura, and Kubo [1] in studies of the second-order optical processes with stochastic models of the intermediate state. Since then, there have been several theoretical developments in the formulation of the time-resolved optical spectrum [2–4]. Most of the investigations [2,4] were performed with the help of models of stochastic processes [5], whereas the analysis in Ref. [3] was done for an analytically solvable and nonstochastic model for the intermediate state [6,7]. The calculations in these papers were done with the help of the density operator method.

In this paper, we will derive the formula of the time-resolved optical spectrum of transient resonant light scattering by means of the formalism of nonequilibrium thermo field dynamics (NETFD) [8–13], which is an operator formalism of quantum systems with *dissipative processes,* and will apply it to the nonstochastic model of a localized-electron and phonon system [3], i.e., the second-order light scattering due to the optically active three electronic states whose intermediate state is dynamically modulated by the phonon interaction mode [14]. Among the merits of NETFD are a straightforward and comprehensible treatment of transient phenomena and a transparent algebraic structure (see, for example, [15–19]). The formula of the time-resolved optical spectrum is derived along the lines of Ref. [4] by means of algebraic treatments within NETFD which are very similar to the ones in quantum mechanics. When a laser pulse impinges on matter the incident photons are absorbed, causing an excitation of the state of the matter system, say the states of localized electrons. The intermediate state of the localized electron is modulated dynamically by a phonon system. The scattered photons, i.e., the photons emitted during the deexcitation, yield a spectrum consisting of instantaneous Raman scattering and of relatively long-time luminescence. The spectrum can be calculated by considering a second-order optical process.

In Sec. II, the method of NETFD is briefly explained. In Sec. III, the formula of the photon counting rate for the second-order optical processes is derived with the help of NETFD. In Sec. IV, we apply the formula obtained to the case of the three-state dynamical model for a localized electron-phonon system. In Sec. V, the limits of slow and fast modulations for the model are investigated. In Sec. VI, we present the profiles of the time-resolved optical spectrum for several typical parameters, which lead to a deeper insight into the nature of the scattering process for the model of a dynamical intermediate state. Section VII is devoted to discussion.

II. TECHNICAL BASICS OF NETFD

NETFD is a unified formalism of dissipative quantum systems including all the aspects of nonequilibrium statistical mechanics, i.e., the Boltzmann, the Fokker-Planck, the Langevin, and the stochastic Liouville equations (see [13] for detail and references). It allows us to deal with dissipative systems by algebraic manipulations similar to the usual quantum mechanics.

Let us begin by listing the basics of NETFD.

(1) Any operator A is associated with its partner (tilde) operator $\tilde{A}$. The *tilde conjugation* is defined by

*Present address: Division of Electrical and Computer Engineering, Faculty of Engineering, Yokohama National University, Tokiwadai, Yokohama 240, Japan.

$$(A_1 A_2)^{\sim} = \tilde{A}_1 \tilde{A}_2 \ , \tag{2.1}$$

$$(c_1 A_1 + c_2 A_2)^{\sim} = c_1^* \tilde{A}_1 + c_2^* \tilde{A}_2 \ , \tag{2.2}$$

$$(\tilde{A})^{\sim} = A \ , \tag{2.3}$$

$$(A^\dagger)^{\sim} = \tilde{A}^\dagger \ , \tag{2.4}$$

where the A's are operators, and c_1 and c_2 are c numbers.

(2) The tilde and nontilde operators at an equal time are mutually commutative, and are related with each other through the relation

$$\langle 1| A^\dagger = \langle 1| \tilde{A} \ . \tag{2.5}$$

(3) The expectation value of an operator A is given by $\langle 1|A|0\rangle$. Observable operators consist only of nontilde operators.

(4) The thermal vacuums $\langle 1|$ and $|0\rangle$ are *tilde invariant,*

$$\langle 1|^{\sim} = \langle 1|, \quad |0\rangle^{\sim} = |0\rangle \ , \tag{2.6}$$

and are normalized as $\langle 1|0\rangle = 1$.

(5) The dynamical evolution of systems is described by the *Schrödinger equation* ($\hbar = 1$)

$$\frac{\partial}{\partial t}|0(t)\rangle = -i\hat{H}^{\text{tot}}|0(t)\rangle \ . \tag{2.7}$$

We usually call the Schrödinger equation the Fokker-Planck equation for coarse grained systems.

(6) The *hat Hamiltonian,* an infinitesimal time-evolution generator $\hat{H}^{\text{tot}}$, satisfies

$$(i\hat{H}^{\text{tot}})^{\sim} = i\hat{H}^{\text{tot}} \ . \tag{2.8}$$

This characteristic is named *tildian.* The tildian hat Hamiltonian is not necessarily a Hermitian operator.

(7) The hat Hamiltonian has zero eigenvalue for the thermal bra vacuum,

$$\langle 1|\hat{H}^{\text{tot}} = 0 \ . \tag{2.9}$$

This is a manifestation of the conservation of probability, i.e.,

$$\langle 1|0(t)\rangle = 1 \ . \tag{2.10}$$

Now, we introduce a set of the states [20]

$$|m,\tilde{n}\rangle = |m\rangle|\tilde{n}\rangle \ , \tag{2.11}$$

where $|m\rangle$ and $|\tilde{n}\rangle$ satisfy

$$a^\dagger a|m\rangle = m|m\rangle, \quad \tilde{a}^\dagger \tilde{a}|\tilde{n}\rangle = n|\tilde{n}\rangle \ , \tag{2.12}$$

$$\langle m|a^\dagger a = \langle m|m, \quad \langle \tilde{n}|\tilde{a}^\dagger \tilde{a} = \langle \tilde{n}|n \ , \tag{2.13}$$

the orthonormality

$$\langle m|m'\rangle = \delta_{m,m'}, \quad \langle \tilde{n}|\tilde{n}'\rangle = \delta_{n,n'} \ , \tag{2.14}$$

and the completeness

$$\sum_m |m\rangle\langle m| = 1, \quad \sum_n |\tilde{n}\rangle\langle \tilde{n}| = 1 \ . \tag{2.15}$$

We see that the orthonormality and the completeness for $|m,\tilde{n}\rangle$ are given, respectively, by

$$\langle m,\tilde{n}|m',\tilde{n}'\rangle = \delta_{m,m'}\delta_{n,n'} \ , \tag{2.16}$$

$$\sum_{m,n} |m,\tilde{n}\rangle\langle m,\tilde{n}| = 1 \ . \tag{2.17}$$

The matrix elements $\langle k,\tilde{l}|A|m,\tilde{n}\rangle$ and $\langle k,\tilde{l}|\tilde{A}|m,\tilde{n}\rangle$ with the operator A consisting only of nontilde operators reduce, respectively, to

$$\begin{aligned}\langle k,\tilde{l}|A|m,\tilde{n}\rangle &= \langle k|A|m\rangle\langle \tilde{l}|\tilde{n}\rangle \\ &= \langle k|A|m\rangle\delta_{l,n} \ ,\end{aligned} \tag{2.18}$$

$$\begin{aligned}\langle k,\tilde{l}|\tilde{A}|m,\tilde{n}\rangle &= \langle k|m\rangle\langle \tilde{l}|\tilde{A}|\tilde{n}\rangle \\ &= \delta_{k,m}\langle l|A|n\rangle^* \\ &= \delta_{k,m}\langle n|A^\dagger|l\rangle \ ,\end{aligned} \tag{2.19}$$

where we used the property

$$|\tilde{n}\rangle = |n\rangle^{\sim} \ . \tag{2.20}$$

Note that the state $|m,\tilde{n}\rangle$ satisfies

$$|m,\tilde{n}\rangle^{\sim} = |n,\tilde{m}\rangle \ . \tag{2.21}$$

We can represent the thermal vacuums as

$$|0(t)\rangle = \sum_{n,m} P_{n,m}(t)|n,\tilde{m}\rangle \ , \tag{2.22}$$

$$\langle 1| = \sum_n \langle n,\tilde{n}| \ . \tag{2.23}$$

The normalization of $\langle 1|0(t)\rangle$ reduces to

$$\begin{aligned}1 = \langle 1|0(t)\rangle &= \sum_k \sum_{n,m} P_{n,m}(t)\langle k,\tilde{k}|n,\tilde{m}\rangle \\ &= \sum_k P_{k,k}(t) \ ,\end{aligned} \tag{2.24}$$

where we used the orthonormality (2.16). With the help of (2.21), we see the tilde invariance of the thermal vacuum $|0(t)\rangle$ in the following way:

$$\begin{aligned}|0(t)\rangle^{\sim} &= \sum_{n,m} P_{n,m}^*(t)|n,\tilde{m}\rangle^{\sim} \\ &= \sum_{n,m} P_{n,m}^*(t)|m,\tilde{n}\rangle \\ &= \sum_{m,n} P_{n,m}^*(t)|n,\tilde{m}\rangle \\ &= |0(t)\rangle \ ,\end{aligned} \tag{2.25}$$

where we used $P_{m,n}^* = P_{n,m}$ in the last equality.

When the hat Hamiltonian $\hat{H}^{\text{tot}}$ in (2.7) can be divided into two parts as

$$\hat{H}^{\text{tot}} = \hat{H} + \hat{H}' \ , \tag{2.26}$$

we can introduce the thermal vacuum ket vector in the interaction representation as

$$|0(t)\rangle_I = e^{i\hat{H}t}|0(t)\rangle \ . \tag{2.27}$$

The Fokker-Planck equation (2.7) then reads

$$\frac{\partial}{\partial t}|0(t)\rangle_I = -i\hat{H}'(t)|0(t)\rangle_I \;, \tag{2.28}$$

where we used

$$\hat{H}'(t) = e^{i\hat{H}t}\hat{H}'e^{-i\hat{H}t} \;. \tag{2.29}$$

This can be formally solved in terms of the state of the system at an initial time t_0 as

$$|0(t)\rangle_I = \hat{S}(t,t_0)|0(t_0)\rangle_I \;, \tag{2.30}$$

with

$$\hat{S}(t,t_0) = \hat{S}(t)\hat{S}^{-1}(t_0) \;, \tag{2.31}$$

where $\hat{S}(t)$ is specified by

$$\frac{d}{dt}\hat{S}(t) = -i\hat{H}'(t)\hat{S}(t) \;, \tag{2.32}$$

with the initial condition $\hat{S}(0)=1$. The thermal vacuum $|0(t)\rangle$ in the Schrödinger representation can be expressed by means of $\hat{S}(t,t_0)$ as

$$|0(t)\rangle = e^{-i\hat{H}t}\hat{S}(t,t_0)e^{i\hat{H}t_0}|0(t_0)\rangle \;. \tag{2.33}$$

Since $\hat{H}$ should satisfy

$$\langle 1|\hat{H} = 0 \;, \tag{2.34}$$

the interaction Hamiltonian $\hat{H}'(t)$ in the interaction representation has the property

$$\langle 1|\hat{H}'(t) = 0 \;. \tag{2.35}$$

Then, (2.32) gives us

$$\langle 1|\hat{S}(t) = \langle 1|\hat{S}(t_0) \;, \tag{2.36}$$

leading to

$$\langle 1|\hat{S}(t,t_0) = \langle 1| \;. \tag{2.37}$$

This is a manifestation of the conservation of probability, $\langle 1|0(t)\rangle = 1$. Note that the thermal bra vacuum in the interaction representation ${}_I\langle 1|$ becomes the same as the one in the Schrödinger representation:

$${}_I\langle 1| = \langle 1|e^{-i\hat{H}t} = \langle 1| \;. \tag{2.38}$$

The overlap $\langle l,\tilde{l}|0(t)\rangle$ is given by

$$\langle l,\tilde{l}|0(t)\rangle = \sum_n \langle l,\tilde{l}|e^{-i\hat{H}t}\hat{S}(t,t_0)e^{i\hat{H}t_0}|n,\tilde{n}\rangle P_{n,n}(t_0) \;, \tag{2.39}$$

where we put for the initial state

$$|0(t_0)\rangle = \sum_n P_{n,n}(t_0)|n,\tilde{n}\rangle \;, \tag{2.40}$$

with

$$\sum_n P_{n,n}(t_0) = 1 \;, \tag{2.41}$$

which is consistent with the normalization $\langle 1|0(t_0)\rangle = 1$. We see that

$$\begin{aligned}\sum_l \langle l,\tilde{l}|0(t)\rangle &= \sum_l\sum_n \langle l,\tilde{l}|e^{-i\hat{H}t}\hat{S}(t,t_0)e^{i\hat{H}t_0}|n,\tilde{n}\rangle P_{n,n}(t_0)\\ &= \sum_n \langle 1|\hat{S}(t,t_0)e^{i\hat{H}t_0}|n,\tilde{n}\rangle P_{n,n}(t_0)\\ &= \sum_n P_{n,n}(t_0) = 1 \;,\end{aligned} \tag{2.42}$$

where we used (2.34), (2.37), and

$$\langle 1|m,\tilde{n}\rangle = \sum_l \langle l,\tilde{l}|m,\tilde{n}\rangle = \sum_l \delta_{l,m}\delta_{l,n} = \delta_{m,n} \;. \tag{2.43}$$

Although the interaction hat Hamiltonian $\hat{H}'$ has the structure

$$\hat{H}' = H' - \tilde{H}' \;, \tag{2.44}$$

the hat Hamiltonian $\hat{H}$ does *not*, in general. Therefore, one needs to calculate the matrix elements

$$\langle l,\tilde{l}|e^{-i\hat{H}t}\hat{S}(t,t_0)e^{i\hat{H}t_0}|n,\tilde{n}\rangle \;, \tag{2.45}$$

in order to obtain the overlap (2.39). Expanding the $\hat{S}$ *matrix* with respect to the order of $\hat{H}'$ as

$$\hat{S}(t,t_0) = \sum_{n=0}^{\infty} \hat{S}^{(n)}(t,t_0) \;, \tag{2.46}$$

we can deal with any order of processes induced by $\hat{H}'$. See Appendix A for the first-order process (the linear response) as the simplest example.

Note that when the hat Hamiltonian $\hat{H}$ has the structure

$$\hat{H} = H - \tilde{H} \;, \tag{2.47}$$

in addition to $\hat{H}'$, the overlap (2.39) becomes the well-known form

$$\begin{aligned}\langle l,\tilde{l}|0(t)\rangle &= \sum_n \langle l|S(t,t_0)|n\rangle\langle\tilde{l}|\tilde{S}(t,t_0)|\tilde{n}\rangle P_{n,n}(t_0)\\ &= \sum_n |\langle l|S(t,t_0)|n\rangle|^2 P_{n,n}(t_0) \;,\end{aligned} \tag{2.48}$$

where we assumed that $|n,\tilde{n}\rangle$ is an eigenfunction of H with a real eigenvalue E_n,

$$H|n,\tilde{n}\rangle = E_n|n,\tilde{n}\rangle, \quad \tilde{H}|n,\tilde{n}\rangle = E_n|n,\tilde{n}\rangle \;. \tag{2.49}$$

Note that, in the case of (2.47),

$$\hat{S}(t,t_0) = S(t,t_0)\tilde{S}(t,t_0) \;, \tag{2.50}$$

where $S(t,t_0)$ contains only nontilde operators and is a unitary operator.

III. SECOND-ORDER OPTICAL PROCESSES

We now consider a system that is composed of a radiation field (R) and a matter system (M):

$$\hat{H}^{\text{tot}} = \hat{H} + \hat{H}_{RM} \;, \tag{3.1}$$

$$\hat{H} = \hat{H}_R + \hat{H}_M \;, \tag{3.2}$$

with

$$\hat{H}_R = H_R - \tilde{H}_R \ , \tag{3.3}$$

$$\hat{H}_{RM} = H_{RM} - \tilde{H}_{RM} \ . \tag{3.4}$$

The Hamiltonians H_R and H_{RM} describe the radiation field and its interaction with the material system, respectively,

$$H_R = \sum_{\mathbf{k}} \omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \ , \tag{3.5}$$

$$H_{RM} = \sum_{\mathbf{k}} g_{\mathbf{k}} a_{\mathbf{k}} M_{\mathbf{k}}^\dagger + \text{H.c.} \ , \tag{3.6}$$

where $a_{\mathbf{k}}^\dagger$ ($a_{\mathbf{k}}$) denotes the creation (annihilation) operator for a photon with energy $\omega_{\mathbf{k}}$, and $M_{\mathbf{k}}^\dagger$ ($M_{\mathbf{k}}$) describes the excitation (deexcitation) operator for the matter system. The strength of the coupling between the photon and the matter systems is specified by the complex coefficient $g_{\mathbf{k}}$. The hat Hamiltonian $\hat{H}_M$ is given when the matter system is specified (see next section).

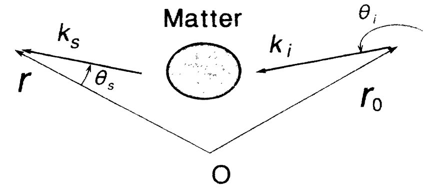

FIG. 1. Setup of the system under consideration.

Let us investigate the second-order optical process of a system with the setup sketched in Fig. 1. We assume that the incident laser pulse with a wave vector $\mathbf{k}_i$, which is generated at time t_0 and position r_0, is scattered by a matter system, and that the scattered light with a wave vector $\mathbf{k}_s$ is detected at time t and position $\mathbf{r}$.

We find the related $\hat{S}$ matrix $\hat{S}^{(2,2)}(t,t_0)$ in

$$\hat{S}^{(4)}(t,t_0) = (-i)^4 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_3} dt_4 \hat{H}_{RM}(t_1)\hat{H}_{RM}(t_2)\hat{H}_{RM}(t_3)\hat{H}_{RM}(t_4) \tag{3.7}$$

$$= \sum_{l=0}^{4} \hat{S}^{(l,4-l)}(t,t_0) \ , \tag{3.8}$$

where the superscript in $\hat{S}^{(m,n)}(t,t_0)$ indicates the order m of H_{RM} and n of $\tilde{H}_{RM}$. The expression $\hat{S}^{(2,2)}$ can be arranged as

$$\hat{S}^{(2,2)}(t,t_0) = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_3} dt_4 [H_{RM}(t_1)H_{RM}(t_2)\tilde{H}_{RM}(t_3)\tilde{H}_{RM}(t_4) + H_{RM}(t_1)\tilde{H}_{RM}(t_2)H_{RM}(t_3)\tilde{H}_{RM}(t_4)$$
$$+ H_{RM}(t_1)\tilde{H}_{RM}(t_2)\tilde{H}_{RM}(t_3)H_{RM}(t_4) + \text{t.c.}] \ , \tag{3.9}$$

where t.c. indicates to take a tilde conjugation. The thermal vacuum state $|0(t)\rangle\rangle$, which is responsible for the second-order optical process, is given by

$$|0(t)\rangle\rangle^{(2,2)} = e^{-i\hat{H}t}\hat{S}^{(2,2)}(t,t_0)e^{i\hat{H}t_0}|0(t_0)\rangle\rangle \ . \tag{3.10}$$

Let us now take the initial condition

$$|0(t_0)\rangle\rangle = |p_i\rangle |0_M(t_0)\rangle\rangle \ , \tag{3.11}$$

where $|0_M(t_0)\rangle\rangle$ is the vacuum ket vector for the matter system, and the incident pulse $|p_i\rangle$ is supposed to be given by

$$|p_i\rangle = \sum_{\mathbf{k},\mathbf{k}'} f_i(\mathbf{k}) f_i^*(\mathbf{k}') e^{-i\mathbf{k}\cdot\mathbf{r}_0 + i\mathbf{k}'\cdot\mathbf{r}_0} |\mathbf{k},\tilde{\mathbf{k}}'\rangle \ , \tag{3.12}$$

where $\mathbf{r}_0$ is the center of the incident pulse and $|\mathbf{k},\tilde{\mathbf{k}}'\rangle = a_{\mathbf{k}}^\dagger \tilde{a}_{\mathbf{k}'}^\dagger |0,\tilde{0}\rangle$. The scattered pulse $|p_s\rangle$ may be given by

$$|p_s\rangle = \sum_{\mathbf{k},\mathbf{k}'} f_s(\mathbf{k}) f_s^*(\mathbf{k}') e^{-i\mathbf{k}\cdot\mathbf{r} + i\mathbf{k}'\cdot\mathbf{r}} |\mathbf{k},\tilde{\mathbf{k}}'\rangle \ , \tag{3.13}$$

where $\mathbf{r}$ is the center of the scattered pulse. Then the thermal bra vacuum becomes

$$\langle\langle 1| = \langle\langle 1_M| \langle p_s| \ , \tag{3.14}$$

and the photon counting rate, detected at $(\mathbf{r},t)$, is proportional to the expectation value $P(t)$ of the matrix element $\langle p_f|\hat{S}^{(2,2)}(t,t_0)|p_i\rangle$ with respect to the thermal vacuums of the matter,

$$P(t) = \langle\langle 1|0(t)\rangle\rangle^{(2,2)}$$
$$= \langle\langle 1_M| \langle p_s| e^{-i\hat{H}t}\hat{S}^{(2,2)}(t,t_0)e^{i\hat{H}t_0}|p_i\rangle |0_M\rangle\rangle \ , \tag{3.15}$$

where $|0_M\rangle\rangle = |0_M(t_0)\rangle\rangle$.

With the assumption

$$M_{\mathbf{k}}|0_M\rangle\rangle = 0, \quad \tilde{M}_{\mathbf{k}}|0_M\rangle\rangle = 0 \ , \tag{3.16}$$

which is the case, for example, when the electronic state coupling to the radiation field is initially in its ground state (see next section), (3.9) reduces to

$$\hat{S}^{(2,2)}(t,t_0) = \hat{S}_1^{(2,2)}(t,t_0) + \hat{S}_2^{(2,2)}(t,t_0)$$
$$+ \hat{S}_3^{(2,2)}(t,t_0) + \text{t.c.} \ , \tag{3.17}$$

where

$$\hat{S}_1^{(2,2)}(t,t_0) = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_3} dt_4 \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} g_{\mathbf{k}_1}^* g_{\mathbf{k}_2} g_{\mathbf{k}_3} g_{\mathbf{k}_4}^* e^{i(\omega_1 t_1 - \omega_2 t_2 - \omega_3 t_3 + \omega_4 t_4)} a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \tilde{a}_{\mathbf{k}_3}^\dagger \tilde{a}_{\mathbf{k}_4}$$
$$\times M_{\mathbf{k}_1}(t_1) M_{\mathbf{k}_2}^\dagger(t_2) \tilde{M}_{\mathbf{k}_3}(t_3) \tilde{M}_{\mathbf{k}_4}^\dagger(t_4) \ , \tag{3.18}$$

$$\hat{S}_2^{(2,2)}(t,t_0)=\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3\int_{t_0}^{t_3}dt_4\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}g^*_{\mathbf{k}_1}g_{\mathbf{k}_2}g_{\mathbf{k}_3}g^*_{\mathbf{k}_4}e^{i(\omega_1t_1-\omega_2t_2-\omega_3t_3+\omega_4t_4)}a^\dagger_{\mathbf{k}_1}\tilde{a}^\dagger_{\mathbf{k}_2}a_{\mathbf{k}_3}\tilde{a}_{\mathbf{k}_4}$$
$$\times M_{\mathbf{k}_1}(t_1)\tilde{M}_{\mathbf{k}_2}(t_2)M^\dagger_{\mathbf{k}_3}(t_3)\tilde{M}^\dagger_{\mathbf{k}_4}(t_4)\;, \tag{3.19}$$

$$\hat{S}_3^{(2,2)}(t,t_0)=\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3\int_{t_0}^{t_3}dt_4\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}g^*_{\mathbf{k}_1}g_{\mathbf{k}_2}g^*_{\mathbf{k}_3}g_{\mathbf{k}_4}e^{i(\omega_1t_1-\omega_2t_2+\omega_3t_3-\omega_4t_4)}a^\dagger_{\mathbf{k}_1}\tilde{a}^\dagger_{\mathbf{k}_2}\tilde{a}_{\mathbf{k}_3}a_{\mathbf{k}_4}$$
$$\times M_{\mathbf{k}_1}(t_1)\tilde{M}_{\mathbf{k}_2}(t_2)\tilde{M}^\dagger_{\mathbf{k}_3}(t_3)M^\dagger_{\mathbf{k}_4}(t_4)\;. \tag{3.20}$$

The assumption (3.16) is not essential in the following formulation; however we will take this for simplicity. Then, the photon counting rate (3.15) becomes

$$P(t)=\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3\int_{t_0}^{t_3}dt_4 2\,\mathrm{Re}[(\mathrm{I})+(\mathrm{II})+(\mathrm{III})] \tag{3.21}$$
$$=P_1(t)+P_2(t)+P_3(t)\;, \tag{3.22}$$

where (I), (II), and (III) are given by

$$(\mathrm{I})=\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}g^*_{\mathbf{k}_1}g_{\mathbf{k}_2}g_{\mathbf{k}_3}g^*_{\mathbf{k}_4}f_s^*(\mathbf{k}_1)f_s(\mathbf{k}_3)f_i(\mathbf{k}_2)f_i^*(\mathbf{k}_4)e^{i(\mathbf{k}_1-\mathbf{k}_3)\cdot\mathbf{r}-i(\mathbf{k}_2-\mathbf{k}_4)\cdot\mathbf{r}_0}$$
$$\times e^{-i\omega_1(t-t_1)+i\omega_3(t-t_3)-i\omega_2(t_2-t_0)+i\omega_4(t_4-t_0)}\langle 1_M|M_{\mathbf{k}_1}(t_1)M^{\dagger\dagger}_{\mathbf{k}_2}(t_2)\tilde{M}_{\mathbf{k}_3}(t_3)\tilde{M}^{\dagger\dagger}_{\mathbf{k}_4}(t_4)|0_M\rangle\;, \tag{3.23}$$

$$(\mathrm{II})=\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}g^*_{\mathbf{k}_1}g_{\mathbf{k}_2}g_{\mathbf{k}_3}g^*_{\mathbf{k}_4}f_s^*(\mathbf{k}_1)f_s(\mathbf{k}_2)f_i(\mathbf{k}_3)f_i^*(\mathbf{k}_4)e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}-i(\mathbf{k}_3-\mathbf{k}_4)\cdot\mathbf{r}_0}$$
$$\times e^{-i\omega_1(t-t_1)+i\omega_2(t-t_2)-i\omega_3(t_3-t_0)+i\omega_4(t_4-t_0)}\langle 1_M|M_{\mathbf{k}_1}(t_1)\tilde{M}_{\mathbf{k}_2}(t_2)M^{\dagger\dagger}_{\mathbf{k}_3}(t_3)\tilde{M}^{\dagger\dagger}_{\mathbf{k}_4}(t_4)|0_M\rangle\;, \tag{3.24}$$

$$(\mathrm{III})=\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}g^*_{\mathbf{k}_1}g_{\mathbf{k}_2}g^*_{\mathbf{k}_3}g_{\mathbf{k}_4}f_s^*(\mathbf{k}_1)f_s(\mathbf{k}_2)f_i^*(\mathbf{k}_3)f_i(\mathbf{k}_4)e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}+i(\mathbf{k}_3-\mathbf{k}_4)\cdot\mathbf{r}_0}$$
$$\times e^{-i\omega_1(t-t_1)+i\omega_2(t-t_2)+i\omega_3(t_3-t_0)-i\omega_4(t_4-t_0)}\langle 1_M|M_{\mathbf{k}_1}(t_1)\tilde{M}_{\mathbf{k}_2}(t_2)\tilde{M}^{\dagger\dagger}_{\mathbf{k}_3}(t_3)M^{\dagger\dagger}_{\mathbf{k}_4}(t_4)|0_M\rangle\;. \tag{3.25}$$

Here, we introduced the symbol $\dagger\dagger$ in order to remind us of the fact that the time evolution is generated generally by a nonunitary operator. In deriving (3.21), we used the expressions of the matrix elements

$$\langle p_s|e^{-i\hat{H}_Rt}a^{\dagger\dagger}_{\mathbf{k}_1}(t_1)a_{\mathbf{k}_2}(t_2)\tilde{a}^{\dagger\dagger}_{\mathbf{k}_3}(t_3)\tilde{a}_{\mathbf{k}_4}(t_4)e^{i\hat{H}_Rt_0}|p_i\rangle$$
$$=\sum_{\mathbf{k},\mathbf{k}'}\sum_{\mathbf{p},\mathbf{p}'}\langle\mathbf{k},\tilde{\mathbf{k}}'|e^{-i\hat{H}_Rt}a^{\dagger\dagger}_{\mathbf{k}_1}(t_1)a_{\mathbf{k}_2}(t_2)\tilde{a}^{\dagger\dagger}_{\mathbf{k}_3}(t_3)\tilde{a}_{\mathbf{k}_4}(t_4)e^{i\hat{H}_Rt_0}|\mathbf{p},\tilde{\mathbf{p}}'\rangle f_s^*(\mathbf{k})f_s(\mathbf{k}')f_i(\mathbf{p})f_i^*(\mathbf{p}')e^{i\mathbf{k}\cdot\mathbf{r}-i\mathbf{k}'\cdot\mathbf{r}-i\mathbf{p}\cdot\mathbf{r}_0+i\mathbf{p}'\cdot\mathbf{r}_0}$$
$$=e^{-i\omega_1t+i\omega_2t_0+i\omega_3t-i\omega_4t_0}f_s^*(\mathbf{k}_1)f_s(\mathbf{k}_3)f_i(\mathbf{k}_2)f_i^*(\mathbf{k}_4)e^{i\mathbf{k}_1\cdot\mathbf{r}-i\mathbf{k}_3\cdot\mathbf{r}-i\mathbf{k}_2\cdot\mathbf{r}_0+i\mathbf{k}_4\cdot\mathbf{r}_0}\;, \tag{3.26}$$

$$\langle p_s|e^{-i\hat{H}_Rt}a^{\dagger\dagger}_{\mathbf{k}_1}(t_1)\tilde{a}^{\dagger\dagger}_{\mathbf{k}_2}(t_2)a_{\mathbf{k}_3}(t_3)\tilde{a}_{\mathbf{k}_4}(t_4)e^{i\hat{H}_Rt_0}|p_i\rangle$$
$$=e^{-i\omega_1t+i\omega_2t+i\omega_3t_0-i\omega_4t_0}f_s^*(\mathbf{k}_1)f_s(\mathbf{k}_2)f_i(\mathbf{k}_3)f_i^*(\mathbf{k}_4)e^{i\mathbf{k}_1\cdot\mathbf{r}-i\mathbf{k}_2\cdot\mathbf{r}-i\mathbf{k}_3\cdot\mathbf{r}_0+i\mathbf{k}_4\cdot\mathbf{r}_0}\;, \tag{3.27}$$

$$\langle p_s|e^{-i\hat{H}_Rt}a^{\dagger\dagger}_{\mathbf{k}_1}(t_1)\tilde{a}^{\dagger\dagger}_{\mathbf{k}_2}(t_2)\tilde{a}_{\mathbf{k}_3}(t_3)a_{\mathbf{k}_4}(t_4)e^{i\hat{H}_Rt_0}|p_i\rangle$$
$$=e^{-i\omega_1t+i\omega_2t-i\omega_3t_0+i\omega_4t_0}f_s^*(\mathbf{k}_1)f_s(\mathbf{k}_2)f_i^*(\mathbf{k}_3)f_i(\mathbf{k}_4)e^{i\mathbf{k}_1\cdot\mathbf{r}-i\mathbf{k}_2\cdot\mathbf{r}+i\mathbf{k}_3\cdot\mathbf{r}_0-i\mathbf{k}_4\cdot\mathbf{r}_0}\;, \tag{3.28}$$

and the property

$$\langle 1|A|0\rangle+\langle 1|\tilde{A}|0\rangle=2\,\mathrm{Re}\langle 1|A|0\rangle\;. \tag{3.29}$$

When the incident pulse is composed of only photons whose wave vectors are parallel with a wave vector $\mathbf{k}_i$, and when the detector is supposed to detect only photons whose wave vectors are parallel with a wave vector $\mathbf{k}_s$, i.e.,

$$f_i(\mathbf{k})=f_i(k)\delta_{\mathbf{k}\|\mathbf{k}_i},\quad f_s(\mathbf{k})=f_s(k)\delta_{\mathbf{k}\|\mathbf{k}_s}\;, \tag{3.30}$$

the expressions for the integrands (I), (II), and (III) in $P(t)$ further reduce to

$$(\mathrm{I})=e^{i\Omega_s(t_1-t_3)-i\Omega_i(t_2-t_4)}F_s^*(t_s-t_1)$$
$$\times F_s(t_s-t_3)F_i(t_2-t_i)F_i^*(t_4-t_i)$$
$$\times\langle 1_M|M_{\bar{k}_s}(t_1)M^{\dagger\dagger}_{\bar{k}_i}(t_2)\tilde{M}_{\bar{k}_s}(t_3)\tilde{M}^{\dagger\dagger}_{\bar{k}_i}(t_4)|0_M\rangle\;, \tag{3.31}$$

$$
\begin{aligned}
(\mathrm{II}) = {} & e^{i\Omega_s(t_1-t_2)-i\Omega_i(t_3-t_4)} F_s^*(t_s-t_1) \\
& \times F_s(t_s-t_2) F_i(t_3-t_i) F_i^*(t_4-t_i) \\
& \times \langle 1_M | M_{\bar{k}_s}(t_1) \tilde{M}_{\bar{k}_s}(t_2) M_{\bar{k}_i}^{\dagger\dagger}(t_3) \tilde{M}_{\bar{k}_i}^{\dagger\dagger}(t_4) | 0_M \rangle \ ,
\end{aligned}
\tag{3.32}
$$

$$
\begin{aligned}
(\mathrm{III}) = {} & e^{i\Omega_s(t_1-t_2)+i\Omega_i(t_3-t_4)} F_s^*(t_s-t_1) \\
& \times F_s(t_s-t_2) F_i^*(t_3-t_i) F_i(t_4-t_i) \\
& \times \langle 1_M | M_{\bar{k}_s}(t_1) \tilde{M}_{\bar{k}_s}(t_2) \tilde{M}_{\bar{k}_i}^{\dagger\dagger}(t_3) M_{\bar{k}_i}^{\dagger\dagger}(t_4) | 0_M \rangle \ ,
\end{aligned}
\tag{3.33}
$$

where we defined

$$
\sum_k g_k f_i(k) e^{-i\omega(t-t_i)} M_k^{\dagger\dagger}(t) = F_i(t-t_i) e^{-i\Omega_i(t-t_i)} M_{\bar{k}_i}^{\dagger\dagger}(t) \ , \tag{3.34}
$$

$$
\sum_k g_k^* f_s^*(k) e^{-i\omega(t_s-t)} M_k(t) = F_s^*(t_s-t) e^{-i\Omega_s(t_s-t)} M_{\bar{k}_s}(t) \ , \tag{3.35}
$$

with

$$
\omega = ck, \quad \Omega_i = c\bar{k}_i, \quad \Omega_s = c\bar{k}_s \ , \tag{3.36}
$$

$$
t_i = t_0 - \frac{r_0}{c}\cos\theta_i, \quad t_s = t - \frac{r}{c}\cos\theta_s \ . \tag{3.37}
$$

Here, we put $k=|\mathbf{k}|$, $k_i=|\mathbf{k}_i|$, $k_s=|\mathbf{k}_s|$, $r_0=|\mathbf{r}_0|$, and $r=|\mathbf{r}|$. The angles θ_i $(\pi/2 \le \theta_i \le \pi)$ and θ_s $(0 \le \theta_s \le \pi/2)$ are shown in Fig. 1. The real function $F_i(t)$ is the envelope function of the incident pulse, whereas the real function $F_s(t)$ is the apparatus function of the detector. The frequencies Ω_i and Ω_s represent, respectively, the mean values of the frequencies constituting the incident and the scattered lights. The time t_i indicates the moment when the incident pulse, generated by the source at t_0, comes to the matter, and the time t_s represents the instant when the photons, which are going to be detected at t, are emitted from the matter. Note that the existence of the apparatus function $F_s(t)$ allows us to observe the time-resolved spectrum in spite of the Heisenberg uncertainty principle with respect to time and energy.

The general formula of the time-resolved spectrum of the photon counting rate for the second-order optical processes is given by (3.21) with (3.31)–(3.33).

IV. A MODEL OF THE MATTER SYSTEM

Now let us apply the formula derived in the previous section to an analytically solvable model of the localized-electron and phonon system [3]. The localized electron has three electronic states which are optically active, as depicted in Fig. 2. The incident photon with energy ω_i is absorbed by the matter with the transition of the localized electron from the ground state $|1,\tilde{1}\rangle$ to the intermediate state $|3,\tilde{3}\rangle$, and the photon with energy ω_s is emitted from the matter with the transition of the localized electron from the intermediate state $|3,\tilde{3}\rangle$ to the final state $|2,\tilde{2}\rangle$. This is the typical situation of Raman $(\omega_i > \omega_s)$ or anti-Raman $(\omega_i < \omega_s)$ scattering. The energy of the intermediate state is modulated dynamically (frequency modulation) by the *phonon interaction mode* which dissipates its energy to the rest of the phonon modes. The modulation of the intermediate state causes the emission of luminescence which greatly reflects the characteristics of the matter system.

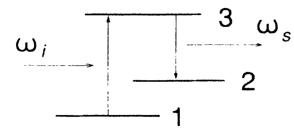

FIG. 2. Energy diagram of the three-state model.

We assume that the phonon modes besides the phonon interaction mode are in the thermal equilibrium state specified by a temperature β^{-1} $(k_B=1)$. The interaction mode can initially (at $t=t_0$) be out of the equilibrium state. We also assume that the electronic state at the initial time $t=t_0$ is in the ground state $|1,\tilde{1}\rangle$.

The matter operators M_k for the model are given by

$$
M_{k_i} = c_1^\dagger c_3, \quad M_{k_s} = c_2^\dagger c_3 \ , \tag{4.1}
$$

where $c_j^\dagger$ (c_j), with $j=1,2,3$, are the creation (annihilation) operators for the jth electronic state. The time-evolution generator $\hat{H}_M$ becomes

$$
\hat{H}_M = H_M - \tilde{H}_M + i\hat{\Pi}_{\mathrm{ph}} \ , \tag{4.2}
$$

with

$$
H_M = H_{\mathrm{el}} + H_{\mathrm{ph}} + H_{\text{el-ph}} \ , \tag{4.3}
$$

$$
H_{\mathrm{el}} = \sum_{j=1}^{3} \omega_j c_j^\dagger c_j, \quad H_{\mathrm{ph}} = \omega_B b^\dagger b \ , \tag{4.4}
$$

$$
H_{\text{el-ph}} = g b^\dagger b c_3^\dagger c_3 \ , \tag{4.5}
$$

$$
\begin{aligned}
\hat{\Pi}_{\mathrm{ph}} = {} & -\kappa[(1+2\bar{n})(b^\dagger b + \tilde{b}^\dagger \tilde{b}) - 2(1+\bar{n})\tilde{b}b \\
& - 2\bar{n}\tilde{b}^\dagger b^\dagger] - 2\kappa\bar{n} \ ,
\end{aligned}
\tag{4.6}
$$

where $b^\dagger(b)$ is the creation (annihilation) operator of the interaction mode of the phonon system, and $\bar{n}$ is the equilibrium number of the interaction mode,

$$
\bar{n} = \frac{1}{e^{\beta\omega_B}-1} \ . \tag{4.7}
$$

The damping generator $\hat{\Pi}_{\mathrm{ph}}$ describes the dissipative time evolution of the interaction mode due to the coupling with the rest of the phonon modes, which are assumed to be in a thermal equilibrium state with a certain temperature β^{-1}.

For simplicity, we will assume that the initial condition for the matter system is given by

$$
|0_M\rangle = |1,\tilde{1}\rangle_{\mathrm{el}} |0_{\mathrm{ph}}\rangle \ , \tag{4.8}
$$

where $|1,\tilde{1}\rangle_{\rm el}$ means that the electronic system is in its ground state, i.e.,

$$c_1^\dagger c_1|1,\tilde{1}\rangle_{\rm el}=1\ , \tag{4.9}$$

$$c_j^\dagger c_j|j,\tilde{j}\rangle_{\rm el}=0\quad(\text{for } j=2,3)\ , \tag{4.10}$$

and the initial thermal vacuum $|0_{\rm ph}\rangle$ for the interaction mode is specified by the thermal state condition

$$b|0_{\rm ph}\rangle=f\tilde{b}^\dagger|0_{\rm ph}\rangle\ , \tag{4.11}$$

with

$$f=\frac{n}{1+n}\ , \tag{4.12}$$

where n is the initial phonon number of the interaction mode.

With the thermal state condition (4.12), we can obtain moments with respect to the corresponding thermal vacuum $|0_{\rm ph}\rangle$, e.g.,

$$\begin{aligned}\langle 1|b^\dagger b|0_{\rm ph}\rangle&=f\langle 1|b^\dagger\tilde{b}^\dagger|0_{\rm ph}\rangle\\&=f\langle 1|\tilde{b}^\dagger b^\dagger|0_{\rm ph}\rangle\\&=f\langle 1|bb^\dagger|0_{\rm ph}\rangle\ ,\end{aligned} \tag{4.13}$$

leading to

$$\langle 1|b^\dagger b|0_{\rm ph}\rangle=n\ . \tag{4.14}$$

At the second equality in (4.13), we used the commutativity between the tilde and nontilde operators, i.e., $[b^\dagger,\tilde{b}^\dagger]=0$, and, at the third equality, the thermal state condition (2.5), i.e., $\langle 1|\tilde{b}^\dagger=\langle 1|b$.

Taking t_0 as the time at which all the representations (the Heisenberg, the Schrödinger, and the interaction representations) coincide, we see that the deexcitation operator $M_j(t)$ of the matter system, for example, has the form

$$M_j(t)=e^{i\hat{H}(t-t_0)}M_je^{-i\hat{H}(t-t_0)} \tag{4.15}$$

$$\begin{aligned}&=e^{-i\omega_{3j}(t-t_0)}e^{i\hat{H}_{\text{el-ph}}(t-t_0)}\\&\quad\times c_j^\dagger c_3e^{-i\hat{H}_{\text{el-ph}}(t-t_0)}\ ,\end{aligned} \tag{4.16}$$

where $\omega_{3j}=\omega_3-\omega_j$, and

$$\hat{H}_{\text{el-ph}}=H_{\text{el-ph}}-\tilde{H}_{\text{el-ph}}+i\hat{\Pi}_{\rm ph}\ . \tag{4.17}$$

The matrix elements in (3.31)–(3.33) can be treated as

$$\begin{aligned}\langle 1_M|M_{\bar{k}_s}(t_1)M_{\bar{k}_i}^{\dagger\dagger}(t_2)\tilde{M}_{\bar{k}_s}(t_3)\tilde{M}_{\bar{k}_i}^{\dagger\dagger}(t_4)|0_M\rangle&=e^{-i\omega_{32}(t_1-t_3)+i\omega_{31}(t_2-t_4)}\langle 1_M|c_2^\dagger c_3e^{-i\hat{H}_{\text{el-ph}}(t_1-t_2)}c_3^\dagger c_1e^{-i\hat{H}_{\text{el-ph}}(t_2-t_3)}\\&\quad\times\tilde{c}_2^\dagger\tilde{c}_3e^{-i\hat{H}_{\text{el-ph}}(t_3-t_4)}\tilde{c}_3^\dagger\tilde{c}_1e^{-i\hat{H}_{\text{el-ph}}(t_4-t_0)}|0_M\rangle\ ,\\&=e^{-i\omega_{32}(t_1-t_3)+i\omega_{31}(t_2-t_4)}g^*(t_1-t_2,t_2-t_3,t_3-t_4;0,\tilde{1};0,\tilde{0};1,\tilde{0})\ ,\end{aligned} \tag{4.18}$$

$$\langle 1_M|M_{\bar{k}_s}(t_1)\tilde{M}_{\bar{k}_s}(t_2)M_{\bar{k}_i}^{\dagger\dagger}(t_3)\tilde{M}_{\bar{k}_i}^{\dagger\dagger}(t_4)|0_M\rangle=e^{-i\omega_{32}(t_1-t_2)+i\omega_{31}(t_3-t_4)}g^*(t_1-t_2,t_2-t_3,t_3-t_4;0,\tilde{1};1,\tilde{1};1,\tilde{0})\ , \tag{4.19}$$

$$\langle 1_M|M_{\bar{k}_s}(t_1)\tilde{M}_{\bar{k}_s}(t_2)\tilde{M}_{\bar{k}_i}^{\dagger\dagger}(t_3)M_{\bar{k}_i}^{\dagger\dagger}(t_4)|0_M\rangle=e^{-i\omega_{32}(t_1-t_2)-i\omega_{31}(t_3-t_4)}g(t_1-t_2,t_2-t_3,t_3-t_4;1,\tilde{0};1,\tilde{1};1,\tilde{0})\ , \tag{4.20}$$

where we introduced

$$\begin{aligned}&g(t_1,t_2,t_3;A_1,\tilde{A}_1;A_2,\tilde{A}_2;A_3,\tilde{A}_3)\\&\quad=\langle 1_M|G(t_1;A_1,\tilde{A}_1)\\&\qquad\times G(t_2;A_2,\tilde{A}_2)G(t_3;A_3,\tilde{A}_3)|0_M\rangle\ ,\end{aligned} \tag{4.21}$$

with

$$G(t_j;A_j,\tilde{A}_j)=\exp(-i\hat{H}_{\text{el-ph}}^{(j)}t_j)\ , \tag{4.22}$$

$$\hat{H}_{\text{el-ph}}^{(j)}=\hat{H}_{\text{el-ph}}^{(A_j,\tilde{A}_j)}=gA_jb^\dagger b-g\tilde{A}_j\tilde{b}^\dagger\tilde{b}+i\hat{\Pi}_{\rm ph}\ . \tag{4.23}$$

Here, for simplicity, we further assume that the phonon interaction mode is in thermal equilibrium with the rest of the phonon modes, i.e., $n=\bar{n}$. Then we have $\hat{H}_M|0_M\rangle=0$ which leads to

$$\hat{\Pi}_{\rm ph}|0_{\rm ph}\rangle=0\ , \tag{4.24}$$

or

$$\hat{H}_{\text{el-ph}}^{(j)}|0_{\rm ph}\rangle=0\quad(\text{for } A_j=\tilde{A}_j=0)\ . \tag{4.25}$$

Inserting (4.18)–(4.20) into (3.31)–(3.33), we obtain

$$\begin{aligned}(\mathrm{I})^*&=e^{-i\Delta\Omega_s(\tau+\mu)+i\Delta\Omega_i(\mu+\sigma)}g(\tau,\mu,\sigma;0,\tilde{1};0,\tilde{0};1,\tilde{0})\\&\quad\times F_s(t_s-t_1)F_s^*(t_s-t_1+\tau+\mu)F_i^*(t_1-\tau-t_i)\\&\quad\times F_i(t_1-\tau-\mu-\sigma-t_i)\ ,\end{aligned} \tag{4.26}$$

$$\begin{aligned}(\mathrm{II})^*&=e^{-i\Delta\Omega_s\tau+i\Delta\Omega_i\sigma}g(\tau,\mu,\sigma;0,\tilde{1};1,\tilde{1};1,\tilde{0})\\&\quad\times F_s(t_s-t_1)F_s^*(t_s+\tau-t_1)F_i^*(t_1-\tau-\mu-t_i)\\&\quad\times F_i(t_1-\tau-\mu-\sigma-t_i)\ ,\end{aligned} \tag{4.27}$$

$$\begin{aligned}(\mathrm{III})&=e^{i\Delta\Omega_s\tau+i\Delta\Omega_i\sigma}g(\tau,\mu,\sigma;1,\tilde{0};1,\tilde{1};1,\tilde{0})\\&\quad\times F_s^*(t_s-t_1)F_s(t_s+\tau-t_1)F_i^*(t_1-\tau-\mu-t_i)\\&\quad\times F_i(t_1-\tau-\mu-\sigma-t_i)\ ,\end{aligned} \tag{4.28}$$

where we introduced the notation

$$\tau=t_1-t_2,\quad \mu=t_2-t_3,\quad \sigma=t_3-t_4\ , \tag{4.29}$$

and

$$\Delta\Omega_i=\Omega_i-\omega_{31},\quad \Delta\Omega_s=\Omega_s-\omega_{32}\ . \tag{4.30}$$

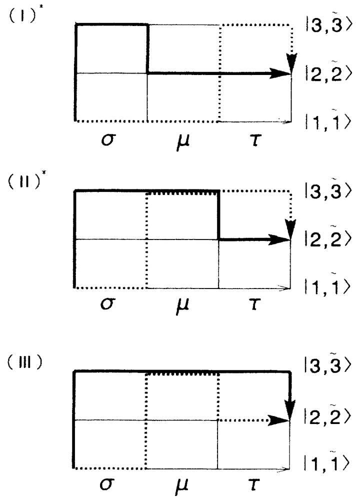

FIG. 3. Diagrammatic expressions of the second-order optical process for the three-state model. The solid line represents the time path among the electronic states described by nontilde operators, and the dotted line by tilde operators.

In Fig. 3, we give a graphical representation of (4.26)–(4.28). We chose to look at the complex conjugate for easy comparison with Ref. [3], i.e., (I)*, (II)*, and (III) above correspond, respectively, to (III), (II), and (I) in Ref. [3].

In order to evaluate

$$g(t_1,t_2,t_3;A_1,\tilde{A}_1;A_2,\tilde{A}_2;A_3,\tilde{A}_3)$$

further, let us rewrite the time-evolution generator $\hat{H}^{(j)}$ in (4.23) as

$$\hat{H}^{(j)}_{\text{el-ph}}=\hat{H}^{(j)}_0+i\hat{\Pi}'_j\ , \tag{4.31}$$

with

$$\hat{H}^{(j)}_0=\tfrac{1}{2}g(A_j+\tilde{A}_j)(b^\dagger b-\tilde{b}^\dagger\tilde{b})\ , \tag{4.32}$$

$$\hat{\Pi}'_j=-\frac{ig}{2}\hat{A}_j(b^\dagger b+\tilde{b}^\dagger\tilde{b})+\hat{\Pi}_{\text{ph}}\ , \tag{4.33}$$

$$=\lambda_j(d_j^\dagger d_j+\tilde{d}_j^\dagger\tilde{d}_j)+2\kappa\bar{n}s_j\ , \tag{4.34}$$

$$=\hat{\Pi}''_j+2\kappa\bar{n}s_j\ , \tag{4.35}$$

where

$$\lambda_j=-\kappa p_j\ , \tag{4.36}$$

$$s_j=\frac{1}{2\bar{n}}\left[1+\frac{ig}{2\kappa}\hat{A}_j-p_j\right]\ , \tag{4.37}$$

$$p_j=\left\{\left[1+\frac{ig}{2\kappa}\hat{A}_j\right]^2+4\bar{n}\frac{ig}{2\kappa}\hat{A}_j\right\}^{1/2}\ , \tag{4.38}$$

$$\hat{A}_j=A_j-\tilde{A}_j\ . \tag{4.39}$$

The operators d_j, $d_j^\dagger$, $\tilde{d}_j$, and $\tilde{d}_j^\dagger$ are defined by

$$d_j^\mu=(Q_j^{-1})^{\mu\nu}b^\nu\ , \tag{4.40}$$

where we have introduced the thermal doublet notation

$$d_j^\mu=\begin{bmatrix} d_j \\ \tilde{d}_j^\dagger \end{bmatrix}\ ,\quad b^\mu=\begin{bmatrix} b \\ \tilde{b}^\dagger \end{bmatrix}\ , \tag{4.41}$$

and the matrix

$$Q_j=\left[\frac{-c}{2\lambda_j}\right]^{1/2}\begin{bmatrix} (a_j-\lambda_j)/c & (a_j+\lambda_j)/c \\ 1 & 1 \end{bmatrix}\ , \tag{4.42}$$

with

$$a_j=\frac{ig}{2}\hat{A}_j+\kappa(1+2\bar{n})\ , \tag{4.43}$$

$$c=2\kappa(1+\bar{n})\ . \tag{4.44}$$

Then we have

$$g(t_1,t_2,t_3;A_1,\tilde{A}_1;A_2,\tilde{A}_2;A_3,\tilde{A}_3)\equiv g(t_1,t_2,t_3;1,2,3)$$

$$=\langle 1_M|e^{-i\hat{H}^{(1)}_0t_1}e^{-i\hat{H}^{(2)}_0t_2}e^{-i\hat{H}^{(3)}_0t_3}e^{\hat{\Pi}'_1t_1}e^{\hat{\Pi}'_2t_2}e^{\hat{\Pi}'_3t_3}|0_M\rangle$$

$$=e^{2\kappa\bar{n}s_1t_1}e^{2\kappa\bar{n}s_2t_2}e^{2\kappa\bar{n}s_3t_3}S(t_1,t_2,t_3;1,2,3)\ , \tag{4.45}$$

with

$$S(t_1,t_2,t_3;1,2,3)=\langle 1_M|e^{\hat{\Pi}''_1t_1}e^{\hat{\Pi}''_2t_2}e^{\hat{\Pi}''_3t_3}|0_M\rangle\ , \tag{4.46}$$

where we used the properties

$$[\hat{H}^{(j)}_0,\hat{\Pi}'_j]=0,\quad \text{therefore } [\hat{H}^{(j)}_0,\hat{\Pi}''_j]=0\ , \tag{4.47}$$

$$\langle 1_M|e^{-i\hat{H}^{(1)}_0t_1}e^{-i\hat{H}^{(2)}_0t_2}e^{-i\hat{H}^{(3)}_0t_3}=1\ . \tag{4.48}$$

Solving the differential equation for $S(t_1,t_2,t_3;1,2,3)$ with a lengthy but simple algebraic manipulation (see Appendix B for details), we finally arrive at

$$g\left[\tau,\mu,\sigma;\begin{bmatrix} 1, & \tilde{0} \\ 0, & \tilde{1}\end{bmatrix};0,\tilde{0};1,\tilde{0}\right]=g\left[\tau,\mu,\sigma;\begin{bmatrix} 1, & \tilde{0} \\ 0, & \tilde{1}\end{bmatrix};1,\tilde{1};1,\tilde{0}\right]$$

$$=g_\pm(\tau,\mu,\sigma)\ , \tag{4.49}$$

where

$$g_\pm(\tau,\mu,\sigma)=\exp\left\{2\kappa\bar{n}\left[\left[\begin{matrix}s(1)\\ s(-1)\end{matrix}\right]\tau+s(1)\sigma\right]\right\}$$
$$\times\left[1-\bar{n}s(1)\left\{1-K(\sigma,1;C_3)\left[1-\left[\begin{matrix}1\\ s(-1)/s(1)\end{matrix}\right]K(\mu,0;C_2)[1-K(\tau,\pm1;C_1)]\right]\right\}\right]^{-1}, \tag{4.50}$$

with

$$K(t,m;C)=1-\{1-\bar{n}p^{-1}(m)[C-s(m)]\}e_m(t), \tag{4.51}$$

$$C_1=C_2K^{-1}(\mu,0;C_2), \tag{4.52}$$

$$C_2=s(1)+[C_3-s(1)]K^{-1}(\sigma,1;C_3), \tag{4.53}$$

$$C_3=\bar{n}^{-1}, \tag{4.54}$$

$$e_m(t)=1-e^{-2\kappa p(m)t}, \tag{4.55}$$

$$s(m)=s_j(\hat{A}_j=m)=\frac{1}{2\bar{n}}\left[1+\frac{ig}{2\kappa}m-p(m)\right], \tag{4.56}$$

$$p(m)=p_j(\hat{A}_j=m)=\left\{\left[1+\frac{ig}{2\kappa}m\right]^2+4\bar{n}\frac{ig}{2\kappa}m\right\}^{1/2}, \tag{4.57}$$

where $m=-1,0,1$.

Assuming that the time resolution $F_s(t)$ of the detector at r is equal to the width $F_i(t)$ of the incident pulse which is supposed to have the Gaussian-form envelope function

$$F_i(t)=F_s(t)=\left[\frac{\delta^2}{\pi}\right]^{1/2}e^{-\delta^2t^2/2}, \tag{4.58}$$

we obtain as a final result for the photon counting rate

$$P(t_s,\Delta\Omega_s,\Delta\Omega_i)=P_1(t_s,\Delta\Omega_s,\Delta\Omega_i)+P_2(t_s,\Delta\Omega_s,\Delta\Omega_i)+P_3(t_s,\Delta\Omega_s,\Delta\Omega_i), \tag{4.59}$$

with

$$P_1(t_s,\Delta\Omega_s,\Delta\Omega_i)=2\,\mathrm{Re}\int_0^\infty d\tau\int_0^\infty d\mu\int_0^\infty d\sigma\, e^{-i\Delta\Omega_s(\tau+\mu)+i\Delta\Omega_i(\mu+\sigma)}\eta_1(t_s,\tau,\mu,\sigma)g_-(\tau,\mu,\sigma), \tag{4.60}$$

$$P_2(t_s,\Delta\Omega_s,\Delta\Omega_i)=2\,\mathrm{Re}\int_0^\infty d\tau\int_0^\infty d\mu\int_0^\infty d\sigma\, e^{-i\Delta\Omega_s\tau+i\Delta\Omega_i\sigma}\eta_2(t_s,\tau,\mu,\sigma)g_-(\tau,\mu,\sigma), \tag{4.61}$$

$$P_3(t_s,\Delta\Omega_s,\Delta\Omega_i)=2\,\mathrm{Re}\int_0^\infty d\tau\int_0^\infty d\mu\int_0^\infty d\sigma\, e^{i\Delta\Omega_s\tau+i\Delta\Omega_i\sigma}\eta_3(t_s,\tau,\mu,\sigma)g_+(\tau,\mu,\sigma), \tag{4.62}$$

where we introduced the functions

$$\eta_1(t_s,\tau,\mu,\sigma)=\left[\frac{\delta^2}{2\pi}\right]^{1/2}\exp\left\{-\frac{\delta^2}{2}\left[[\tfrac{1}{2}(\tau+\sigma)-t_s]^2+\tfrac{1}{2}(\tau+\mu)^2+\tfrac{1}{2}(\sigma+\mu)^2\right]\right\}, \tag{4.63}$$

$$\eta_2(t_s,\tau,\mu,\sigma)=\left[\frac{\delta^2}{2\pi}\right]^{1/2}\exp\left\{-\frac{\delta^2}{2}\left[[\tfrac{1}{2}(\tau+\sigma)]^2+\tfrac{1}{2}(\tau+\mu-t_s)^2+\tfrac{1}{2}(\sigma+\mu-t_s)^2\right]\right\}, \tag{4.64}$$

$$\eta_3(t_s,\tau,\mu,\sigma)=\eta_2(t_s,\tau,\mu,\sigma). \tag{4.65}$$

Here, we put the origin of time at $t_i=0$ with the condition that the distance between the light source and the matter is long enough, and that the detector is quite apart from the matter, i.e., $r_0,r\to\infty, t_0\to-\infty, t\to\infty$ keeping t_s finite [see (3.37)].

The result (4.59) is in complete correspondence with those derived by means of the density operator method where the phase-space method was used to solve the master equation of the system [3].

V. SLOW AND FAST MODULATION

The effect of the phonon modulation can be characterized by the parameter [5]

$$\alpha=\frac{g\sqrt{\bar{n}(\bar{n}+1)}}{2\kappa}. \tag{5.1}$$

For a slow modulation, $\alpha\gg1$, whereas for a fast modulation, $\alpha\ll1$.

A. Slow modulation

In the case of slow modulation ($\alpha\gg1$), $g_\pm(\tau,\mu,\nu)$ in (4.50) reduce to

$$g_\pm(\tau,\mu,\sigma)=[1+\bar{n}-\bar{n}h(\tau,\mu,\sigma)]^{-1}e^{-2\kappa\bar{n}(\tau+\sigma)}$$
$$=\frac{1}{1+\bar{n}}e^{-2\kappa\bar{n}(\tau+\sigma)}\sum_{l=0}^{\infty}e^{-\beta l\omega}[h(\tau,\mu,\sigma)]^l, \tag{5.2}$$

with

$$h(\tau,\mu,\sigma)=e^{-i[\pm g-2\kappa i(1+2\bar{n})]\tau}e^{-i[g-2\kappa i(1+2\bar{n})]\sigma}$$
$$-(1+\bar{n})(1-e^{-2\kappa\mu})(1-e^{-i[g-2\kappa i(1+2\bar{n})]\sigma})$$
$$\times(1-e^{-i[\pm g-2\kappa i(1+2\bar{n})]\tau}) \quad (5.3)$$
$$\simeq e^{-i[\pm g-2\kappa i(1-2\bar{n})]\tau}e^{-i[g-2\kappa i(1+2\bar{n})]\sigma} . \quad (5.4)$$

We see that (5.2) with (5.4) can be derived by

$$g_{\pm}(\tau,\mu,\sigma)=\frac{1}{1+\bar{n}}\sum_{l=0}^{\infty}e^{-\beta l\omega}e^{-i\langle l,\bar{l}|\hat{H}^{(\pm1)}_{\text{el-ph}}|l,\bar{l}\rangle\tau}$$
$$\times e^{-i\langle l,\bar{l}|\hat{H}^{(+1)}_{\text{el-ph}}|l,\bar{l}\rangle\sigma} , \quad (5.5)$$

with

$$\langle l,\bar{l}|\hat{H}^{(j)}_{\text{el-ph}}|l,\bar{l}\rangle=g\hat{A}_j l-2\kappa i[\bar{n}+(1+2\bar{n})l] . \quad (5.6)$$

The expression (5.5) indicates that, for slow modulation, the scattered light consists of the superposition of each light scattered by the intermediate electronic state, coupled to the l-phonon state ($l=1,2,3,\ldots$), with the weight $e^{\beta l\omega}/(1+\bar{n})$ of the canonical ensemble.

B. Fast modulation

In the case of fast modulation ($\alpha\ll1$), as can be seen in the investigation of Appendix C, the modulation of the phonon system can be taken into account by a random force operator $d\Omega(t)=d\Omega^{\dagger}(t)$ of a stationary stochastic process, i.e., a quantum Gaussian process,

$$\langle d\Omega(t)\rangle=\langle d\tilde{\Omega}(t)\rangle=0 , \quad (5.7)$$
$$g^2\langle d\Omega(t)d\Omega(s)\rangle=g^2\langle d\tilde{\Omega}(t)d\Omega(s)\rangle$$
$$=2\kappa^2\alpha^2e^{-2\kappa|t-s|}dt\,ds . \quad (5.8)$$

The latter correlation reduces to

$$g^2\langle d\Omega(t)d\Omega(s)\rangle=g^2\langle d\tilde{\Omega}(t)d\Omega(s)\rangle$$
$$=4\kappa\alpha^2\delta(t-s)dt\,ds , \quad (5.9)$$

in the limit of $\kappa\to\infty$, i.e., the limit of extremely fast modulation yielding a quantum Wiener process.

The time evolution of the system is described by the quantum stochastic Liouville equation of the Stratonovich type [11–13] as

$$d|0_f(t)\rangle=-i\hat{H}_{f,t}dt\circ|0_f(t)\rangle , \quad (5.10)$$

with

$$\hat{H}_{f,t}dt=\bar{n}g\hat{A}\,dt+gA\,d\Omega(t)-g\tilde{A}\,d\tilde{\Omega}(t) . \quad (5.11)$$

The symbol $\circ$ indicates the Stratonovich stochastic multiplication. The stochastic Liouville equation (5.10) can be written in the form of the Ito type equation [11–13], for the extreme limit $\kappa\to\infty$, as

$$d|0_f(t)\rangle=-i\hat{\mathcal{H}}_{f,t}|0_f(t)\rangle , \quad (5.12)$$

with

$$\hat{\mathcal{H}}_{f,t}dt=\hat{H}_{f,t}dt-i2\kappa\alpha^2\hat{A}^2dt . \quad (5.13)$$

Taking the random average $\langle\cdots\rangle$ of (5.12) with respect to the random process (5.8), we obtain the Fokker-Planck equation of the system as

$$\frac{\partial}{\partial t}|0(t)\rangle=-i\hat{H}|0(t)\rangle , \quad (5.14)$$

with

$$|0(t)\rangle=\Big\langle|0_f(t)\rangle\Big\rangle \quad (5.15)$$
$$\hat{H}=\Big\langle\hat{\mathcal{H}}_{f,t}\Big\rangle=\bar{n}g\hat{A}-i2\kappa\alpha^2\hat{A}^2 , \quad (5.16)$$

where we used the characteristics of the Ito multiplication

$$\langle A\,d\Omega(t)\rangle=0 . \quad (5.17)$$

This Fokker-Planck equation gives us

$$g_{\pm}(\tau,\mu,\sigma)=\exp\{[\mp i\bar{n}g-2\kappa\alpha^2]\tau\}$$
$$\times\exp\{[-i\bar{n}g-2\kappa\alpha^2]\sigma\} . \quad (5.18)$$

Note that the Langevin equation for c_3 of the Stratonovich type is given by

$$dc_3(t)=-i[(\omega_3+\bar{n}g)+g\,d\Omega(t)]\circ c_3(t) . \quad (5.19)$$

This shows that, for fast modulation, the system reduces to the model of phase modulation investigated by Kubo when he introduced the stochastic Liouville equation [21,5] (see also [22]).

VI. PROFILES OF TIME-RESOLVED SPECTRUM

In Figs. 4–14, we list the profiles of the time-resolved optical spectrum in the model of the three-state localized electron and phonon for typical parameters. The profiles $P(t_s,\Delta\Omega_s)$ are shown with the axes $\Delta\Omega_s$ and t_s. The former is the distance of the frequency Ω_s from the energy separation ω_{32} between the intermediate and the final electronic states. The latter is the time when the matter emits the absorbed light. The origin of the time axis, i.e., $t_s=0$, represents the moment at which the peak of the incident pulse is scattered by the matter.

For every profile, we fixed the parameter δ at the value $\delta=0.5$, which is the width of the envelope function of the incident pulse, and of the apparatus function of the detector. The other parameters for each profile are listed in Table I.

We put $\Delta\Omega_i=1.0$ for Fig. 4, and $\Delta\Omega_i=-1.0$ for Fig. 5, while the other parameters are the same. We see that the former intensity of the spectrum is larger than the latter. This is because, in the former case, the incident pulse is absorbed and/or scattered extensively by the matter, since there are a lot of modulated intermediate electronic states in the energy region larger than ω_{32} corresponding to the number of phonons of the interaction mode. On the other hand, in the latter case, only the tail of the incident pulse, which is in the energy region larger than ω_{32}, is absorbed and/or scattered by the matter. We observe also that, in the former case, the Raman and luminescence components are hard to distinguish, and that, in the latter case, they are well separated. The Raman component is found in Fig. 5 as a Gaussian profile

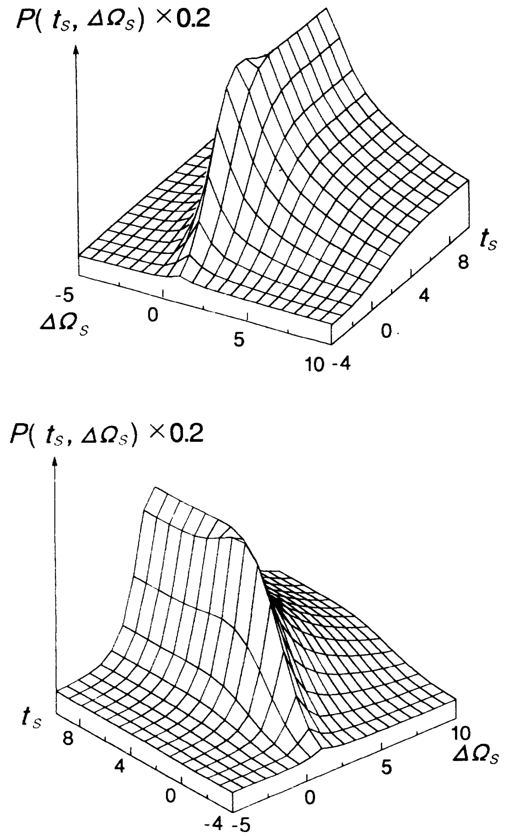

FIG. 4. $\Delta\Omega_i=1.0$, $g=1.0$, $2\kappa=0.5$, $\bar{n}=10.0$, $\alpha=21.0$.

centered at the origin, $(t_s,\Delta\Omega_s)=(0,0)$, which reflects the position and shape of the incident pulse. We will investigate the case $\Delta\Omega_i=-1.0$ much more deeply in the following. Note that time and frequency in every figure are scaled by $|\Delta\Omega_i|$, i.e., t_s should be interpreted as $|\Delta\Omega_i|t_s$ and $\Delta\Omega_s$ as $\Delta\Omega_g/|\Delta\Omega_i|$.

Between Figs. 5 and 6, we made 2κ ten times larger, keeping the other parameters fixed. We observe that, in Fig. 6, the intensities of both Raman and luminescence components are reduced approximately by a factor of $\frac{1}{5}$, and that the peak of the luminescence shifts to larger

TABLE I. Parameters for each profile.

Fig. no.	$\Delta\Omega_i$	g	2κ	$\bar{n}$	α
4	1.0	1.0	0.5	10.0	21.0
5	−1.0	1.0	0.5	10.0	21.0
6	−1.0	1.0	5.0	10.0	21.0
7	−1.0	1.0	5.0	5.0	1.10
8	−1.0	1.0	5.0	2.5	0.592
9	−1.0	2.0	5.0	5.0	2.19
10	−1.0	0.5	5.0	5.0	0.548
11	−1.0	1.0	10.0	5.0	0.548
12	−1.0	1.0	2.5	5.0	2.19
13	−1.0	2.0	0.05	1.0	56.6
14	−1.0	1.0	10.0	1.0	0.141

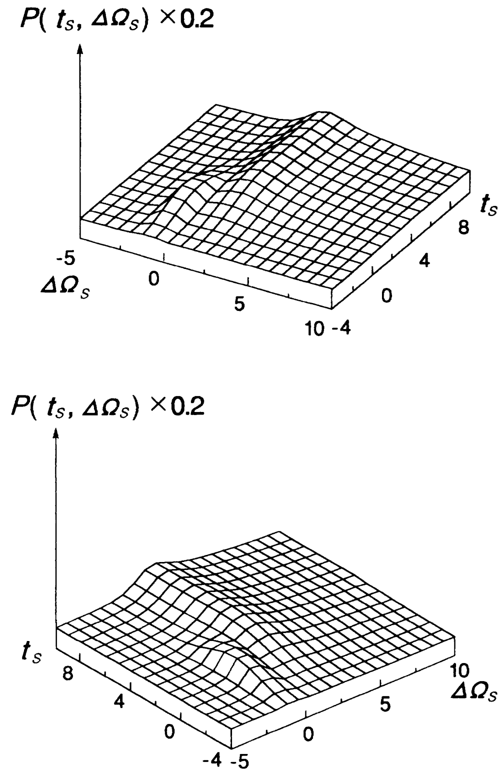

FIG. 5. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=0.5$, $\bar{n}=10.0$, $\alpha=21.0$.

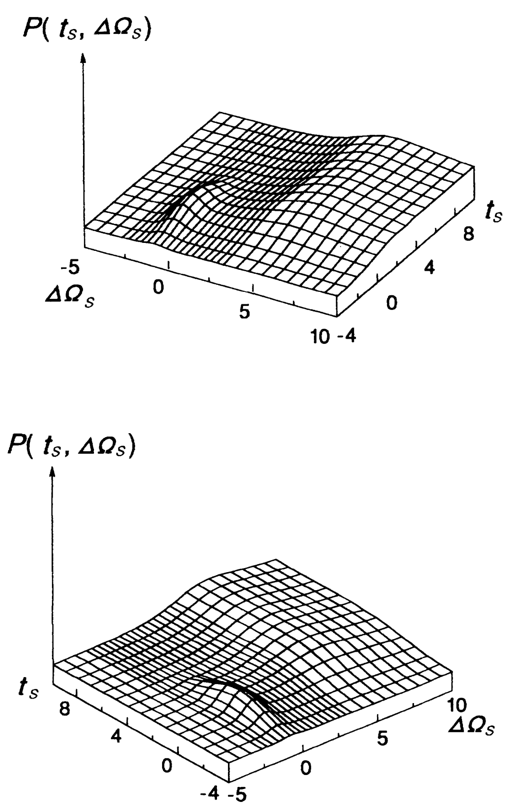

FIG. 6. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=5.0$, $\bar{n}=10.0$, $\alpha=2.10$.

$\Delta\Omega_s$ which is consistent with the characteristics observed in the absorption spectra of the model investigated in Refs. [23,19]. As 2κ becomes larger, so does the width of the phonon levels. Therefore, for larger 2κ, the overlapping among the adjacent phonon levels is getting larger, which may cause the shift of the peak of luminescence component to larger $\Delta\Omega_s$.

Among Figs. 6, 7, and 8, we varied $\bar{n}$, which indicates the temperature of the matter [see (4.7)]. When the value of $\bar{n}$ gets smaller (i.e., the temperature of the matter gets lower), the profile $P(t,\Delta\Omega_s)$ becomes larger, and the positions of the peaks for Raman and luminescence components become closer. The lower the temperature of the material becomes, the fewer the number of phonons and the smaller the influence of the modulation on the intermediate electronic state. This is again consistent with the observations in Refs. [23,19].

Among Figs. 9, 7, and 10, we changed g. We see that, as g becomes smaller, the photon counting rate becomes larger. Since the value of g measures the strength of coupling between the intermediate electronic state and the phonon interaction mode, the smaller g indicates that the modulation to the intermediate electronic state is getting inefficient. This makes the intensity of the profile larger. Note that the distance between the neighboring levels of the interaction mode is equal to g [see (5.6)].

Let us consider here how the parameter α characterizes the profiles. For Figs. 6 and 9, the values of α are close, and the profiles are alike. Similarly, Figs. 8 and 10 have nearly the same profiles. On the other hand, Figs.

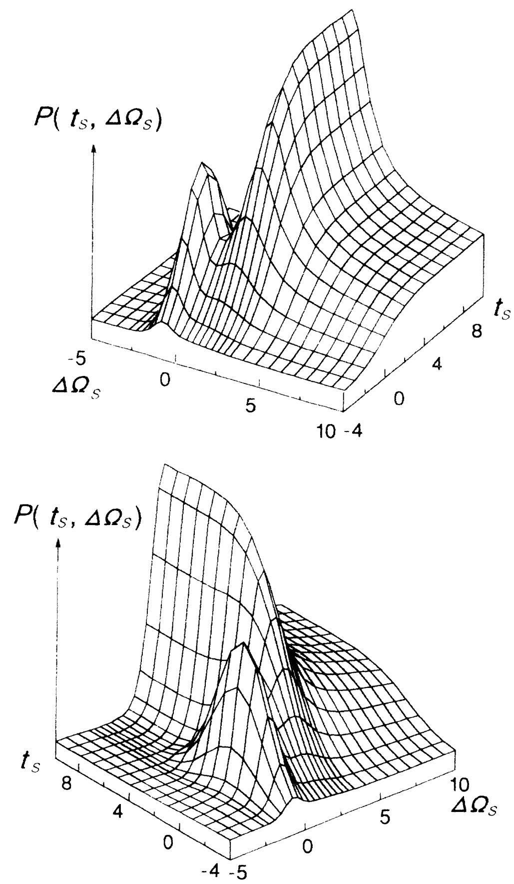

FIG. 8. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=5.0$, $\bar{n}=2.5$, $\alpha=0.592$.

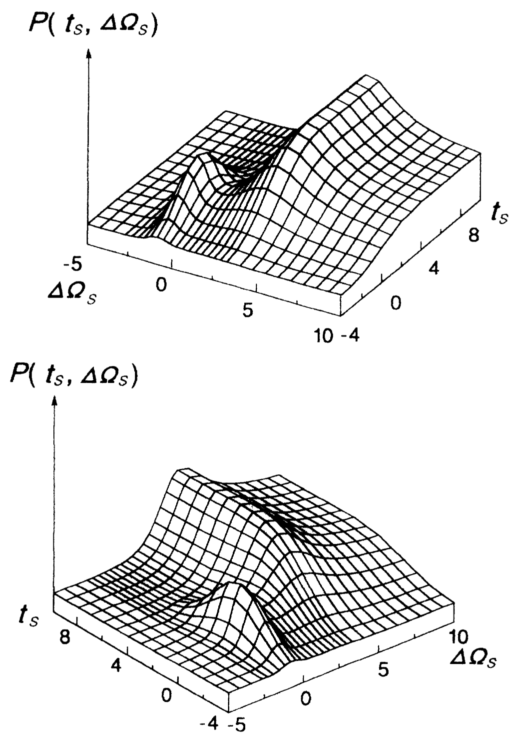

FIG. 7. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=5.0$, $\bar{n}=5.0$, $\alpha=1.10$.

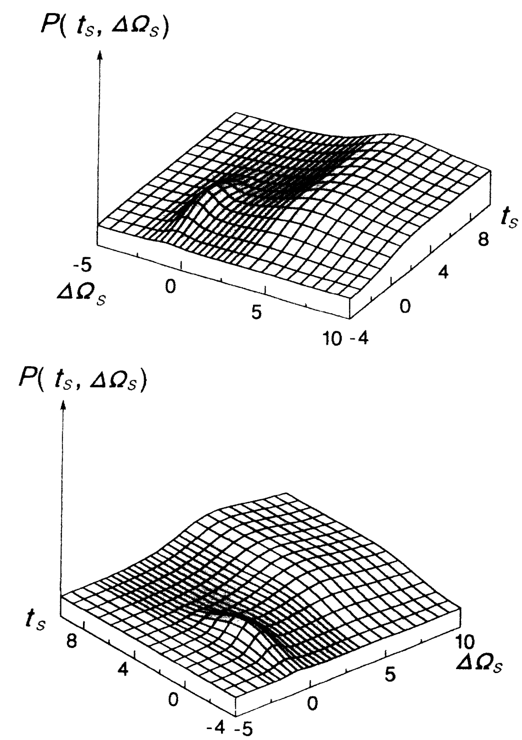

FIG. 9. $\Delta\Omega_i=-1.0$, $g=2.0$, $2\kappa=5.0$, $\bar{n}=5.0$, $\alpha=2.19$.

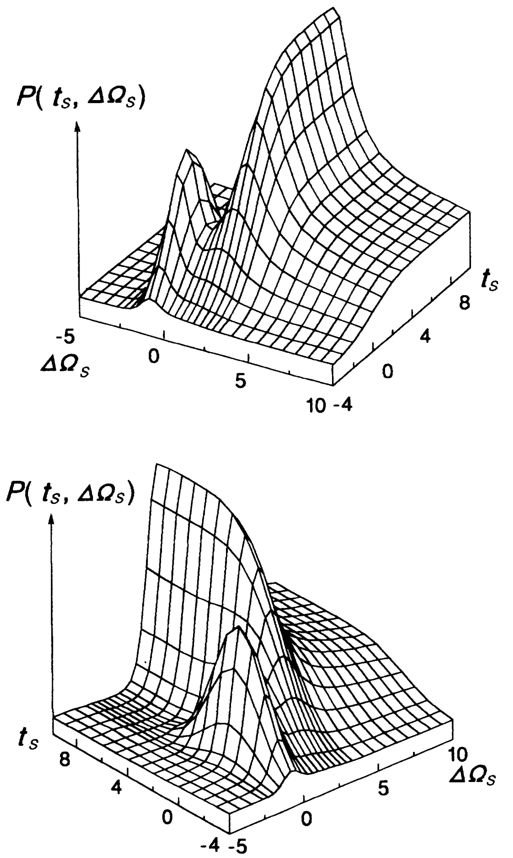

FIG. 10. $\Delta\Omega_i=-1.0$, $g=0.5$, $2\kappa=5.0$, $\bar{n}=5.0$, $\alpha=0.548$.

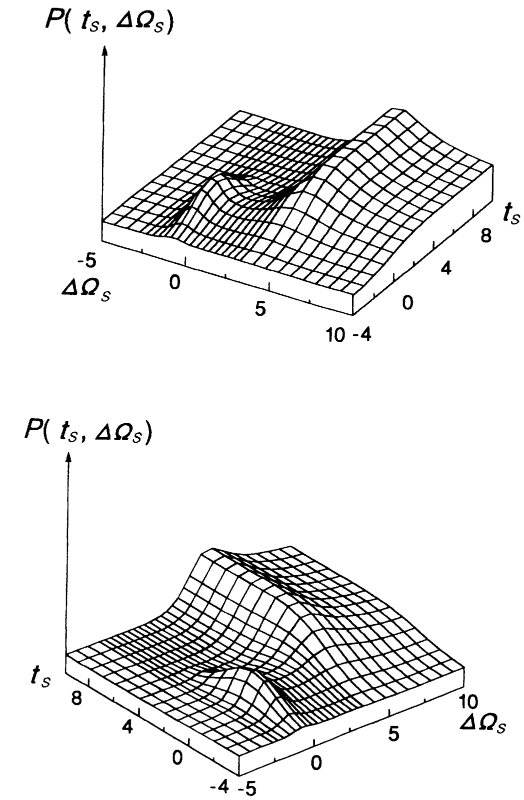

FIG. 11. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=10.0$, $\bar{n}=5.0$, $\alpha=0.548$.

11 and 12 have, respectively, just the same value of α as the cases of Figs. 10 and 9, but their profiles are not like each other. Rather, the profiles of Figs. 11 and 9 look similar, as do those of Figs. 12 and 10. Therefore one cannot distinguish the shape of the luminescence profile only by the parameter α for the present dynamical model. This is a contrast with the cases in the stochastic model where the parameter α characterizes the profile of the time-resolved spectrum [5].

In Figs. 13 and 14, we put the limiting cases of the slow and the fast modulations. The former can be analyzed by substituting (5.5) for $g_{\pm}(\tau,\mu,\sigma)$ in the formula (4.59), and the latter by substituting (5.18) in (4.59). In Fig. 13, we observe the phonon sideband in the profile of the luminescence component. Note that the widths of the phonon sidebands are convoluted by that of the apparatus function $F_s(t)$, causing a larger width than the expected one, i.e., $2\kappa[\bar{n}+(1+2\bar{n})l]$, for the lth sideband [see (5.5)]. In Fig. 14, we see that the luminescence component changes its profile with respect to $\Delta\Omega_s$ from a Gaussian to a Lorentzian shape in the early stage of its time evolution. This is consistent with the investigation performed by Kubo, Toda, and Hashitsume [5].

Note that in the case of $\kappa=0$ only the phonon levels excited directly by the incident pulse can emit luminescence. On the other hand, in the case of $g=0$, only the Raman component appears, since there is no modulation due to phonons for the intermediate electronic state, i.e.,

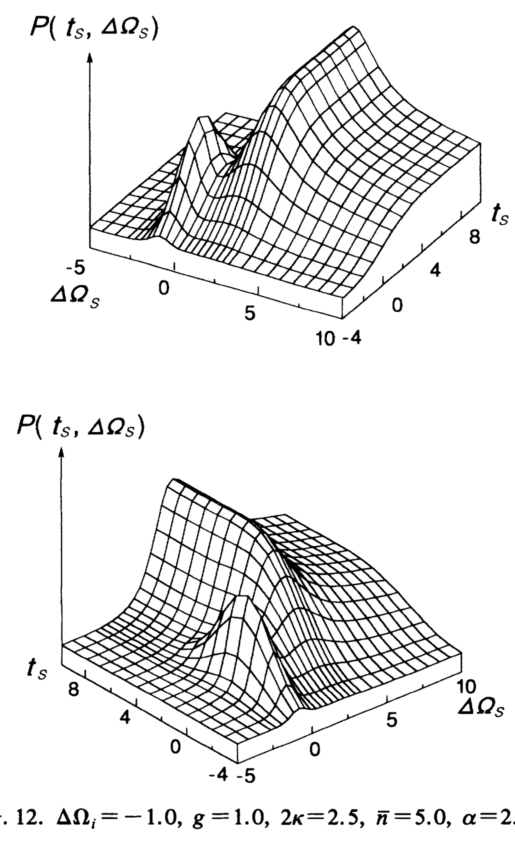

FIG. 12. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=2.5$, $\bar{n}=5.0$, $\alpha=2.19$.

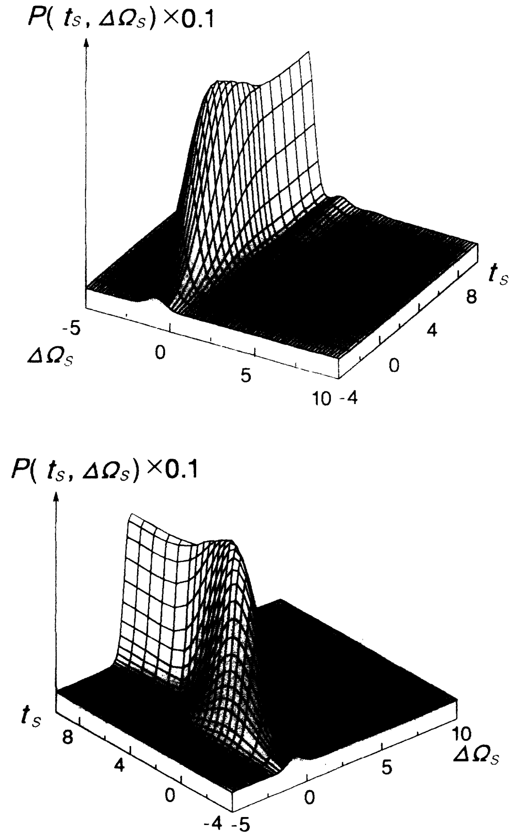

FIG. 13. $\Delta\Omega_i=-1.0$, $g=2.0$, $2\kappa=0.05$, $\bar{n}=1.0$, $\alpha=56.6$.

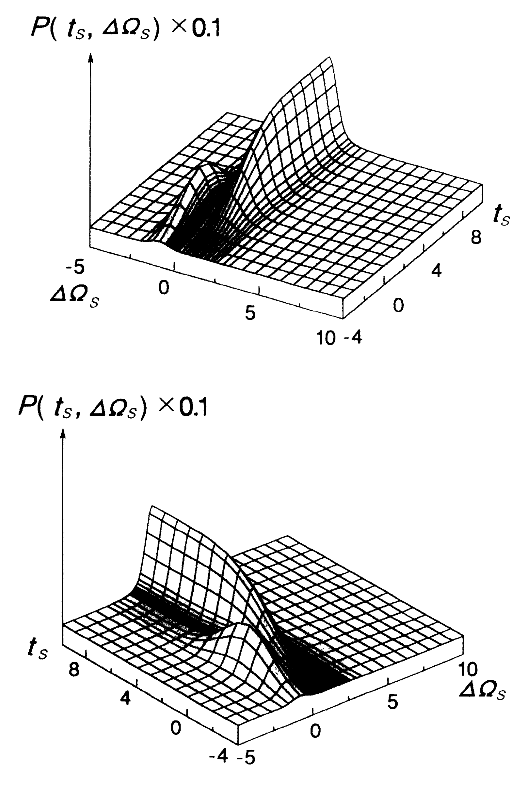

FIG. 14. $\Delta\Omega_i=-1.0$, $g=1.0$, $2\kappa=10.0$, $\bar{n}=1.0$, $\alpha=0.141$.

a purely quantum mechanical light scattering problem mediated by three electronic states.

VII. DISCUSSION

We derived a general formula of the time-resolved optical spectrum for transient resonant light scattering by means of the formalism of NETFD. The formula is applied to the second-order light scattering due to a localized electron which has three optically active electronic states whose intermediate state is dynamically modulated by phonons.

The derivation of the formula of the spectrum and its application showed that the algebraic manipulations within NETFD serve a transparent and straightforward methodology which enables us to treat nonequilibrium transient and dissipative systems, common in macroscopic quantum systems (e.g., mesoscopic quantum systems), much more easily by a similar process as in quantum mechanics and in quantum field theory.

The investigations of the profiles of the luminescence component in time-resolved spectrum revealed, by a single formula, how the stochastic character comes out in the fast modulation limit, and how the dynamical behavior of the phonon system causing the modulation of the intermediate electronic state comes out in the slow modulation limit. This was possible with the help of the solvability of the model, which gave us the analytical expression for the formula of the profile which mediates between the fast and slow modulation limits.

Although we restricted ourselves to a simple case where the phonon interaction mode is in a thermal equilibrium state with the rest of the phonon modes, the present formula can be applied to a further nonequilibrium transient situation where the phonon interaction mode and the rest of the phonon modes are initially out of equilibrium. Application of the derived formula to a more realistic model of a localized-electron and phonon system without the introduction of the phonon interaction mode, and to other systems, such as excitons, would be interesting future problems.

ACKNOWLEDGMENTS

One of the authors (T.A.) would like to thank Dr. T. Iwasaki and Dr. F. H. Willeboordse for helpful discussions and for taking an interest in nonequilibrium statistical physics and the method of NETFD in spite of their unexpected somewhat delicate and difficult situations.

APPENDIX A: LINEAR RESPONSE OF MATERIAL SYSTEMS

Let us consider the linear response to the external radiation field of the system specified by $\hat{H}$. Since the deformation of the thermal vacuum is given by

$$\delta|0(t)\rangle = e^{-i\hat{H}t}\hat{S}^{(1)}(t,t_0)e^{i\hat{H}t_0}|0(t_0)\rangle , \tag{A1}$$

with

$$\hat{S}^{(1)}(t,t_0) = -i\int_{t_0}^{t} dt' \hat{H}_{RM}(t') , \tag{A2}$$

the linear response of an observable

$$Q(t)=\sum_{\mathbf{k}} Q_{\mathbf{k}}^{\dagger}(t)+\text{H.c.} \tag{A3}$$

is given by

$$\delta\langle Q(t)\rangle=-\sum_{\mathbf{q}}\sum_{\mathbf{k}}\int_0^t dt'\Phi_{\mathbf{q},\mathbf{k}}(t,t')\,\mathrm{Re}[g_{\mathbf{k}}\alpha_{\mathbf{k}}(t')] , \tag{A4}$$

with

$$\Phi_{\mathbf{q},\mathbf{k}}(t,t')=i\langle 1_M|[Q_{\mathbf{q}}(t),M_{\mathbf{k}}^{\dagger}(t')]|0_M\rangle+\text{c.c.} \tag{A5}$$

Here, we assumed that the state of the external radiation field is the coherent state defined by

$$a_{\mathbf{k}}|\alpha\rangle=\alpha_{\mathbf{k}}|\alpha\rangle , \tag{A6}$$

and that the field is given by

$$\mathrm{Re}g_{\mathbf{k}}\alpha_{\mathbf{k}}(t)=\mathrm{Re}g_{\mathbf{k}}^{*}\alpha_{\mathbf{k}}^{*}(t)=|g_{\mathbf{k}}\alpha_{\mathbf{k}}|\cos(\omega_{\mathbf{k}}t+\phi) . \tag{A7}$$

APPENDIX B: DERIVATION OF $g_{\pm}(t_1,t_2,t_3)$

Rewriting the function $S(t_1,t_2,t_3;1,2,3)$ defined by (4.46) as

$$S(t_1,t_2,t_3;1,2,3)=\langle 1_M|e^{\hat{\Pi}_1''t_1}|0_M(t_2,t_3;2,3)\rangle , \tag{B1}$$

with

$$|0_M(t_2,t_3;2,3)\rangle=e^{\hat{\Pi}_2''t_2}e^{\hat{\Pi}_3''t_3}|0_M\rangle , \tag{B2}$$

we have

$$\frac{d}{dt_1}S(t_1,t_2,t_3;1,2,3)=2\lambda_1\langle 1|d_1^{\dagger}d_1e^{\hat{\Pi}_1''t_1}|0_M(t_2,t_3;2,3)\rangle \tag{B3}$$

$$=c\left[1-\frac{a_1-\lambda_1}{c}\right]\frac{f(t_1,t_2,t_3;1,2,3)-(a_1+\lambda_1)/c}{1-f(t_1,t_2,t_3;1,2,3)}S(t_1,t_2,t_3;1,2,3) \tag{B4}$$

$$=-\left\{\frac{d}{dt_1}\ln[1-r+re^{2\lambda_1t_1}]\right\}S(t_1,t_2,t_3;1,2,3) , \tag{B5}$$

where

$$f(t_1,t_2,t_3;1,2,3)=\frac{f_1(t_1,t_2,t_3,1,2,3)}{f_2(t_1,t_2,t_3;1,2,3)} , \tag{B6}$$

with

$$\begin{bmatrix} f_1(t_1,t_2,t_3;1,2,3) \\ f_2(t_1,t_2,t_3;1,2,3)\end{bmatrix}=Q_1e^{\tau_3\lambda_1t_1}\begin{bmatrix} f_1(t_2,t_3;2,3) \\ f_2(t_2,t_3;2,3)\end{bmatrix} \tag{B7}$$

and

$$r=r(t_2,t_3;1,2,3)=\frac{[c-(a_1-\lambda_1)]f_1(t_2,t_3,2,3)}{[c-(a_1-\lambda_1)]f_1(t_2,t_3,2,3)+[c+(a_1-\lambda_1)]f_2(t_2,t_3,2,3)} . \tag{B8}$$

Here, $f_1(t_2,t_3;2,3)$ and $f_2(t_2,t_3;2,3)$ are defined through the relation

$$\begin{bmatrix} d_1 \\ \tilde{d}_1^{\dagger}\end{bmatrix}|0_M(t_2,t_3;2,3)\rangle =\begin{bmatrix} f_1(t_2,t_3;2,3) \\ f_2(t_2,t_3;2,3)\end{bmatrix}e^{\hat{\Pi}_2''t_2}e^{\hat{\Pi}_3''t_3}\tilde{b}^{\dagger}|0_M\rangle , \tag{B9}$$

and are given by

$$\begin{bmatrix} f_1(t_2,t_3;2,3) \\ f_2(t_2,t_3;2,3)\end{bmatrix}=Q_1^{-1}Q_2e^{\tau_3\lambda_2t_2}Q_2^{-1}Q_3e^{\tau_3\lambda_3t_3}Q_3^{-1}\begin{bmatrix} f \\ 1\end{bmatrix} . \tag{B10}$$

In deriving (B5), we introduced the annihilation and creation operators

$$\gamma_1(t_1)^{\mu}=\begin{bmatrix}\gamma_1(t_1) \\ \tilde{\gamma}_1^{\#}(t_1)\end{bmatrix},\quad \bar{\gamma}_1(t_1)^{\mu}=(\gamma_1^{\#}(t_1)\ \ -\tilde{\gamma}_1(t_1)) , \tag{B11}$$

which are defined by

$$\begin{aligned}\gamma_1(t_1)^{\mu}&=B(t_1,t_2,t_3;1,2,3)^{\mu\nu}b_1(t_1)^{\nu} ,\\ \bar{\gamma}_1(t_1)^{\mu}&=\bar{b}_1(t_1)^{\nu}B^{-1}(t_1,t_2,t_3;1,2,3)^{\nu\mu} ,\end{aligned} \tag{B12}$$

with the help of the time-dependent Bogoliubov transformation

$$B(t_1,t_2,t_3;1,2,3)^{\mu\nu}=\begin{bmatrix} Z_1 & 0 \\ 0 & Z_2\end{bmatrix}\times\begin{bmatrix} 1 & -f(t_1,t_2,t_3;1,2,3) \\ -1 & 1\end{bmatrix} , \tag{B13}$$

with

$$Z_1Z_2=[1-f(t_1,t_2,t_3;1,2,3)]^{-1} . \tag{B14}$$

Here, $f(t_1,t_2,t_3;1,2,3)$ is given by (B6), and the time-dependent operators $b(t)^{\mu}$ and $\bar{b}(t)^{\mu}$ are defined by

$$b_1(t_1)^\mu = e^{-\hat{\Pi}'_1 t_1} b^\mu e^{\hat{\Pi}'_1 t_1} = \begin{bmatrix} b_1(t_1) \\ \tilde{b}_1^{\dagger\dagger}(t_1) \end{bmatrix},$$

$$\bar{b}_1(t_1)^\mu = e^{-\hat{\Pi}'_1 t_1} \bar{b}^\mu e^{\hat{\Pi}'_1 t_1} = (b_1^{\dagger\dagger}(t_1) \quad -\tilde{b}_1(t_1)) . \tag{B15}$$

The annihilation and creation operators satisfy

$$\gamma_1(t_1)|0_M(t_2,t_3;2,3)\rangle = 0 , \tag{B16}$$

$$\langle 1_M | e^{\hat{\Pi}''_1 t_1} \tilde{\gamma}_1^{\#}(t_1) = 0 . \tag{B17}$$

The differential equation (B5) can be solved as

$$S(t_1,t_2,t_3;1,2,3) = [1 - r + re^{2\lambda_1 t_1}]^{-1} , \tag{B18}$$

with r being given by (B8).

With the help of the time-dependent Bogoliubov transformation (B13), we can rewrite $\hat{\Pi}''$, defined in (4.35), in terms of the annihilation and creation operators as

$$\hat{\Pi}'' = \lambda_1(d_1^\dagger d_1 + \tilde{d}_1^\dagger \tilde{d}_1) \tag{B19}$$

$$\begin{aligned} &= \frac{c}{2}\left\{ Z_2^2 \left[1 - \frac{a_1-\lambda_1}{c}\right]\left[1 - \frac{a_1+\lambda_1}{c}\right] \tilde{\gamma}_{1,t_1}\gamma_{1,t_1} \right. \\ &\quad + Z_1 Z_2 \left[1 - \frac{a_1-\lambda_1}{c}\right]\left[f(t_1,t_2,t_3;1,2,3) - \frac{a_1+\lambda_1}{c}\right](\tilde{\gamma}_{1,t_1}^{\#}\tilde{\gamma}_{1,t_1} + 1) \\ &\quad + Z_1 Z_2 \left[f(t_1,t_2,t_3;1,2,3) - \frac{a_1-\lambda_1}{c}\right]\left[1 - \frac{a_1+\lambda_1}{c}\right]\gamma_{1,t_1}^{\#}\gamma_{1,t_1} \\ &\quad \left. + Z_1^2 \left[f(t_1,t_2,t_3;1,2,3) - \frac{a_1-\lambda_1}{c}\right]\left[f(t_1,t_2,t_3;1,2,3) - \frac{a_1+\lambda_1}{c}\right]\gamma_{1,t_1}^{\#}\tilde{\gamma}_{1,t_1}^{\#} \right\} + \text{t.c.} , \end{aligned} \tag{B20}$$

where

$$\gamma_{1,t_1}^\mu = \begin{bmatrix} \gamma_{1,t_1} \\ \tilde{\gamma}_{1,t_1}^{\#} \end{bmatrix}, \quad \bar{\gamma}_{1,t_1}^\mu = \begin{bmatrix} \gamma_{1,t_1}^{\#} & -\tilde{\gamma}_{1,t_1} \end{bmatrix} \tag{B21}$$

is defined through the relation

$$\gamma_1(t_1)^\mu = e^{-\hat{\Pi}'_1 t_1} \gamma_{1,t_1}^\mu e^{\hat{\Pi}'_1 t_1}, \quad \bar{\gamma}_1(t_1)^\mu = e^{-\hat{\Pi}'_1 t_1} \bar{\gamma}_{1,t_1}^\mu e^{\hat{\Pi}'_1 t_1} . \tag{B22}$$

Here, we dropped the subscript j, for simplicity.

The expression (B20) is the normal ordered form of the generator $\hat{\Pi}''$, whereas the expression (B19) is the diagonalized form of the generator. Note that, in the usual quantum mechanics or quantum field theory, the operator which diagonalizes a Hamiltonian and the operator which defines the normal ordering are the same. It is a special feature in transient nonequilibrium situations that the diagonalizing operator for the time-evolution generator within NETFD is different from the normal ordering operator.

APPENDIX C: THE AUTOCORRELATION OF $gb^{\dagger\dagger}(t)b(t)$

With the help of the thermal state condition (4.11), the autocorrelation of the operator $gb^\dagger b$ can be calculated as

$$\begin{aligned} &\langle gb^{\dagger\dagger}(t)b(t)gb^{\dagger\dagger}(s)b(s)\rangle_c \\ &\quad = \langle 1_{\text{ph}}|gb^{\dagger\dagger}(t)b(t)gb^{\dagger\dagger}(s)b(s)|0_{\text{ph}}\rangle - g^2 n(t)n(s) \\ &\quad = g^2 n(s)[1+n(s)]e^{-2\kappa(t-s)}, \quad t \ge s , \end{aligned} \tag{C1}$$

where

$$n(t) = \langle 1_{\text{ph}}|b^{\dagger\dagger}(t)b(t)|0_{\text{ph}}\rangle = \bar{n} + \Delta n e^{-2\kappa t} , \tag{C2}$$

with $\Delta n = n - \bar{n}$. In the stationary case, i.e., $\Delta n = 0$, the autocorrelation reduces to

$$\langle gb^{\dagger\dagger}(t)b(t)gb^{\dagger\dagger}(s)b(s)\rangle_c = g^2\bar{n}(\bar{n}+1)e^{-2\kappa(t-s)} , \quad t \ge s . \tag{C3}$$

We see that the parameter α is the ratio of the intensity of the correlation, $g\sqrt{\bar{n}(\bar{n}+1)}$, and the relaxation rate of the correlation, 2κ.

[1] T. Takagawara, E. Hanamura, and R. Kubo, J. Phys. Soc. Jpn. **43**, 802 (1977); **43**, 811 (1977); **43**, 1522 (1977).
[2] M. Aihara and A. Kotani, Solid State Commun. **46**, 751 (1983).
[3] T. Arimitsu and M. Ban, J. Phys. Soc. Jpn. **53**, 76 (1984).
[4] K. Maruyama, F. Shibata, and M. Aihara, Physica A **153**, 441 (1988).
[5] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II* (Springer, Berlin, 1985).
[6] T. Arimitsu and M. Ban, J. Phys. Soc. Jpn. **53**, 74 (1984).
[7] M. Ban and T. Arimitsu, J. Phys. Soc. Jpn. **53**, 939 (1984).
[8] T. Arimitsu and H. Umezawa, Prog. Theor. Phys. **75**, 429 (1985).
[9] T. Arimitsu and H. Umezawa, Prog. Theor. Phys. **77**, 32

(1987).
[10] T. Arimitsu and H. Umezawa, Prog. Theor. Phys. **77**, 53 (1987).
[11] T. Arimitsu, in *Thermal Field Theories,* edited by H. Ezawa, T. Arimitsu, and Y. Hashimoto (North-Holland, Amsterdam, 1991), p. 207.
[12] T. Arimitsu, Phys. Lett. **153**, 163 (1991).
[13] T. Arimitsu, Bussei Kenkyu **60**, 491 (1993), and references therein.
[14] N. Arimitsu and T. Arimitsu, in *Proceedings of the 3rd Workshop on Thermal Field Theories and their Applications,* edited by G. Kunstatter and R. Kobes (World Scientific, Singapore, 1994).
[15] M. Ban and T. Arimitsu, Physica A **146**, 89 (1987).
[16] T. Tominaga, M. Ban, T. Arimitsu, J. Pradko, and H. Umezawa, Physica A **149**, 26 (1988).
[17] T. Tominaga, T. Arimitsu, J. Pradko, and H. Umezawa, Physica A **150**, 97 (1988).
[18] T. Iwasaki, T. Arimitsu, and F. H. Willeboordse, in *Thermal Field Theories* (Ref. [11]), p. 459.
[19] T. Arimitsu, F. H. Willeboordse, and T. Iwasaki, Physica A **182**, 214 (1992).
[20] Y. Takahashi and H. Umezawa, Collect. Phenom. **2**, 55 (1975).
[21] R. Kubo, J. Math. Phys. **4**, 174 (1963).
[22] F. Shibata and T. Arimitsu, J. Phys. Soc. Jpn. **49**, 891 (1980).
[23] T. Arimitsu, M. Ban, and F. Shibata, Physics A **123**, 131 (1984).

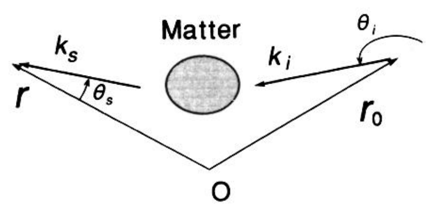

FIG. 1. Setup of the system under consideration.

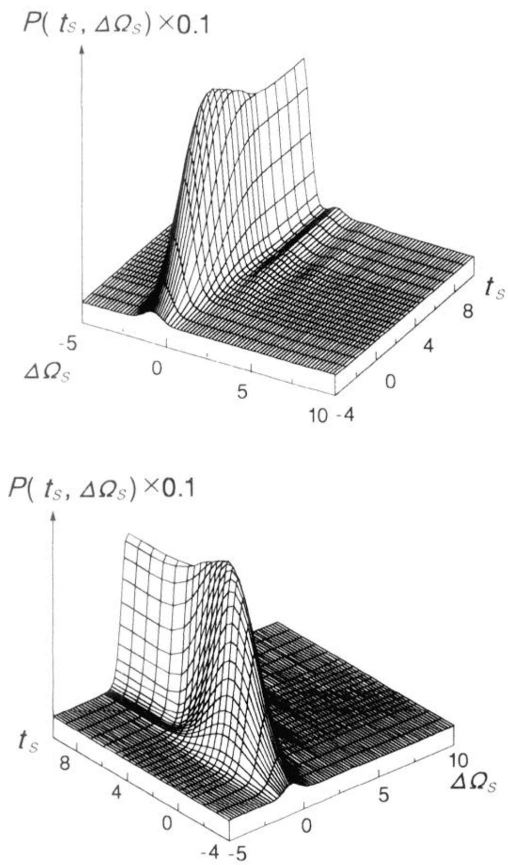

FIG. 13. $\Delta\Omega_i = -1.0$, $g = 2.0$, $2\kappa = 0.05$, $\bar{n} = 1.0$, $\alpha = 56.6$.

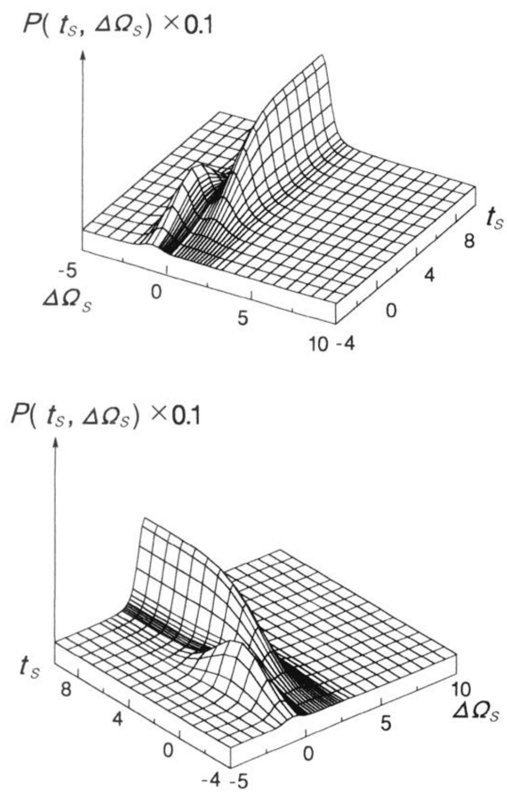

FIG. 14. $\Delta\Omega_i = -1.0$, $g = 1.0$, $2\kappa = 10.0$, $\bar{n} = 1.0$, $\alpha = 0.141$.